Development of ZIF-8 membranes: opportunities and challenges for commercial applications

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Metal organic framework (MOF) membranes have attracted significant attentions in recent years because of their potentials in gas and liquid separations and other applications such as catalysis and chemical sensors, etc. More than half of the MOF membrane publications up to date are related to ZIF-8 system, because of its easy synthesis, relatively high stability, and excellent gas separation performance, which allows many novel ideas to be easily implemented. Extensive studies have shown that ZIF-8 membranes hold great potentials in gas separations, but may face great challenges in liquid separations mainly because of their poor stability. This is also a common observation for other MOF membranes. As such, in this article we use ZIF-8 membrane as a prototype and focus on its development in gas separations for the discussions of the most concerned issues related to membrane commercialization including membrane synthesis, separation performance, stability, process reproducibility, and finally on the opportunities and challenges that MOF membranes may face in industrial applications.

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Introduction

Membrane technology offers great energy benefit in the separation of bulk gas and liquid mixtures since the separation can be carried out without phase separation. In an optimal membrane process design, the energy of the entire system is mainly determined by the membrane selectivity, so it should be the first important design parameter to consider. The higher the selectivity, the lower the energy consumption can be achieved [1,2•]. To save membrane cost, the membrane permeance is the second important design parameter which should also be as high as possible. The third design parameter is pressure ratio between the feed and permeate in order to meet the product purity requirement. Hence, a membrane should be robust enough to hold a certain transmembrane pressure drop (TMP).

As a new type of ordered porous materials, MOFs hold great potentials to provide both high selectivity and high permeability because of their uniform pore size for sharp molecular sieving and high porosity for fast transport rate. ZIF-8 is a small pore MOF which consists of zinc ions coordinated with 2-methyl imidazolate ligands, forming a SOD zeolite structure with connection window size of 0.34 nm calculated from the crystallographic structure. ZIF-8 is first reported by Chen et al. [3••] and Yaghi et al. [4]. ZIF-8 has many advantages: It is one of the most stable MOF structures [5]. The starting materials are cheap and easily available. The synthesis is relative easy. Wiebcke et al. first reported a fast and room temperature synthesis protocol using methanol as solvent [6••]. We first reported the synthesis in aqueous solution [7••]. The first ZIF-8 membrane was reported by Caro [8••]. The pore size is suitable to separate a number of important gas mixtures including H_2/CO_2, CO_2/N_2, H_2/CH_4, and most notably, C_2/C_3 and propylene/propane. However, there are also many challenges in the MOF membrane preparation and applications, such as brittleness, cracks, reproducibility, process scalability, etc. These challenges have significantly slowed down the commercialization roadmap of the counterpart zeolite membranes. In addition, MOFs are mechanically softer and chemically weaker compared to zeolites. All of these challenges and weaknesses have cast a big concern to the future of MOF membranes [9-11]. Nevertheless, the fascinating MOF structures have attracted more and more talent researchers into the field and many novel ideas have been proposed to tackle these challenges in recent years. Hence, it is worthy to revisit this topic, especially from the practical application point of view.

Membrane synthesis

Like other crystalline membrane materials such as zeolites, the membrane performance is related to many factors such as pore size, structure flexibility, orientation, and thickness. Since all MOF membranes developed thus far are polycrystalline, hence grain boundaries and pinholes are important membrane microstructures that if not properly sealed can be a major source of defects. It is worthy to note that the maximum size difference between any gas molecules is less than 0.3 nm, which is beyond the resolution of most SEM and TEM equipment. Hence, even a membrane appears compact under SEM or TEM inspection, the membrane could still fail to offer good separation performance. Hence, gas separation membranes are particularly sensitive to defects, and this has imposed a big challenge to membrane preparation. Although many novel membrane fabrication methods have been developed which can be found in details in a number of review articles [12-13,14••,15], only the *in situ* crystallization, seeded growth, and counter-diffusion (CD) methods, which are illustrated in Figure 1, have yielded membranes with decent gas separation performance.

The normal *in situ* crystallization method is simple but suffers from poor heterogeneous nucleation on the surface of supports. Many methods including surface modification of the support with metal coordination agents [16-18], coating a ZnO layer [19-22] or using polymer with metal chelating groups [23], are proposed to enrich the metal ions on the support. These methods improve not only the process reproducibility, but also the adhesion between the membrane and support.

The seeded growth method uses a seed layer to by-pass the nucleation stage and promote growth on the support surface. This method is able to control membrane orientation, thickness and grain boundary structure, and hence often leads to a better membrane performance [24]. The seed layer is typically prepared by dip-coating or rubbing [25,26], but both methods suffer from non-uniformity. Jeong et al. developed a microwave assistant seeding technique in which a uniform seed layer can be formed *in situ* on the support surface. After seeded growth, high quality ZIF-8 membranes with good propylene/propane separation performance are achieved [27].

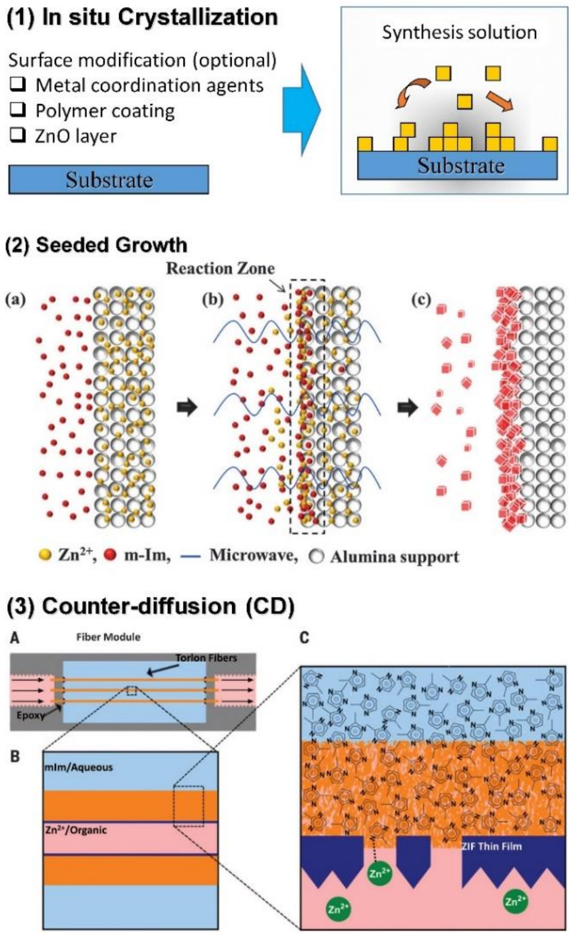

Figure 1: Illustrations of the three most effective ZIF-8 membrane fabrication methods. (1) *in situ* crystallization; (2) a microwave assisted seeded growth process [27]; (3) an interfacial microfluidic counter-diffusion method [28••].

The CD method was first developed by Wang et al.[29••] utilizing the unique coordination chemistry of MOFs which are typically formed from two precursors, one is the metal salt which is soluble in either water or organic solvents, and the other is the organic ligand which is in most cases soluble only in organic solvent. 2-methylimidazole is one of the few imidazoles that are soluble in water, and hence ZIF-8 can be synthesized in pure aqueous solution [7••]. A number of good progresses have been made in this method. Jeong et al. developed a two-step CD process in which the support is first soaked in one precursor solution and then immersed in another precursor solution[30••]. Nair et al. developed an interfacial microfluidic flow processing method in which the precursor solutions are supplied separately from two sides of the hollow fiber support. The membrane can be formed at any position of the support [28••,31]. A number of other studies also reported the flow process where the precursor solutions are cycled either from one side or both sides of the support [32-34]. Cycling the precursor solution can promote not only the product yield, but also the crystallization rate [28••,31]. In-situ TEM observation on ZIF-8 crystal growth confirmed that the crystallization rate is much faster in a flow system than that in a static solution [35].

The support is also an important factor that will affect the membrane quality. The surface chemistry, roughness, and mechanical strength of the support sometimes will greatly affect the membrane growth, the adhesion, and the integrity of the final membrane. Commonly used supports include ceramics and polymers. In most cases the support should be inert since the support should be robust and stable in practical applications. However, inert supports typically have poor heterogeneous nucleation and weak adhesion. This is particular an issue in the *in situ* crystallization method as discussed previously. While in the seeded growth method, the effect of the support can be largely eliminated by the seed layer. Supports with a certain degree of roughness can enhance the adhesion, but a smooth surface is often needed to achieve a more uniformly oriented and thinner membrane. Ceramic supports have much stronger mechanical strength than polymer supports, so presumably ceramic supports should be beneficial for the polycrystalline ZIF-8 membranes, which is brittle and fragile in nature. However, a number of reports have showed that under low TMP conditions polymer supported ZIF-8 membranes are able to achieve similar gas separation performances as those on ceramic supports [23,28••,31]. While under high TMP the membrane performance in both cases is unknown and need study more.

Compared to zeolite membranes, ZIF-8 system has many advantages towards commercialization, as summarized below.

- The synthesis can be carried out at room temperature, or at temperature below the boiling point of the solvent used. This eliminates the use of expensive autoclaves and makes the process much easier to handle.
- The synthesis time is short. The synthesis time can be further reduced by coupling with microwave heating [8••] or rapid thermal deposition [36].
- Since MOF syntheses do not require organic structure directing agents, there is no need for thermal sintering which is one of the major steps to form defects in zeolite membranes. The mild synthetic conditions allow the use of polymers as supports [23,29••,31,37•,38-43,44•], which could significantly reduce the membrane cost.
- The counter-diffusion method can repair defects *in situ* [30••].

Gas separation performance

The pore size of ZIF-8 based on the crystallographic structure data is around 0.34 nm, which is similar to the kinetic diameter of CO_2. However, the gas permeation data exhibited only moderate selectivities for hydrogen and CO_2 over other gases. For example, the selectivities of H_2/CO_2, H_2/N_2

and H_2/CH_4 are typically around 4, 9, and 13, respectively. Such low selectivities will be difficult to compete with polymeric membranes and hence the potential of ZIF-8 membranes in these gas separations will be limited. A sharp molecular sieving is found between ethane/propane and propylene/propane [45••,46••], which indicates the effective pore size of ZIF-8 is around 0.42 nm. This discrepancy in pore size is typically attributed to the flopping motion of the methyl group attached to the imidazole. However, even for zeolites whose structure is often considered rigid, the effective pore size is also found approx. 0.05 nm larger than the crystallographic pore size [47]. Detailed adsorption studies of ZIF-8 showed that the adsorption isotherm should be modelled by two structures: one is obtained at normal condition and the other at high pressure [48]. Change between these two structures is occurred at a relative adsorption pressure of 2×10^{-4}. Most of the reported permeation data are based on single-component and hence the reported selectivities are ideal selectivities. For many porous materials the mixture selectivities can be very different from the ideal ones due to effects such as single-file diffusion or selective adsorption, etc. Fortunately, for ZIF-8 membranes there is not much difference [49]. The reason is probably because that the ZIF-8 structure is composed of large cages connected with short channels, so even the single file effect or preferable adsorption occurs in the short channels, the molecules will redistribute inside the large cages.

The efficient separation of propylene and propane over ZIF-8 membranes is an exciting discovery because it is an industrially important system [46••]. This separation is first realized by Li et al. from the kinetic adsorption studies over chlorated-ZIF-8 powder [50]. The size difference between these two molecules is around 0.02 nm, while the reported membrane selectivity is as high up to 150 [23]. The separation is apparently based on the kinetic difference because their adsorption capacities are almost the same. Hence, this system clearly shows that the structure of MOF is rigid enough to provide sharp molecular sieving, although the effective pore size is not exact the same as that is calculated from the crystallographic structure data. One reason is probably because ZIF-8 structure is based on a stable connection. Recently, MOF structures based on stable triangle connections were also shown to give excellent molecular sieving effect [51]. Propylene is the second largest gas product after ethylene. It is mainly produced from the fluid catalytic cracking process which yields about 70% propylene and 30% propane. The separation is currently achieved by distillation. Because of the close boiling points of these two gases, the distillation process requires more than 200 separation trays, making it one of the most energy and capital intensive processes in petrochemical industry. The superstructure of the membrane-distillation hybrid system is shown in Figure 2a, which covers different situations including the pure distillation process, the membrane-distillation hybrid process, and the pure single-stage membrane process. The simulated energy consumption of the membrane-distillation hybrid system at different membrane selectivity and pressure ratio is shown in Figure 2b. It shows that a membrane with selectivity higher than 10 can help reduce the energy consumption from distillation. A membrane with selectivity of 30 and 100 can reduce 40% and 80% energy, respectively. Figure 2c shows the separation performance of ZIF-8 membranes in comparison with other types of membranes. Clearly, the performance of ZIF-8 membranes achieved so far is not only much better than any other types of membranes, but also high enough to achieve up to 80% energy saving as predicted from modelling. However, most of the permeation tests in laboratory are carried out at room temperature, with 50:50 feed composition, and under no pressure drop. In real applications, the temperature is around 50^{o}C, feed contains 70% ethylene, and the pressure is about 18 bars [52]. As such, how to maintain the high membrane performance at real conditions will be a crucial step for commercialization.

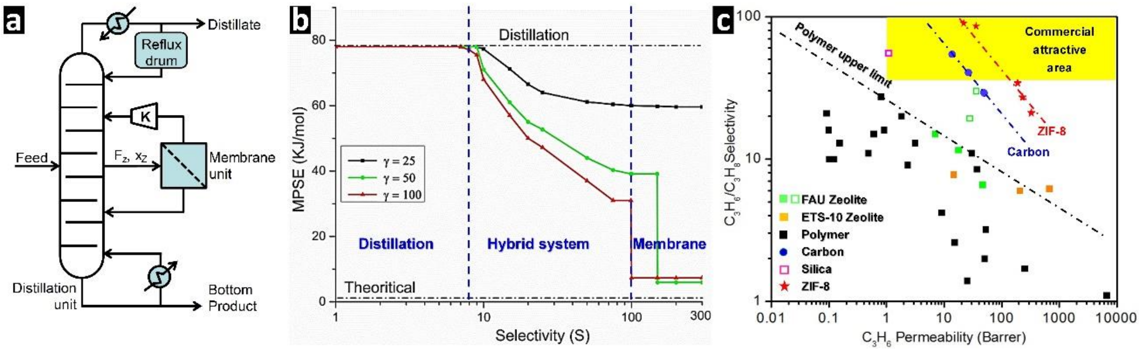

Figure 2: (a) the superstructure of the membrane-distillation system [2•]; (b) The simulated energy consumption for the separation of propylene/propane at different membrane selectivity and pressure ratio γ [2•]. A sharp drop in energy in the third stage indicates that the hybrid system is downgraded into a single-stage membrane process. (c) Performance comparison of ZIF-8 membranes to other membrane systems for the separation of propylene/propane [46••].

Membrane stability

From the bond strength calculations, ZIF-8 is one of the most stable MOF structures [5]. This is also confirmed by TEM studies where high resolution TEM images of the ZIF-8 structure can be achieved owing to its excellent stability [53•]. Lin et al. did systematic stability studies of ZIF-8 membranes [54••,55-56]. Below is the summary of their main conclusions.

- ZIF-8 membrane can maintain structural integrity up to 150^{o}C.
- ZIF-8 membrane is not stable in liquid. The membrane is damaged in less than 10 hours exposure to water during a pervaporation test. The membrane is less stable than powder because it contains more defects. We also observed that ZIF-8 membrane is not stable in organic solvents (unpublished data). In this study, a ZIF-8 membrane was used to separate the mixture of ethanol and propanol. The membrane showed excellent selectivity initially (~35), but disappeared after about one-month running. Lin et al. further found that the ZIF-8 membrane degradation in liquid is a dynamic dissolution process. By adding

precursors to the liquid the dissolution process is retarded. Since most MOF and ZIF materials are based on the same coordination chemistry, this dissolution mechanism should apply to all MOF membranes.

- For gas separation, the membrane is much more stable. In ambient conditions the membrane permeance drops only 25% after 35 days off-steam testing and the selectivity remained almost the same.

Jeong et al. compared the stability of ZIF-8 membranes prepared by two methods, one by counter-diffusion using methanol as solvent (CD-ZIF-8), and the other by microwave assisted seeding followed by secondary growth in aqueous solution (MW-ZIF-8). They found MW-ZIF-8 is more stable than CD-ZIF-8 and the reason is because MW-ZIF-8 contains less defects [57]. Lin et al.[58] and Yang et al.[59] found that the membrane stability can be improved by surface modification with hydrophobic ligands. However, the membrane stability under real applications still remains an open question.

Mechanical strength and process reproducibility

Many process reproducibility issues are related to the poor mechanical strength of ZIF-8. The structure is found very fragile and special care is required during solvent exchange. Direct removal of big solvent such as N,N-dimethyl formamide (DMF) or strong binding solvent such as water will cause structural collapse. Methanol has a small size and weak interaction with ZIF-8 structure and hence is commonly used as an exchanging solvent. The exchange rate is also an important factor. Using mixed solvent or saturated methanol vapor can slow down the exchange rate and therefore lead to better membrane quality [49].

The mechanical strength under pressure is another big challenge. Pan et al. found that the propylene/propane selectivity decreases from 61 to 14 when TMP increases from 0 to 3 bars [20].

The reason seems related to structure flexibility instead of physical damage since the selectivity can be largely restored when TMP is recovered. Nair et al. observed a similar trend in their studies [31,43].

A good progress was made by Pan et al. recently using coating as an effective approach to eliminate defects [60••]. They applied a PDMS coating on defective ZIF-8 membranes and found that all membranes after treatment showed very high propylene to propane selectivity. Very interesting, the membrane selectivity after treatment increases with pressure. When TMP increased from 0 to 6 bars, the propylene/propane selectivity increased from 93 to 105, while when TMP released back to zero, the separation factor returned back to 95, very close to the initial value. The intrinsic-hydrophobic PDMS coating also significantly improved the hydrolytic stability of the membrane. The membrane exhibited excellent long-term stability even using humidified-state feed gases. Coating has been widely used in polymer membrane preparation as a remedy approach. Hence, this finding represents an important progress towards commercialization.

One should also note that the effect of structure flexibility is not always negative. Very recently, Caro et al. used an electrical field to distort the ZIF-8 structure, which can fine tune the gas separation performance [61].

Perspectives of ZIF-8 membranes in industrial applications

There are thus far no major industrial gas separation processes using crystalline porous membranes. The future of MOF membranes will largely depends on whether it can find an industrial application.

All three synthetic methods are able to fabricate high quality ZIF-8 membranes on hollow fiber supports. A number of post-treatment methods have been developed to further improve the membrane separation performance [62] or hydrothermal stability [58,59]. The CD method with cycling precursor streams from both sides indicates that a continuous synthesis process can be designed. Hence, the membrane productivity may not be a major issue. Similar to polymer membranes, coating is likely to be an essential step in membrane fabrication to eliminate defects. Considering that the CD method can also repair defects *in situ*, the membrane reproducibility issue may not be as bad as it appears in the existing literature. Polymer is likely to be used as a support material because of its cheap price. Water used as solvent has apparent advantages in terms of cost and environmental impact compared to toxic and flammable organic solvents. Hence, even though the membrane cost may not be as cheap as those of polymer membranes, ZIF-8 membranes are still much more economical than other inorganic membranes.

The application of MOF membranes in liquid separations has been recently reviewed [63]. However, for ZIF-8 membrane it is unlikely suitable for liquid separations because of its poor stability in both water and organic solvents. However, for gas separation the long-term membrane stability under ambient conditions seems good. Because the effective pore size of ZIF-8 is about 0.07 nm larger than its crystallographic pore size, which makes it less selective and thus less competitive for H_2 and CO_2 separations. The membrane showed sharp molecular sieving for C_2/C_3 and propylene/propane mixtures, both are highly valuable systems in petrochemical industry. The selectivity is high enough to bring up to 80% energy reduction from the existing distillation process. Such a huge energy benefit will serve as a strong driving force to promote its commercialization. However, the membrane stability under real streams remains unknown. All the membrane permeation tests are carried out under conditions far away from the real separation conditions. The main challenge under real conditions is probably the mechanic strength under high pressure. The highest TMP tested so far is about 6 bars, while the pressure in real conditions is around 18 bars. How to maintain the high separation performance under such high pressure is unknown.

There are almost no studies on other membrane challenges such as fouling and concentration polarization. Since the highest permeance of propylene reported so far is less than 100 GPU, concentration polarization will not be a major issue [64•]. However, fouling by heavy hydrocarbons can be another big challenge in real applications.

Conclusions

ZIF-8 as an eminent example of MOF membranes have shown very promising performance for the separation of propylene/propane. The current membrane synthetic methods are capable to fabricate ZIF-8 membrane modules suitable for industrial applications at competitive cost. Although there are still a number challenges in membrane stability and process reproducibility, there is no technically unsolvable barriers to stop it from commercialization. The high value and large scale of the propylene/propane system and the potential energy benefit that can be achieved by a ZIF-8 membrane compared to the current distillation process will serve as a strong driving force to promote its commercialization. The successful implement of ZIF-8 membrane in industry will greatly benefit the development of MOF membranes.

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