

프로필렌 분리를 위한 ZIF-8 분리막의 연구 동향

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Research Trend on ZIF-8 Membranes for Propylene Separation

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요약: 고순도 프로필렌(프로펜)은 옥탄가를 높이는 화합물이며 산업적으로 중요한 화합물들의 원료가 된다. 프로판 혼합물로부터 프로펜을 정제하는 것은 비슷한 끓는점으로 인해 기술적으로 어려우며, 큰 비용이 요구된다. ZIF-8 분리막은 분자체 메커니즘에 의해 효율적으로 프로판으로부터 프로필렌을 분리할 수 있는 가능성 때문에 많은 연구가 진행되고 있다. ZIF-8 분리막에 대한 관심이 커지는 것은 소위 “gate opening” 효과 때문이다. 프로필렌/프로판 혼합물로부터 프로필렌 분리를 높이기 위해 “gate opening” 효과는 분리막 기공을 확장시켜 더 크고 무거운 프로판은 피드 흐름에 유지시키며, 프로필렌만 선택적으로 투과할 수 있도록 한다. 본 논문에서는 ZIF-8 분리막 제조에 널리 적용되는 방법들과 분리막을 통한 프로필렌 투과도 및 선택도에 영향을 주는 인자들에 대해 살펴보고자 한다.

Abstract: High purity propylene (propene) is an octane-enhancing chemical and also feedstock to industrially important chemicals. Purification of propylene from propane mixture is technologically and financially challenging because of their close boiling points. ZIF-8 membrane has been increasingly researched due to its great potential to separate propylene from propane effectively by molecular sieving. The increasing interest in ZIF-8 membranes lies in the so called “gate opening” effect. The gate opening effect enlarges the membrane pores and preferentially allows propylene to permeate through the membrane pores, while retaining the larger and heavier propane molecules in the feed stream in order to effect high propylene separation from propylene/propane mixture. In this paper, the widely accepted methods of ZIF-8 membrane preparation and parameters affecting propylene permeation and selectivity in ZIF-8 membrane are identified and reviewed.

Keywords: ZIF-8 membrane, propylene purification, crystal growth, microporous media, gas enrichment

1. Introduction

Separation of propylene or propene (C₃H₆) from propane (C₃H₈) is technically and financially challenging due to their close boiling points, high volatility and condensability characters. The separation of propylene from propylene/propane mixture is performed by an

energy-intensive cryogenic process that requires over 100 contacting stages and large energy input for maintaining high reflux ratios[1-3]. The cryogenic distillation reportedly consumes over 20 GJ of energy per ton of propylene produced, uses non-renewable energy resources and emits significant greenhouse gases (GHGs) and air contaminants. The U.S. Department of Energy

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asserted[4] that the present propylene/propane separation is the most energy-intensive distillation.

Pressure swing adsorption (PSA) and membrane technologies are the less energy intensive alternatives for propylene/propane purification than the cryogenic distillation. In PSA, propylene is selectively adsorbed on porous solid adsorbents at a relatively high pressure. The adsorbed propylene is then desorbed from the solids by lowering the pressure[5]. A more detailed approach on PSA for propylene/propane separation by utilizing 8-ring silica-chabazite (SiCHA) and zeolite 4 Å is reported previously[6].

The selection of SiCHA adsorbent was based on the diffusivity ratio. SiCHA reportedly showed propylene diffusivity of 1.1×10^{-9} cm²/s and propane diffusivity of 5.6×10^{-13} cm²/s with diffusivity ratio of over 2,000 at 353 K. The diffusivity ratio was increased to 46,000 at lower temperature of 303 K. In a different presentation, the propylene and propane uptakes by SiCHA were 95 mg/g and 8 mg/g at square root time of 10 min^{0.5}, respectively, the ratio of which is by a factor of 12[7]. The higher diffusivity and propylene uptake inside the adsorbent was attributed to the higher affinity of the SiCHA material for the propylene. The other adsorbents considered promising for propylene/propane separation are Ag⁺ exchanged Amberlyst-15 resin (Ag+resin)[8], AgNO₃/SiO₂[9], AlPO₄-14[10], zeolite 4 Å[11], zeolite 13X[12], Ag/SBA-15[13] and combination of these adsorbents[9,14].

Fig. 1 shows the comparison of purity and recovery of propylene by PSA. The performance comparison suggests that adsorbents such as zeolite 4 Å, AgNO₃/SiO₂, SiCHA, Ag/SBA-15 and AlPO₄-14 are excellent adsorbents for propylene purification from propylene/propane mixture due to their high propylene purity and recovery, all of which fall within the viable region. Despite the high propylene purity of greater than 95%, Ag⁺ exchanged Amberlyst-15 resin and zeolite 13X, are not considered to be viable for propylene purification due to their extremely low recovery of less than 40%. Zeolite 4 Å also performed poorly in term of its recovery when multiple component species (propylene, pro-

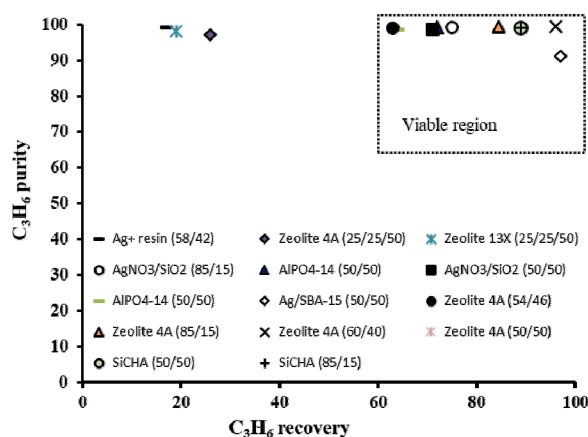


Fig. 1. Purity-recovery of propylene by PSA using different adsorbents with different feed composition of propylene/propane/nitrogen. For examples, Ag+resin (58/42) refers to 58% of propylene and 42% of propane in the feed, whereas Zeolite 4 Å (25/25/50) refers to 25% of propylene, 25% of propane and 50% of nitrogen by volume.

pane and nitrogen) are fed into the feed stream.

In addition to PSA, membrane technology is another alternative for propylene purification that is increasingly gaining attraction, especially in the academia. Membranes are considered a more promising candidate to separate, enrich and purify propylene from its mixture than PSA due to the higher energy saving potential, less complication in the unit operation and that the membrane separation requires relatively low capital upfront investment[15,16].

In membrane separation, selectivity or separation factor which is a measure of the capacity of a membrane to transport and separate gases is used instead of the purity that is widely used in PSA to gauge the latter's performance. The selectivity however is related to the quality of propylene in that, the higher the selectivity, the higher the purity of propylene. To gauge the membrane's productivity, permeability or permselectivity is used instead of the recovery which is commonly used in PSA.

Separation factor in membrane separation is measured by considering the molecular interaction that exists between the gas and membrane wall, and between the gas molecules. It can be determined using the ratio of the observed gas permeability or permselectivities. The

permeance of propylene in a binary gas system containing propylene (*species i*) and propane (*species j*), K_i^{mix} , is defined as [17],

$$K_i^{mix} = \frac{J_i^{mix}}{\Delta p_{ln,i}} \quad (1)$$

where J_i^{mix} is the volume flux of propylene in the gas mixture that permeate through the ZIF membranes. J_j^{mix} is the volume flux of the propane gas. Δp is the pressure difference between the feed and permeate side of the membranes. The separation factor, $\alpha_{i/j}^{sep}$, is calculated by taking the ratio of the observed gas permeance of propylene to that of propane,

$$\alpha_{i/j}^{sep} = \frac{K_i^{mix}}{K_j^{mix}} \quad (2)$$

The theoretical permeability can be calculated using [18,19],

$$K = \frac{\varepsilon}{z\tau\Re T} \left\{ \frac{P_{avg} r_p^2}{8\mu} + \left[\frac{2(r_p - r_g)}{3} \sqrt{\frac{8\Re T}{\pi M}} + \frac{1}{\varepsilon} (D_s \rho_m f) \right] \right\}, \quad (3)$$

for $r_p \geq r_g$

where, ε is the membrane porosity, z is gas compressibility factor, \Re is universal gas constant, T is temperature, P_{avg} is average pressure, r_p is membrane pore size, μ is gas viscosity, r_g is gas radius, M is gas molecular weight, D_s is surface diffusivity, ρ_m is membrane density, and f is loading or affinity factor.

Permeation of a gas species in a *micro*-porous membrane is contributed by two primary transport mechanisms represented by the last two terms in equation (3). The first is Knudsen-molecular sieving mechanism represented by the second term from the right hand side of the equation. The permeation by this mechanism depends on the molecular weight, size of the gas species and the membrane's pore size. The second mechanism is surface affinity or surface adsorption represented by the last term of the equation that facilitates adsorption and diffusion of the gas along the pore wall. The con-

tribution of membrane affinity becomes significant when the membrane's pore size is in the micro-porosity regime and the process is operated at low temperature and high pressure regions.

Metal organic frameworks (MOFs) membranes are known to contain pores of nanometer scale [20-22], which lies in the *micro*-porosity regime of < 2 nm. In addition, the MOFs exhibit well-ordered porous structures and chemical functionalities [23-28], which are conducive to separation of gas molecules of various species. Of particular interest are zeolitic imidazolate frameworks (ZIFs); a subclass of MOFs having the same zeolite sodalite (SOD) topology; whose crystals were reportedly grown to form molecular sieve membrane for gas separation application. Extensive review on the different type of ZIF membranes from their synthesis level to their overall performance in gas separation for variety of species can be found in the literature [29].

For separation of propylene from propylene/propane mixture, ZIF-8 appears to be in the current research limelight considering its theoretical aperture of 0.34 nm, which is smaller than the kinetic diameter of propylene molecule of 0.40 nm and propane molecule of 0.43 nm. Another factor that ZIF-8 earns researchers' attraction as the preferred material over the other types of ZIF materials for propylene-propane separation stems from the so called "gate opening" effect that allows propylene (despite its larger molecular size than the membrane's aperture) to selectively permeate through the membrane pores and retain the larger propane molecules in the feed stream by molecular sieving in order to effect high propylene separation from propylene/propane mixture. As a result, ZIF-8 membrane was selected to separate propylene from propane in a series of the previous work [30-39]. Due to the increasing interest in ZIF-8 for propylene-propane separation, the widely used approaches of laboratory scale ZIF-8 membrane syntheses are reviewed. The parameters affecting propylene permeation in ZIF-8 membrane and recent progress that has been made in the field are also presented in the paper.

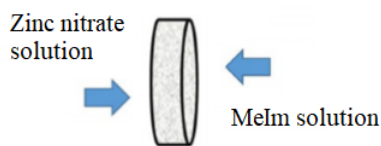


Fig. 2. Schematic procedure for ZIF-8 membrane synthesis following contra-diffusion in *in-situ* growth method.

2. ZIF-8 Membrane Preparation Methods

Generally, ZIF-8 membranes are prepared by following 3 methods, i.e., *in-situ* growth on a porous support, secondary growth by seeding and electrospray deposition. These methods involve contacting the porous support with a precursor synthesis solution, after which the membrane is treated with solvent to form pores or functionalized the surface pores to improve membrane affinity for particular species. ZIF-8 membranes can be grown on porous ceramic and polymeric supports of different geometry such as flat sheet, tubular, or hollow fiber. Other techniques considered innovative may come from the extended version of the 3 methods described earlier. These include the counter-diffusion, microwave irradiation, rapid thermal deposition and micro-channelling through pumping of the precursor solution, which may fall under the *in-situ* or secondary growth method.

2.1. *In-situ* growth technique

In-situ growth method, also referred to as primary synthesis or *in-situ* crystallization, involves growing the ZIF-8 crystals directly on a pristine porous support. The support can be made from metal oxide such as titania or alumina. The technique is accomplished by immersing the support in a precursor solution, allowing sufficient amount of time for the nucleation to proceed at an elevated temperature so that the crystals can grow on the support and eventually form the membrane on the support's surface. In order to reduce the time taken for the seed crystals to grow, microwave heating is usually applied during the synthesis to facilitate the nucleation[29].

In addition, the support surface can be conditioned by

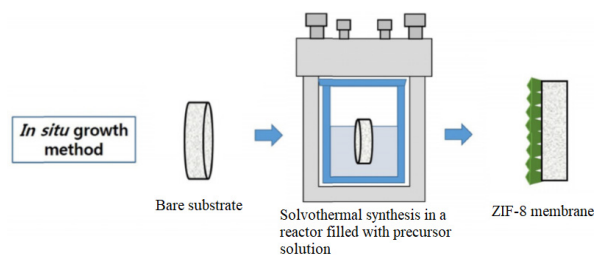


Fig. 3. Schematic procedure for ZIF-8 membrane synthesis following *in-situ* growth method[29].

contacting it with organic ligands, solvents or chemical agents on the surface or opposite to the surface (via contra-diffusion by means of pumping such as shown schematically in Fig. 2) in order to improve the heterogeneous nucleation, to yield smoother, more even surface and to establish firmly anchored crystals into the support for better mechanical stability[22,29,39].

In ZIF-8 membrane synthesis, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is normally selected as the zinc source and 2-methylimidazole (MeIm, $\text{C}_4\text{H}_6\text{N}_2$) is used as the ligand source. Zinc nitrate was preferred because it reportedly resulted in both seed layers and membranes with better microstructures than the other zinc salts with excellent propylene/propane separation factor of 80[40] and 105[41], respectively when synthesized under microwave irradiation.

The two solutions containing the metal and ligand sources are mixed and stirred continuously. The support is then dipped in the seed suspension (or the precursor solution) and repeated (if necessary) to obtain defect free seed layer or to form membranes on top of each other (asymmetrical layer-by-layer). The seeded support is then placed in the secondary growth solution for few hours until the membrane is formed, taken out carefully and then rinsed thoroughly with fresh solvent to remove loose particles from the membrane's surface. The membrane is immersed again in fresh solvent for few days to allow for solvent exchange to take place. The membrane is finally dried prior to use. Fig. 3 shows the schematic procedure for ZIF-8 membrane synthesis following *in-situ* growth method.

2.2. Secondary growth technique

The secondary growth method reportedly offers better control of membrane microstructures than the *in-situ* growth method. This method requires attachment of ZIF-8 seeds onto the porous support prior to the crystal growth to provide sites for crystallization and improve control over the growth of the crystals. The seeds are attached onto the support surface by following 2 alternative routes; chemical (dip or slip coating approach) or physical attachment (rubbing mediated seeding)[29,39]. In chemical attachment, the support is seeded by dip-coating it in the saturated precursor solution (colloidal suspension) and then heat treated by either solvothermal processing or microwave irradiation to facilitate rapid nucleation and growth of the crystals to form the membrane[40,41].

In the secondary growth with physically attached seeds, ZIF-8 seeds dispersed in a solvent are used. The seeds are obtained after the precipitates are separated from the colloidal dispersion by centrifugation and washed with solvent and dried at room temperature under vacuum. The seeds are dispersed in the solvent by sonication to form ZIF-8 seed suspension. The seeds from the suspension are attached onto the support's surface by various seeding methods such as dip-coating, spin coating, etc.

Sodium formate (NaCOOH) is sometimes used together with the seed suspension as a deprotonating agent during the dip-coating process to complete the deprotonation of imidazole, improve the uniformity of the membrane and "heal" defects in the membrane[22,28]. Alternatively, ammonium hydroxide and 3-aminopropyltriethoxysilane (APTES) can also be used for the same purposes[22,38]. The procedure in the *in-situ* growth is repeated to develop the ZIF-8 membrane. Fig. 4 illustrates ZIF-8 membrane synthesis following the secondary growth method.

In another development, ZnO seeds were used instead of ZIF-8 crystals. The former was then converted into the ZIF-8 membrane. The motive for choosing this approach was to gain increased adhesion of the ZIF-8 membrane with the support. The method involves dis-

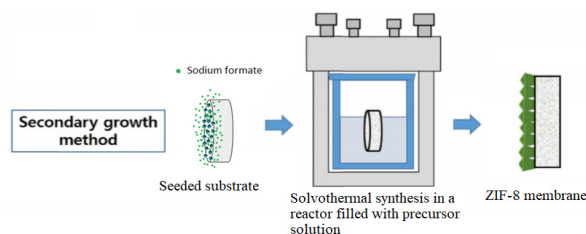


Fig. 4. Schematic illustration of ZIF-8 membrane synthesis from secondary growth method using sodium formate[29].

persion of ZnO seeds in a solvent such as dimethylformamide (DMF), methanol or water. The selected alumina substrate was then dip-coated into the ZnO solution followed by drying at 100°C for 12 hours and sintering at 450°C for 2 hours to form ZnO membrane. The ZnO membrane was then converted into ZIF-8 membrane by immersing the former in 2-methylimidazole solution[42]. This reactive seeding approach reportedly yielded mechanically strong yet flexible ZIF-8 membrane because the amphoteric nature of ZnO induced the electrophoresis of spatially charged dispersed particles in the solution.

2.3. Electrospray deposition

Electrospray deposition applies an electrostatic force on the seed solution at the tip of a capillary and the surface tension forces of the droplet. This method is relatively new and it offers a significant reduction in synthesis time and precursor consumption and easy control of membrane thickness, as well as simplification in the activation process[31]. Electrospray deposition method provides continuous evaporation-induced nucleation and crystallization to form ZIF-8 membrane in a single step, vis-à-vis multiple steps in the dip-coating, extended nucleation, crystallization and drying of the *in-situ* and secondary growth methods. This eases the scalability of the process for commercial application. Electrospray deposition requires that clean porous support be heated to a designated temperature from 70°C to 80°C before the precursor solution is sprayed on the hot support through the nozzle. The operating parameters affecting the membrane quality from electrospray deposition depend largely on the applied voltage, the di-

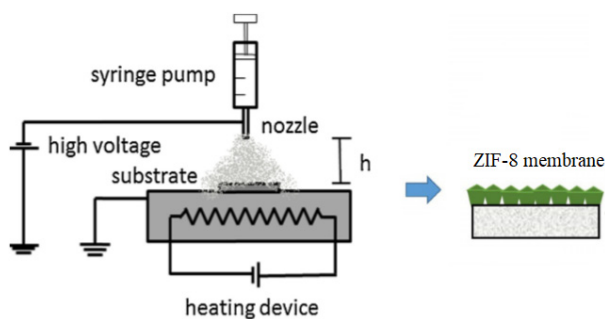


Fig. 5. Electro spray deposition setup where h is the distance between the nozzle tip and the support[31].

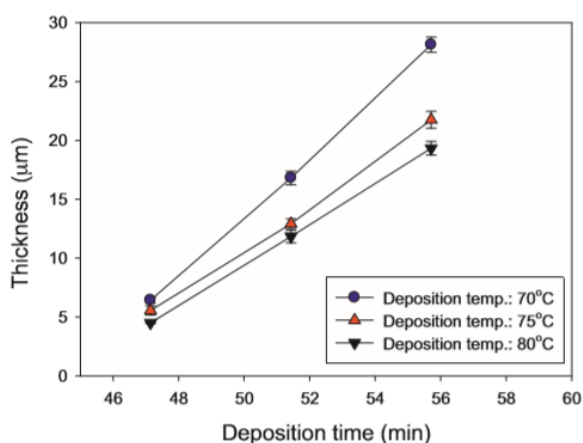


Fig. 6. Thickness of ZIF-8 membrane as a function of deposition temperature and time[31].

stance between the nozzle tip and the support, and the support or deposition temperature.

Fig. 5 depicts the schematic diagram of electro spray deposition using porous α -alumina disc as the support (or substrate) onto which the ZIF-8 precursor solution was sprayed. It reportedly produced well-intergrown and continuous membranes having thickness of about $28 \mu\text{m}$ in less than an hour when the following conditions were applied: substrate temperature of 70°C , flowrate of 0.7 mL/hr , voltage of 8 kV , and the distance between the nozzle tip and substrate hot surface, h , was maintained at 2 cm .

In electro spray deposition, the thickness of ZIF-8 membrane was found to be influenced predominantly by the deposition temperature and time such as shown in Fig. 6. By keeping the other parameters constant, the

membrane's thickness increased with increasing deposition time and decreased with increasing deposition temperature[31]. The decreased thickness with increasing deposition temperature was due to higher evaporation rates at higher temperature. Controlling the membrane's thickness is important in electro spray deposition because unnecessarily thick membrane development would create higher resistance to flow and limit the membrane's productivity. Since ZIF-8 membrane prepared by electro spray deposition is relatively new, it has not been applied for propylene/propane separation, despite its potential scalability.

3. Propylene Permeability and Selectivity in ZIF-8 Membranes

ZIF-8 membrane surface area defines how much gas can be accommodated per gram of the membrane material. High surface area is preferred since it is the indicator of greater amount of gas that can be adsorbed onto the membrane's pore surface. Higher surface area is correlated reciprocally with smaller average pore radii. The smaller the pore size, the greater the separation factor is. ZIF-8 exhibits inherent pore of 11.6 \AA with a small 6-membered ring pore aperture of 3.4 \AA [43]. ZIF-8 reportedly demonstrated surface area of $868 \text{ m}^2/\text{g}$ [44], $1,079 \text{ m}^2/\text{g}$ [45] up to ca. $1,700 \text{ m}^2/\text{g}$ [46], which is considered high. The increase in selectivity of propylene from 48.6 to 90.2 when water/methanol ratio was increased from 1/3 to 3/1 during ZIF-8 synthesis as reported previously came from the higher surface area of the membrane with tighter grain boundary structures as a result of complete ZnO into ZIF-8 conversion at higher water/methanol mixture[42]. Although ZIF-8 membrane generally exhibits high surface area, there is still room for improvement by creatively designing the membrane at the micro synthesis level.

Beside the membrane surface area, the properties of the gas molecules also play an important role in the permeability of the gases across the microporous membranes through molecular sieving. The molecular char-

Table 1. Propylene-propane Properties for Consideration in Separation by Relative Diffusivity and Molecular Sieving

Gas	Molecular diameter (nm)	T _c (K)	P _c (MPa)	MW (g/mol)
Propylene, C ₃ H ₆	0.40	369.55	4.23	42.08
Propane, C ₃ H ₈	0.43	365.57	4.66	44.10

acteristics include the molecular diameter, critical temperature, critical pressure and molecular weight of the gas species[47]. Table 1 shows that propylene exhibits smaller diameter and is lighter molecule than propane, thus the former is more diffusive in nature. The selectivity based on the relative diffusivity of propylene and propane is 1.02 by taking the inverse of the square root of the ratio of their molecular weights, which is extremely low for an effective physical separation.

ZIF-8 is claimed to exhibit the theoretical aperture of 0.34 nm, which is smaller than the molecular diameter of the gases. Despite its smaller pore size, ZIF-8 was reported to be able to open its pore aperture exclusively for propylene molecules on pressurization but exclude the propane molecules from entering its pore structure by the so called “gate opening” effect. This is possible due to the flipping motion of the ligand upon pressure increase or the introduction of the guest molecules in the ZIF-8 pore mouths or opening. Another view of this possibility is due to the orientation of the propylene molecule that fits nicely through the 8-membered oxygen ring of the ZIF-8 membrane at a specific angle. As a result separation of propylene from propane is possible and separation factor of higher than 20 was reportedly observed from the experiment. In a series of previous investigation, propylene/propane separation of ~130 was also possible from numerical simulation[48-50].

ZIF-8 membranes outperformed most of polymer based membranes for propylene/propane separation, the latter of which are still confined within the limitation demarcated by the Robeson’s upper boundary. It was reported that ZIF-8 membrane prepared by secondary growth method demonstrated separation factor of 29[30], 31[32], 35[33] and 89[34] for the propylene/propane system. Attempts to increase the separation factor us-

ing counter diffusion method in the synthesis of ZIF-8 membrane did not yield a promising result. Counter diffusion method yielded separation factor of merely 40[35] and 50[36]. Efforts to improve the propylene-propane separation factor from 59[51] to 71[21] by counter diffusion resulted in marked increase of membrane thickness, and reduced propylene permeance from $25.00 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s Pa}$ to $3.51 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s Pa}$, respectively.

Another attempt to use different technique, which was rapid thermal deposition, also did not give satisfactory separation level. With separation factor of merely 30 using rapid thermal deposition[16], a more recent attempt to improve the selectivity further was to use ultrathin ZIF-8 membranes on polymeric hollow fibers. However, the selectivity of 46 was achieved from this effort[20]. Further researches on improving ZIF-8 membrane performance seem to have made a little progress ever since. Comparison of separation performance of the results reported in the previous works is summarized in Table 2.

In a renewed interest to improve the separation performance of ZIF-8 membranes for propylene separation, sodium formate was introduced during the synthesis of ZIF-8 membranes on porous alumina support based on one step *in-situ*[21], counter-diffusion concept. The resulting membrane showed a separation factor of 71 for propylene/propane system[22]. They confirmed the role of sodium formate in the improved separation factor, the excess amount of which, led to rapid formation of ZIF-8 layer at the support interface. When sodium formate was tried in the counter-diffusion-based *in-situ* and microwave-assisted seeding technique, the propylene permeance was reduced by 75% while the separation factor increased to more than 6 times[26]. Learning that the secondary growth method has suc-

Table 2. Summary on the Binary Propylene/propane Past Performances by ZIF-8 Membranes from Different Synthesis Techniques

Preparation method	Thickness (μm)	C_3H_6 permeance ($10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$)	$\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation factor*	Reference**
Secondary growth	2.5	4.21	29	[30]
	2.5	4.82	31	[32]
	2.2	8.44	35	[33]
	3.0	0.88	89	[34]
Microwave irradiation	1.2	188.00	80	[40]
	-	-	105	[41]
Counter diffusion	1.0	19.50	40	[35]
	1.5	4.24	50	[36]
	80.0	25.00	59	[51]
	1.5	3.51	71	[21]
Rapid thermal deposition	5.0~20.0	2.90	30	[16]

* Knudsen separation factor for propylene/propane mixture = 1.

** Propylene/propane separation of 130 was observed from numerical simulation[48-50].

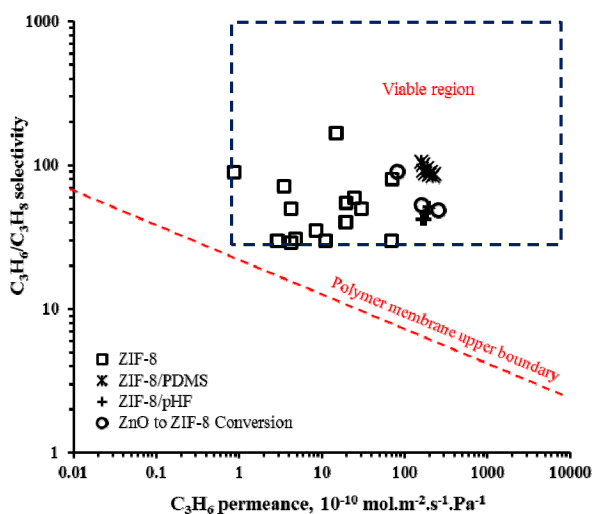


Fig. 7. Selectivity-permeance plot of ZIF-8 by secondary growth, modified ZIF-8 and ZIF-8 by reactive seeding (ZnO to ZIF-8 conversion) with viable region and upper limit of polymeric membrane for propylene/propane separation.

cessfully yielded the highest separation factor of 105 under microwave irradiation, the motivation to enhance the quality of ZIF-8 membrane further by introducing sodium formate in the membrane synthesis by the secondary growth method is on-going. The microwave synthesis however has not received widespread attention due to the limited accessibility and scalability for research and commercial application.

Fig. 7 shows the selectivity-permeance plot of ZIF-8 with viable region and upper limit of polymeric membrane for propylene/propane separation. The viable region considered commercially attractive is located in the upper right quadrant[52]. All the ZIF-8 membranes, regardless of their preparation methods fall within the region of interest. However, the modified ZIF-8 membranes with polydimethylsiloxane (PDMS) resulted in an unusually high permeance under high feeding pressures[53]. The PDMS coating was claimed to penetrate into the underneath ZIF-8 polycrystalline membrane, blocking the inter-crystalline defects and also hindering the flexibility of the ZIF-8 framework that caused the defects.

The ZIF-8 membranes prepared from ZnO via secondary growth also demonstrated significant propylene permeance of $258.3 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$, although at reduced selectivity of 48.6[42]. The application of ultrathin ZIF-8 membranes on polymeric hollow fibers (ZIF-8/pPHF)[20] too, resulted in improved permeance, rendering the membrane commercially viable despite lower propylene selectivity than ZIF-8/PDMS and ZIF-8 membrane prepared from the reactive seeding approach.

4. Navigating the Course for Improved ZIF-8 Membrane Performance

In-situ synthesis and seeded growth techniques that were originally developed for the synthesis of zeolite membranes have been successfully adapted to grow continuous ZIF-8 membranes. The resulting ZIF-8 membranes from these techniques demonstrate consistently high separation factor for propylene/propane separation. Other emerging techniques such as counter-diffusion synthesis and *in-situ* growth of ZIF-8 into solid-state nano-channel through pumping of the precursor solution into the pore surface substrate[54] are now capable of producing ZIF-8 membranes with enhanced microstructure, separation ability and healing property that prevent formation of defects in the membranes. This so-called “self-healing” property stems from the rapid re-crystallization of the ZIF-8 seeds in every direction which promotes the crystal growth, prevents and heals defect formation by filling up the micro gaps that exist between the crystals during the membrane synthesis.

The promising application of ZIF-8 membrane for propylene/propane separations by molecular sieve mechanism is made possible by the gate-opening effect which begins to be understood and increasingly gaining wider attention. Currently, the observed increase in selectivity is thought to come from the pore opening by flipping motion of the ligand upon pressure increase. Another view considers that the ZIF-8 material property which exhibits greater affinity for propylene (especially at higher pressure) to be the reason for the increased selectivity by preferential adsorption.

The contribution of membrane affinity for propylene is significant for ZIF-8 membrane because the membrane pore size lies in the *micro*-porosity regime. It was reported that zeolite 4 Å demonstrated kinetic selectivity of 223 allegedly due to the higher affinity of propylene than propane[55]. The kinetic selectivity is by the ratio of Henry’s constant multiplies the square root of the ratio of the diffusion coefficient of propylene to propane. The kinetic selectivity of pure silica chabazite (SiCHA) of 28 is reported[8] due to the low-

er affinity of propylene for the material than zeolite 4 Å. In a separate work, the incorporation of Fe²⁺ into a molecular sieve membrane was also seen to increase the C₃H₆/C₃H₈ sorption selectivity by 11%[56]. Thus, ZIF-8 membrane, modified by ligand exchange to improve propylene affinity, is expected to attract future researches. This would lead to the innovation of a newly hybrid membrane system with enhanced separation properties.

Although the innovative procedures in ZIF-8 membrane development have shown marked improvement in the propylene separation from propylene/propane mixture, the trade-off between selectivity and permeability in the membrane separation is quite revealing. Finding the most effective way to maximize the selectivity-permeability further is needed. The optimization of the operational parameters which is considered significant in improving the selectivity is important in order to ease the commercial development of ZIF-8 membranes and to enable wide-spread applications of the membranes in the industrial scale propylene purification. Advanced optimization techniques such as multi-objective optimization, response surface methodology and artificial neural network to optimize the operation of the integrated membrane system are considered a useful tool to achieve the objective. The one factor at a time (OFAT) technique such as varying one factor while keeping the other factors constant considered popular in the industry and academia failed to search for the global optimum[57].

Finally, the permeability-selectivity plot that is presently used to gauge the ZIF-8 membrane performance is expected to be replaced by purity-recovery plot for a more meaningful presentation of the membrane performance. This conversion not only provides useful information about the membrane’s performance, but also makes comparison between membrane and the other more established separation techniques such as PSA and cryogenic distillation possible. Overcoming the barriers for practical applications, such as improving the reliability and scalability of membrane processing, reducing membrane cost and evaluating the overall membrane

performance and long-term stability using real industrial gas streams should also be the focus of future efforts. This would enable wide-spread applications of the membranes in the industrial propylene purification.

5. Conclusion

ZIF-8 membranes demonstrated promising candidate for effective propylene/propane separation. The innovative ZIF-8 method such as addition of sodium formate as deprotonating agent during the membrane synthesis results in continuous, well-intergrown ZIF-8 crystal layer on α -Al₂O₃ support and provides the uniquely discovered re-crystallization that promote the self-healing effect. Preparation of ZIF-8 by innovative techniques should also lead to the development of membranes with increased number of affinitive sites, high surface area and narrow pore size distribution that are requisites for an excellent propylene selectivity.

Unconventional ZIF-8 membranes prepared by ligand-induced perm-selectivity that enhance the propylene separation by material affinity are expected to attract future researches. Hypotheses to explain the favorable outcomes from the material syntheses are discussed to guide future researches. This would lead to the innovation of a new membrane system with enhanced separation properties. The optimization of the operational parameters which is considered significant in improving the selectivity of the membrane unit operation is also important in order to ease the commercial development of ZIF-8 membranes and to chart the future for continuous improvement of ZIF-8 performance.

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