Defect-dependent Stability of Highly Propylene-Selective Zeolitic-Imidazolate Framework ZIF-8 Membranes

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Abstract

Membranes of ZIF-8, a prototypical zeolitic-imidazolate framework (ZIF) with a sodalite topology, have shown excellent propylene/propane separation performances based on molecular sieving mechanism. Although the long-term stability of ZIF-8 membranes is of critical importance for their practical applications, there are only a few studies reported on the subject. Here, we report the long-term binary propylene/propane performances of ZIF-8 membranes prepared by two distinctive synthesis methods. A battery of characterizations was employed to explain how different synthetic protocols led to the formation of ZIF-8 membranes with different bulk defect densities and surface defects, thereby affecting the long-term membrane stability. Finally, a post-synthetic ligand treatment is proposed as an effective means to mitigate the defects of ZIF-8 membranes, resulting in improved long-term separation performances.

Keywords: Zeolitic-imidazolate frameworks, gas separation, membranes, defects, long-term stability

1. Introduction

Membrane-based gas separation [1, 2] is of great interest as an alternative to conventional energy-intensive processes such as distillation because it is more energy-efficient, eco-friendly and cost-effective. In particular, membrane-based separation of propylene/propane mixture has been extensively studied by using polymer membranes [3, 4], carbon molecular sieve membranes [5, 6], and zeolite membranes [7]. There are, however, no propylene/propane separation membranes commercially available due to the limitations of current membrane materials and processing techniques with respect to the performance requirements such as separation factors and propylene permeances and/or the operational requirements such as chemical/mechanical stabilities and long-term performance stabilities.

Zeolitic-imidazolate frameworks (ZIFs) are a subclass of metal-organic frameworks (MOFs), possessing zeolite topologies originated from the metal-ligand-metal bond angle of 145° similar to the T-O-T bond angle in zeolites [8]. ZIFs have well-defined micro pores with relatively good chemical and thermal stabilities as compared to other MOFs [9]. A prototypical ZIF-8, composed of zinc ions interconnected with 2-methylimidazoles, is a particularly promising material for the kinetic separation of propylene/propane [10, 11] due to its effective pore size of $\sim 4 \text{ \AA}$ [12], which is in between the sizes of propylene and propane.

Several synthesis methods [13-16] have been developed for polycrystalline ZIF-8 membranes. However, only a handful of those resulted in highly propylene-selective membranes. Lai and co-workers were the first to report high-quality ZIF-8 membranes prepared using seeded growth in an aqueous precursor solution for light hydrocarbon separation [17] and for propylene/propane separation [18]. Hara et al. reported ZIF-8 membranes synthesized by the counter-diffusion method showing good propylene/propane separation [19-21]. Nair and co-

workers demonstrated ZIF-8 membrane grown on polymeric hollow fiber by interfacial microfluidic membrane processing (IMMP) for propylene/propane separation [16, 22]. Our group has reported several synthesis methods including counter-diffusion-based *in situ* growth [13, 14] (hereafter CD method), microwave-seeding and secondary growth [15] (hereafter, MW method), and most recent heteroepitaxial secondary growth [23] to prepare high-quality ZIF-8 and ZIF-67 (Co-substitute ZIF-8) membranes with unprecedented propylene/propane separation performances.

Defects in crystalline porous materials such as zeolites and MOFs are inevitable and studied widely [24-26]. Although limited, there are a few studies on the defects in ZIF-8. Tian et al. [27] reported surface compositions of ZIF-8 thin films by using X-ray photoelectron spectroscopy (XPS) and discovered various surface terminal groups including carbonates, water/hydroxides, and secondary amines in addition to 2-methylimidazoles. Cheng et al. [28] studied water-treated ZIF-8 for H₂ adsorption and found that water treatment led to water-terminated defects, thereby inducing enhanced H₂ uptake by 77% at ambient temperature. By drawing an analogy with zeolites, Zhang et al. [29] computationally characterized and categorized various possible point defects in ZIF-8 into linker vacancy, metal vacancy, and dangling linker. Based on the activation energies of defect formation, they concluded that those defects can be formed even in ambient conditions (in particular dangling linkers can form even at room temperature for ~ 1 hr).

The long-term stability of ZIF-8 membranes is crucial for their potential commercial applications. To the best of our best knowledge, however, there are only a few such studies reported so far [22, 30]. Liu et al.[30] studied the long-term stability of ZIF-8 membranes synthesized using the aqueous secondary growth recipe [17]. Their ZIF-8 membranes exhibited

1 stable propylene/propane separation performances over 40 days at 35 °C. Recently, Eum et al.
2 [22] reported the long-term stability of ZIF-8 membranes on polymeric hollow fiber membrane
3 fabricated by IMMP with an equimolar binary propylene/propane at 25 °C at 1 bar. During the
4 30 days of continuous operation, both selectivity and gas permeances were maintained.

5 Herein, we report the time-dependent selectivity and permeation behaviors of high-
6 quality ZIF-8 membranes prepared by the CD and MW methods. The time-dependent separation
7 performances of ZIF-8 membranes depend upon synthesis recipes. Upon a battery of
8 characterizations, we attribute the recipe-dependent long-term stability of ZIF-8 membranes to
9 defects including surface defects resulting from different synthesis conditions. In addition, the
10 effect of atmospheric water on membrane gas transport and separation performance is discussed.
11 Finally, we show a post-synthetic ligand treatment as an effective means to stabilize ZIF-8
12 membranes.

2. Materials and methods

2.1. Chemicals

Alpha-Al₂O₃ powder (CR6, Baikowski) was used to prepare alumina disks and polyvinyl alcohol (PVA 500, Duksan) was used as a binder for alumina disk preparation. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%, Sigma-Aldrich) and zinc chloride (ZnCl₂, 99.99%, anhydrous, Alfa Aesar) were used as metal sources. 2-methylimidazole (C₄H₆N₂, 99%, Sigma-Aldrich) was used as an organic ligand and sodium formate (HCO₂Na, 99%, Sigma-Aldrich) was utilized as a deprotonating agent. Methanol (CH₃OH, >99%, Alfa Aesar) and deionized water were used as solvents.

2.2. Preparation of porous α -Al₂O₃ supports, ZIF-8 powders, and ZIF-8 membranes

Porous α -Al₂O₃ disks (diameter ~ 22 mm and thickness ~ 2 mm) were used as supports and prepared by following a previously reported procedure [14, 15]. Briefly, 10 g of α -Al₂O₃ powders was mixed with 1 ml of an aqueous PVA binder solution. The binder solution was prepared by dissolving 3 g of polyvinyl alcohol in a mixture of 95 ml of D.I. water and 5 ml of 1 M HNO₃. 2.1 g of the alumina and binder mixture was then pressed at 10 t for 1 min. The supports were sintered at 1100 °C for 2 hrs and one side of the sintered supports was polished with a sand paper (grit# 800). Before usage, a support was immersed in methanol and sonicated for 1 min followed by drying at 120 °C for 1 hr.

ZIF-8 membranes were synthesized using both the CD method and the MW method as reported previously from our group [13-15]. For CD-ZIF-8 membranes, a metal precursor solution and a ligand precursor solution were prepared by dissolving 0.98 g of zinc chloride in 40 mL of methanol and by dissolving 5.19 g of 2-methylimidazole (hereafter mIm) and 0.5 g of

sodium formate in 40 mL of methanol, respectively. Sodium formate was dried in an oven at 100 °C for 6 hrs under vacuum prior to usage. An alumina support was soaked in the metal precursor solution for 1 hr. The support saturated with the metal solution was inserted into a Teflon holder and then placed vertically into a Teflon-lined autoclave filled with 40 ml of the ligand solution followed by solvothermal treatment at 120 °C for 4 hrs. After cooled down to room temperature, the sample was rinsed several times with methanol and immersed in 35 ml of fresh methanol for 12 hrs. The back side of the sample was polished with sand papers (grit # 350) to remove crystals formed on the back side. Finally, the membranes were washed in 35 ml of fresh methanol for 5 days and dried at room temperature for 5 hrs and 60 °C for 1 hr. Homogeneously-formed ZIF-8 crystals were collected from the residual solution after membrane synthesis. The crystals (hereafter CD-ZIF-8 crystals) were washed and centrifuged for 4 times with fresh methanol followed by drying at 70 °C under vacuum for 12 hrs.

MW-ZIF-8 membranes were synthesized using our previously reported microwave method [15]. For microwave-assisted seeding, 2.43 g of zinc nitrate hexahydrate was dissolved in 40 ml of methanol and 2.59 g of mIm and 0.125 g of sodium formate were dissolved in 30 ml of methanol. A dried alumina support was placed vertically with the polished side facing down using a Teflon holder and soaked in the metal precursor solution for 1 hr. Afterwards the metal-soaked support was inserted in a microwave-resistant glass tube filled with the ligand precursor solution. Microwave irradiation was immediately applied with the power of 100 W for 1.5 min. After cooled down to room temperature, the seeded support was thoroughly rinsed with methanol and kept in 35 ml of fresh methanol for 1 day followed by drying at 60 °C for 4 hrs. The secondary growth of the ZIF-8 seed layer was carried out based on the aqueous recipe reported elsewhere [18]. For secondary growth, aqueous metal and ligand precursor solutions were

1 prepared by dissolving 0.11 g of zinc nitrate hexahydrate and 2.27 g of m-Im in 20 ml of DI
2 water, respectively. The seeded alumina disk was placed vertically using a Teflon holder in a
3 beaker. Meanwhile, the metal precursor solution was added into the 20 ml of the ligand precursor
4 solution and stirred for 2 min. Then the aqueous solution mixture was poured into the beaker
5 containing the seeded support. The beaker is then placed in a static oven at 30 °C for 6 hrs. The
6 resulting membrane was then washed in 35 ml of fresh methanol for 5 days and dried at 60 °C
7 for 6 hrs. Similar to CD-ZIF-8 powers, homogeneously-formed ZIF-8 crystals after the
8 secondary growth (hereafter MW-ZIF-8 crystals) were collected, washed and dried.

9 **2.3. Propylene/propane gas permeation test**

10 Propylene/propane binary gas permeation measurements were carried out at room
11 temperature under atmospheric pressure using the Wicke–Kallenbach technique (see Fig. S1a).
12 An equimolar propylene/propane mixture was used as a feed. The feed and argon sweeping gases
13 were supplied to the feed and permeate sides at a flow rate of 100 cc/ min, respectively. The
14 composition of the permeate side stream was analyzed using a gas chromatography (Agilent GC
15 7890A equipped with a column of HP-PLOT/Q). For thermal activation studies, as-dried ZIF-8
16 membranes were subjected to further drying at 100 °C for 12 hrs under vacuum and gas drying
17 units were installed to dehumidifying feed gases. During off-stream measurements, two different
18 arrangements were devised depending on whether the permeation cell containing a ZIF-8
19 membrane inside is opened to ambient condition (open cell) or isolated from ambient condition
20 (closed cell) after each measurement (see Figure S1b). All permeation cells were kept in a fume
21 hood (RH: 30 ~ 80 %) regardless of open or closed cell arrangements.

22 **2.4. Characterizations**

X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex II powder X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Electron micrographs were taken using a JEOL JSM-7500F operating at 5 keV acceleration voltage and 15 mm working distance. Solid state nuclear magnetic resonance (NMR) spectroscopy of ZIF-8 powders were taken by using a Varian INOVA 400 MHz solid-state NMR spectrometer equipped with a 7.5 mm CP/MAS probe for ^{15}N NMR (40.52 MHz) spectra. It is operated at 10 kHz of constant spinning frequency with 4 s of a pulse delay time and 1 ms of a contact time. ZIF-8 powders were packed into 7.5 mm zirconia rotors and sealed with Kel-F short caps. Infra-red spectra were collected using a NICOLET IR100 FT-IR spectrometer. Pulverized ZIF-8 particles were homogeneously mixed with KBr and pelletized for IR measurements. Note that it is repeated at least three times for each sample. Thermal gravimetric analysis (TGA) of ZIF-8 powders were conducted using a TGA system (Q50, TA instrument) from room temperature to 800 °C with a ramp rate of 5 °C/min under nitrogen environment. N₂ adsorption measurements were conducted using an ASAP 2000 (Micrometrics). X-ray photoelectron spectra were collected on an Omicron XPS instrument with a DAR 400 dual Mg/Al X-ray source. The survey spectra were collected over an energy range of -10 – 1100 at 1 eV/step with 100 eV pass energy. High resolution spectra for individual element (C 1s, N 1s, O 1s, and Zn 2p) were collected over the energy range of 20 eV at 0.05 eV/step and pass energy of 50 eV. Data analysis was performed using CasaXPS software (Casa Software, Ltd.) and peaks were fitted with a range of 1.5 – 2.5 fwhm.

3. Results and discussion

3.1. Comparison of CD-ZIF-8 and MW-ZIF-8 membranes

ZIF-8 membranes were synthesized using two different synthesis protocols, the CD method (denoted CD-ZIF-8 membranes) and the MW method (denoted MW-ZIF-8 membranes). It should be noted that there are several differences in the two methods: solvent (methanol vs. water), deprotonating agent (with vs. without), zinc source (zinc chloride anhydrous vs. zinc nitrate hexahydrate), reaction time (30 min vs. 6 hrs), and reaction temperature (120 °C vs. 30 °C) as summarized in detail in Table 1.

Table 1 Synthesis conditions of CD-ZIF-8 and MW-ZIF-8 power samples

	CD-ZIF-8	MW-ZIF-8
Zinc source	Zinc chloride (anhydrous)	Zinc nitrate hexahydrate
Solvent	Methanol	D.I. water
Deprotonator	Sodium formate	None
Reaction temperature	120 °C	30 °C
Reaction time	30 min*	6 hrs
Drying condition	R.T. for 5 hrs 60 °C for 1 hr	60 °C for 6 hrs

* Although the overall reaction time of CD-ZIF-8 powder and membrane synthesis is 4 hrs, the majority of crystals formed in 30 mins as evidenced by XRD in previously reported by Kwon et al.[14]

Fig. 1 shows electron micrographs of CD-ZIF-8 and MW-ZIF-8 membranes before and after 60 days of off-stream measurements. As can be seen in Figs. 1 and S2, as-synthesized membranes possess different microstructures in grain size and thickness: the MW-ZIF-8 membrane is ~ 1.6 µm thick with grains of ~ 1 µm in size (Figs. 1a and S2a) while the CD-ZIF-8 membrane is ~ 1 µm thick with grains of ~ 0.5 µm in size (Figs. 1c and S2c). Even after 60 days

of off-stream measurements, no significant changes in the membrane microstructures were observed under SEM (see Fig. S2b and S2d). Fig. 2 presents the XRD patterns of the membranes before and after the off-stream measurements. The (110) peak intensity of the MW-ZIF-8 membrane is slightly greater than that of the CD-ZIF-8 membrane likely due to the fact that the former is thicker than the latter. Furthermore, there is little change in the XRD patterns even after 60 days of off-stream measurements, indicating that the crystallinities of both membranes were not compromised.

Figure 1 SEM images of as-synthesized CD-ZIF-8 and MW-ZIF-8 membranes (a, c) and after 60 days of off-stream measurement (b, d).

Figure 2 XRD patterns of (a) ZIF-8 simulated pattern, CD-ZIF-8 membrane (b) before and (c) after 60 days of off-stream measurements, and MW-ZIF-8 membrane (d) before and (e) after 60 days of off-stream measurements.

Fig. 3 compares the time-dependent off-stream propylene/propane binary gas separation performances of ZIF-8 membranes (see Table S1 for the absolute performances of the membranes). The propylene permeance of the CD-ZIF-8 membrane dropped by ~75% of its initial value while the selectivity increased 6 times of its initial value after 60 days of measurement. In contrast, the MW-ZIF-8 membrane showed much stable separation performance: although the propylene permeance decreased by ~ 25%, the selectivity remained constant even after 60 days of measurement. This drastic contrast in the long-term permeation behaviors of the CD-ZIF-8 and MW-ZIF-8 membranes is likely due to the difference in their defects including surface defects (i.e., the CD-ZIF-8 membrane is more defective, thereby more prone to change). It should be noted that the MW-ZIF-8 membranes are not as stable as previously reported ZIF-8 membranes by Lin and coworkers [30] even though the MW-ZIF-8

membranes were prepared under the similar aqueous secondary growth conditions as for the membranes by Lin and coworkers [30].

Figure 3 Time-dependent performances of (—■—) CD-ZIF-8 and (—●—) MW-ZIF-8 membranes. Note that separation factors and propylene permeances are normalized with respect to the initial values.

3.2. Defects of ZIF-8 membranes

Formation of defects in crystalline materials depends on kinetic variables such as temperature, chemical compositions, etc. In general, given similar conditions, the faster the crystals form, the more defective the crystals become due to the kinetic trapping of structures at local energy minima. The CD membranes were more rapidly synthesized as compared to the MW membranes due in part to the presence of a deprotonating agent (i.e., sodium formate). It is our hypothesis that the faster CD method produces more defective ZIF-8 membranes (both in grains and grain boundaries), thereby more reactive and less stable than the slower MW method. Moreover, Zhang et al. [29] reported in their recent work on computational characterization of point defects in ZIF-8 that when formate ions are present in an aqueous solution, linker vacancy formation is favorable under both synthesis and post-synthesis steps. It was hypothesized that

formates may play an important role in the formation of defects (both bulk and surface) in ZIF-8 (CD-ZIF-8 crystals) during the synthesis step by increasing the reaction rate as a deprotonator as well as by competing with mIm as a modulating agent [31].

To prove the above-mentioned hypothesis, homogeneously-grown ZIF-8 crystals were collected from the mother solution of the CD-ZIF-8 membrane synthesis as well as from the mother solution after the secondary growth of the MW-ZIF-8 membranes (denoted CD-ZIF-8 and MW-ZIF-8, respectively). As summarized in Table 1, CD-ZIF-8 powders were prepared in methanol using zinc chloride in the presence of sodium formate while MW-ZIF-8 crystals were prepared in water using zinc nitrate without sodium formate. Though both ZIF-8 powder samples show well-faceted crystals (Fig. 4), the CD-ZIF-8 crystals are much bigger than the MW-ZIF-8 crystals, indicating that the crystallization of the CD-ZIF-8 is faster than that of the MW-ZIF-8 likely due to the higher synthesis temperature and the presence of sodium formate.

Figure 4 SEM images of (a) CD-ZIF-8 and (b) MW-ZIF-8 powders

Figure 5 presents the normalized ^{15}N solid state NMR spectra for CD-ZIF-8 and MW-ZIF-8 powders. As shown in the figure, the CD-ZIF-8 peak is noticeably broader than that of MW-ZIF-8, clearly implying that the CD-ZIF-8 is more defective than MW-ZIF-8. N_2 adsorption

analyses were conducted for both ZIF-8 particles and their BET surface areas are summarized in Table 2. Cheng et al. [28] related the reduction in the surface area of ZIF-8 crystals to the defects: the more defective the crystals, the smaller the surface area. As can be seen in the table, the CD-ZIF-8 exhibits substantially reduced surface area (~ 21% less) compared to the MW-ZIF-8, suggesting that the CD-ZIF-8 crystals are likely more defective than the MW-ZIF-8 crystals. Furthermore, the FT-IR spectra of the selected vibrations (see Fig. 6) were compared. As shown in the figure, given the similar sample amounts, the CD-ZIF-8 sample displayed notably less absorbances than the MW-ZIF-8 samples, indicating that the CD-ZIF-8 sample is possibly more defective as observed by Cheng et al. [28]. This observation is further corroborated by TGA results (see Fig. 7), showing that the weight loss started at ~ 400 °C for the CD-ZIF-8 power sample which is substantially lower than ~ 560 °C for the MW-ZIF-8 sample. Initial weight loss of MW-ZIF-8 at 100 °C is likely due to the removal of water trapped in framework during synthesis (note that water was used as a solvent). Besides, when both CD-ZIF-8 and MW-ZIF-8 membranes were exposed to steam and ligand vapor at 145 °C, as shown in Fig. S3, the CD-ZIF-8 membrane underwent a rather dramatic change while the MW-ZIF-8 membrane remained intact, consistent with the above observation that the CD-ZIF-8 membrane is more defective, thereby less stable [32].

Surface termination of ZIF-8 membranes may vary depending on synthesis methods. Specifically, ZIF-8 membranes are likely to be terminated with zinc rich surfaces [33] and under coordinated zinc sites are saturated by negatively charged components available in synthetic and/or post synthetic conditions [27]. Surface terminations of as-synthesized CD- and MW-ZIF-8 membranes were investigated by XPS (see Figure 8). Both membranes exhibited a negligible difference in the N spectra, whereas the clear presence of formate moieties was observed in the

CD-ZIF-8 membrane in the C spectra. The O spectra showed the relatively strong peaks of carbonate and hydroxide terminal groups in the MW-ZIF-8 membrane as compared to the CD-ZIF-8 membrane. This XPS observation strongly suggests that MW-ZIF-8 membranes are mostly terminated with carbonates and hydroxides due to the water in the synthesis solution while CD-ZIF-8 membranes are likely terminated with formates along with the water-associated terminal groups. It is our hypothesis that the formate terminal groups are less stable in the presence of residual and/or ambient water than the water-originated surface terminal groups such as hydroxides and carbonates.

Preceding results suggest that as compared to MW-ZIF-8 membranes, CD-ZIF-8 membranes possess more bulk defects (i.e., more defective grains) and more reactive surfaces (i.e., more reactive grain boundaries and external surfaces). As a result, CD-ZIF-8 membranes are more prone to undergoing changes not only in their local structures but also their surface structures in the presence of water. These structural changes might result in the improved grain boundary structures, thereby reducing the propylene permeance while enhancing the propylene/propane separation factor.

Table 2 Surface areas of ZIF-8 powder samples. The reference values of ZIF-8* were taken from Park et al.[8]

	Langmuir surface area ² (m /g)	BET surface area ² (m /g)
CD-ZIF-8	1882.4	1160.1
MW-ZIF-8	2387.5	1474.8
ZIF-8*	1810	1630

Figure 5 ^{15}N solid state NMR spectra of CD-ZIF-8 (—) and MW-ZIF-8 (—) powders.

Figure 6 FT-IR spectra of CD-ZIF-8 (—) and MW-ZIF-8 (—) powders: (a) C=C-N twisting (out-of-plane bending, 995cm^{-1}), (b) =C-H bending and C-N bending (1146 cm^{-1}), (c) C-H symmetric and asymmetric stretching of CH_3 (2932 and 2957cm^{-1} , respectively), and (d) =C-H asymmetric stretching (3134 cm^{-1})

Figure 7 Thermal Gravimetric Analysis (TGA) results of CD-ZIF-8 (—) and MW-ZIF-8 (—) powders.

Figure 8 Comparison of high resolution XPS spectra of CD-ZIF-8 (bottom) and MW-ZIF-8 (top) membranes. N, C, O and Zn from the left.

3.3. Thermal activation of CD-ZIF-8 membranes prior to off-stream measurement

As mentioned above, we hypothesized that the ambient water molecules as well as the residual water molecules in the framework might lead to changes in both bulk and surface structures of more defective CD-ZIF-8 membranes, consequently affecting their performance during the off-stream measurements. It is worthy of mentioning here that relative humidity in Texas (RH: 30 ~ 80 % in a fume hood) is significantly higher than that in Arizona (RH: 20.9 ~ 23.6 %) [30]. It is reminded that the long-term stability measurements were conducted in an open cell arrangement where the membranes were exposed to ambient conditions between permeation measurements (Figure S1b). To test this above-mentioned hypothesis, first, we dried the CD-ZIF-8 membranes at 100 °C for 12 hrs under vacuum to remove any solvent molecules trapped in the framework. Second, to prevent ambient water molecules from contacting ZIF-8 membranes in-between permeation measurements, we isolated the permeation cell between the permeation measurements (i.e., closed cell arrangement) by capping the four union fittings connected to the cell (Fig. S1b). The CD-ZIF-8 membrane dried at 100 °C before the off-stream measurement and kept in a closed cell is denoted CD-ZIF-8-100-C while maintained in an opened cell is named CD-ZIF-8-100-O.

After membranes were additionally activated at 100 °C under vacuum, as presented in Fig. S6, the selectivities remained the same while the propylene permeances dropped significantly. It is surmised that the additional activation at 100 °C for 12 hrs under vacuum might have decreased the sticking coefficients of gases on the membrane surface due to the rearrangement of surface terminal groups, thereby reducing gas adsorption which in turn resulted in decreased permeances but similar selectivities. The time-dependent off-stream measurement results are plotted in Fig. 9. Several observations can be made. First, the propylene permeances

of CD-ZIF-8 membranes regardless of open vs closed cell arrangement, when further activated at 100 °C for 12 hrs under vacuum, decreased less than that of the as-activated membranes. The time-dependent selectivity of the CD-ZIF-8 membranes after further activation, however, shows a stark contrast depending on whether the cell is open or closed between the measurements: when open, the selectivity increases while when closed, the selectivity is relatively stable, though slightly decreased. This relatively stable selectivity and propylene permeance of the CD-ZIF-8-100-C membranes can be explained by the fact that the membranes are completely isolated from ambient water before and during the measurements. With no water interacting with defects (both bulk and surface defects), the membranes show more stable long-term performances.

Figure 9 Time-dependent separation performances of (—■—) CD-ZIF-8 and (—▲—) CD-ZIF-8-100-O, (—◆—) CD-ZIF-8-100-C. Note that separation factors and propylene permeances are normalized with respect to the initial values.

3.4. Post-synthetic ligand treatment to stabilize the performance of CD-ZIF-8 membranes

Based on the observations made above, in order to stabilize the performance of CD-ZIF-8 membranes, we reasoned it critical to reduce their defects (in particular, surface defects). We reckoned that post-synthetic ligand treatment (PL) might reduce more reactive defects such as formate terminal groups, thereby stabilizing CD-ZIF-8 membranes. It is noted that post-synthetic

1 ligand treatment was used to stabilize defective ZIF-67 membranes in our recent report [23]. CD-
2 ZIF-8 membranes were post-synthetically treated at 60 and 120 °C in aqueous ligand (mM)
3 solutions with two different ligand concentrations (15 and 25 wt. %) and named according to
4 treatment conditions (denoted CD-PL-120-15, CD-PL-120-25, and CD-PL-60-25, respectively),
5 as described in the Supplementary Information. After the post-synthetic ligand treatment, as seen
6 in the electron micrographs (Fig. 10), ZIF-8 membranes treated at 120 °C regardless of ligand
7 concentrations underwent more drastic morphological change than CD-PL-60-25. The XRD
8 patterns of the treated membranes (see Fig. 11) suggest that while all membranes retained crystal
9 structures, when treated in 25 wt. % ligand solutions, the crystallinities of the membranes were
10 somewhat compromised as evidenced by the reduction in the (110) peak intensity. The
11 membranes treated at 120 °C did not show any gas separation regardless of the ligand
12 concentrations. On the contrary, as shown in Fig. 12, the membranes treated at 60 °C with 25 wt.
13 % ligand concentration exhibited much enhanced long-term stability as compared with untreated
14 CD-ZIF-8 membranes: the separation factor initially increased two folds then remained
15 unchanged while the permeance value dropped initially and then stabilized. Table S2 shows the
16 absolute values of binary gas performance data. After post-synthetic ligand treatment, the
17 propylene permeance of the CD-ZIF-8 membrane was decreased while its selectivity was
18 increased. The enhanced selectivity with decreased permeance is most likely due to the healing
19 of the grain boundary defects by the post-synthetic ligand treatment, leading to the reduction in
20 the non-selective diffusion pathways. This explanation is supported by the XPS analysis after the
21 hydrothermal ligand treatment as presented in Figure S6. As shown in the figure, the more
22 reactive secondary amine and formate moieties were notably decreased while the less reactive
23 hydroxide and carbonate moieties increased. This strongly suggests that the hydrothermal ligand

treatment saturates under coordinated surface zinc sites with more stable surface terminal groups such as hydroxide moieties, thereby making the membranes more stable.

Figure 10 SEM images of top (upper) and cross-sectional (lower) views of (a, b) CD-PL-60-25, (c, d) CD-PL-120-15, and (e, f) CD-PL-120-25, respectively

Figure 11 XRD patterns of (a) CD-ZIF-8, (b) CD-PL-120-15, (c) CD-PL-120-25, and (d) CD-PL-60-25 membranes

Figure 12 Time-dependent propylene/propane separation performances of CD-ZIF-8 membranes (ZIF-8-PL-60-25) (—●—) before and (—■—) after ligand treatment. Note that separation factors and propylene permeances are normalized with respect to the initial values.

4. Conclusion

In conclusion, we report the time-dependent propylene/propane separation performances of highly propylene-selective ZIF-8 membranes prepared by two different synthesis methods, counter-diffusion-based *in situ* (CD method) and microwave-assisted seeding and secondary growth (MW method). ZIF-8 membranes prepared by the CD method (CD-ZIF-8 membranes) were found to be less stable than those by the MW method (MW-ZIF-8 membranes). The propylene permeance of CD-ZIF-8 membranes was reduced by ~ 75% after 60 days while their propylene/propane selectivity increased more than 6 times. The relative instability of CD-ZIF-8 membranes was attributed to the more defective nature (both bulk and surface) of the CD-ZIF-8 membranes resulting from the faster crystallization in combination with other synthesis parameters such as the presence of sodium formate. It was shown that the high energy defect sites on the CD-ZIF-8 membranes likely underwent local structural changes, especially on the grain boundaries in the presence of ambient water, resulting in the dynamic permeation behaviors of the membranes. Lastly, the long-term stability of the CD-ZIF-8 membranes was

improved by post-synthetically treating the membranes in an aqueous ligand solution possibly resulting from the reduction of defects upon the treatment. The current study is a significant step forward in the practical applications of these promising ZIF-8 membranes by not only providing understanding on the long-term stability of the membranes but also offering ways to improve their stability.

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Supporting Information

Defect-dependent Stability of Highly Propylene-Selective Zeolitic-Imidazolate Framework ZIF-8 Membranes

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6. Binary gas permeation test

Figure S1 Schematic diagram of binary gas permeation in Wicke-Kallenbach technique (a) and different permeation cell arrangements (b). The permeation cell is connected to feed, sweep, and permeate lines, accordingly to start measurement. After measurement, the cell is disconnected, marked with asterisks, and kept with membrane inside the cell remained opened, exposed to ambient atmosphere (18~21 °C, RH: 30~ 80%). For thermal activation studies, for controlled measurements, the selected cell remained closed after each permeation measurement until next measurement.

7. Comparison of CD-M-ZIF-8 and MW-W-ZIF-8 membranes

7.1. Comparison of microstructure of CD and MW-ZIF-8 membranes

Figure S2 SEM images of cross-sectional views of as-synthesized CD-ZIF-8 and MW-ZIF-8 membranes (a, c) and after 60days of off-stream measurement (b, d), respectively.

7.2. Absolute values of the off-stream measurements of as-synthesized CD-ZIF-8 and MW-ZIF-8 membranes

Table S1 Permeances and separation factors of ZIF-8 membranes presented in Figure 3

Day	Separation factor		Propylene permeance $\times 10^{-10} \text{ mol/Pa} \cdot \text{m}^2 \cdot \text{s}$	
	CD-ZIF-8	MW-ZIF-8	CD-ZIF-8	MW-ZIF-8
0	14.97	207.57	296.14	157.84
0.25	19.02	212.14	288.66	159.58
0.5	20.01	212.64	280.22	162.57
1	21.41	210.44	272.07	160.89
3	24.06	216.32	252.20	166.27
5	27.40	219.80	282.53	161.74
10	32.48	215.99	256.94	148.31
15	51.90	222.23	109.89	137.11
30	88.88	236.40	81.07	129.37
60	95.14	231.84	75.47	121.18

8. Defects of ZIF-8 membranes

Figure S3 SEM images of CD-ZIF-8 and MW-ZIF-8 membranes hydrothermally treated in the presence of ligand at 145 °C for 9 and 24 hrs. Each membrane was inserted in Teflon-lined autoclaves with 1.5g of 2-methylimidazole and 1ml of water without direct contacting with any solvent and incubated in preheated convection oven at 145°C. After post-synthetic hydrothermal treatments in vapor phase, CD-ZIF-8 membrane lost crystal facets, whereas, MW-ZIF-8 membrane showed negligible changes even after 24 hrs at 145 °C. This work is from recent publication of Kwon et al.[1]

9. Thermal activation of CD-M-ZIF-8 prior to off-stream measurement

Figure S4 XRD patterns of simulated ZIF-8 pattern, CD-ZIF-8 and CD-ZIF-8-100 membranes

Figure S5 Off-stream measurement of CD-ZIF-8 and CD-ZIF-8-100-O, CD--ZIF-8-100-C membranes

1 **Table S2** Table of absolute values of the off-stream measurements in Figure 6

Day	Separation factor			Propylene permeance ⁻¹⁰ (10 ² mol/Pa·m · s)		
	CD-M-ZIF-8	CD-M-ZIF-8- 100-O	CD-M-ZIF-8- 100-C	CD-M-ZIF-8	CD-M-ZIF-8- 100-O	CD-M-ZIF-8- 100-C
0	54.06	63.56	52.90	134.18	66.03	71.67
5	64.24	84.28	51.39	105.47	55.80	66.47
10	N/A	N/A	49.33	N/A	N/A	57.53
15	80.11	82.68	49.14	88.5	53.05	54.29
30	83.01	86.13	43.39	84.9	52.78	49.93

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10. Post-synthetic ligand treatment to stabilize membrane performance

Hydrothermal ligand treatment was conducted post-synthetically to stabilize CD- ZIF-8 membranes. Ligand solution is prepared by dissolving 3 mg and 5 mg 2-methylimidazole in 20 ml water to prepare 15 wt% and 25 wt% ligand solutions, respectively. As-synthesized CD-ZIF-8 membranes were inserted vertically using house-made Teflon holder in Teflon-lined autoclave with 20 ml of aqueous ligand solution. Autoclaves were incubated in pre-heated convection oven at 60 and 120 °C for 4 hours followed by cool down to room temperature. Membranes were washed in 30 ml fresh methanol for 1 day followed by drying at room temperature for 12 hours.

Figure S6 Comparison of high resolution XPS spectra of CD- ZIF-8 and CD-PL-60-25 membranes

1 **Reference**

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