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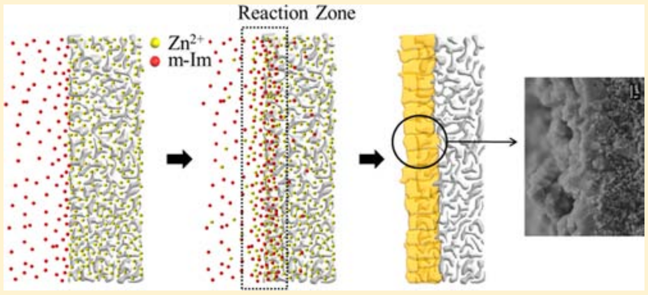
In Situ Synthesis of Thin Zeolitic−Imidazolate Framework ZIF-8 Membranes Exhibiting Exceptionally High Propylene/Propane Separation

Hyuk Taek Kwon[†] and Hae-Kwon Jeong*[,†,‡]

[†]Artie McFerrin Department of Chemical Engineering [‡]Materials Science and Engineering Program, Texas A&M University, College Station, TX-77843, United States

Ⓢ *Supporting Information*



ABSTRACT: Metal−organic frameworks (MOFs) are a class of hybrid porous crystalline materials comprising of metal centers coordinated to organic linkers. Owing to their well-defined pores and cavities in the scale of molecules combined with abundant surface chemistry, MOFs offer unprecedented opportunities for a wide range of applications including membrane-based gas separations. It is not straightforward (often requiring multiple steps) to prepare membranes of MOFs due to the fact that the heterogeneous nucleation and growth of MOF crystals on porous supports are not generally favored. Furthermore, the performance of polycrystalline MOF membranes strongly depends on the membrane microstructure, in particular, the grain boundary structure. Here we report a simple one step *in situ* method based on a counter-diffusion concept to prepare well-intergrown ZIF-8 membranes with significantly enhanced microstructure, resulting in exceptionally high separation performance toward propylene over propane.

■ INTRODUCTION

Due to the close physical properties, olefin/paraffin separation (such as propylene/propane) is quite challenging, yet commercially very important.[1−3] Separation of olefin/paraffin mixtures is traditionally performed using highly energy-intensive cryogenic distillation.[1,3] Membranes have therefore gained tremendous interest as an energy-efficient alternative technology. It has been proposed that in order for membranes to be commercially viable a minimum propylene permeability of 1 Barrer and a propylene selectivity of 35 are required.[4] So far, there have been many different types of membranes studied including polymer,[3] zeolite,[5] carbon molecular sieve,[6−8] mixed matrix,[9] and facilitated transport membranes.[10] However, most of these membranes suffer from certain limitations one way or another. For example, most of polymeric membranes do not meet the selectivity/permeability threshold while suffering from low reliability and durability.[3] The selectivity/permeability performance targets are met neither by more robust membranes, such as zeolites and ceramics, nor by mixed matrix membranes consisting of highly selective phases dispersed in polymer matrix until recently. Facilitated transport membranes can be easily poisoned by small amount of impurities, while carbon molecular sieve membranes are brittle and difficult to scale-up the production. Accordingly, it is evident that new material paradigms are essential to successfully address this energy-intensive yet industrially important separation.

Metal−organic frameworks (MOFs) are a new class of nanoporous organic−inorganic hybrid materials that exhibit regular crystalline lattices with rigid pore structures.[11−13] With unprecedented control over pore size and chemical/physical properties via a judicious choice of organic linkers, MOFs offer unique opportunities to overcome the limitations of not only current membrane materials but also conventional membrane system design/integration and operation.[14−16] An important subclass of MOFs, especially when considering gas separation applications, is zeolitic-imidazolate frameworks (ZIFs).[17−19] ZIFs consist of metal nodes (usually zinc or cobalt) connected to imidazole (or its derivative) linkers and exhibit zeolite-like structures due to the metal−linker−metal bond angle of ∼145° (close to the T−O−T angle found in zeolites).[17] ZIFs have been extensively investigated for gas separation membranes mainly due to their exceptional stability and ultramicropores.[20−25] Of particular interest is ZIF-8 composed of Zn and 2-methylimidazole ligands, forming the sodalite (SOD) zeolite structure with large cavities (11.6 Å) and small pore apertures (3.4 Å).[17] Recently Li et al.[26] have reported that propylene (∼4 Å) diffuses in ZIF-8 2 orders of magnitude faster than propane (∼4.3 Å),[27] suggesting that high-quality ZIF-8 membranes could effectively distinguish propylene from propane based on size.

So far, several research groups have reported diverse synthesis protocols for ZIF films and membranes.[16,28] In order to achieve well-intergrown ZIF membranes, it is critical to favor the heterogeneous nucleation and crystal growth of ZIFs

Received: April 20, 2013
Published: June 12, 2013

dx.doi.org/10.1021/ja403849c | *J. Am. Chem. Soc.* 2013, 135, 10763−10768

on porous supports over the homogeneous nucleation and crystal growth in solutions. To promote the heterogeneous nucleation and crystal growth, a number of different strategies have been devised including the chemical modification of support surfaces[20,25] and the anchoring of seed crystals on supports,[29−31] making ZIF membrane synthesis complicated. The added complexity not only increases the cost of membrane manufacturing but also often leads to poor membrane microstructure (i.e., grain boundary structure). Indeed, none of ZIF membranes reported so far has shown any impressive gas separation performance.[16] The only exception is the ZIF-8 membranes reported by Lai and co-workers,[31] showing excellent propylene/propane separation performance. The membranes were synthesized using a secondary (or seeded) growth method in which preformed seed crystals are deposited on supports followed by subsequent growth of the seed crystals into well-intergrown films. However, an increased number of steps involved in secondary growth can add to the complexity of the synthesis process, thereby potentially causing reproducibility issues.[16] In contrast, though conceptually simpler and less complicated than secondary growth, an *in situ* method has failed to yield ZIF membranes with high gas separation performance.

Reaction systems where reacting species are physically separated and brought into contact by diffusion (such as interfacial and counter-diffusion synthesis) have been used to create MOF films and membranes.[32,33] Self-supporting HKUST-1 hollow shell-membranes were synthesized at the interface between two immiscible liquids in which metal ions and ligand molecules meet and react.[32] These HKUST-1 membranes were found to be selective toward small molecules.[32] ZIF-8 membranes were prepared on porous polymer supports using a counter-diffusion concept in which the supports physically separate metal ions and ligand molecules.[33] However, These ZIF-8 membranes have not shown any good gas separation performance, likely due to their poor grain boundary structure.[33]

Here we report a new *in situ* approach for the synthesis of well-intergrown ZIF-8 membranes with significantly enhanced microstructure. Our synthesis method is based on a counter-diffusion concept in which a metal precursor solution is soaked in porous α-alumina supports followed by rapid solvothermal reaction in a ligand solution. Due to the nature of the counter-diffusion concept, the new method offers unique opportunities, such as healing defective membranes (i.e., poorly intergrown) as well as significantly reducing the consumption of costly ligands and organic solvents. The ZIF-8 membranes show excellent propylene/propane separation performance and exhibit exceptional mechanical strength. The technique appears to be potentially general evidenced by the successful synthesis of well-intergrown membranes of prototypical ZIFs, such as ZIF-7 and SIM-1.

■ MATERIALS AND METHOD

Chemicals. Zinc chloride ($ZnCl_2$, 99.99%, Alfa Aesar), 2-methylimidazole ($C_4H_6N_2$, 99%, Sigma-Aldrich), sodium formate (NaCOOH, > 95%, Sigma-Aldrich), and methanol (CH_3OH, > 99%, Alfa Aesar) were used as a metal source, a ligand, a deprotonating agent, and a solvent for the synthesis of ZIF-8 membranes, respectively. All of the chemicals were used as purchased without further purification.

Preparation of ZIF-8 Membranes. In a typical synthesis, 0.98 g of zinc chloride was dissolved in 40 mL of methanol (solution A), and 5.19 g of 2-methylimidazole (hereafter mIm) and 0.5 g of sodium formate was dissolved in 40 mL of methanol (solution B). A homemade α-Al_2O_3 disk (porosity = 46%, diameter = 22 mm, and thickness = 2 mm) was soaked in the solution A for 1 h. The disk saturated with the zinc salt solution was positioned vertically in a Teflon-lined autoclave containing the solution B. Then, the autoclave was subjected to solvothermal synthesis for 4 h at 120 °C. After synthesis, the membrane sample was rinsed with methanol several times and immersed in methanol under stirring for 1 day. Afterward, one side of the supported membranes was polished with sand paper manually since films are formed on both sides of supports. Additional washing of 4 days was conducted before drying in an oven at 60 °C for 12 h for further characterizations.

Healing of Defective ZIF-8 Membranes. Defective membranes were synthesized in a similar manner described above but using recycled precursor solutions (details explained in Results and Discussion section below). A poorly intergrown ZIF-8 membrane was loaded into a homemade diffusion cell (Figure S9). A ligand solution (2.27 g of 2-methyimidazole in 20 mL of D.I. water) was poured into the support side of the diffusion cell and kept for 1 h in order to saturate the support. A metal solution (0.11 g of zinc nitrate hexahydrate in 20 mL of D.I. water) was supplied into the membrane side of the diffusion cell. Finally, the diffusion cell is kept in an oven at 30 °C for 6 h for the healing process. The healed membrane is washed in methanol for 5 days under stirring followed by drying at 60 °C for 6 h.

Characterization. X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex II powder X-ray diffractometer with Cu−Kα radiation (λ = 1.5406 Å). Electron micrographs were taken using a JEOL JSM-7500F operating with 5 keV acceleration voltage and 15 mm working distance.

Propylene/Propane Gas Permeation Tests. Propylene/propane single and binary gas permeation measurements were carried out at various temperatures under atmospheric pressure by the Wicke−Kallenbach technique (Figure S5). The feed and argon sweeping gases were supplied to the feed and permeate sides at a flow rate of 100 cc/min, respectively. For a binary measurement, an equimolar propylene/propane mixture was used as a feed. The composition of the permeate side stream was analyzed using a gas chromatography (Agilent GC 7890A equipped with a column of HP-PLOT/Q).

■ RESULTS AND DISCUSSION

Figure 1 illustrates the synthesis of continuous and defect-free supported ZIF-8 membranes using one step *in situ* growth based on counter-diffusion concept. As illustrated in the figure,

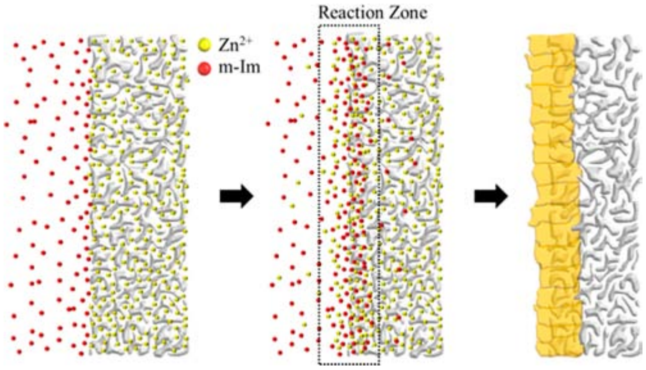


Figure 1. Schematic illustration of the membrane synthesis using the counter-diffusion-based *in situ* method: (1) A porous alumina support saturated with a metal precursor solution is placed in a ligand solution containing sodium formate; (2) the diffusion of metal ions and ligand molecules cause the formation of a “reaction zone” at the interface; and (3) rapid heterogeneous nucleation/crystal growth in the vicinity at the interface leads to the continuous well-intergrown ZIF-8 membranes.

porous α-Al_2O_3 supports are soaked with a metal ion solution, and the supports containing metal ions are then subjected to solvothermal growth in a ligand solution. Upon contact, the concentration gradients enable metal ions and ligand molecules to diffuse from the support into the solution and from the solution into the support, respectively. Therefore, relatively high concentrations of both metal ions and ligand molecules are maintained in the vicinity of the support ("reaction zone") during the solvothermal treatment. It should be noted that in a typical counter-diffusion concept,[33] two solutions (i.e., metal ions and ligand molecules) are provided from the opposite sides of the supports, resulting in much longer diffusion length as compared to our case. Since reaction (crystallization) and diffusion occur simultaneously, it is critically important to consider both of these competing kinetic processes. For example, if the reaction rate is too slow as compared to the diffusion rate (i.e., low Thiele modulus which is the ratio of diffusion and reaction time constants), most of the metal ions will completely diffuse from the support to the solution, favoring the homogeneous nucleation and crystal growth. Ideally, the reaction should be faster than the diffusion (i.e., high Thiele modulus) so that the heterogeneous nucleation and growth can happen before metal ions are depleted from the support. One can increase the Thiele modulus by raising the reaction rate by increasing temperature and/or by adding catalysts. In this study, sodium formate was added as a deprotonator to the ligand solution to increase the reaction rate,[25,34] maintaining relatively high Thiele modulus.

Figure 2 presents the XRD patterns and SEM images of the films grown for various growth times (see Figure S1 for the complete set). As can be seen in the figure, a substantial heterogeneous formation of phase-pure ZIF-8 crystals can be observed even after 2 min of the solvothermal growth, strongly suggesting the relatively high precursor concentrations at the support surface (i.e., reaction zone). After 30 min, the crystal growth appears to be completed so that the grain size and the film thickness of ca. 1.5 μm do not change even with further growth. In general, forming well-intergrown polycrystalline framework membranes with a thickness of ca. 1.5 μm is not straightforward using *in situ* methods. In a typical *in situ* method, heterogeneous nucleation and crystal growth are in competition with homogeneous nucleation and crystal growth. To prevent excessive homogeneous crystal formation, it is often necessary to maintain precursor concentrations low. This results in a much smaller number of nuclei and their growth into bigger crystals in a longer time scale as compared to the case with high precursor concentrations. Indeed, MOF membranes synthesized by *in situ* method have thicknesses in the rage of tens of micrometers,[20,22,23,35] compromising gas permeances through the membranes (i.e., low flux). However, in our method, throughout the crystallization, relatively high precursor concentrations are maintained near the supports. This high precursor concentration, combined with the presence of the catalyst, leads to the fast formation of a large number of nuclei and their subsequent crystal growth in the vicinity of the support surfaces, resulting in the formation of substantially thinner ZIF-8 membranes (ca. 1.5 μm) than typical *in situ* grown membranes. Furthermore, the self-limiting crystal growth, in which the crystals can grow only where the ligand molecules and metal ions are in contact, significantly limits further crystal growth. Another important observation is that a fraction of ZIF-8 crystals are formed inside the support (Figure 2d), which potentially enhances the mechanical stability of the membranes (more discussion follows).

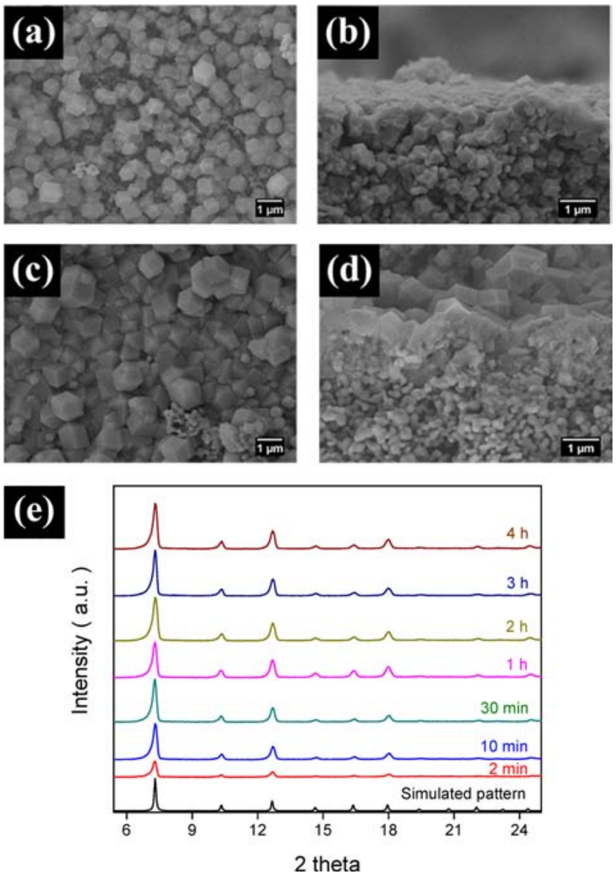


Figure 2. SEM images of ZIF-8 membranes grown for 2 min (a, b) and for 30 min (c, d), and XRD patterns of ZIF-8 membranes as a function of growth time (e). Fast heterogeneous nucleation/crystal growth is due to the presence of a catalyst (i.e., sodium formate) and the relatively high concentration of both metal ions and ligand molecules in the vicinity of the interface.

In order to synthesize continuous well-intergrown ZIF-8 membranes using the counter-diffusion-based *in situ* method (hereafter, CD-based *in situ* method), it was found necessary to have metal ions inside supports as well as the presence of sodium formate in the ligand solution. When supports were soaked with ligand molecules along with sodium formate or when sodium formate was absent in the ligand solution even with metal ions inside the supports, no substantial heterogeneous crystal growth was observed (Figure S2). It is our hypothesis that unfavorable heterogeneous crystal growth in both of these cases is primarily due to the relatively low Thiele modulus (i.e., slow reaction as compared to diffusion). If ligand and sodium formate molecules are contained in supports prior to the solvothermal treatment in a metal solution, it is expected that the chemical potential gradient of the solvent (methanol) causes the solvent to diffuse from the ligand side (inside the supports) to the metal ion side (outside the supports). The diffusion of the solvent further promotes the diffusion of ligand molecules, leading to the quick depletion of ligand molecules inside the supports, thereby limiting heterogeneous crystal formation. On the other hand, without sodium formate, which deprotonates ligand molecules, the reaction rate is relatively low as compared to the diffusion rate, favoring homogeneous nucleation and crystal growth. If our hypothesis is true, one can expect significantly enhanced heterogeneous crystal growth even with supports soaked with ligand molecules when the Thiele modulus is increased by increasing reaction rate. Indeed, this was the case when the excess amount of sodium formate was added either in the ligand solution alone or in both the metal ion and ligand solutions. Though not well-intergrown, continuous ZIF-8 films with high surface coverage were observed (Figure S3 and S4). In addition to enhancing the reaction rate by deprotonating ligand molecules, sodium formate is expected to play an important role in facilitating the crystal intergrowth[25,36,37] as well as the heterogeneous crystal growth.[35]

The separation performance of ZIF-8 membranes was evaluated by performing 50/50 propylene/propane binary gas permeation measurements in a Wicke−Kallenbach setup (Figure S5). Figure 3 displays the room-temperature propylene/propane separation performance of ZIF-8 membranes prepared for varying membrane growth times. Membranes grown even for 10 min started to show a moderate separation factor (∼ 3). As membranes were grown for longer times, the separation factor increases and then reaches at a plateau (∼50). ZIF-8 membranes prepared by the CD-based *in situ* method are in stark contrast with those synthesized by conventional *in situ* method[35] showing no separation toward the mixture (Figure S6). In fact, none of ZIF-8 membranes reported so far[20,24,25,29,38] have shown any good propylene/propane selectivity. The only exception is the ZIF-8 membranes reported by Pan et al.[31] that showed excellent propylene/propane separation factors (average 35) similar to that of the current membranes. The drastically enhanced separation performance strongly suggests that the ZIF-8 membranes prepared via CD-based *in situ* method possess much better grain boundary structure as compared to those synthesized by other methods. When compared with other membranes reported in literature (Figure 4), our ZIF-8 membranes notably outperform both polymeric and zeolite membranes with respect to the separation factor and the propylene permeability. Furthermore, our membranes are close to the upper bound of carbon membranes while meeting the proposed requirement[4] (a minimum permeability of 1 Barrer and selectivity of 35) for commercial application.

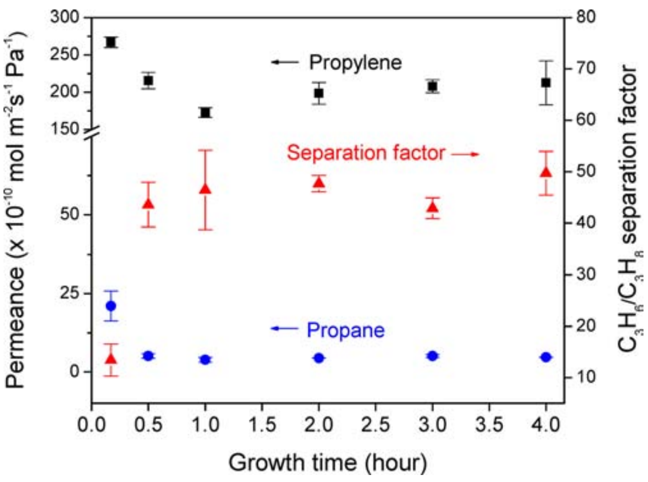


Figure 3. Propylene/propane separation performance of ZIF-8 membranes as a function of growth time at room temperature. ZIF-8 membranes show excellent proplylene/propane separation factor (∼50) even after growing for 30 min.

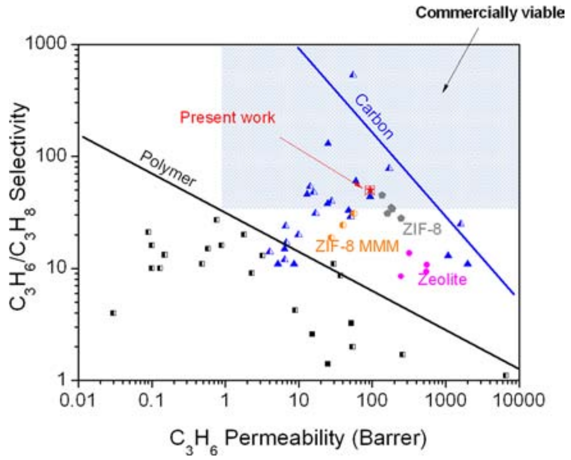


Figure 4. Comparison of the propylene/propane separation performance of our ZIF-8 membranes with those of other membranes reported in the literatures. Half- and full-filled symbols indicate separation data from single and binary gas permeation measurements, respectively. The shaded area in the graph implies the performance requirement of a membrane (a minimum permeability of 1 Barrer and selectivity of 35) for commercial application. The solid lines are the so-called Robison upper bound. Triangle: Carbon membrane;[6−8] circle: zeolite membrane;[5] rectangle: polymer membrane;[3] pentagon: ZIF-8 membrane;[31] hexagon: ZIF-8 mixed matrix membrane;[9] star: ZIF-8 membrane in this work.

The temperature dependences of both single and binary propylene/propane separation performance of the membranes (grown for 4 h) are presented in Figure S7. In both cases, the permeances of propylene decrease, while those of propane increase slightly as temperature rises, which is consistent with the previous report.[31] This leads to a decrease in propylene/propane separation factor and ideal selectivity as the temperature increases. These trends can be explained by the surface diffusion model[39−41] in which the diffusion through microporous materials is described as an activation process composed of adsorption and subsequent diffusion of molecules by hopping along adsorbent surface. Therefore, the permeance of gas molecules depends on both the heat of adsorption and the activation energy for gas diffusion (i.e., $P \sim \exp\left((\Delta H_{\mathrm{ads}} - E_{\mathrm{a}})/RT\right)$). The heats of adsorption of propylene and propane on ZIF-8 are 30 and 34 kJ/mol, respectively, while the diffusional activation energies for propylene and propane are 9.7 and 74 kJ/mol.[26] As such, as the temperature increases, the permeance of proplyene decreases, while that of propylene increases.

When ZIF-8 membranes are applied in a large commercial scale, we envision membrane modules (similar to commercial polymer or ceramic membrane modules) with each module packed with a number of cylindrical membranes. As is often the case for commercial ceramic membrane modules, one has no choice but to discard the expensive membrane modules when there form defects in the individual membrane in the modules because it is often too costly to disassemble the modules and to identify and replace the defective membranes. Given the fact that membranes will develop defects and cracks, it is highly desirable if defective membranes can be healed *in situ* without disassembling and discarding the expensive membrane modules. As illustrated in Figure S8, the self-limiting nature of the counter-diffusion concept enables the defective membranes to be identified (since crystals grow preferentially from defects or cracks where the separated metal ions and ligand molecules are in contact) and to be healed readily without completely disassembling the membrane modules. To prove the concept of this unique defect-healing capability, a poorly intergrown ZIF-8 membrane was subjected to a custom-made diffusion cell where metal ions are provided from the membrane side, while ligand molecules are supplied from the support side (Figure S9). Figure 5 shows the micrographs of the ZIF-8 membrane before and after the healing process. As can be seen in Figure 5c,d, the intercrystal gaps were completely filled with newly grown crystals (see the red arrows). The newly grown crystals have distinctive morphology possibly due to the difference in recipe (water vs methanol) and the confined crystal growth in the intercrystal spaces. It is important to note that the thickness of the membrane did not change after the healing process, not compromising the flux owing to the self-limiting feature of the counter-diffusion concept (Figure S10). The separation performance of the healed membranes is presented in Table S1. After healing, the permeance was dramatically reduced as the propylene/propane selectivity decreased to ~10. This reduced performance after healing is possibly due to the insufficient healing and/or compromised grain boundary defects upon healing. Further investigation is currently under way.

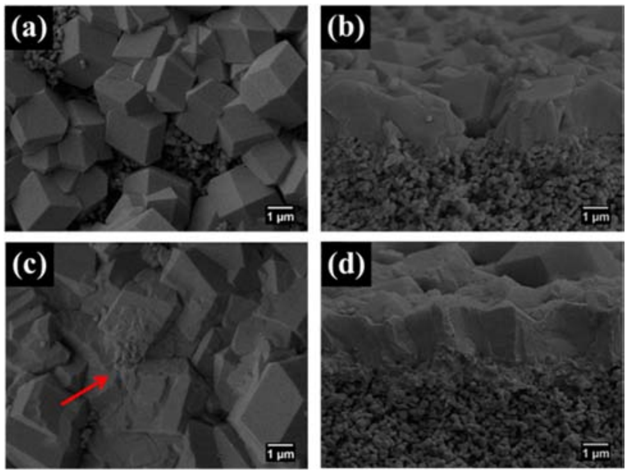


Figure 5. SEM images of ZIF-8 membranes before (a, b) and after (c, d) the healing process. Red arrow indicates newly grown crystals that have distinctive morphology possibly due to the difference in recipe (water vs methanol) and the confined crystal growth in the intercrystal spaces.

Organic ligands and solvents (mostly organic) used for the typical synthesis of MOFs are costly and environmentally harmful. It is, therefore, very attractive if the consumption of organic ligands and solvents can be drastically reduced. Conceptually, the CD-based *in situ* method requires a significantly less amount of precursor solutions than conventional methods since the precursor solutions can be recycled. As a proof-of-concept, the ligand solution was recycled to grow ZIF-8 membranes multiple times (Figures 6 and S11). As can be seen in the figures, well-intergrown continuous ZIF-8 membranes were formed even after the ligand solution was recycled three times. The more the solution is recycled, the bigger the grains become, which can be explained by the formation of a smaller number of nuclei as the ligand concentration drops due to the increased number of recycling. ZIF-8 membranes grown from the ligand solutions after recycled four times are not well-intergrown though continuous, mainly owing to the depletion of ligand molecules. These poorly intergrown membranes can be made into well-intergrown membranes by healing the membranes using the CD-based *in situ* method. The separation performance of the membranes synthesized in a recycled ligand solution was tested and showed good separation performance (Table S2).

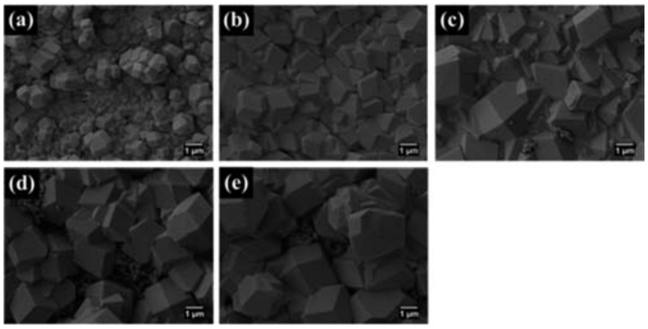


Figure 6. SEM images of ZIF-8 membranes synthesized with a ligand solution recycled; once (a), twice (b), three times (c), four times (d), and five times (e). Well-intergrown continuous ZIF-8 membranes were formed even after the ligand solution was recycled three times.

The mechanical stability of polycrystalline ZIF-8 membranes is also an important issue for their practical applications. The mechanical stability of ZIF-8 membranes was tested using a sonication method.[42−44] No substantial degradation of the films was observed even after subjected to intensive sonication for 2 h (Figure S12), strongly suggesting the excellent mechanical stability of ZIF-8 membranes. The gas separation properties of the membranes were also tested (Table S3). The membranes maintained excellent propylene/propane separation performance, though the separation factor was slightly dropped as the sonication time increases. This slight drop in the selectivity is likely due to the fact that the grain boundary structure of the membranes was somewhat compromised upon the sonication process.

Finally, ZIF-7 and SIM-1 membranes were synthesized using our CD-based *in situ* method to demonstrate its potentially general applicability (Figure S13 and S14). Even though these membranes show some cracks, given the fact that ZIFs are quite robust as compared to other MOFs (such as IRMOFs), chances are likely that the cracks formed during activation process. For example, it is well-known that rather bulky solvent molecules (e.g, dimethylforamide) used for ZIF-7 synthesis are included in the framework cages, thereby making activation without crack formation very difficult. Further studies to prevent crack formation are currently under way.

■ CONCLUSION

In conclusion, we have developed a one-step *in situ* synthesis technique for high-quality MOF membranes based on the concept of counter diffusion. This simple yet highly versatile method enabled the rapid preparation of well-intergrown ZIF-8 membranes with excellent microstructure. The high-quality ZIF-8 membranes showed an excellent separation performance of a propylene/propane (50/50) mixture (selectivity ~55). Furthermore, the ZIF-8 membranes were found to be mechanically very strong with their separation performance maintained high even after 2 h of intensive sonication. The unique feature of the counter-diffusion concept allowed the poorly intergrown membranes to be healed. In addition, the costly precursor solutions can be recycled multiple times for membrane synthesis. Finally, prototypical ZIF-7 and SIM-1 membranes were also successfully synthesized using our method, proving its general applicability. Considering its unique features including postsynthetic healing and reduced precursor consumption, the simple general method reported here enabling the synthesis of high-quality MOF membranes with excellent microstructure offers unique opportunities for potential large-scale practical applications of MOF membranes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures and tables and experimental procedures for ZIF-7 and SIM-1 membranes are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hjeong7@mail.che.tamu.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

H.-K.J. acknowledges the financial support from the National Science Foundation (CBET-1132157). H.-K.J. and H. K. are grateful for the financial support from the Mary Kay O'Conner Process Safety Center in the Artie McFerrin Department of Chemical Engineering at Texas A&M University and Texas Engineering Experiment Station. H.-K.J. and H. K. acknowledge Dr. Sonny Sachdeva's contribution on optimizing the synthesis recipe for SIM-1 membranes. The FE-SEM acquisition was supported by the National Science Foundation under grant no. DBI-0116835, the VP for Research Office, and the TX Eng. Exp. Station.

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