crystals

Article

Propylene-Selective Thin Zeolitic Imidazolate Framework Membranes on Ceramic Tubes by Microwave Seeding and Solvothermal Secondary Growth

Jingze Sun [1], Chen Yu [1] and Hae-Kwon Jeong [1,2,*]

1 Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA; jingzesun93@gmail.com (J.S.); yuchen_hi@tamu.edu (C.Y.)
2 Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3122, USA
* Correspondence: hjeong7@tamu.edu

Received: 26 August 2018; Accepted: 17 September 2018; Published: 21 September 2018

Abstract: Zeolitic imidazolate framework (ZIF-8) membranes have attracted tremendous interest for their high-resolution kinetic separation of propylene/propane mixtures. Current polycrystalline ZIF-8 membranes are supported mostly on planar ceramic substrates (e.g., alumina disks) because of their high thermal, chemical, and mechanical stabilities and facile manufacturing in the labs. Planar supports are, however, not scalable for practical separation applications owing to their low packing density (typically 30–500 m^2/m^3). On the other hand, ceramic tubes provide order-of-magnitude higher packing densities than planar supports (i.e., much higher membrane areas per module). Here, we report polycrystalline ZIF-8 membranes with thicknesses of ~1.2 µm grown on the bore side of commercially-available ceramic tubes using the microwave seeding and secondary growth technique. The tubular ZIF-8 membranes showed excellent propylene/propane separation factors of ~80, exceeding all currently-reported ZIF-8 membranes on ceramic tubes. It was found that the secondary growth time was critical to enhance the propylene/propane separation factor of the membranes. Membranes were also grown on the shell side of tubular supports, showing the versatility of our technique.

Keywords: zeolitic imidazolate frameworks; gas separation; propylene/propane separation; polycrystalline membranes; ceramic tubular supports

1. Introduction

Metal–organic frameworks (MOFs) are a class of new crystalline nanoporous materials, formed by metal nodes and organic linkers connected via coordination bonds [1,2]. Because of their unique structural features, MOFs have attracted a great deal of interest for membrane-based gas separations [3,4]. Zeolitic imidazolate frameworks (ZIFs) [5–8], a sub-class of MOFs, consisting of divalent metal centers (e.g., Zn^{2+}) interconnected with imidazole-based linkers, have been extensively investigated as membrane materials for gas separations, mainly because of their exceptional chemical/thermal stabilities and their ultra-microporosities.

Among several ZIFs, membranes of ZIF-8 (zeolitic imidazolate frameworks), which consists of zinc ions and 2-methylimdazolates, have shown promising gas separation performances, in particular for propylene/propane separation [9,10]. Following the well-acclaimed pioneering work by Bux et al. [11], as well as Pan and Lai et al. [12], several groups reported polycrystalline ZIF-8 membranes supported on alumina disks exhibiting propylene/propane separation factors as high as ~200 [13–16].

Polycrystalline ZIF membranes with high separation performances have been supported mostly by planar ceramic (alumina) substrates [11,13–24].

For their practical applications, however, it is of critical importance to be able to package ZIF membranes into modules with large surface-area-to-volume ratios [25–28]. With a packing density of 30–500 m^2/m^3 (only ~5–20 m^2 membrane area per module), clearly current planar substrates are not scalable [29]. Scalable supports investigated so far include ceramic tubes [30–37], ceramic hollow fibers [37–39], and polymeric hollow fibers [40–46].

Nair group was the first to report polycrystalline ZIF-8 membranes on polymer hollow fibers via interfacial fluidic method [28,41,42]. Similar strategies also were used by other groups to grow ZIF-8 membranes on polymeric hollow fibers [47–49]. Chen et al. [45] and Li et al. [46] reported preparation of ultra-thin ZIF-8 membranes on TiO_2-modified and ZnO-modified polymer hollow fibers, respectively. Jeong and co-workers have recently reported propylene-selective ZIF-8 membranes on polymer hollow fibers using the microwave seeding and secondary growth method [44]. Despite their early success and great potential, only a few of the ZIF-8 membranes supported on polymer hollow fibers either tested or showed decent propylene/propane separation performances. Furthermore, it is expected to be quite challenging for ZIF-8 membranes on polymer hollow fibers to break into the market in a foreseeable future, given the fact that there are no commercial polycrystalline membranes (e.g., zeolite membranes) supported on polymer hollow fibers. Most commercial polymeric hollow fibers are not as thermally, mechanically, and chemically stable as ceramic supports, limiting their applications under mild conditions. There are even fewer reports on the use of ceramic hollow fibers as supports for ZIF-8 membranes [50]. It is not likely that fragile ceramic hollow fibers can be used for commercial applications.

Ceramic tubes are practical and promising supports for ZIF-8 membranes for large-scale gas separation membrane applications because they are not only chemically and thermally stable but also mechanically robust, while offering significantly-improved packing density compared with planar supports [51]. To the best of our knowledge, ceramic tubes are the only substrate used for commercial polycrystalline molecular-sieve membranes for pervaporation applications (e.g., ZEBREX^{TM} of Mitsubishi Chemical, Mitsubishi Chemical, Tokyo, Japan) [52].

Carreon et al. [53] first synthesized polycrystalline ZIF-8 membrane on the internal surface of alumina tubes via the manual rubbing seeding method, showing CO_2/CH_4 separation performance. Yamaguchi et al. [30] prepared ZIF-8 on ceramic tubes with counter-diffusion methods, exhibiting a propylene/propane separation factor of 59 with relatively low propylene permeance of 7.5 GPU (gas permeation unit, 1 GPU = 3.35×10^{-10} mol s^{-1} Pa^{-1} m^{-2}). With interfacial control via two immiscible solvents, they were able to obtain higher propylene permeance of 36 GPU, but a lower propylene/propane separation factor of 12 [54]. Tanaka et al. [32,55] prepared in situ ZIF-8 membranes on ceramic tubes via surface modification. The resulting membranes with the thickness of ~1 μm exhibited a propylene/propane separation factor of 36 and corresponding propylene permeance of 27 GPU (permeability of ~6 Barrer, see Table S1). This barely meets the minimum propylene permeability of 1 Barrer and minimum propylene/propane separation factor of 35 by Colling et al. [56] in order for membranes to be commercially-viable based on three-stage membrane processes to obtain 99.6% propylene purity with 40.5% of energy reduction. In general, secondary (or seeded) growth results in polycrystalline membranes with improved microstructures (i.e., better grain boundary and lower thickness) as compared with in situ growth, thereby showing better separation performances.

Here, we report the facile preparation of thin ZIF-8 membranes on scalable ceramic tubes using microwave seeding and secondary growth. High-quality ZIF-8 seed layers were readily formed on ceramic tubes. Furthermore, the unique counter-diffusion and microwave heating enabled us to control the location of seed layers, that is, either on the bore side or on the shell side, consequently the location of membrane. After secondary growth, the resulting tubular ZIF-8 membranes on the bore side of the tubes showed the average propylene/propane separation factor of ~80, indicating improved grain boundary structure. Furthermore, the membranes are one of the thinnest ZIF-8 membranes prepared on ceramic tubes, thereby showing a propylene permeance of more than 60 GPU.

2. Materials and Methods

Chemicals: Zinc nitrate hexahydrate (98%, Sigma-Aldrich, Saint Louis, MO, USA) was used as a metal source while 2-methylimidazole (99%, Sigma-Aldrich, Saint Louis, MO, USA) was used as an organic ligand source. Sodium formate (American Chemical Society (ACS) reagents, ≥99%, Sigma-Aldrich, Saint Louis, MO, USA) was used as a modulator for microwave seeding process. Methanol (ACS, absolute, low acetone, 99.8+%, Alfa Aesar, Haverhill, MA, USA) was used as solvent.

Tubular supports: Symmetrical ceramic tubes (named NS-1 by the vendor) were purchased from Noritake Co. (Nagoya, Japan), with no further treatment. The inner diameter of the support is 10 mm. The estimated packing density is around 700 m^2/m^3. According to the manufacturer, these supports were made of high purity alpha-alumina, with a mean pore diameter of 0.15 μm and a mean porosity of 35–40%. The N_2 permeance of the bare tube is 9.5×10^{-7} mol pa^{-1} m^{-2} s^{-1}. The maximum load is 246 N and the radial crushing strength is higher than 40 MPa. Scanning electron micrograph (SEM) images of pristine ceramic supports have been included in Figure S1.

Microwave (MW) seeding procedures: The microwave seeding and secondary growth procedures were adopted from a previously published paper [15] from our group with slight modifications. The ceramic tubes were wrapped with Teflon tapes on the shell side to limit the reaction to only the bore side. The ceramic tubes were then immersed into the zinc solution for 1 h. The zinc solution was prepared by dissolving 2.43 g of zinc nitrate hexahydrate into 40 mL of methanol. For each tube, 2.59 g 2-mIm and 0.125 g sodium formate were dissolved into 30 mL of methanol. After the soaking, soaked ceramic tubes were transferred into microwave-inert reaction chambers with the ligand solution in them. A 100-W microwave was immediately introduced for 90 s after the transferring. After cooling down for 30 min, the ceramic tubes were washed with 40 mL of fresh methanol for 1 day inside a beaker on a Big Bill Thermolyne shaker (M49125, produced by Thermal Fisher Scientific, MA, USA). A similar seeding procedure was adopted to prepare seed layers on the shell sides of tubes. To limit the formation of seed layers on the shell side, both ends of tubes were sealed with epoxy resin.

Secondary growth procedures: The secondary growth solution was prepared following the recipe by Pan et al. [12] by dissolving 0.11 g of zinc nitrate hexahydrate and 2.27 g 2-mIm into 40 mL of D.I water. The tube was wrapped again with Teflon tapes and immersed into a Teflon-lined autoclave with the secondary growth solution in it. The secondary growth was carried out for 5 d inside a convective oven at 30 °C. After the secondary growth, with Teflon tapes removed, the tube was washed with fresh methanol for 60 h, followed by drying at 60 °C before permeation tests. The washing procedure is similar to the one previously mentioned. Similarly, the seed layers on the shell sides of tubes were secondarily grown into membranes by sealing both ends of the seeded tubes with epoxy resin.

Acid treatment and the reuse of tubes: Our tubular supports were reused repeatedly by immerging the tubes in 1 mol/L hydrochloride acids for 1 min under ultra-sonication and four more minutes without ultra-sonication, followed by extensive washing. The surface of the tubes was then regenerated by thermal treatment at 1100 °C for 4 h. The tubes were further sonicated in methanol and washed with fresh methanol, and then dried completely before using again.

Characterizations and permeation tests: Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku Miniflex II powder X-ray diffractometer (Rigaku Corporation, USA) with Cu-Kα radiation (λ = 1.5406 A°) with a step size of 0.020 degrees. Scanning electron micrographs (SEM) were collected using a JEOL (Tokyo, Japan) JSM-7500F operating at 2 keV acceleration voltage and working distances of 15 mm. The gas separation performances of ZIF-8 tubular membranes were tested using a home-made Wicke–Kallenbach setup [57] under atmospheric pressure. The 50:50 mixture of propylene and propane was supplied to a feed side, while the permeate side was swept by argon. The total flow rates of both sides were maintained at 100 mL/min. The gas compositions of the permeate side were analyzed using an Agilent (CA, USA) GC 7890A gas chromatography (equipped with HP-PLOT/Q column).

3. Results and Discussion

Figure 1 displays a schematic illustration for our microwave seeding and secondary growth technique following the previously reported procedure [15]. To confine formation of seed layers on the bore sides of tubes, the shell sides of tubes were sealed using Teflon tape only during both the seeding and during later secondary growth. An alumina tube soaked with a zinc solution was immersed in a ligand solution, followed by microwave heating (Figure 1a). ZIF-8 crystals were then formed rapidly on the bore side surface (Figure 1b). Subsequent secondary growth of the seeded support led to formation of polycrystalline ZIF-8 membranes (Figure 1c).

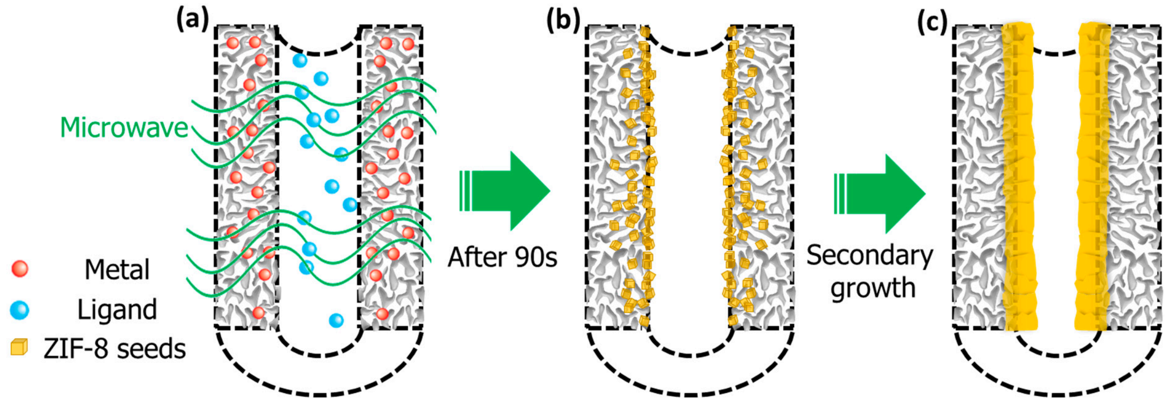

Figure 1. A schematic illustration of (**a**) microwave seeding; (**b**) seeded tube; and (**c**) polycrystalline membrane after secondary growth. ZIF-8—zeolitic imidazolate framework.

Figure 2 shows ZIF-8 seed layers formed on either the bore side or the shell side of alumina tubes. The support surfaces were covered by densely-packed ZIF-8 nanocrystals with an average size of ~50 nm (see Figure 2). These nanocrystals of ZIF-8 exhibit clear facets as well as narrow size distribution. As demonstrated in our earlier report [15], the seed crystals appear to be strongly attached on the support surfaces. The seed layers with high packing density and uniform nanocrystals that are strongly attached to supports are expected to lead formation of thin ZIF-8 membranes after secondary growth, as illustrated in Figure S2. It is worth mentioning here that the unique microwave heating in combination of counter-diffusion of zinc ions and ligands enables rapid formation of nanocrystals not only on the external surface but also inside porous supports (that is, inter-particle pores of supports) [15]. The seed crystals inside supports are expected grow into grains interlocked between alumina grains, thereby increasing the mechanical strength of membranes after secondary growth.

As shown in Figure 3a, ZIF-8 seed layers were grown into continuous, well-intergrown membranes after being subjected to the secondary growth in an aqueous solution at 30 °C for 6 h. Because of the difficulty of taking X-ray diffraction on ZIF-8 membranes grown on the shell sides of tubes, the phase and crystallinity of the membranes were indirectly confirmed using the powder X-ray diffraction of powders scratched from the inner surface of the support (see Figure S3). The average thickness of the membranes was estimated to be ~1.2 μm (see the inset of Figure 3a), which is among the thinnest ZIF-8 membranes grown on either ceramic tubes/hollow fibers or polymer hollow fibers. Interestingly (see Table S1), many of the seeds deposited deeply inside the support did not grow further, likely because of the self-limiting nature of the growth. The propylene/propane separation performance of the membranes was tested in a Wicke–Kallenbach setup (Figure S4) with equal-molar propylene/propane mixture as a feed. The average propylene/propane separation factor of the membranes was ~20, which is much lower than those (~30–200) of our previous ZIF-8 membranes prepared similarly on alumina disks [15,16]. This was attributed to the fact that with a tubular geometry and the ligand solution present in the inner cylinder space, mass transfer limitation might be generated. In other words, with planar supports, concentration of ligand in the vicinity of support is maintained at a relatively high level because of the more effective convective mass transfer, which is not the case for tubular supports. After a series of experiments, we discovered that increasing the secondary growth time is most effective in improving tubular ZIF-8 membranes. Surprisingly, the thickness of the membranes remained unchanged even after extending the secondary growth time to 5 d (see Figure 3b). This can be explained based on the mass transfer limitation in the cylindrical geometry as described above, under which grains do not grow further, yet grain boundary structure may improve.

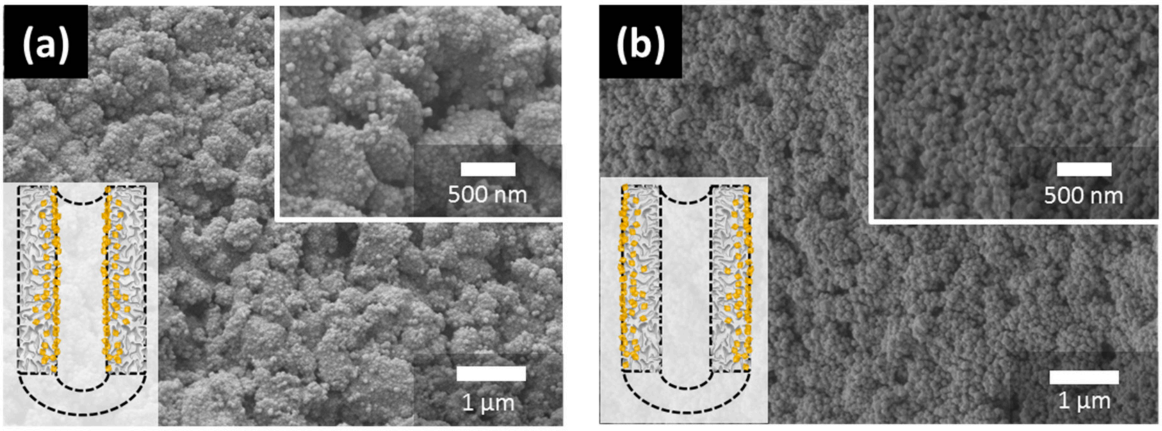

Figure 2. Scanning electron micrographs (SEMs) of ZIF-8 seed layers on the (**a**) bore side and (**b**) shell side of alumina tubes after microwave seeding.

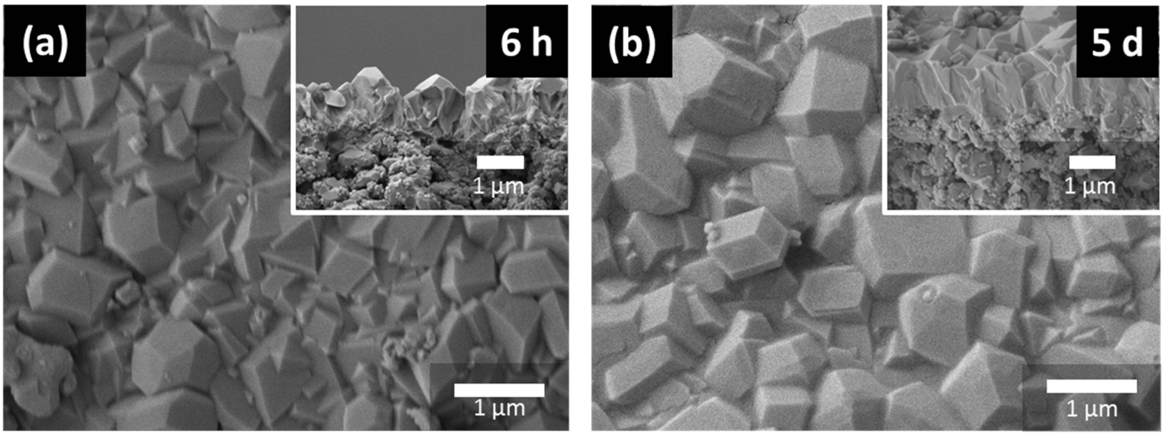

Figure 3. SEMs of ZIF-8 membranes grown on the bore side of alumina tubes at secondary-growth times of 6 h (**a**) and 5 days (**b**). Cross-sectional images are shown as insets.

Figure 4 presents the propylene/propane binary separation performances of tubular ZIF-8 membranes as a function of the secondary growth time. As can be seen, the separation factor increased as the secondary growth time increased, while the propylene permeance underwent relatively little change. The secondary growth time of five days resulted in the separation factor of ~80, which is the highest reported for tubular ZIF-8 membranes (see Table S1). A further extension of the secondary time to eight days was found no significant increase in the separation factor.

The propylene/propane separation performance of our ZIF-8 tubular membranes is compared with representative ZIF-8 polycrystalline membranes on various supports, as well as other membranes (see Figure 5a). Figure 5b compares our ZIF-8 membranes with propylene-selective ZIF-8 membranes on ceramic tubes. Table 1 summarizes and compares ZIF-8 membranes reported on scalable supports. As can be observed, our tubular membranes are significantly more propylene-selective as compared with previously reported tubular membranes, which can be attributed to the high-quality seed layers by microwave seeding, as well as to the better control over grain boundary structure by elongated secondary growth. Similar improvement can also be found for permeance (see Figure S5).

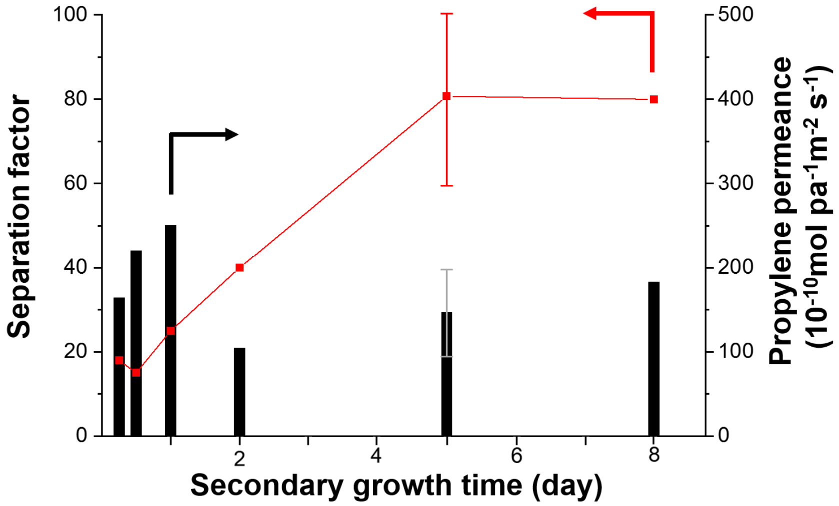

Figure 4. Binary propylene/propane separation factors and propylene permeances of ZIF-8 tubular membranes with increasing secondary growth time. Additional samples (five membranes from three batches) were synthesized to generate the standard error bar.

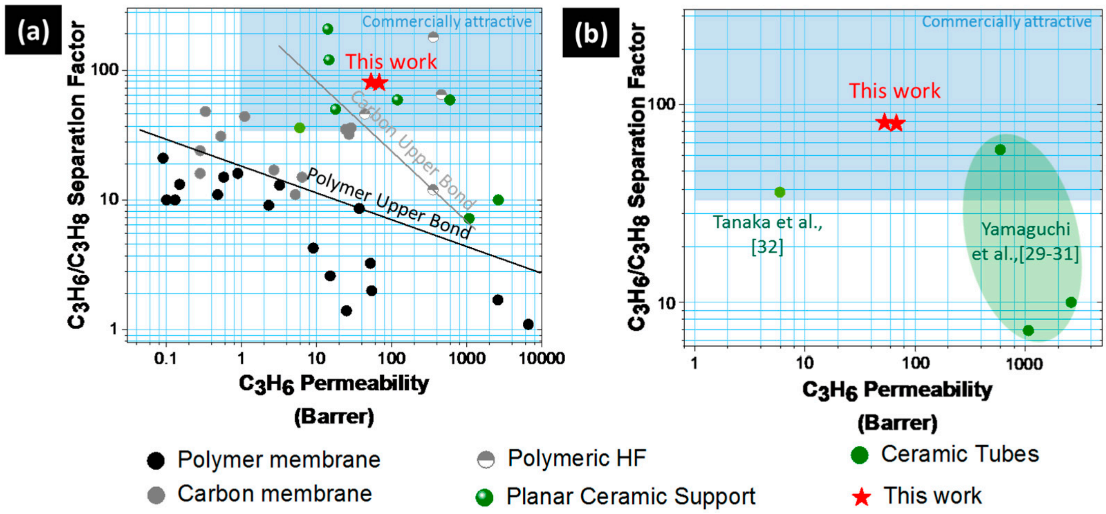

Figure 5. Propylene/propane separation performance of our ZIF-8 tubular ZIF-8 membranes in comparison with (**a**) all other membranes and (**b**) other ZIF-8 membranes supported on ceramic tubes. HF stands for hollow fiber.

As alumina tubes are relatively expensive, we attempted to find out whether or not tubes can be reused. ZIF-8 films on tubular supports were dissolved in a diluted hydrochloric acid solution. After extended washing in Deionized (DI) water, the tubes were thermally treated at 1100 °C for 4 h. The regenerated tubes were used to grow ZIF-8 membranes. In this way, tubular supports were regenerated several times. The performance of the resulting ZIF-8 membranes showed similar/better separation performances as those of the membranes on fresh tubes (see Table S2). All the separation data in Figures 4 and 5 were generated by membranes on reused supports.

Table 1. Propylene-selective zeolitic imidazolate framework (ZIF-8) membranes on polymer hollow fibers and ceramic tubes. SF stands for separation factor.

	Year	Group	Permeance ($\times 10^{-10}$ mol s^{-1} Pa^{-1} m^{-2})	Permeabilit Barrer	SF	Thickness (µm)	Membrane Position	Method	Ref.
Polymeric hollow fibers	2014	Nair	135	355	12	8.8	Internal	Interfacial fluidic processing	[39]
	2015		220	460	65	7	Internal	Interfacial fluidic processing	[40]
	2015		150	355	180	8	Internal	Interfacial fluidic	[41]
	2017	Li & Zhang	215400	109	70	0.017	External	Gel-vapor deposition	[46]
	2018	Jeong	185	44	46	0.8	Internal	Microwave seeding and secondary growth	[44]
Ceramic capillary tubes	2014	Yamaguchi	25	597	59	80	External	Counter-diffusion	[29]
	2015		220	2628	10	40	External	Counter-diffusion with interface control by two immiscible solvents	[31]
	2015		120	1075	7.2	30	External	Counter-diffusion with interface control by two immiscible solvents	[30]
Ceramic tubes	2017	Tanaka	100	30	36	1	Internal	Surface modification with (3-Aminopropyl)triethoxysilate (APTES)	[32]

To further prove the versatility of our microwave seeding and secondary growth technique, membranes were prepared on the shell sides of supports. Although the membranes show similar morphology, they are quite a lot thicker (~1.8 μm) than the bore-side membranes (see Figure 6). As opposed to growing on the bore side, growing on the shell side of a tube is similar to growing on a planar support in terms of mass transfer, consequently leading to thicker membranes.

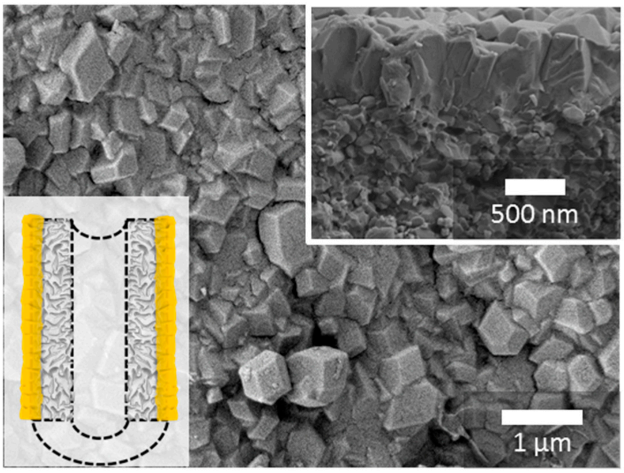

Figure 6. Top-view and cross-section (inserted) SEM micrographs of ZIF-8 membranes on the shell side of tubular supports. The secondary growth was performed at 30 °C for 6 h.

4. Conclusions

Here, we synthesized high-quality ZIF-8 polycrystalline membranes on ceramic tubular supports with a thickness of ~1.2 μm using the microwave seeding and secondary growth technique. Compared with the currently reported tubular ZIF-8 membranes, the tubular ZIF-8 membranes showed an excellent propylene/propane separation factor of ~80 and propylene permeance as high as 56 GPU. This improved separation performance of our membranes is likely the because of the fact that (1) the unique nature of microwave seeding led to rapid formation of high-quality seed layers that are strongly attached to supports and (2) the extended secondary growth time in a cylindrical support geometry enabled improvement in the grain boundary structure without further growing grains. The versatility of the current technique enabled formation of ZIF-8 membranes on the shell-sides of tubular supports. High-performance tubular ZIF membranes are expected to be a major step towards their practical application because of the high packing density of tubular configuration, along with the high chemical and mechanical stabilities of ceramic supports.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/8/10/373/s1, Figure S1. Top-view SEM images of pristine tubular support on its inner side (a) and outer side (b); Figure S2. Schematic illustrations on common reasons for a low-quality seeding layer; Figure S3. PXRD pattern of powder sample scratched from the inner surface of the tubular membrane and the simulated pattern; Figure S4. Optical images of loading tubular membranes into the test module (a) and a schematic illustration of its gas connections (b); Figure S5. Permeance and separation factors of propylene/propane separation for ZIF-8 membrane on ceramic tubular supports; Table S1. Typical ZIF-8 tubular membranes targeting propylene/propane separation; Table S2. ZIF-8 membrane on new (unrecycled) tubes.

Author Contributions: Investigation, C.Y. and J.S.; Supervision, H.-K.J.; Writing—original draft, J.S.; Writing—review & editing, H.-K.J.

Funding: H.-K.J. acknowledges the financial support from the National Science Foundation (CBET-1510530 and CMMI-1561897).

Acknowledgments: This publication was made possible in part by NPRP grant number 8-001-2-001 from the Qatar National Research Fund (a member of the Qatar Foundation). The statements made herein are solely the responsibility of the authors. The National Science Foundation supported the FE-SEM acquisition under Grant DBI-0116835, the VP for Research Office, and the Texas A&M Engineering Experimental Station.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Carne, A.; Carbonell, C.; Imaz, I.; Maspoch, D. Nanoscale metal-organic materials. *Chem. Soc. Rev.* **2011**, *40*, 291–305. [CrossRef] [PubMed]
2. Shekhah, O.; Liu, J.; Fischer, R.A.; Woll, C. MOF thin films: Existing and future applications. *Chem. Soc. Rev.* **2011**, *40*, 1081–1106. [CrossRef] [PubMed]
3. Rodenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; Xamena, F.X.L.I.; Gascon, J. Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nat. Mater.* **2015**, *14*, 48–55. [CrossRef] [PubMed]
4. Qiu, S.; Xue, M.; Zhu, G. Metal-organic framework membranes: From synthesis to separation application. *Chem. Soc. Rev.* **2014**, *43*, 6116–6140. [CrossRef] [PubMed]
5. Wang, B.; Cote, A.P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O.M. Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs. *Nature* **2008**, *453*, 207–211. [CrossRef] [PubMed]
6. Morris, W.; Doonan, C.J.; Furukawa, H.; Banerjee, R.; Yaghi, O.M. Crystals as molecules: Postsynthesis covalent functionalization of zeolitic imidazolate frameworks. *J. Am. Chem. Soc.* **2008**, *130*, 12626–12627. [CrossRef] [PubMed]
7. Park, K.S.; Ni, Z.; Cote, A.P.; Choi, J.Y.; Huang, R.D.; Uribe-Romo, F.J.; Chae, H.K.; O'Keeffe, M.; Yaghi, O.M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *PNAS* **2006**, *103*, 10186–10191. [CrossRef] [PubMed]
8. Hayashi, H.; Cote, A.P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O.M. Zeolite a imidazolate frameworks. *Nat. Mater.* **2007**, *6*, 501–506. [CrossRef] [PubMed]
9. Ravanchi, M.T.; Kaghazchi, T.; Kargari, A. Application of membrane separation processes in petrochemical industry: A review. *Desalination* **2009**, *235*, 199–244. [CrossRef]
10. Eldridge, R.B. Olefin/paraffin separation technology: A review. *Ind. Eng. Chem. Res.* **1993**, *32*, 2208–2212. [CrossRef]
11. Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J.R. Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. *J. Am. Chem. Soc.* **2009**, *131*, 16000–16001. [CrossRef] [PubMed]
12. Pan, Y.C.; Li, T.; Lestari, G.; Lai, Z.P. Effective separation of propylene/propane binary mixtures by zif-8 membranes. *J. Membr. Sci.* **2012**, *390*, 93–98. [CrossRef]
13. Ramu, G.; Lee, M.; Jeong, H.-K. Effects of zinc salts on the microstructure and performance of zeolitic-imidazolate framework zif-8 membranes for propylene/propane separation. *Microporous Mesoporous Mater.* **2018**, *259*, 155–162. [CrossRef]
14. Kwon, H.T.; Jeong, H.K.; Lee, A.S.; An, H.S.; Lee, J.S. Heteroepitaxially grown zeolitic imidazolate framework membranes with unprecedented propylene/propane separation performances. *J. Am. Chem. Soc.* **2015**, *137*, 12304–12311. [CrossRef] [PubMed]
15. Kwon, H.T.; Jeong, H.K. Highly propylene-selective supported zeolite-imidazolate framework (zif-8) membranes synthesized by rapid microwave-assisted seeding and secondary growth. *Chem. Commun.* **2013**, *49*, 3854–3856. [CrossRef] [PubMed]
16. Lee, M.J.; Kwon, H.T.; Jeong, H.K. Defect-dependent stability of highly propylene-selective zeolitic-imidazolate framework zif-8 membranes. *J. Membr. Sci.* **2017**, *529*, 105–113. [CrossRef]
17. Huang, Y.; Zhang, Y.; Chen, X.; Wu, D.; Yi, Z.; Cao, R. Bimetallic alloy nanocrystals encapsulated in zif-8 for synergistic catalysis of ethylene oxidative degradation. *Chem. Commun.* **2014**, *50*, 10115–10117. [CrossRef] [PubMed]
18. McCarthy, M.C.; Varela-Guerrero, V.; Barnett, G.V.; Jeong, H.K. Synthesis of zeolitic imidazolate framework films and membranes with controlled microstructures. *Langmuir* **2010**, *26*, 14636–14641. [CrossRef] [PubMed]
19. Li, Y.S.; Bux, H.; Feldhoff, A.; Li, G.L.; Yang, W.S.; Caro, J. Controllable synthesis of metal–organic frameworks: From mof nanorods to oriented mof membranes. *Adv. Mater.* **2010**, *22*, 3322–3326. [CrossRef] [PubMed]
20. Li, Y.S.; Liang, F.Y.; Bux, H.; Feldhoff, A.; Yang, W.S.; Caro, J. Molecular sieve membrane: Supported metal–organic framework with high hydrogen selectivity. *Angew. Chem. Int. Ed.* **2010**, *122*, 558–561. [CrossRef]
21. Pan, Y.; Lai, Z. Sharp separation of c2/c3 hydrocarbon mixtures by zeolitic imidazolate framework-8 (zif-8) membranes synthesized in aqueous solutions. *Chem. Commun.* **2011**, *47*, 10275–10277. [CrossRef] [PubMed]

22. Shah, M.; Kwon, H.T.; Tran, V.; Sachdeva, S.; Jeong, H.-K. One step in situ synthesis of supported zeolitic imidazolate framework zif-8 membranes: Role of sodium formate. *Microporous Mesoporous Mater.* **2013**, *165*, 63–69. [CrossRef]
23. Li, L.; Yao, J.; Chen, R.; He, L.; Wang, K.; Wang, H. Infiltration of precursors into a porous alumina support for zif-8 membrane synthesis. *Microporous Mesoporous Mater.* **2013**, *168*, 15–18. [CrossRef]
24. Kwon, H.T.; Jeong, H.-K.; Lee, A.S.; An, H.S.; Lee, T.; Jang, E.; Lee, J.S.; Choi, J. Defect-induced ripening of zeolitic-imidazolate framework zif-8 and its implication to vapor-phase membrane synthesis. *Chem. Commun.* **2016**, *52*, 11669–11672. [CrossRef] [PubMed]
25. Bissett, H.; Zah, J.; Krieg, H.M. Manufacture and optimization of tubular ceramic membrane supports. *Powder Technol.* **2008**, *181*, 57–66. [CrossRef]
26. Biesheuvel, P.M.; Breedveld, V.; Higler, A.P.; Verweij, H. Graded membrane supports produced by centrifugal casting of a slightly polydisperse suspension. *Chem. Eng. Sci.* **2001**, *56*, 3517–3525. [CrossRef]
27. Pina, M.; Arruebo, M.; Felipe, M.; Fleta, F.; Bernal, M.; Coronas, J.; Menendez, M.; Santamaria, J. A semi-continuous method for the synthesis of naa zeolite membranes on tubular supports. *J. Membr. Sci.* **2004**, *244*, 141–150. [CrossRef]
28. Baker, R.W.; Low, B.T. Gas separation membrane materials: A perspective. *Macromolecules* **2014**, *47*, 6999–7013. [CrossRef]
29. Harlacher, T.; Wessling, M. Gas–gas separation by membranes. In *Progress in Filtration and Separation*; Elsevier: New York, NY, USA, 2015; pp. 557–584.
30. Hara, N.; Yoshimune, M.; Negishi, H.; Haraya, K.; Hara, S.; Yamaguchi, T. Diffusive separation of propylene/propane with zif-8 membranes. *J. Membr. Sci.* **2014**, *450*, 215–223. [CrossRef]
31. Hara, N.; Yoshimune, M.; Negishi, H.; Haraya, K.; Hara, S.; Yamaguchi, T. Effect of temperature on synthesis of zif-8 membranes for propylene/propane separation by counter diffusion method. *J. Jpn. Pet. Inst.* **2015**, *58*, 237–244. [CrossRef]
32. Tanaka, S.; Okubo, K.; Kida, K.; Sugita, M.; Takewaki, T. Grain size control of zif-8 membranes by seeding-free aqueous synthesis and their performances in propylene/propane separation. *J. Membr. Sci.* **2017**, *544*, 306–311. [CrossRef]
33. Wang, N.; Liu, T.; Shen, H.; Ji, S.; Li, J.R.; Zhang, R. Ceramic tubular mof hybrid membrane fabricated through in situ layer-by-layer self-assembly for nanofiltration. *AlChE J.* **2016**, *62*, 538–546. [CrossRef]
34. Xie, Z.; Yang, J.; Wang, J.; Bai, J.; Yin, H.; Yuan, B.; Lu, J.; Zhang, Y.; Zhou, L.; Duan, C. Deposition of chemically modified α-al 2 o 3 particles for high performance zif-8 membrane on a macroporous tube. *Chem. Commun.* **2012**, *48*, 5977–5979. [CrossRef] [PubMed]
35. Zhang, K.; Lively, R.P.; Zhang, C.; Koros, W.J.; Chance, R.R. Investigating the intrinsic ethanol/water separation capability of zif-8: An adsorption and diffusion study. *J. Phys. Chem. C* **2013**, *117*, 7214–7225. [CrossRef]
36. Zhang, X.; Liu, Y.; Li, S.; Kong, L.; Liu, H.; Li, Y.; Han, W.; Yeung, K.L.; Zhu, W.; Yang, W. New membrane architecture with high performance: Zif-8 membrane supported on vertically aligned zno nanorods for gas permeation and separation. *Chem. Mater.* **2014**, *26*, 1975–1981. [CrossRef]
37. Sun, Y.; Zhang, R.; Zhao, C.; Wang, N.; Xie, Y.; Li, J.-R. Self-modified fabrication of inner skin zif-8 tubular membranes by a counter diffusion assisted secondary growth method. *RSC Adv.* **2014**, *4*, 33007–33012. [CrossRef]
38. Wang, X.; Sun, M.; Meng, B.; Tan, X.; Liu, J.; Wang, S.; Liu, S. Formation of continuous and highly permeable zif-8 membranes on porous alumina and zinc oxide hollow fibers. *Chem. Commun.* **2016**, *52*, 13448–13451. [CrossRef] [PubMed]
39. Xu, G.; Yao, J.; Wang, K.; He, L.; Webley, P.A.; Chen, C.-S.; Wang, H. Preparation of zif-8 membranes supported on ceramic hollow fibers from a concentrated synthesis gel. *J. Membr. Sci.* **2011**, *385*, 187–193. [CrossRef]
40. Brown, A.J.; Brunelli, N.A.; Eum, K.; Rashidi, F.; Johnson, J.; Koros, W.J.; Jones, C.W.; Nair, S. Interfacial microfluidic processing of metal-organic framework hollow fiber membranes. *Science* **2014**, *345*, 72–75. [CrossRef] [PubMed]
41. Eum, K.; Rownaghi, A.; Choi, D.; Bhave, R.R.; Jones, C.W.; Nair, S. Fluidic processing of high-performance zif-8 membranes on polymeric hollow fibers: Mechanistic insights and microstructure control. *Adv. Funct. Mater.* **2016**, *26*, 5011–5018. [CrossRef]

42. Eum, K.; Ma, C.; Rownaghi, A.; Jones, C.W.; Nair, S. Zif-8 membranes via interfacial microfluidic processing in polymeric hollow fibers: Efficient propylene separation at elevated pressures. *ACS Appl. Mater. Interfaces* **2016**, *8*, 25337–25342. [CrossRef] [PubMed]
43. Brown, A.J.; Johnson, J.; Lydon, M.E.; Koros, W.J.; Jones, C.W.; Nair, S. Continuous polycrystalline zeolitic imidazolate framework-90 membranes on polymeric hollow fibers. *Angew. Chem. Int. Ed.* **2012**, *51*, 10615–10618. [CrossRef] [PubMed]
44. Lee, M.J.; Hamid, M.R.A.; Lee, J.; Kim, J.S.; Lee, Y.M.; Jeong, H.-K. Ultrathin zeolitic-imidazolate framework zif-8 membranes on polymeric hollow fibers for propylene/propane separation. *J. Membr. Sci.* **2018**, *559*, 28–34. [CrossRef]
45. Hou, J.; Sutrisna, P.D.; Zhang, Y.; Chen, V. Formation of ultrathin, continuous metal–organic framework membranes on flexible polymer substrates. *Angew. Chem. Int. Ed.* **2016**, *55*, 3947–3951. [CrossRef] [PubMed]
46. Li, W.; Su, P.; Li, Z.; Xu, Z.; Wang, F.; Ou, H.; Zhang, J.; Zhang, G.; Zeng, E. Ultrathin metal–organic framework membrane production by gel–vapour deposition. *Nat. Commun.* **2017**, *8*, 406. [CrossRef] [PubMed]
47. Cacho-Bailo, F.; Catalan-Aguirre, S.; Etxeberria-Benavides, M.; Karvan, O.; Sebastian, V.; Tellez, C.; Coronas, J. Metal-organic framework membranes on the inner-side of a polymeric hollow fiber by microfluidic synthesis. *J. Membr. Sci.* **2015**, *476*, 277–285. [CrossRef]
48. Marti, A.M.; Wickramanayake, W.; Dahe, G.; Sekizkardes, A.; Bank, T.L.; Hopkinson, D.P.; Venna, S.R. Continuous flow processing of zif-8 membranes on polymeric porous hollow fiber supports for CO_2 capture. *ACS Appl. Mater. Interfaces* **2017**, *9*, 5678–5682. [CrossRef] [PubMed]
49. Biswal, B.P.; Bhaskar, A.; Banerjee, R.; Kharul, U.K. Selective interfacial synthesis of metal–organic frameworks on a polybenzimidazole hollow fiber membrane for gas separation. *Nanoscale* **2015**, *7*, 7291–7298. [CrossRef] [PubMed]
50. Pan, Y.; Wang, B.; Lai, Z. Synthesis of ceramic hollow fiber supported zeolitic imidazolate framework-8 (zif-8) membranes with high hydrogen permeability. *J. Membr. Sci.* **2012**, *421*, 292–298. [CrossRef]
51. Zhou, J.; Zhang, X.; Wang, Y.; Larbot, A.; Hu, X. Elaboration and characterization of tubular macroporous ceramic support for membranes from kaolin and dolomite. *J. Porous Mater.* **2010**, *17*, 1–9. [CrossRef]
52. Huang, A.; Dou, W.; Caro, J.r. Steam-stable zeolitic imidazolate framework zif-90 membrane with hydrogen selectivity through covalent functionalization. *J. Am. Chem. Soc.* **2010**, *132*, 15562–15564. [CrossRef] [PubMed]
53. Venna, S.R.; Carreon, M.A. Highly permeable zeolite imidazolate framework-8 membranes for CO_2/CH_4 separation. *J. Am. Chem. Soc.* **2009**, *132*, 76–78. [CrossRef] [PubMed]
54. Hara, N.; Yoshimune, M.; Negishi, H.; Haraya, K.; Hara, S.; Yamaguchi, T. Zif-8 membranes prepared at miscible and immiscible liquid–liquid interfaces. *Microporous Mesoporous Mater.* **2015**, *206*, 75–80. [CrossRef]
55. Tanaka, S.; Shimada, T.; Fujita, K.; Miyake, Y.; Kida, K.; Yogo, K.; Denayer, J.F.; Sugita, M.; Takewaki, T. Seeding-free aqueous synthesis of zeolitic imidazolate framework-8 membranes: How to trigger preferential heterogeneous nucleation and membrane growth in aqueous rapid reaction solution. *J. Membr. Sci.* **2014**, *472*, 29–38. [CrossRef]
56. Colling, C.W.; Huff, G.A., Jr.; Bartels, J.V. Processes Using Solid Perm-Selective Membranes in Multiple Groups for Simultaneous Recovery of Specified Products from a Fluid Mixture. U.S. Patent US20040004040A1, 1 August 2004.
57. Soukup, K.; Schneider, P.; Šolcová, O. Comparison of wicke–kallenbach and graham's diffusion cells for obtaining transport characteristics of porous solids. *Chem. Eng. Sci.* **2008**, *63*, 1003–1011. [CrossRef]