ZIF-8 Membrane Separation Performance Tuning by Vapor Phase Ligand Treatment

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Abstract: Vapor phase ligand treatment (VPLT) of 2-amino-benzimidazole (2abIm) for 2-methylimidazole (2mIm) in ZIF-8 membranes prepared by two different methods (LIPS: ligand induced perme-selectivation and RTD: rapid thermal deposition) results in a notable shift of the molecular level cut-off to smaller molecules establishing selectivity improvements from ca. 1.8 to 5 for O2/N2; 2.2 to 32 for CO2/CH4; 2.4 to 24 for CO2/N2; 4.8 to 140 for H2/CH4 and 5.2 to 126 for H2/N2. Stable (based on a one-week test) oxygen-selective air separation membranes made by LIPS and RTD membranes exhibit fast and gradual evolution upon exposure to 2abIm-VPLT, respectively, reflecting differences in their thickness and microstructure. Functional reversibility is demonstrated by showing that the original permeation properties of the VPLT-LIPS membranes can be recovered upon 2mIm-VPLT.

Metal–organic framework (MOF) membranes are an emerging class of separation agents,[1–6] offering the potential for much needed energy efficiency improvements.[7] However, the lack of low-cost scalable synthesis is a major hindrance for their adaptation in industrial practice. The recent introduction of an all-vapor-phase robust method for MOF membrane synthesis called ligand induced perme-selectivation (LIPS),[8] holds promise for overcoming this obstacle.

The LIPS approach evolved from earlier work on all-vapor MOF film formation on non-porous supports,[9] which showed that a zinc oxide film made by atomic layer deposition (ALD) could be converted to a polycrystalline ZIF-8 film by 2-methylimidazole (2mIm) vapor treatment. In the LIPS process, the pores of mesoporous (ca. 3 nm) γ-alumina support are blocked by a deposit formed using diethylzinc/water ALD. The deposited oxide is then subjected to a 2abIm vapor treatment. The resulting thin (ca. 100–200 nm) and pore-confined deposit is not highly crystalline but exhibits propane/propylene separation performance comparable or superior to other ZIF-8 membranes made by various approaches that include liquid phase processing.[10–15]

In an effort to expand the range of separations for MOF membranes made by all-vapor-phase processing, here we demonstrate the facile modification of ZIF-8 membranes made by LIPS (LIPS-ZIF-8) through a vapor phase ligand treatment (VPLT) method to tune their separation performance towards smaller molecules. VPLT is found to (i) proceed rapidly in LIPS membranes compared to thicker ZIF-8 membranes made by rapid thermal deposition (RTD)[16] and (ii) be functionally reversible, i.e., upon exposure to 2mIm vapors, VPLT membranes regain their original propylene selective performance.

ZIF-8 membranes (hereafter LIPS-ZIF-8) were synthesized by LIPS as reported previously.[8] VPLT was then performed on as-made LIPS-ZIF-8 membranes by exposing them to sublimated 2abIm vapor at 180°C for 40 min (Scheme 1). The treated membrane (denoted as 2abIm-VPLT-LIPS-ZIF-8) shows a visible color change on its surface. 2abIm is dark yellow, whereas 2mIm is white. Since heating of LIPS-ZIF-8 membrane without 2abIm does not lead to color change, the characteristic color change upon VPLT, shown in the photos included in Scheme 1, is indicative of membrane modification by 2abIm incorporation.

Figure 1A,B shows the 1100–1350 cm−1 range of attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of LIPS-ZIF-8 membranes before and after VPLT, along with ATR-FTIR of 2mIm and 2abIm powders. The entire range of collected ATR-FTIR spectra can be found in Supporting information (Figure S1). A broad-band attributable to water could be observed at ca. 1600 cm−1 and 3600 cm−1, and a CO2 band could be observed at 2300 cm−1 and in the 3600–3800 cm−1 range because the analysis was performed at atmospheric conditions without any treatment.[17] ATR-FTIR on 2abIm powder showed a band at approximately 1280 cm−1, which was not observed with 2mIm.
According to the literature, the adsorption at 1280 cm\(^{-1}\) is due to the C–N stretching vibrations.\(^{[19]}\) The incorporation of 2abIm in VPLT-LIPS-ZIF-8 membrane is supported by the emergence of a band around 1270 cm\(^{-1}\), close to 1280 cm\(^{-1}\), that cannot be seen in pure LIPS-ZIF-8 membrane. The band shift between powder and membrane could be indicative of 2abIm interacting with neighboring zinc atoms through deprotonation.\(^{[19]}\) Consistently, digestion \(^1\)H-NMR spectroscopy of 2abIm-VPLT-LIPS-ZIF-8 membrane confirms the presence of 2abIm with a 2abIm:2mIm molar ratio of 61:39. Detailed \(^1\)H-NMR information can be found in Figure S2. The assignments of the bands after digestion of the ZIFs layer were based on the bands observed for the solution \(^1\)H-NMR of pure organic ligands (Figure S2). In Figure 1C, the XRD pattern of 2abIm-VPLT-LIPS-ZIF-8 shows weak ZIF-8 reflections of similar intensity as in the original LIPS-ZIF-8 membrane. It is noted that the weak peak intensity for LIPS-ZIF-8 membranes is in agreement with the earlier LIPS report\(^{[8]}\) where it was attributed to the nano-confined (γ-alumina has ca. 3 nm pores) and mostly amorphous structure of the selective layer. Top view SEM imaging also reveals no discernible changes. Figure 1D shows featureless surfaces (characteristic for LIPS membranes) before and after VPLT, due to the absence of a highly crystalline deposit outside the pores of the γ-alumina.

From the results shown above, it is indicated that a considerable amount of 2abIm was incorporated in the LIPS-ZIF-8 membrane by VPLT, without altering the confined microstructure of the deposit. Further work is required to elucidate the type of interactions responsible for the incorporation of 2abIm in the ZIF film, for example, by ligand exchange or other mechanisms.

The separation performance of the 2abIm-VPLT-LIPS-ZIF-8 membranes was determined by single component time-lag dead-end (H\(_2\), CO\(_2\), O\(_2\), N\(_2\), and CH\(_4\)) and Wicke–Kallenbach (C\(_3\)H\(_6\) and C\(_3\)H\(_8\)) methods (Figure 2A). The LIPS-ZIF-8 membrane displayed a clear cut-off between propylene and propane with separation factor of about 75 and propylene permeance of 5.5 × 10\(^{-10}\) mol m\(^{-2}\) Pa\(^{-1}\) s\(^{-1}\). Upon VPLT, permeances decreased with more pronounced reductions corresponding to larger molecules. For example, propylene permeance dropped to 4.0 × 10\(^{-10}\) mol m\(^{-2}\) Pa\(^{-1}\) s\(^{-1}\), and the molecular sieve cut-off region shifted from propylene (ca. 4.0 Å) to oxygen (ca. 3.5 Å). Figure 2B shows the ideal selectivities for industrially important gas pairs (O\(_2\)/N\(_2\), CO\(_2)/\)CH\(_4\), CO\(_2//N\(_2\), and H\(_2)/\)CH\(_4\)) before and after VPLT. Upon VPLT, the selectivity of 2abIm-VPLT-LIPS-ZIF-8 membrane increased by more than ca. 2.5, 7, 9, 18, and 24-fold for O\(_2//\)N\(_2\), CO\(_2//\)CH\(_4\), CO\(_2//\)N\(_2\), H\(_2//\)CH\(_4\), and H\(_2//\)N\(_2\), respectively. The 2abIm-VPLT-LIPS-ZIF-8 membranes also exhibit a second permeation cut-off after propylene. Similarly to ZIF-8 membrane, which also shows multiple cut-offs (i.e., at propylene and isobutane), the second cut-off is at too low a permeance (3 × 10\(^{-10}\) mol m\(^{-2}\) Pa\(^{-1}\) s\(^{-1}\)) to be of practical significance.\(^{[10]}\) The observed change (reduced permeability and improved selectivity) for light gases is in agreement with the expected reduction of the effective pore size of ZIF-8 by incorporation of the bulkier 2abIm ligand. Recently, Babu et al. reported the stiffening of ZIF-8 membrane by rapid heat...
membranes. Results from both single gas and mixtures with performance, which has not been reported before for MOF
O₂/N₂ separation factor of 4.2–5.0 close to the upper bound CO₂/CH₄ selectivity by enhanced CO₂ adsorption. [22]

Figure 2. A) Gas permeation properties of 2abIm-VPLT-LIPS-ZIF-8 membrane by the time-lag (H₂, CO₂, O₂, N₂, CH₄) or Wicke–Kallenbach (C₃H₆, C₃H₈) methods at 25°C. B) Permeoselctivity of gas pairs before and after 2abIm-VPLT. Error bars are derived from five independently prepared membranes. C) O₂/N₂ mixture (21/79) separation properties of a 2abIm-VPLT-LIPS-ZIF-8 membrane as a function of temperature at a feed pressure of 7 bar(a) and 1 bar(a) sweep-free permeate. D) C₃H₆, C₃H₈, O₂, and N₂ permeances for LIPS-ZIF-8 membranes upon sequential VPLT with 2abIm and 2mIm showing reversible performance.

Figure 3. H₂, CO₂, and CH₄ permeances and H₂/CH₄ and CO₂/CH₄ selectivities for ZIF-8 membranes follow a similar gradual trend, as shown in Figure 3. H₂, CO₂, and CH₄ permeances and H₂/CH₄ and CO₂/CH₄ selectivities reach after 24 h similar levels to those obtained after only 40 min of 2abIm-VPLT on LIPS-ZIF-8 membranes. The requirement for lengthy treatment is a processing disadvantage for RTD membranes but offers the

Figure 3. H₂/CH₄, and B) CO₂/CH₄ gas permeation properties (at 25°C) of a 2abIm-VPLT-RTD-ZIF-8 membrane as a function of VPLT time.

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opportunity for precise tuning of permeance-selectivity combinations to match process scale requirements.

In summary, we have reported that the vapor phase treatment of ZIF-8 membranes with 2abIm can be used to tune their separation performance toward smaller molecules. While VPLT is expected to be widely applicable for ZIF and other MOF membranes made by various methods, the all-vapor combination of VPLT and LIPS is particularly attractive for scalable membrane fabrication.

Acknowledgements

This work was supported as part of the Center for Gas Separations, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0001015 (membrane synthesis), and the US National Science Foundation under Award CBET-1705687 (gas permeation testing and membrane characterization).

Conflict of interest

The authors declare no conflict of interest.

Keywords: ligand-induced permselectivity · membranes · metal–organic frameworks · vapor phase · ZIF-8


Manuscript received: July 28, 2019
Version of record online: ■ ■ ■ ■ ■
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Oxygen separation from air and other gas separations are enabled by a facile vapor phase ligand treatment method (VPLT) for the modification of ZIF membranes. The changes of permeation properties are reversible and can be gradual allowing for tailoring performance to applications.