

SUMMARY

Membrane-based separation has become a promising alternative to traditional separation processes to capture CO₂ owing to the great features such as energy efficiency and environmental friendliness. Polymers are easy to process and have been commercialized. However, most commercial polymer membranes suffer from a trade-off relation between gas permeability and selectivity. Porous organic frameworks (POFs) are an emerging class of microporous polymers, which may have high CO₂ permeability and selectivity when being processed into membranes due to their intrinsic porosity and strong CO₂ adsorption ability. However, using POFs as membranes are still at the infancy stage due to their insolubility in most common solvents.

Thus, this thesis focusses on the development of porous organic frameworks (POFs) membranes for various CO₂ separation applications, including biogas upgrading, (Chapter 2), post-combustion CO₂ capture (Chapter 3 and 4) and pre-combustion capture (Chapter 5). The fully organic nature together with the excellent thermal and chemical stabilities make POFs promising to be used as membranes for CO₂ separation.

Part I (Chapter 1) gives an introduction on different types of POFs along with their structures and applications in gas separation either in the form of mixed-matrix membranes (MMMs) or pure POF membranes. Some basic definitions and separation mechanisms are also discussed for better understanding the following chapters. POFs can have a crystalline or amorphous structure, thus we choose two types of POFs for membrane preparation. One is a crystalline POF, azine-linked covalent organic frameworks (ACOF-1) (**Part II**) and the other is an amorphous POF, benzimidazole-linked polymers (BILP-101) (**Part III**).

Part II includes **Chapter 2** and **3**. In Chapter 2, we first focus on the synthesis and characterization of an ACOF-1. ACOF-1 was chosen because of its relatively small pore size ($\sim 9.4 \text{ \AA}$) and high CO₂ adsorption capacity. Diffusion reflectance infrared Fourier transform (DRIFT) and solid-state ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy confirms the successful synthesis of ACOF-1 with the

formation of characteristic C=N band. N₂ adsorption suggests a microporous structure. powder X-ray diffraction (PXRD) pattern reveals the good crystallinity. The CO₂ uptake of ACOF-1 at 1 bar, 3.92 mmol·g⁻¹, is much higher than that of CH₄, 0.92 mmol·g⁻¹, which demonstrates its selectivity towards CO₂. ACOF-1 was incorporated into Matrimid® to prepare MMMs. Cross-sectional scanning electron microscopy (SEM) images and Raman spectroscopy of the resulting membranes indicate a good dispersion of ACOF-1 in the polymer matrix. The ACOF-1 containing mixed-matrix membranes (MMMs) were tested for CO₂/CH₄ separation at 308 K. The gas permeability increases with ACOF-1 loading and the 16 wt.% COF loading MMM shows an increase of more than doubling of the CO₂ permeability compared to the bare Matrimid® membrane, together with slightly higher CO₂/CH₄ selectivities. The increase in gas permeability is attributed to the additional gas transport pathways introduced by the porous ACOF-1 network, while the slightly higher CO₂/CH₄ selectivities can be rationalized by the selective adsorption of CO₂ over CH₄ in the N-rich ACOF-1 through dipole-quadrupole interactions.

In Chapter 3, ACOF-1 was further incorporated into 3 different polymer matrices (low flux-mid selectivity Matrimid®, mid flux-high selectivity Polyactive™ and high flux-low selectivity 6FDA:DAM) to investigate the influence of polymeric components on post-combustion CO₂ capture. For Matrimid® and 6FDA:DAM, an overall enhancement of the polymer's separation properties could be achieved, in case of Polyactive™ penetration of the more flexible polymer into the COF porosity resulted in a decreased membrane permeability. The best improvement was obtained for Matrimid®-based MMMs, for which the CO₂/N₂ selectivity increases from 29 to 35, together with an enhancement in CO₂ permeability from 9.5 to 17.7 Barrer for 16 wt.% COF loading, was observed. All the composite membranes show a higher selectivity, which is attributed to the favorable CO₂ adsorption ability of ACOF-1. This chapter demonstrates that the combination of the filler-polymeric matrix pair chosen is crucial for POF based MMMs. Overall, **Part II** presents ACOF-1 as an interesting candidate to prepare MMMs for CO₂ separation.

Part III comprises **Chapter 4 and 5**. In this part, the main focus is on the development of BILP membranes for post-combustion (Chapter 4) as well as for pre-combustion (Chapter 5). BILP-101 was selected because of its ultra-microporous structure (reported pore size ~

5.4 Å) and high stability. In Chapter 4, BILPs with large and small porosity (BILP-101 and RT-BILP-101) were synthesized through controlling the initial polymerization rate. RT-BILP-101 with lower porosity was synthesized at room temperature, increasing the nucleation rate and resulting in smaller particle size and porosity. The incorporation of both BILPs into Matrimid® to prepare MMMs resulted in an increased gas permeability with loading for both CO₂ and N₂, attributed to the introduction of fast transport ways by porous BILPs. MMMs fabricated with RT-BILP-101 exhibits a higher gas permeability than BILP-101 MMMs at the same loading. The best improvement was achieved by 24 wt.% RT-BILP-101 MMMs, for which the CO₂ permeability increases 2.8 times, from 9.6 to 26.5 Barrer. The selectivity remained constant upon BILP addition and is still determined by the polymer matrix.

Chapter 5 describes the further engineering of BILP-101 into pure POF membranes. Using the interfacial polymerization method, free standing BILP-101 films were formed at a benzene-water interface. DRIFTS and ¹³C CP/MAS) NMR spectroscopies confirm the same chemical connectivity as BILP spherical particles synthesized in Chapter 4. SEM, TEM and AFM supported the formation of sheet-like morphology. BILP-101 membrane films were further fabricated in a similar manner onto porous α-Al₂O₃ supports with a top layer of γ-Al₂O₃. The obtained membranes demonstrated a high potential for pre-combustion CO₂ capture with an ultrahigh H₂ selectivity (up to 40) at elevated temperature (423 K) together with high-pressure resistance. Even at 10 bar absolute feed pressure and 423 K the membrane still exhibits a H₂/CO₂ selectivity of 25. In addition, the membrane remained stable under alternating dry and humidified gas mixtures at 423 K during 800 h of operation. The separation performance was even slightly improved during this 800 h long hydrocycling test. The supported BILP membranes were also selective in the H₂/N₂ separation with selectivity values up to 87. All results point to the interpretation that these membranes are operated by molecular sieving and can be used for a wider range of gas separation applications.

Overall, the obtained results in this thesis demonstrate that POFs are promising candidates to be applied in membrane fields for CO₂ separation. The fully organic nature makes POFs attractive and easy to be incorporated into polymers to prepare defect-free MMMs due to their excellent compatibility. Another alternative method, interfacial polymerization, offers an interesting outlook for the preparation of defect-free pure POF membranes. The combination of the above two preparation methods with the rich chemistry of POFs may open the door to the rational design of versatile POF membranes for a wide range of separations.

Samenvatting