

Synthesis of Thin Film Composite Metal-Organic Frameworks Membranes on Polymer Supports

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ABSTRACT**Synthesis of Thin Film Composite Metal-Organic Frameworks Membranes on Polymer Supports**

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Since the discovery of size-selective metal-organic frameworks (MOF) researchers have tried to manufacture them into gas separation membranes. ZIF-8 became the most studied MOF for membrane applications mainly because of its simple synthesis, good chemical and thermal stability, recent commercial availability and attractive pore size.

The aim of this work is to develop convenient methods for growing ZIF thin layers on polymer supports to obtain defect-free ZIF membranes with good gas separation properties. We present new approaches for ZIF membranes preparation on polymers.

We introduce zinc oxide nanoparticles in the support as a secondary metal source for ZIF-8 growth. Initially the ZnO particles were incorporated into the polymer matrix and later on the surface of the polymer by magnetron sputtering. In both cases, the ZnO facilitated to create more nucleation opportunities and improved the ZIF-8 growth compared to the synthesis without using ZnO. By employing the secondary seeded growth method, we were able to obtain thin (900 nm) ZIF-8 layer with good gas separation performance.

Next, we propose a metal-chelating polymer as a suitable support for growing ZIF layers. Defect-free ZIF-8 films with a thickness of 600 nm could be obtained by a contra-diffusion method. ZIF-8 membranes were tested for permeation of hydrogen and hydrocarbons, and one of the highest selectivities reported so far for hydrogen/propane, and propylene/propane was obtained.

Another promising method to facilitate the growth of MOFs on polymeric supports is the chemical functionalization of the support surface with functional groups, which can complex metal ions and which can covalently bond the MOF crystals. We functionalized the surface of a common porous polymeric membrane with amine groups, which took part in the reaction to form ZIF-8 nanocrystals. We observed an enhancement in adhesion between the ZIF layer and the support. The effect of parameters of the contra-diffusion experiment (such as temperature lower than room temperature and synthesis times shorter than 1 hour) on ZIF-8 membrane properties was evaluated. We could prepare one of the thinnest (around 200 nm) yet selective ZIF-8 films reported.

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1 Chapter

1.1 Introduction

The importance of membrane technology for gas separation has increased during the last two decades. Development of gas separation membrane focuses on materials which can offer high permeability combined with reasonable selectivity. Organic polymers are the dominating material for commercial gas-separation membranes thanks to their convenient manufacture and mechanical strength. Inorganic materials possess several advantages relative to polymers such as defined pore sizes and high thermal and chemical stability, however, till now, they are too expensive for most industrial applications.

A relatively new group of hybrid porous materials called metal-organic frameworks (MOF) attracted research interest thanks to their exciting potential for various fields. MOFs are built up of metal or metal cluster centers bonded by organic ligands. A much-researched subclass of MOFs are zeolitic imidazolate frameworks (ZIF) which have a network ordered in an analogous fashion to that of silicon and oxygen in zeolites. However, their coordination network is mechanically less stiff and brittle compared to zeolites. [1] In general, ZIFs possess desired properties such as crystallinity, microporosity, high surface area, and exceptional thermal and chemical stability [2, 3].

ZIFs can be incorporated into a polymer matrix similarly to zeolites to improve selective properties of the mixed-matrix membrane (MMM), or they can be grown on the surface of a porous support to serve as a selective layer of a composite membrane. Thin dense MOF layers

have been successfully synthesized on inorganic supports and offered superior selective properties. However polymeric supports possess several advantages over ceramic supports. They are much cheaper, lighter and they can be easily produced in modules on a large scale.

Herein, we present new methods for growing ZIF thin layers on polymer supports while aiming to obtain thin (less than 1 μm) and defect-free ZIF membranes with high gas permeance and selectivity performance.

1.2 Dissertation structure and goals

This dissertation is composed of six chapters which all address the topic of synthesis and performance of MOF thin film composite membranes prepared on a polymer support.

Chapter 1 introduces the subject of MOF membranes and offers a recent literature review about the employment of MOF materials in the membranes field. Different approaches used for MOF membrane fabrication are explained on examples from literature. The area of growing MOF membranes on various polymer supports is discussed in more detail.

Chapter 2 provides results from our very first approach for developing ZIF-8 membrane on a polymer support. A porous mixed-matrix membrane composed of polyetherimide (PEI) and zinc oxide nanoparticles was fabricated and applied as support for the ZIF-8 layer. It was assumed that presence of zinc oxide in the support would be beneficial for the ZIF-8 growth and would enhance the affinity between the two layers. Different seeding methods were studied, and secondary growth conditions were optimized. Final coating with the fast permeating polymer silicon rubber was introduced as defects-sealing and a protective layer.

Chapter 3 presents an interesting double-metal-source method when zinc oxide sputter coatings served as effective seeding layers for ZIF-8 growth. By a sputtering technique commercial polyacrylonitrile (PAN) supports were coated with a 90 nm thin zinc oxide layer, which was transformed to ZIF-8 during the subsequent growth step. The obtained ZIF-8 layer was only 900 nm thick and was tested for hydrogen/propane and propylene/propane separation.

Chapter 4 introduces a contra-diffusion method and an uncommon polymer called poly thiosemicarbazide (PTSC) which can bind metal ions and form chelates. The metal and ligand concentrations were adjusted to produce a very compact ZIF-8 layer that displayed interference colors due to its smooth surface and extreme thinness (around 600 nm). High performance for hydrogen/propane (8300) and propylene/propane (150) selectivity were measured.

Chapter 5 also focuses on the contra-diffusion method and tries to offer an answer to the question: "How thin is the thinnest yet selective ZIF-8 layer?" Two chemical surface modifications with ethylenediamine and histamine are introduced to enhance the zinc binding ability of the PEI support and thus improve the ZIF-8 layer's adhesion to the support. The effect of a low temperature ZIF-8 synthesis and short reaction times on the final membrane thickness and gas separation performance was studied. ZIF-8 layers as thin as 200 nm were prepared. Coating with the fast permeating polymer poly(trimethylsilyl)propyne (PTMSP) showed to be a promising approach for boosting selectivity of very thin ZIF-8 layers.

Chapter 6 summarizes the conclusions of this dissertation and offers plans for future work in this area.

1.3 Literature review: Employment of MOFs in the membrane field

1.3.1 Definition of metal-organic frameworks

Metal-organic frameworks as a new group of porous materials were introduced about 25 years ago by the pioneering work of the research group under professor Omar Yaghi, who authored the first report on design and synthesis of an exceptionally stable and highly porous MOF in 1999 [4]. These hybrid materials have been defined by the chemical community through IUPAC as *“a Coordination Network with organic ligands containing potential voids.”* While the coordination network is defined as *“a coordination compound extending, through repeating coordination entities, in 1 dimension, but with crosslinks between two or more individual chains, loops or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions.”*[5] And the coordination entity is *“an ion or neutral molecule that is composed of a central atom, usually that of metal, to which is attached a surrounding array of atoms or groups of atoms, each of which is called a ligand.”* [6] MOFs belong to the group of Coordination Polymers materials.

The existence of a vast number of combinations of metals and organic linkers gives theoretically almost unlimited number of possible MOF structures [7, 8]. However, only some of them are being deeply researched and tested for potential applications because they showed reasonable thermal and chemical stability and can be synthesized relatively easily in high purity and crystallinity. Beside their high surface area and porosity, the main MOF's advantage are their tunable properties such as their pore size and shape and pore surface chemistry. It was also reported that MOFs are relatively flexible structures and phenomena like “gate opening”, “breathing” and “linker dynamics” have been observed under pressure of the guest molecule,

which could be used in their application in gas storage [9-11]. Moreover, MOF has caught attention to be potentially useful also in other applications, including gas adsorption and separation [12], catalysis [13], chemical sensors [14], drug delivery [15] and other biomedical applications [16, 17].

MOF materials became an interesting material indeed also for the membrane community. Already in 2005, Sanchez *et al.* [18] reported their expectation of using these new hybrid materials for membranes and in separation devices. On the following pages a review about the MOF membranes development over the past decade is delivered.

1.3.2 Types of MOF membranes

There are two different ways how MOFs are being used in membranes (Fig. 1.1).

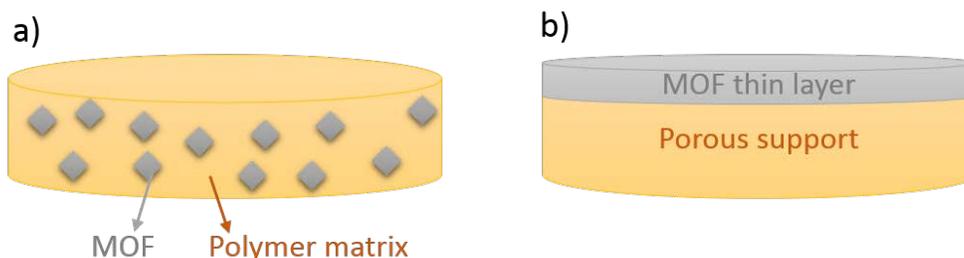


Fig. 1.1 Schematic illustration of the two modes how MOF are employed in membranes: a) as fillers in mixed-matrix membrane, or b) as thin film layers grown on a support

Similarly to other porous materials MOFs can serve as fillers in a polymer matrix to produce mixed-matrix membranes (MMM). In 1973, researchers Paul and Kemp [19] reported one of the first MMM for gas separation composed of zeolite particles (molecular sieve type 5A) incorporated in silicon rubber membrane. They studied how the presence of these adsorptive

fillers in membranes changes the diffusion time lag of gases. Later, Kulprathipanja *et al.* [20] reported an increase of oxygen/nitrogen selectivity, when silicalite was added in a cellulose acetate matrix. Since then, numerous works have been published to present the successful synthesis of MMM composed of various fillers in different polymers [21].

The primary purpose of adding fillers into a polymer matrix is to increase the selectivity of the final membrane in comparison to the pristine polymer membrane. When using the mixed-matrix membrane approach, we may benefit from the excellent processability and mechanical properties of the polymer and at the same time from the high permeability and selectivity properties of the filler particle. The traditional filler is an inorganic material such as zeolite, carbon molecular sieve, mesoporous silica, nonporous silica, metal oxide or carbon nanotube. An ideal mixed-matrix membrane (as shown in Fig. 4 a) is a matrix with perfect adhesion between polymer and fillers without gaps at the interface and aggregation or sedimentation of the particles. However, the traditional fillers (if not chemically functionalized) often suffer from poor adhesion to the polymer matrix, and this results in the formation of non-selective defects and voids at the filler-polymer interface, which will dramatically affect the performance of the MMM. Since MOFs are hybrid materials with an organic component like organic polymers, one can expect that the affinity between MOF and polymer may be enhanced compared to traditional fillers in MMM [22]. There is an interesting approach recently reported about surface cross-linking of ZIF-8/polyimide MMM by Wijenayake *et al.* [23, 24] Their MMM was composed of 33.3 wt. % ZIF-8 in 6FDA-durene and the surface was cross-linked by reacting with ethylenediamine

vapor. The tests showed, that permselective properties of as-prepared MMM fall above the most recent permeability-selectivity trade-off lines for H_2/CO_2 , H_2/N_2 , and H_2/CH_4 gas couples.

The other approach is to form a MOF layer on a support to produce thin film composite membranes (Fig. 1.1b). All projects within this thesis deal with growing MOF layers on a polymer support; therefore the literature review provided here is about the recent development in the synthesis of thin MOF membranes on various supports.

1.3.2.1 The MOF film synthesis methods

When forming MOF layers, we aim to obtain compact, thin, defect-free and selective MOF layers on a support. There are various growing methods, which have been shown as promising techniques for growing MOF films (Fig. 1.2). Most of them have been inspired by the techniques originally developed for the preparation of zeolite membranes. We can divide them into the four following categories:

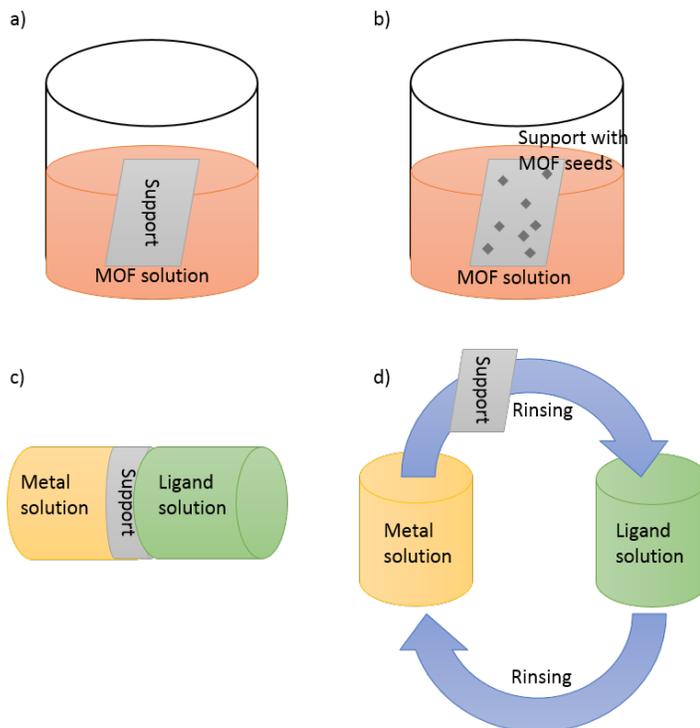


Fig. 1.2 Schematic illustration of four main methods for growing MOF films: a) direct growth, b) secondary seeded growth, c) contra-diffusion method, d) layer-by-layer method.

1. *In-situ* (direct) growth

The *in-situ* growth is a one-step procedure, in which the support is immersed in the MOF growth solution without any crystals previously attached to the surface (Fig. 1.2 a). The nucleation, growth, and intergrowth of MOF occur during the same fabrication step. The main advantage of the direct growth is its simple, quick and straightforward approach for obtaining MOF layers. However, there are only a few examples in the literature showing that this one-step method led to well-intergrown, continuous and selective MOF films.

2. Secondary (seeded) growth

Secondary seeded growth consists of two main fabrication steps (Fig. 1.2 b). Initially, the seeding MOF crystals are attached to the support by using a seeding method. Then the seeded support is immersed into the growth solution to form a continuous MOF layer. The seeds are the nucleation centers which enhance the MOF layer growth and its attachment to the support during the secondary growth.

3. Contra-diffusion growth

The support is placed between the solution of metal source and solution of ligand source (Fig. 1.2 c). These two reactants contra-diffuse through the support to the opposite solution, and as they meet, they react and form MOF crystals. As the process continues, the MOF layer can be obtained on the support surface or also inside the support's pores. Contra-diffusion method is considered as a self-limiting method because the reactants diffuse through spaces which are not covered by MOF layer and thus seal any pinholes.

4. Layer-by-layer method

The principle of this method is to repeat an arbitrary number of cycles of immersing the support in the metal source solution, rinsing it, then immersing in the ligand source solution and rinsing it (Fig. 1.2 d). As the name of this method suggests, the desired film is grown by forming an ultrathin sublayer on top of another layer. The method is convenient when we need to control the thickness of MOF film.

In each of these methods there are numerous parameters (such as synthesis temperature and pressure, time and reactant concentrations), which should be optimized to obtain thin selective MOF layers without defects.

1.3.2.2 The MOFs used for membranes

Although there are over 50,000 MOFs in The Cambridge Crystallographic Data Centre, only a few of them are being deeply researched for applications in the membranes field. Without any doubt, the most studied is the subgroup of MOF called zeolitic imidazolate frameworks (ZIF). ZIFs are composed of tetrahedrally-coordinated transition metal ions (such as Zn, Co, Cu) which are connected by imidazolate linkers. Their name came from the fact that the metal-imidazole-metal angle is similar to the 145° Si-O-Si angle in zeolites and thus ZIFs take zeolite-like topologies (Fig. 1.3).

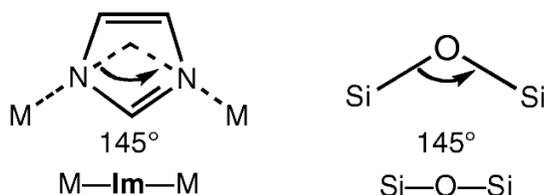


Fig. 1.3 Schematic illustration of the angle in ZIFs and zeolites (adopted from [3]).

More than one hundred ZIF materials have been introduced so far. Many of them have an attractive window size (less than 7 \AA) for the molecular sieving-based membrane in gas and vapor

separations [3, 25, 26]. In the 2015 review authors Zhang and Koros [27] admonished that over 70 % of total published work on the topic of ZIF-enabled membranes deals with ZIF-8.

ZIF-8 is composed of tetrahedrally coordinated zinc ions which are connected by 2-methylimidazole bridges. It has a sodalite (SOD) topology (Fig. 1.4) with the theoretical crystallographic size of aperture 3.4 Å. However, it was reported that the effective size is somewhat larger; around 4.2 Å. This proportion is ideal for separating propylene from propane. The ZIF-8's synthesis protocol is convenient because it can be prepared at room temperature and in an aqueous medium within few minutes. It also possesses an excellent thermal and chemical stability. These features made this framework a promising membrane material.

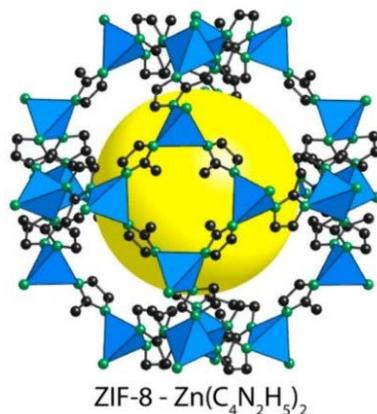


Fig. 1.4 Schematic model of the ZIF-8 structure, nitrogen atoms are green, carbons are black, and the blue pyramids show tetrahedrally coordinated zinc ions (adopted from [3]).

1.3.2.3 MOF membranes prepared on inorganic supports

One of the first MOF membranes was prepared by Guo *et al.* [28] in 2009. A film of HKUST-1 which is an MOF structure composed of copper ions and benzene tricarboxylic acid ligands was

synthesized by a so-called “twin copper source” growth method. They used a copper net not only as a support but also as a source of the copper during the MOF layer synthesis. The gas separation tests showed that the prepared membrane is more permeable and selective for H₂ over other studied gasses with the selectivity for H₂/N₂ of 7.

About the same time, a continuous ZIF-8 membrane (Fig. 1.5) was developed by Professor Caro’s research group who has presented its fabrication on an asymmetric porous titania support [29]. They prepared an around 40 μm thick ZIF-8 layer by direct growth method using microwave-assisted heating, which allowed them to shorten the synthesis time to only 4 hours. The membrane showed a separation factor of 11.2 for an equimolar hydrogen/methane mixture.

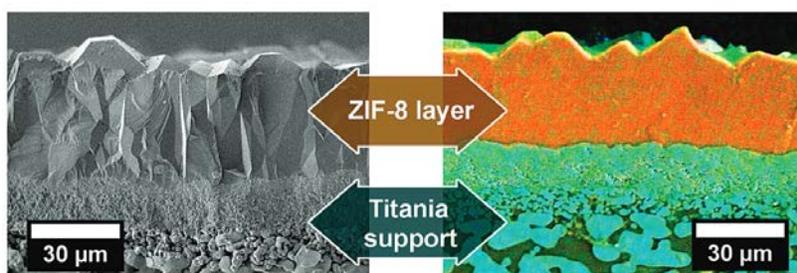


Fig. 1.5 SEM image (left) and EDXS mapping of the ZIF-8 membrane prepared on a titania support (adopted from [29]).

The same group reported the preparation of several other MOF composite membranes such as manganese(II) formate [30], ZIF-22 [31], ZIF-90 [32, 33], ZIF-7 [34] and ZIF-100 [35]. Among the developments they proposed was also an enhancement of the MOF adhesion to the ceramic support by modification of the supports for instance by polyethyleneimine, polydopamine [35, 36], graphene oxide [37] or amino-functionalized silanes. The polydopamine coating (Fig. 1.6)

was originally inspired by the ability of marine mussels to stick to almost any kind of surface as it was described in 2007 by Lee *et al.* [38].

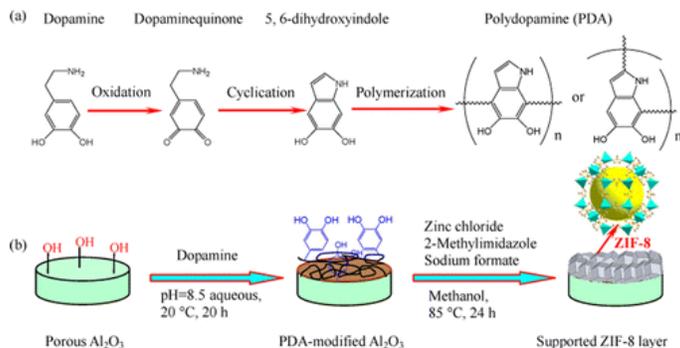


Fig. 1.6 Schematic illustration of the synthesis of ZIF-8 membrane on a polydopamine modified support (adopted from [35]).

The MOF membranes showed the desired molecular-sieving transport and a sharp cut-off between H_2 and other permeants such as CO_2 , CH_4 and propane. Later, they prepared a ZIF-8 membrane supported by an alumina disk [39] with a preferred orientation of crystal grains by secondary seeded growth method (Fig. 1.7.), and a sharp molecular sieve separation was observed for an equimolar $\text{H}_2/\text{C}_3\text{H}_8$ mixture with a separation factor above 300.

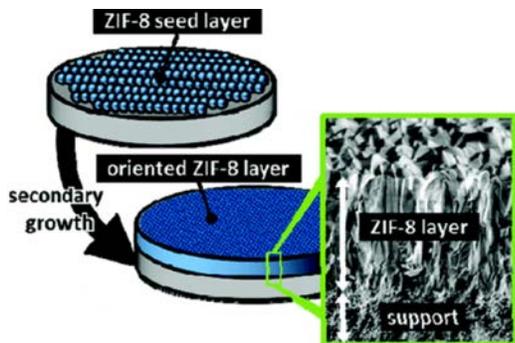


Fig. 1.7 ZIF-8 membrane on an alumina disc support prepared by secondary seeded growth method (adopted from [39]).

The research groups around professors Christof Wöll and Roland A. Fisher [40-44] achieved significant developments in growing MOF layers. In 2007, they [45] developed the layer-by-layer method for forming MOF films on supports.

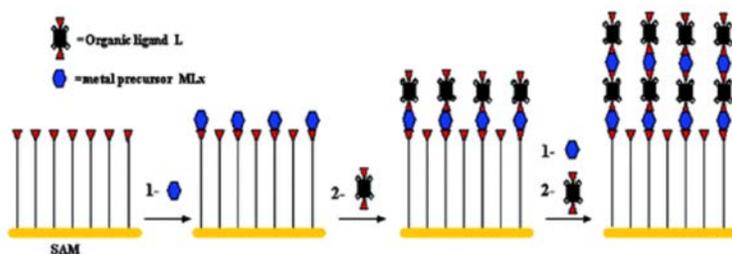


Fig. 1.8 Illustration of the step-by-step growth of the MOF on the substrates, by repeated immersion cycles, first in a solution of metal precursor and subsequently in a solution of organic ligand (adopted from [45]).

Using this method which is also named liquid epitaxy they prepared a film of HKUST-1. They used a support functionalized with COOH-groups, which can bind copper ions and thus serve as a link

between the support and the growing MOF layer. This step-by-step approach enables to study the kinetics of each step in MOF films formation [46, 47] and it also can be used for growing novel MOF-like layers using a different combination of more metals or ligands [48].

An interesting example of applying this method was provided by Shekhah *et al.* [49] for growing ZIF-8 membrane on a porous support. They obtained an ultrathin (0.5–1 μm) ZIF-8 layer, which was tested for gas separation by the time lag technique (constant-volume-variable-pressure) with vacuum on the permeate side. They showed that the selectivity of the membrane for propylene over propane and for methane over n-butane decreased by time and they noted that a quick reading of the values at non-equilibrium state could lead to overestimating the selectivity performance for these gas mixtures. The same group very recently reported preparation of several MOF films on functionalized inorganic substrates by combining the liquid epitaxy technique with spin coating [50], which showed to be an efficient next generation procedure for MOF formation with the possibility to scale-up.

Professors Joseph T. Hupp and Omar K. Farha with their groups have as well contributed to the field of MOF films. Although their primary focus was on MOF synthesis and their application in gas sorption [51-54], they have as well prepared ZIF-8 [55] and other MOF films [56, 57]. They have used a chemical modification of the support to improve adhesion of ZIF-8 crystals through deposition of APTES-functionalized $\alpha\text{-Al}_2\text{O}_3$ particles onto a macroporous support [55]. Their membrane achieved a H_2/N_2 ideal selectivity of 15.4.

The group of professor Hae-Kwon Jeong [58-60] reported in 2008 a microwave-induced thermal deposition for obtaining MOF thin films. They prepared membranes of HKUST-1 [61], ZIF-7 and

ZIF-8 [62] on alumina supports with the lack of macroscopic cracks or defects while reaching relatively high separation performance. The ZIF-8 membranes prepared by microwave-assisted seeding and secondary growth showed an average propylene-propane selectivity of about 40. The same group very recently presented microwave-assisted synthesis to prepare a hybrid cobalt-ZIF-8 membrane by mixing zinc and cobalt metal sources [63]. They observed enhanced performance for propylene/propane separation (separation factor about 120) compared to the original ZIF-8 membrane (separation factor about 60).

Experience with zeolites membranes helped professor Huanting Wang and his research group to introduce several significant developments in growing thin MOF membranes. Xu *et al.* [64] prepared ZIF-8 membrane supported on ceramic hollow fibers from a synthesis gel which was composed of ZIF-8 reactants at relatively high concentration. The permeation tests of their membrane showed selectivities of H_2/CO_2 , N_2/CO_2 and CH_4/CO_2 to be about ten times greater than the corresponding Knudsen selectivities. They observed a significant decrease of CO_2 permeance (about four times) within the first 12 hours of the permeation experiment which also resulted in lower fluxes of the other studied gasses. They explained it by the strong CO_2 adsorption in the micro-cavities of ZIF-8 membranes which partially blocked the gas transport. Hu *et al.* [65] recently reported preparation of ZIF-8 membranes by contra-diffusion on an alumina support, which was initially seeded by a hybrid mixture of ZIF-8 and graphene oxide nanosheets. They obtained very thin and compact ZIF-8 membranes, which showed an ideal selectivity of 12 for propylene/propane separation.

In 2011, the Professor Zhiping Lai's research team reported a greener, convenient room-temperature synthesis of ZIF-8 crystals using water as the solvent medium [66]. Before that, ZIF-8 was mostly synthesized in organic solvents, mainly DMF or DMAc and at higher temperatures (around 100 °C). Their synthesis solution with the relatively high molar ratio between zinc and imidazole (1:70) resulted in obtaining 85 nm large ZIF-8 crystals within only 5 min after mixing the reactants together. Later, they also presented the ZIF-8 membrane fabrication in an aqueous solution by the secondary seeded method (Fig. 1.9) [67, 68]. The achieved separation factors for mixtures of ethane/propane, ethylene/propylene, and ethylene/propane were around 80, 10 and 167, respectively. The ZIF-8 membrane was also synthesized on a yttria-stabilized zirconia fiber supports with high permeability for hydrogen [69]. The ideal selectivity for H₂/C₃H₈ was calculated as 1100, and the mixed gas measurements showed that the separation factor for this gas pair was about 470.

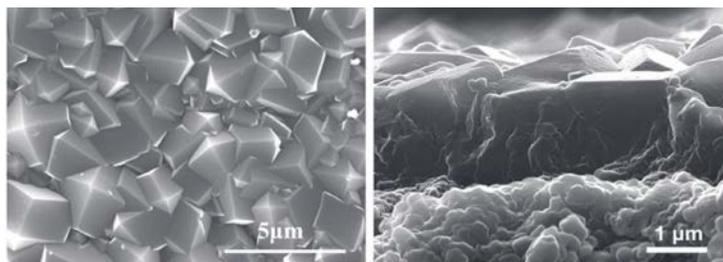


Fig. 1.9 SEM images of the surface (left) and the cross-section (right) of the ZIF-8 membrane prepared in aqueous solution (adopted from [67]).

Often MOF layers have been grown on supports modified by various materials. An interesting example of growing MOFs on a layer of a covalent-organic framework (COF) was recently

presented by Fu *et al.* [70]. The COF-MOF composite membrane was prepared as schematically shown in Fig. 1.10. First, the ceramic support was coated with a polyaniline (PANI) layer, which played the role of an anchor for the next COF layer because of the imine groups' content. In the second step, the PANI coated support was immersed in the mother solution of COF-300 (this COF is composed of terephthalaldehyde and tetra-(4-anilyl)-methane). In the last step, they synthesized the MOF layer on a COF-PANI support; two different MOFs were studied: $\text{Zn}_2(\text{bdc})_2(\text{dabco})$ and ZIF-8. The authors claimed that the performance of their membrane for H_2/CO_2 separation is unique because of the combination of the properties of COF and MOF and because of a very thin and selective layer at the interface of these two materials. The separation factor for H_2/CO_2 of the COF-300-ZIF-8 membrane reached 13.5 which is almost double compared to the separation factors of the pure ZIF-8 and COF-300 membranes.

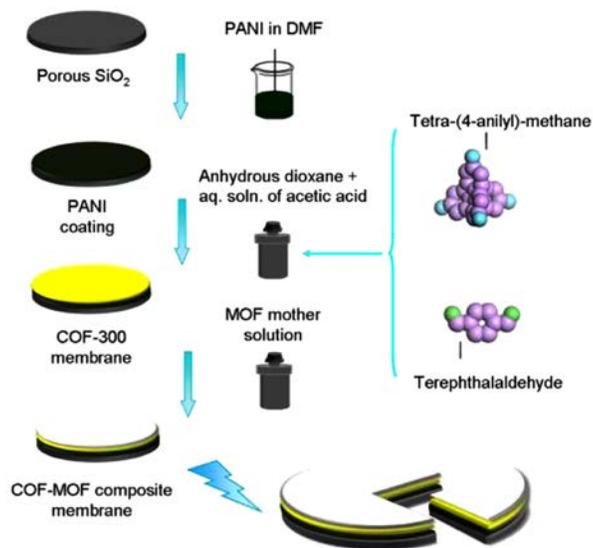


Fig. 1.10 Schematic illustration of the COF-MOF composite membrane preparation (adopted from [70]).

It has been reported [63, 71-77] that adsorption and other properties of MOFs can be tuned through a post-synthetic ligand and cation exchange strategy. Wang *et al.* [78] recently prepared ZIF-67 (MOF composed of cobalt ions and methylimidazole ligands) membranes on alumina supports and investigated how the performance for propylene/propane separation would change with substituting the cobalt ion with the zinc ion. The separation factor increased from 1.4 for the parent ZIF-67 membrane to 50 for the 90% zinc-substituted ZIF-67 membrane.

1.3.2.4 MOF membranes prepared on polymeric supports

The examples mentioned so far were dealing with the synthesis of MOF films on inorganic supports. The inorganic supports have the advantage of being robust and very inert materials. They can be used for growing MOF layers by the solvothermal method, and they are not damaged by high temperatures or organic solvents. In the laboratory it is also convenient to prepare the MOF films on ceramic disks because they do not bend and thus the risk of cracks formation in the MOF layer is low. The membrane's handling and testing are not difficult.

However, the scalable and competitive fabrication of MOF composite membranes would be more realistic, if porous polymer membranes could be used as the supporting material. Porous polymer supports are much cheaper than ceramic ones because they can be manufactured with high speed on continuously operating machines. Moreover, the polymeric materials can have better compatibilities with MOFs compared to ceramic substrates.

In 2010 Centrone *et al.* [79] reported for the first time preparation of a MOF film on a polymer material. They synthesized films of MIL-47 on a polyacrylonitrile (PAN) substrate. MIL-47 is a

framework composed of vanadium(III) oxide octahedra and terephthalate linkers [80]. They immersed PAN substrates directly in the MIL-47 synthesis solution and heated it with microwaves to 200 °C for different time intervals (5 s to 30 min). They highlighted the role of the substrate polymer chemistry on the MOF growth and observed that MIL-47 does not grow on substrates like Teflon or on poly(ethylene terephthalate), which cannot be functionalized with carboxylic groups. The carboxylic groups play the role of a link between the substrate and the growing MOF layer.

Yao *et al.* [81] in 2011 designed and applied an innovative contra-diffusion growth method for fabrication of ZIF-8 films. The nylon membrane was mounted between the solution of the zinc source and the solutions of the imidazole source, and the ZIF-8 growth occurred directly on the nylon membrane by contra-diffusion of the reactants through the membrane (Fig. 1.11). They studied the effect of time (16-72 h) on the ZIF-8 layer properties. They also observed different sizes of ZIF-8 crystals on the side of the nylon membrane, which faced the zinc solution from those, which faced the imidazole solution. Although they obtained ZIF-8 layers, which did not possess good selective properties for gas separation, (the H₂/N₂ selectivity was in the range of the corresponding Knudsen selectivity), their contribution for the following research attempts to grow MOF films on polymers was important.

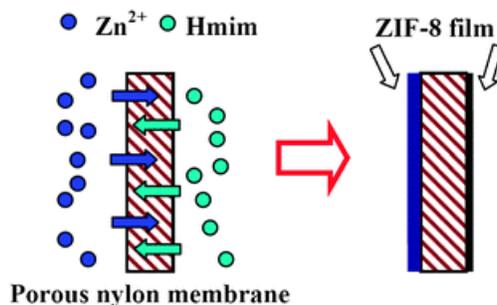


Fig. 1.11 Schematic illustration of the contra-diffusion method (adopted from [81]).

Ge *et al.* [82] prepared the ZIF-8 membrane on an asymmetric porous polyethersulfone substrate by the secondary seeded growth method. Among other experiments, they studied the importance of the seeding step for obtaining a compact, dense ZIF-8 layer, and they observed a poor performance of the sample without pre-attached seeds. The final ZIF-8 membranes were around 7 μm thick and showed good hydrogen separation; the selectivities for H_2/N_2 , H_2/Ar , H_2/O_2 , and H_2/CH_4 all exceeded Knudsen selectivity about four times.

Brown *et al.* [83] prepared a ZIF-90 membrane on the outer surface of a polyamide-imide Torlon hollow fiber (Fig. 1.12). The selected material Torlon is a chemically resistant polymer, and it can tolerate high feed pressures without the plasticization. They applied secondary seeded growth approach and also observed that non-seeded fibers resulted in a low quality of the final ZIF-90 layer. The ZIF-90 seeds were deposited on the surface by a dip-coating technique. The secondary growth was conducted at a relatively low temperature (65 $^\circ\text{C}$) using methanol as the solvent. The obtained membranes were about 5 μm thick, and they were further tested for gas and liquid permeation. In the pervaporation of organic solvents, the ZIF-90/Torlon fiber membranes showed good separation properties for linear *n*-hexane over cyclic hydrocarbons such as benzene

and cyclohexane. The gas permeation offered selectivities for CO₂/N₂ and CO₂/CH₄ well above the corresponding Knudsen values.

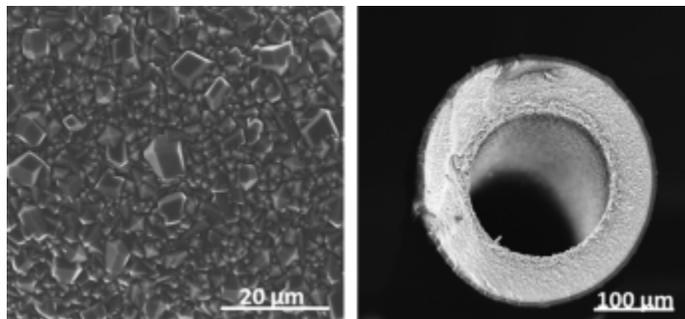


Fig. 1.12 SEM images of the top surface (left) and the cross-section (right) of the ZIF-90/Torlon hollow fiber (adopted from [83]).

ZIF-8 crystal coatings on polyimide substrate were reported by Jin *et al.* [84] who suggested a repeating of several direct growth cycles to obtain a well-intergrowth ZIF-8 layer of suitable thickness. The membrane was tested as a catalyst for the Knoevenagel reaction [85, 86], because the ZIF-8 showed similar catalytic behavior as a weak base.

Ben *et al.* [87] synthesized a HKUST-1 membrane by solvothermal growth on a layer of poly(methyl methacrylate) substrate, which was initially hydrolyzed by sulfuric acid and thus converted into poly(methacrylic acid). They also showed that preparation of a free-standing MOF film is possible by dissolving the substrate underneath the MOF layer.

Wu *et al.* [88] produced free-standing MOF membranes which grew on electrospun fibrous mats. The non-woven nanofibrous mats were composed of polystyrene and low addition of the MOF

crystals. The final membranes were prepared by the secondary growth and tested for gas permeation of N₂ and CO₂.

Our group [89] prepared a ZIF-8 membrane on a mixed-matrix substrate containing zinc oxide nanoparticles. The secondary seeded growth method was used, and silicon rubber coating of the final ZIF-8 layer was introduced as an option for increasing the flexibility of final membrane as well as increasing the selectivity properties via plugging potential pinholes. Later, we grew ZIF-8 membranes by the conversion of sputtered zinc oxide layers on a PAN support, which promoted the MOF growth and improved adhesion [90]. Recently, we applied the contra-diffusion method for growing ZIF-8 membrane on a metal-chelating polymer (poly-thiosemicarbazide) which can bind zinc ions and thus increase the affinity to the growing ZIF-8 film. Ideal selectivity above 100 was observed for propylene/propane separation [91].

Cacho-Bailo *et al.* [92] prepared ZIF-8 membranes on a polysulfone support through a two-steps synthesis approach. A layer of micro-sized ZIF-8 crystals was initially formed and served as a seeding layer for the subsequent secondary growth of nanosized intergrown ZIF-8 crystals, which formed the final continuous film. The membrane showed good separation properties for hydrogen over nitrogen (~12) and methane (~10).

Li *et al.* [93] reported a modification of the polymer support to enhance the adhesion to the growing MOF layer. They studied the synthesis of Cu₃(BTC)₂ and ZIF-8 layers on PAN hollow fibers which were in the first step hydrolyzed and the obtained deprotonated carboxyl group served as binding sites for the copper or zinc ion. Moreover, the stiffness and compression strength of the PAN fibers have been improved after hydrolysis of nitrile groups. That was useful in preventing

the formation of cracks in the MOF layer under applied pressure which can be caused by compression of the polymer support. The obtained membranes were tested for gas separation, and a relatively high hydrogen permeance ($7 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) with a separation factor of ~ 7 for hydrogen/carbon dioxide mixture coupled with thermal and pressure stability was observed.

The same group also reported preparation of a so-called trinity MOF membrane [94]. Polysulfone hollow fibers were used as support which was initially drop-coated by a mixture of polydimethylsiloxane (PDMS) and larger MOF crystals. Then the MOF layer was grown on such mixed-polymer-MOF layer. The primary function of the interlayer was to provide seeds for the subsequent MOF growth and thus increase the adhesion of the MOF layer. The trinity membrane reached selectivity of 21 for H_2/CO_2 and 7 for N_2/CO_2 .

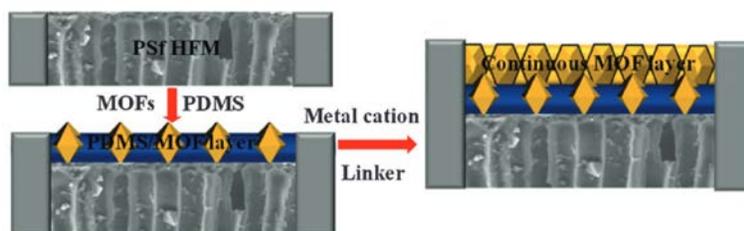


Fig. 1.13 Schematic illustration of the trinity MOF membrane preparation (adopted from [94]).

Mao *et al.* [95] presented a room temperature, pressure assisted method for growing a HKUST-1 membrane on polyvinylidene fluoride (PVDF) hollow fibers within 40 min. Copper hydroxide nanostrands on the surface served as a copper source for the KHUST-1 growth (Fig. 1.14).

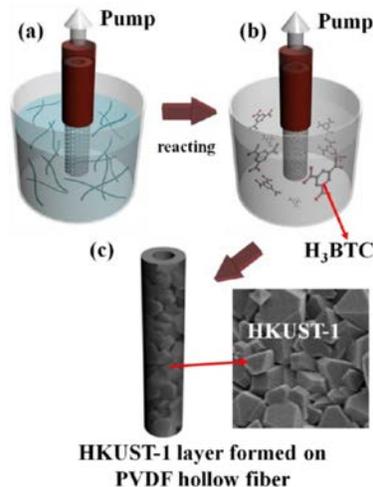


Fig. 1.14 Schematic illustration of the preparation of HKUST-1 membrane on a PVDF hollow fiber by pressure assisted method (adopted from [95]).

An innovative technique employing a microfluidic system was presented by Brown *et al.* [96] for the preparation of MOF hollow fiber membranes. The principle was somewhat similar to the contra-diffusion method however they used different solvents for dissolving the metal source and the ligand source (Fig. 1.15). Moreover, these two selected solvents (water and octanol) were not miscible, and thus the MOF formation happened at the interface of these solutions. The aqueous metal solution was flowing from the outer side of the hollow fiber and the organic ligand solution from the inner side of the hollow fiber. It was shown, that by altering the synthesis parameters, one could control the location of the MOF grow (at inner and outer surfaces, or in the bulk of the fibers). The advantage of the microfluidic approach is low consumption of reactants thanks to the fact that they were recycled and the other main benefit is using only one modul for both: the synthesis and the permeation test of the MOF membranes. The permeation tests for H₂/C₃H₈ and C₃H₆/C₃H₈ offered separation factors 370 and 12, respectively.

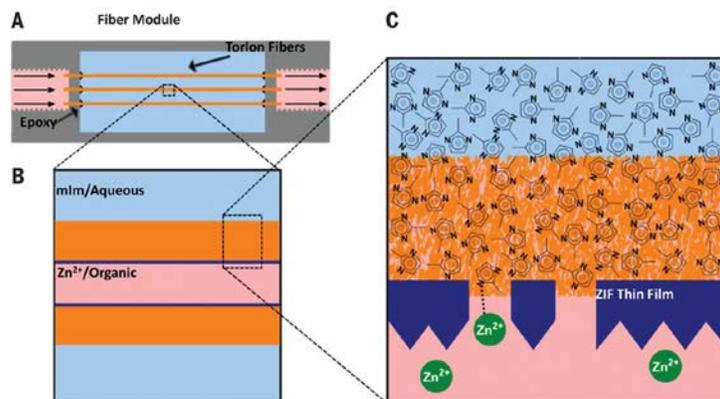


Fig. 1.15 Schematic illustration of the interfacial synthesis of ZIF-8 membrane using the microfluidic approach (adopted from [96]).

The microfluidic method has also been applied by Cacho-Bailo *et al.* [97, 98] for the preparation of ZIF-7, ZIF-8 and ZIF-93 membranes on polymeric hollow fibers. Their ZIF-7 membrane reached a separation factor above 30 for hydrogen/methane. Lately, they proposed the thermal annealing for enhancement of the MOF–polymer adhesion [99]. The MOF composite hollow fiber membranes were slowly heated to 175 °C for one day, and the annealed membranes showed a significant increase in the gas selectivity. Recently, they prepared membranes of SIM-1 (a MOF structure also known as ZIF-94 or $\text{Zn}(\text{4-methyl-5-imidazolecarboxaldehyde})_2$), which was post-treated by an imine-condensation reaction that caused rearrangement of sod structure into a less dense rho structure [100]. This resulted in an increase of the CO_2 permeance without compromising the selectivity.

Guo *et al.* [101] used an intermediate layer composed of a mixture of ZIF-8 seeds in gelatin, which was applied on a PVDF hollow fiber before the ZIF-8 secondary growth step. Their composite membrane was proposed and tested for small dyes removal in waste water treatment.

Sun *et al.* [102] used oriented nano–microstructure arrays modified nickel foams for providing nucleation centers and directing the MOF growth. The obtained membranes were firmly fixed on the nickel foam and offered good separation performance, especially for the H₂/CO₂ mixture.

Zhou *et al.* [103] investigated the effect of polydopamine (PDA) coating as a provider of nucleation centers for the MOF growth and confirmed, that PDA enhanced the MOF growth on various polymer supports such as polypropylene, polyethylene, polystyrene and polyvinylidene fluoride.

An interfacial synthesis (Fig. 1.16) similar to the interfacial polymerization commonly used for fabrication of reverse osmosis membranes was used for obtaining MOF films on polymers by Li *et al.* [104] The metal and ligand source were separately dissolved in non-miscible solvents. The polymer support was soaked overnight with the aqueous zinc solution and then let to react for 1 hour with the ligand organic solution. The ZIF-8 membrane was tested for dye removal (Rose Bengal) from water, ethanol, and isopropanol. Recently, the same group [105] developed further the interfacial synthesis and reached the enhanced performance of the ZIF-8 membrane for nanofiltration application.

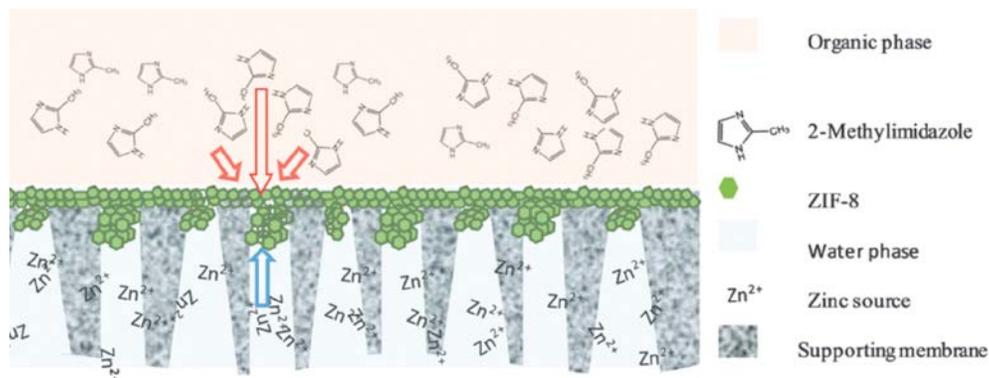


Fig. 1.16 Schematic illustration of the interfacial synthesis of ZIF-8 layer (adopted from [104]).

Shamsaei *et al.* [106] modified the polymer support with vapors of ethylene diamine to introduce amine groups on the surface. The amine groups functioned as binding sites for the zinc ions and subsequently enhanced the adhesion of the growing MOF layer. By contra-diffusion method they prepared ultrathin (only around 200 nm) ZIF-8 layer which had high hydrogen permeance ($2.05 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) and selectivities around 10 for H₂/N₂ and 13 for H₂/CO₂. Additionally, they reported ZIF-8 membrane [107] performance for other gasses reaching propylene/propane selectivity of 27 and hydrogen/propane selectivity of 2259. Recently, they developed a hybrid ZIF-8 membrane [108] grown on polydopamine-coated carbon nanotubes and nanofiber networks which acted as a pseudo-seed and a nano-scaffold for the construction of a dense ZIF-8 film (Fig. 1.17). By contra-diffusion, they obtained a ZIF-8 layer with a thickness of 100-200 nm and with one the highest hydrogen permeances ($2.87 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) reported. Moreover, this layer was shown to grow on a PES support as well as on the alumina AAO disk.

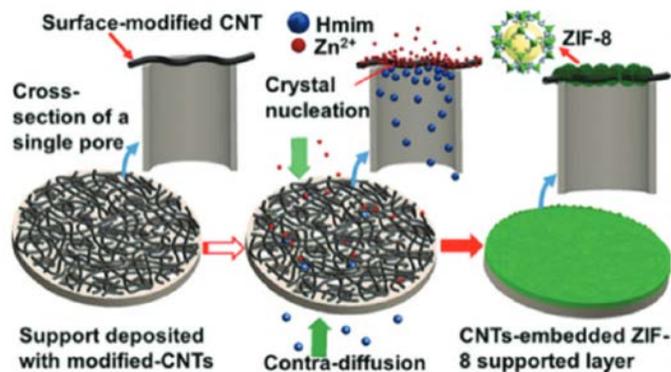


Fig. 1.17 Schematic illustration of the preparation of ZIF-8 membrane on a CNT net (adopted from [108]).

Stassen *et al.* [109] developed a chemical vapor deposition method for formation of MOF films. The ZIF-8 film was formed after the substrates with very thin sputtered zinc oxide layers were exposed to the vapors of 2-methylimidazole. This method enabled to control the thickness of ZIF films by choosing the thickness of the zinc oxide layer, which serves as the zinc source for ZIF-8 growth. It is a useful technique for lift-off patterning or for depositing MOF films on brittle structures. Although the authors had not prepared and tested a membrane via this method, it is likely that it can be a promising approach for MOF membranes formation too.

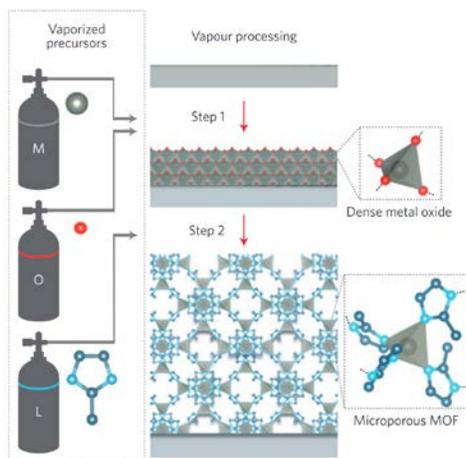


Fig. 1.18 Schematic illustration of the chemical vapor deposition of MOF films (adopted from [109]).

Campbell *et al.* [110] prepared HKUST-1 membranes by direct *in-situ* growth on a polyimide support, which was previously chemically modified with a 1,2,4-benzenetricarboxylic anhydride to functionalize the support with tricarboxylate groups. This functional group can bind copper ions and thus enhance the MOF layer growth and its adhesion to the support. The obtained membrane was tested for organic solvent nanofiltration (OSN). The same group has also used the interfacial synthesis [111] for MOF membrane fabrication and observed improved performance for the OSN applications.

1.3.3 MOF membranes for specific applications

The MOF membranes in most of the mentioned literature examples have been tested for various gas separation applications. The most common are the hydrogen separation (H_2/N_2 , H_2/CO_2 ,

H₂/CH₄, H₂/C₂H₆, H₂/C₃H₈), natural gas/biogas purification (CO₂/CH₄), postcombustion carbon capture (CO₂/N₂) and olefin/paraffin separation (ethylene/ethane, propylene/propane).

Since the ZIF membranes prepared within the projects of this dissertation have been tested for hydrogen/propane and propylene/propane separation, a brief introduction is provided for these two applications and the membranes currently employed.

1.3.3.1 Hydrogen separation

The world energy consumption has been increasing during the past decades. Although the global primary energy consumption rose by just 1.0 % in 2015, according to some predictions, it may almost double in 2050. Above 80 % of the world's energy is obtained from fossil fuels such as coal, oil and natural gas [112]. CO₂ emissions from the combustion of fossil fuels gave rise to the global warming problem. Therefore, there is a logic demand for cleaner and more efficient energy. Hydrogen production technologies have the potential to eliminate carbon emissions and dependency on oil. However, there are no natural hydrogen deposits and the dominant technology for direct hydrogen production is a steam reforming of methane, which is energetically demanding process. The hydrogen separation membranes offer a potential path for economic hydrogen production.

During the gasification process when hydrocarbon fossil or organic fuels react with a controlled amount of oxygen and steam, a synthesis gas, or syngas is produced. After the water gas shift reaction the gas is composed primarily of hydrogen and carbon dioxide. The desired membrane material for hydrogen separation has to possess excellent thermal, chemical, and mechanical stability at the high temperature and pressure.

A recent review from Ockwig and Nenoff [113] offers a general comparison of the recent membrane materials used for hydrogen separation (Tab. 1.1). The polymeric membranes are the cheapest and their production is simple. However, their thermal resistance is limited, and in many cases they do not possess the sufficient selectivity and permeance. Their other advantages are the high flexibility and the option to modify them by chemical functionalization.

The silica, zeolite, metal, and carbon membranes are thermally much more stable, and their performance regarding flux and hydrogen selectivity is higher compared to polymers. However, they do not have desired robust mechanical properties, and that makes their processing and modular design tough and economically difficult.

Tab. 1.1 Comparison of membrane classes for hydrogen separation (adopted from [113]).

	metallic: Pd, Ta, V, Nb, and alloys		ceramic: silica, alumina, zirconia, titania, and zeolites		carbon: porous carbons, ^a single-wall carbon nanotubes	polymer: polyesters, ethers, imides, urethanes, etc.	
	dense	porous	dense	porous	porous	dense	porous
<i>T</i> range (°C)	300–600		600–900	200–600	500–900	<100	
selectivity	> 1000		> 1000	5–139	4–20	low	
flux	60–300		6–80	60–300	10–200	low	
mechanical issues	phase transitions		brittle		very brittle	swelling and compaction	
chemical stability	poisoned by H ₂ S, HCl, CO ₂ , SO _x		potential degradation with H ₂ O, H ₂ S or CO ₂		oxidizing and susceptible to organic vapors	degraded H ₂ S, HCl, CO ₂ , SO _x	
transport mechanism ^a	SolD	SolD/MS	SolD	MS	SolD/MS	SolD	MS

^a KD, Knudson diffusion; SurD, surface diffusion; CC, capillary condensation; MS, molecular sieving; SolD, solution diffusion.

Beyond these membranes hybrid and composite films are considered as promising hydrogen separation membranes. ZIF-8 membranes [27] have been also tested for hydrogen separation. The intrinsic selectivities for H₂/N₂ and H₂/CH₄ are around 10. Although the reported H₂/higher hydrocarbons selectivities are relatively high (above 1000), according to Zhang and Koros [27] it is not likely that ZIF-8 membranes would be employed by industry because they are not competitive with state-of-the-art glassy polyimides [114].

1.3.3.2 Propylene/propane separation

Products made of polypropylene are common in our daily life. This important polymer is made from propylene, which is produced from fossil fuels as one of the byproducts during ethylene and gasoline production by steam cracking and fluid catalytic cracking processes, respectively. Besides being the raw material for plastics production, propylene is also important for the production of other chemicals such as propylene oxide, acrylonitrile, cumene, butyraldehyde, and acrylic acid.

The output of hydrocarbons cracking is not a pure propylene but a mixture of propylene with propane which has to be further separated. Up to now the dominating separation method for this mixture is cryogenic distillation. However, the distillation is highly demanding energy process with an energy consumption of around 1.2×10^{14} BTU/year [115, 116].

The molecular diameter of propylene and propane are very close and thus use of common polymeric membranes for this kind of separation is difficult. Broadly studied glassy polyimides and their derivatives have shown a promising permselective performance [117]. Zeolites and carbon molecular sieve membranes offer desired selective properties, however, they are too expensive to be considered as an attractive option.

It has been reported [118] that ZIF-8's effective aperture size is 4.0–4.2 Å which is exactly the size between the diameter of propylene and propane. According to the already mentioned review [27], the propylene/propane separation is the only high-potential industrial application for ZIF-8 membranes. Several works have applied ZIF-8 membrane or mixed-matrix membranes with ZIF-8 fillers for propylene/propane separation and showed promising separation performance with relatively high propylene fluxes and selectivities ranging above 20.

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2 Chapter: Zeolite-imidazolate framework (ZIF-8) membrane synthesis on a mixed-matrix substrate*

2.1 Abstract

A thin, dense, compact and hydrogen selective ZIF-8 membrane was synthesized on a polymer/metal oxide mixed-matrix support by secondary seeding method. A new concept of incorporating ZnO particles into the support and a PDMS coating of ZIF-8 layer is introduced as improvement for preparing ZIF/polymer composite membranes.

2.2 Introduction

In the field of gas separation the importance of membrane technology has increased during the last two decades. Membranes compete with the traditional separation techniques like the cryogenic distillation or the separation by solvents/sorbents. Organic polymers are the dominating material for the commercial gas-separation membranes. Inorganic materials generally possess several advantages relative to polymers such as the defined pore sizes and the high thermal and chemical stability [1], but for many technical applications they are too expensive.

The work presented here combines the economical processing of polymer membranes with the promising properties of the relatively new crystalline zeolitic imidazolate frameworks (ZIFs).

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ZIFs are a subclass of metalorganic frameworks (MOFs). ZIFs are built of metal center ions (or metal clusters) connected by imidazolate ligands or their derivatives. In general, ZIFs possess desired properties such as crystallinity, microporosity, high surface area, and exceptional thermal and chemical stability. [2, 3]

The ZIFs structure is similar to zeolites since the angle metal-imidazole-metal is the same (145°) as the Si-O-Si angle in zeolite's structure. However, because ZIFs are built of a coordination network, they are mechanically less stiff and brittle compared to zeolites. [4] This results in a high degree of framework flexibility and effects such as 'breathing', 'gate opening', and 'linker dynamics' were reported. [5, 6]

During the past decade, more than 90 different ZIFs structures have been synthesized; for our ZIF membrane, the ZIF-8 was chosen. ZIF-8 has sodalite like topology; 2-methylimidazole serves as bridging ligand between zinc central ions. It was reported that ZIF-8 possesses large cavities with diameters of 11.6 \AA with small apertures of diameters of 3.4 \AA . [2] ZIF-8 has been studied as potential compound for application in gas separation [7-14], pervaporation [15], catalysis [16], and sensing [17]. In the field of membranes it offers desired molecular sieving effects for gas separation. There are two possible usages of ZIF-8 for membranes. It can be incorporated inside a polymer matrix to improve selective properties of the membrane [18-20] or it can be grown on the surface of a porous support to serve as a selective layer of a composite membrane. [7-14]

Most of the recently published works related to ZIF-8 membranes are focusing on growing compact, thin, crack-less and selective ZIF-8 layers on porous supports. The used support is mostly an inorganic material such as alpha-alumina [8, 9, 12, 13, 14, 21, 22] or titania [10]. In

general, fabrication of a thin layer of ZIFs follows either in-situ growth or secondary seeded growth. In-situ growth is a one-step procedure, in which the support is immersed in the growth solution without any crystals previously attached to the surface. During the same fabrication step the nucleation, growth and intergrowth of ZIFs occur. This technique was used recently by Shah *et al.* [23] when they synthesized ZIF-8 membrane on an alumina support. Secondary seeded growth consists of two main fabrication steps. First the seeding ZIF crystals are attached to the support by using one of the seeding methods and then the seeded support is immersed into the growth solution. An interesting example of a successful synthesis of ZIF-8 layer by the secondary seeded growth is the work of Pan *et al.* [12] in which they prepared very thin and selective layers of ZIF-8 on alumina discs. The adhesion of the ZIF-layer on the ceramic support can be improved by organic modification of the ceramic surface [8, 24-26]. The scalable and competitive fabrication of ZIF composite membranes would be much easier, if porous polymer membranes could be used as supporting layer. Porous polymer supports are much cheaper than ceramic ones, because they can be manufactured with high speed on continuously operating machines. In spite of this polymeric membranes have seldom been applied as ZIF supports. One reason is the usually bad adhesion of the ZIF layer on the polymer surface. Ge *et al.* [7] prepared porous polyethersulfone supported ZIF-8 membranes which showed good hydrogen separation, their selectivities H_2/N_2 , H_2/Ar , H_2/O_2 and H_2/CH_4 all exceeded Knudsen selectivity by about 4 times. Different technique for growth of ZIF-8 layer on nylon support was used by Yao *et al.* [11] The nylon was placed between solution of zinc source and solution of imidazole source and by contra-diffusion the growth of ZIF-8 layer occurred firstly inside nylon pores and subsequently on the surface in the form of thin ZIF-8 layer. Brown *et al.* prepared a ZIF-90 layer on the outer surface

of a polyamide-imide hollow fiber [27]. Very recently ZIF-8 crystal coatings on polyimide substrate were reported by Jin *et al.* [28] who tested the membrane as catalyst for Knoevenagel reaction.

Here, we report the synthesis of ZIF-8 membrane on a tailor-made porous polyetherimide/zinc oxide mixed-matrix support. Fig. 2.1 shows schematically the constituting layers of our membrane. A polyester non-woven was coated with a solution of a commercial polyetherimide (PEI, Ultem® 1000) mixed with zinc oxide nanoparticles. The coating and the following precipitation in a water bath was done on a continuously working membrane casting machine. A thin, compact ZIF-8 layer was prepared by secondary seeded method.

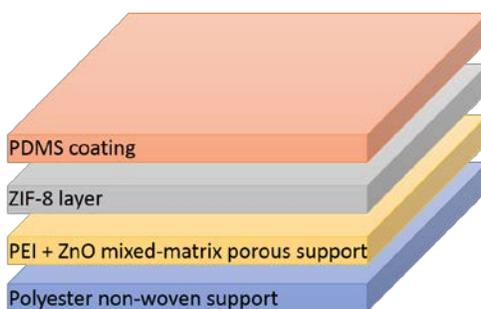


Fig. 2.1 Schematic illustration of the composing layers of the ZIF-8 membrane

2.3 Experimental details

Materials: Polyetherimide (Ultem®1000) was purchased from Sabic, Polydimethylsiloxane (Dehesive 940) was purchased from Wacker, Polyester nonwoven support (PE 05TH-100) was purchased from HIROSE and g-butyrolactone (GBL) was purchased from DAEJUNG Chemicals & Metals CO. LTD. Zinc oxide nanopowder (ZnO), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$),

sodium hydroxide (NaOH) and 2-methylimidazole were supplied by Sigma-Aldrich. Methanol was supplied by Fluka Analytical, iso-octane by Fisher Scientific and N-dimethylacetamide (DMAc) by Acros Organics. All chemicals were used as purchased directly without further purification.

Synthesis of porous support: The porous PEI+ZnO supports were fabricated by non-solvent induced phase separation. A solution consisting of ZnO nanopowder (20 g), GBL (55 g) and DMAc (101 g) was sonicated for 30 min. Subsequently PEI (34 g) was added to this dispersion and stirred at 75 °C for 10 hours to dissolve. After cooling down to room temperature the solution was cast on a polyester support using a casting machine with water at room temperature as coagulation bath by phase inversion method. Prior to the ZIF-8 seeding step, membranes were polished with 1500 grit SiC sandpaper and washed under running water. After polishing, they were sonicated for 30 s in deionized water.

Synthesis of ZIF-8 crystals: The recipe of ZIF-8 crystals synthesis was adopted from Pan *et al.* [12]. $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (1.17 g) and 2-methylimidazole (22.7 g) were dissolved in 88 mL deionized water. The solution was stirred at room temperature for 12 hours. The crystals were obtained by centrifugation (10,000 RPM for 10min) and washed 3 times with DI water and 3 times with methanol. Then the obtained white powder was dried at 45 °C in oven and kept for next step.

Seeding procedure: Seeding step combines two methods: rubbing and dip-coating. From ZIF-8 powder and DI water a ZIF-8 paste at a mass ration 1:10 was prepared. The surface of supports was wiped with ZIF-8 paste along axis direction 3 times with a foam brush and left dried for 2 hours at room temperature. Then the supports were dip-coated in 1.0 wt.% seed suspension for 5 s. After dip-coating step, membranes were dried at room temperature for 12 hours.

Secondary growth: Two solutions were prepared separately: $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (0.22 g) was dissolved in 15 mL of water and 2-methylimidazole (4.54 g) was dissolved in 65 mL water. The pH value of the used water was changed to the value $\text{pH}=9.5$ by addition of NaOH. Then the first solution was rapidly added to the second one. The seeded membranes were placed vertically to a glass beaker in order to avoid sedimentation of crystals and left for ZIF-8 layer growth for 36 hours at $45 \text{ }^\circ\text{C}$ in oven. A control experiment was conducted by growing ZIF-8 on PEI support without zinc oxide fillers. The desired compact ZIF-8 layer was not formed and we observed poor coverage of the support even after secondary growth.

Careful drying and PDMS coating: After secondary growth the membranes were washed sequentially with methanol (50 wt.%), pure methanol, mixture of methanol and iso-octane (1:1), pure iso-octane and finally dip-coated for 20 s in PDMS (2 wt.%) solution. This process ensured slow exchange of solvents inside the ZIF-8 pores. The PDMS layer should fill possible pinholes and it should add to the final membrane more flexibility and resistance of handling damages.

Permeation tests: Single gas permeation tests were performed using an apparatus with constant feed pressure at room temperature. The volume of the permeating gas and the time needed to permeate this volume was measured by a soap film flowmeter (10 mL) and stopwatch. From the known area of membrane A , the transmembrane partial pressure difference Δp_i , the volume of permeating gas V_i and the time t the permeance was calculated:

$$J_i = \frac{V_i}{A \Delta p_i t} \quad (2.1)$$

Each experimental value of volume and time for a particular gas was measured after reaching steady-state which is characterized by constant time value needed for certain volume of permeating gas. A measure of the ability of a membrane to separate two gases, i and j , is the ratio of their permeances, α_{ij} , called the membrane selectivity

$$\alpha_{ij} = \frac{J_i}{J_j} \quad (2.2)$$

Characterization: Scanning electron microscopy (SEM) images of the surfaces and cross-sections of membranes were carried out with FEI Quanta 200FEG SEM. Samples were first coated with either iridium or gold by sputtering under vacuum. X-ray diffraction (XRD) patterns were carried out with a diffractometer Bruker D8 Advance, Cu radiation (40kV, 40 mA scan range 5 to 30 degree).

2.4 Results and discussion

To achieve a good growth of a compact and gap-free ZIF-8 layer on the polymer support is a challenging task. Our support membrane is a mixed matrix membrane which is composed of ZnO (loading 36 wt. %) nanoparticles (size < 100 nm) incorporated in a PEI matrix. The SEM images (Fig. 2.2) of the support's cross-section confirmed that there was no sedimentation of agglomeration of the particles across the membrane.

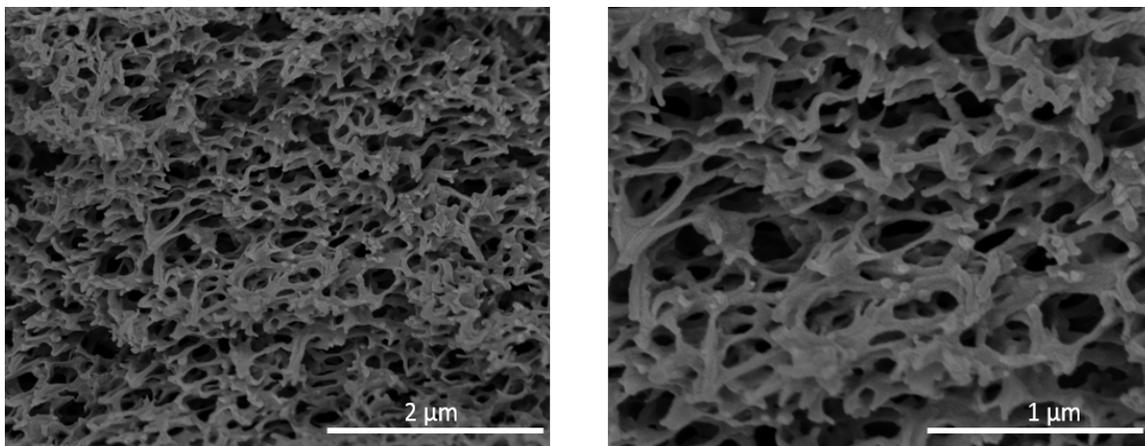


Fig. 2.2 SEM images of cross-section area of the PEI/ZnO mixed-matrix support

The ZnO particles are assumed to have a positive effect on the growth of ZIF-8 crystals mainly because zinc ions can serve as a secondary metal source for formation of ZIF-8 crystals. This improves the adhesion of the ZIF-8 layer to the supporting membrane. Since for better ZIF-8 growth it is important to use a very porous surface, the PEI/ZnO support was polished with ultrafine sandpaper which resulted in a rougher surface with opened pore structure.

The PEI/ZnO support was in the next step seeded with ZIF-8 crystals, which were prepared according to Pan *et al.* [12] recipe. The seeding step is important because the seeds on the support surface act as good base layer for the gap-free growth of ZIF-8 during secondary growth. Several methods including dip-coating in solutions with different ZIF-8 concentration or rubbing with dried ZIF-8 powder, have been tried to plant the ZIF-8 seeds on the support.

From our observation the method of combination of rubbing with ZIF-8 paste using a foam brush and dip-coating in ZIF-8 solution (1 wt. %) was the best method for placing ZIF-8 seeds on the

support. This seeding technique was used and recommended also by Liu *et al.* [29] when preparing NaA zeolite membranes. The SEM image (Fig. 2.3 a) confirms that ZIF-8 seeds are dispersed continuously and equally across the whole support's surface. Moreover, because of opened pores of the support, the ZIF-8 seeds are allowed to enter partially inside the pores of the support and they can serve as roots for the final ZIF-8 layer.

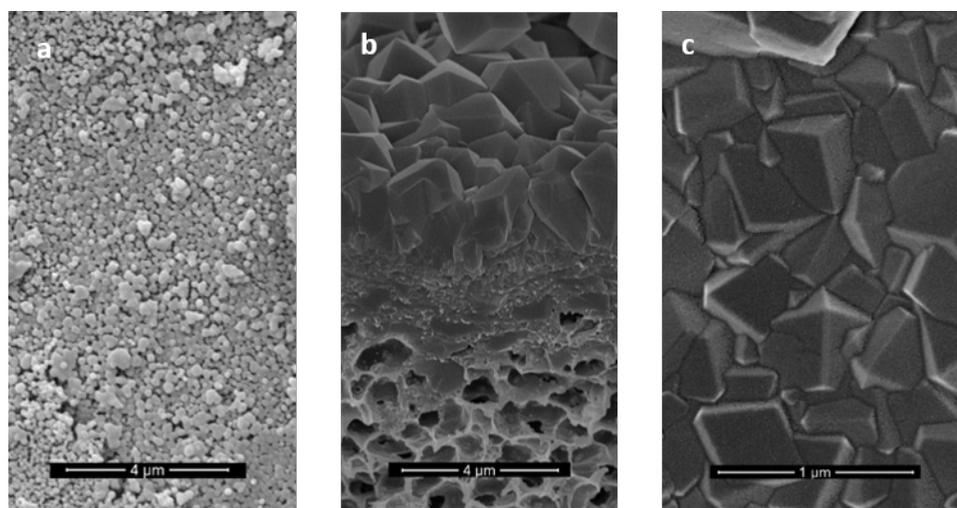


Fig. 2.3 SEM images a) after seeding step with ZIF-8 crystals, b) cross-section and c) top-view of ZIF-8 membrane (without PDMS coating).

Several recipes [7-14] for secondary ZIF-8 growth solution have been proposed by different authors. In this work, the one proposed by Pan *et al.* [12] with some alterations was used because of its advantages including low synthesis temperature, using water instead of organic solvents and relatively short growth time. We changed the original procedure and doubled the concentration of the reactants and we increased the pH from around 7 to 9.5.

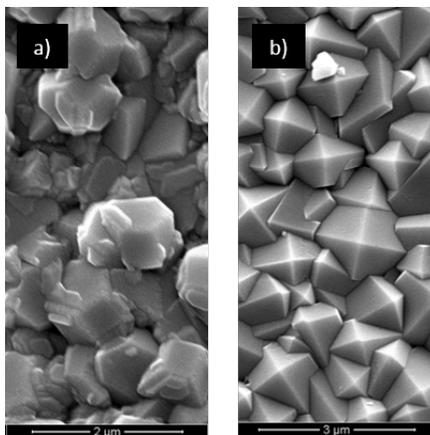


Fig. 2.4 Effect of the pH value of the water used for ZIF-8 membrane synthesis. SEM of membrane prepared using water of a) pH = 7 and b) pH = 9.5.

These modifications showed a positive effect on the compactness of the final ZIF-8 layer (Fig. 2.4), especially on the intergrowth of crystals. Other authors [8, 30] have also reported that addition of alkaline solution such a sodium formate to the synthesis solution improves growth and intergrowth of ZIF-8 crystals. The imidazole ligands must be first deprotonated before ZIF-8 layers could continue to grow. With the increasing pH, the amount of deprotonated 2-methylimidazole increases and growth of ZIF-8 crystals occurs in more directions [31]. Seeded membranes were left in growth solution for 36 hours at 45 °C. The SEM image of the cross-section (Fig. 2.2b) shows that thickness of ZIF-8 layer is $\sim 1.5 \mu\text{m}$.

The formation of the ZIF-8 crystals has been confirmed by X-ray diffraction analysis. Fig. 2.5 shows a diffractogram of the prepared ZIF-8 powder, the ZIF-8 composite membrane and PE/PEI/ZnO support. The ZIF-8 characteristic XRD pattern was obtained and the positions of peaks are in agreement with previously reported XRD analysis of ZIF-8. [2]

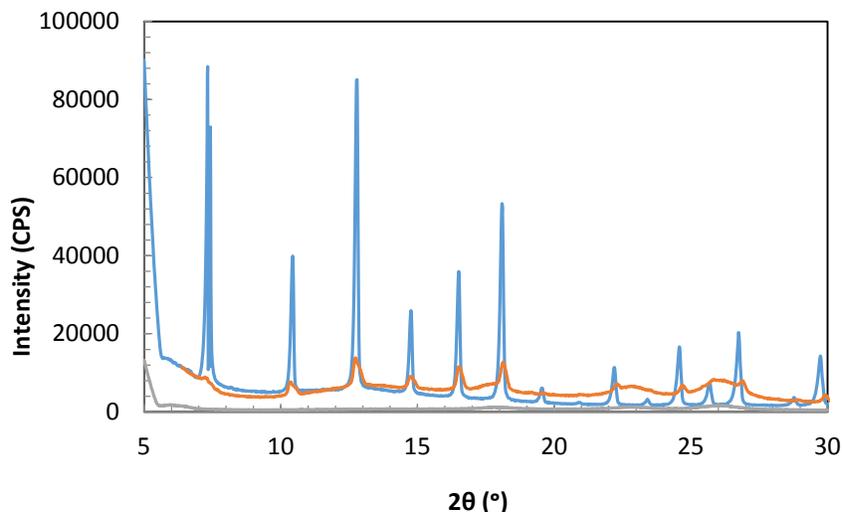


Fig. 2.5 X-ray diffractogram of ZIF-8 powder (blue), ZIF-8 membrane (red) and mixed-matrix support (green).

A top-view of the synthesized ZIF-8 layer is shown in Fig. 2.3 c. It can be seen that the layer is very dense and compact and no cracks are present. The shape and good intergrowth of crystals is very similar and comparable to those ZIF-8 layers obtained by synthesis on inorganic supports. [8, 12, 13]

After the synthesis of the ZIF-8 layer, the membranes were dried applying a solvent exchange to prevent formation of cracks. Wet membranes after secondary growth were dipped sequentially in 50 wt. % methanol solution, in pure methanol, in a solution of methanol and iso-octane, then in pure iso-octane and finally in iso-octane containing 2 wt. % polydimethylsiloxane. Final coating with silicone rubber was applied in order to protect the ZIF-8 layer and to fill potential pinholes. The ZIF-8 membrane is expected to be size-selective, i.e. the small hydrogen molecule permeates faster than the larger hydrocarbons. Silicone rubber is reverse selective, the larger hydrocarbon

molecules permeate faster than hydrogen. Nevertheless, a thin silicone rubber coating can drastically enhance the hydrogen/hydrocarbon selectivity, because it eliminates the viscous flux through pinholes. [32]

Gas permeation and selectivity properties of the ZIF-8 composite membranes were tested using a Millipore permeation cell (active membrane area 2.8 cm²) with constant feed pressure of 1 bar. The permeation of hydrogen was 1.6×10^{-6} mol.m⁻².s⁻¹.Pa⁻¹ which is about 4 times higher than reported for ZIF-8 membrane prepared on polyethersulfone support [7] but two times less than the one prepared on nylon support [11] by the contra-diffusion method. This difference is caused mostly by the different thickness of ZIF-8 layer, which was determined by SEM picture of cross-section for this work to be about ~ 1.5 μm which is less than those reported on polyethersulfone (~ 7.2 μm) or on nylon (~ 16 μm). High permeance for hydrogen as well as high hydrogen selectivity is desirable for application such as purification and recovery of hydrogen from hydrocarbons in refinery streams in the petrochemical industry. Our membrane showed a relatively high ideal selectivity for the couple H₂/C₃H₈ ($\alpha = 22.4$) which exceeded more than 4 times the corresponding Knudsen selectivity.

2.5 Conclusions

In conclusion, we successfully prepared a compact thin ZIF-8 layer on an organic/inorganic mixed-matrix support by the secondary seeded growth method. ZIF-8 crystals were synthesized from aqueous solution at relatively low temperature (45 °C) and atmospheric pressure. The membrane showed high hydrogen permeance and a selectivity for H₂/C₃H₈ exceeding Knudsen selectivity 4 times.

2.6 Acknowledgment

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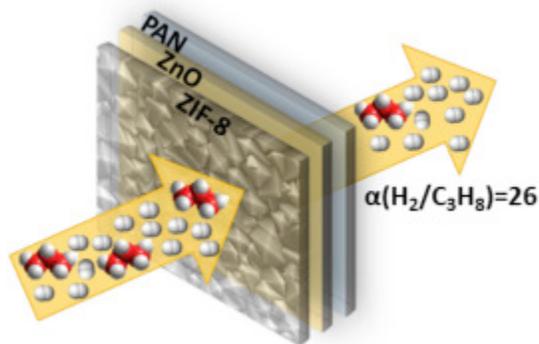
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3 Chapter: Synthesis of polymer supported ZIF-8 membranes via conversion of sputtered zinc oxide layers*



3.1 Abstract

ZIF-8 composite membranes were synthesized at room temperature from aqueous solution by a double-zinc-source method on polyacrylonitrile (PAN) porous supports. The support was coated with zinc oxide (ZnO) by magnetron sputtering prior to ZIF-8 growth to improve the nucleation as well as the adhesion between the ZIF-8 layer and support. By this method, we were able to grow a continuous, dense, very thin (900 nm) ZIF-8 layer on a polymeric support. The developed ZIF-8 membranes had a gas permeance of $1.23 \times 10^{-7} \text{ mol m}^{-2} \text{ sec}^{-1} \text{ Pa}^{-1}$ for hydrogen and a selectivity of 26 for hydrogen/propane gases which is five times higher than the Knudsen selectivity. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis were done to characterize the membranes.

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3.2 Introduction

Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal-organic frameworks (MOFs) with extended three-dimensional structures from tetrahedral metal ions (e.g., Zn, Co) bridged by imidazolate linkers. ZIFs have been extensively studied in the past decade for various applications such as gas adsorption and separation [1-8], sensors [9, 10] and chemical catalysis [11].

Similar to zeolites, ZIFs can be grown as a continuous thin layer on a substrate like ceramic discs or polymeric membranes. Significant work has been done by several research groups about MOF/ceramic composites [12, 13]; however, polymer substrates could be more attractive due to their much lower price and process feasibility.

When MOF's are grown on ceramic supports, we face only few restrictions for temperature and solvents [14-19]. This is different for polymeric supports; synthesis temperature is limited, and solvents which do not attack the polymer have to be selected (water and alcohols are preferred). Several publications presenting successful preparation of MOF layers on polymer supports appeared in the last four years. Among proposed synthesis methods are contra-diffusion methods [20, 21], *in-situ* methods [22, 23], secondary seeded growth methods [24, 25], interfacial approaches [8, 26, 27] and others [28-30].

Recently, several articles have been published about a "dual metal source" method for the formation of MOFs layers [31]. The advantage of this approach is that the substrate contains a

metal source, which provides the required metal ions for initiation of nucleation with high density and a continuous growth of MOFs crystals.

HKUST-1 membranes were synthesized by "twin copper source" technique using copper net [32] and copper hydroxide nanostrands [30] as the metal source in the reaction system. Kang *et al.* [33] synthesized a $\text{Ni}_2(\text{L-asp})_2(\text{bipy})$ membrane substrated by a nickel net which also acted as the metal source. Hu *et al.* [34] presented a reactive seeding method that involves an aluminum substrate as the aluminum precursor reacting with the organic ligand and forming the seed layer of MIL-53

In this work, we used the double-zinc-source method to manufacture ZIF-8 membranes on a polymeric substrate. Zinc oxide (ZnO), an excellent metal source for ZIF-8, has been used in this work and several articles conveyed that presence of ZnO or Zn on the substrate is favorable for ZIF-8 growth [35-40].

Here, we coated very thin ZnO layers on polyacrylonitrile (PAN) support membranes by magnetron sputtering and then the ZIF-8 growth was conducted following both in-situ and secondary seeded growth method. The ZIF-8 membranes developed by secondary growth method were very thin (900 nm), yet showed a good $\text{H}_2/\text{C}_3\text{H}_8$ selectivity. The main advantage of the proposed double-zinc-source method is a quick formation of ZIF-8 nucleation seeds directly on the PAN support via transformation of the coated ZnO layer. Other benefits are the use of water as a solvent, room temperature synthesis and relatively short synthesis time.

3.3 Experimental methods

Materials: The polyacrylonitrile (PAN) support membrane was obtained from GMT Membrantechnik GmbH (Rheinfelden), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) ($\geq 99.0\%$), sodium hydroxide (NaOH) ($\geq 97.0\%$) and 2-methylimidazole (99 %) were supplied by Sigma-Aldrich. Methanol (99.80 %) was supplied by Fluka Analytical. All chemicals were used as received without further purification.

ZnO deposition: PAN membranes were fixed on the metal pallet in the sputter instrument with two-sided carbon tape. Sputter deposition of ZnO was carried out by radio frequency (RF) magnetron sputtering system of ESCRD4 from Equipment Support Company Ltd., equipped with 2" ZnO target (Plasmaterials, 99.99%). The depositions were performed at room temperature at RF power of 75 W with argon as the sputter gas at 100mTorr. The thickness of deposited layer can be adjusted by the length of the deposition time. In our experiments, the deposition duration of 1 hour was used to obtain ~90 nm thick ZnO layer.

Synthesis of the ZIF-8 layer: Two preparation methods (Method A and Method B) were used for ZIF-8 growth on PAN-ZnO support. Method A: 5.9 g of 2-methylimidazole was dissolved in 80 mL of DI water of pH=9.5. The pH value of the used water was adjusted by addition of NaOH. The PAN-ZnO support was directly immersed vertically in the 2-methylimidazole aqueous solution at room temperature for 6 hours. Method B: PAN-ZnO support was dip-coated for 10 sec in 2-methylimidazole solution (3.2 g in 23 mL DI water (pH=9.5)). Then the membrane was dip-coated for 10 sec in zinc nitrate solution (0.25 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 23 mL DI water (pH=9.5)). Such dip-coated membrane was immersed in a secondary growth solution which was prepared as follows: Two solutions were prepared separately: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.50 g) was dissolved in 40 mL of DI

water (pH=9.5), and 2-methylimidazole (6 g) was dissolved in 40 mL of DI water (pH=9.5). Then the first solution was rapidly added to the second one. The membrane was placed vertically in a glass beaker, and the growth was continued for 6 hours at room temperature. After the growth, the membranes were washed with methanol several times to remove excess traces of ZIF-8 crystals before drying at room temperature overnight.

Characterization: Scanning electron microscopy (SEM) images of the surfaces and cross-sections of membranes were carried out with FEI Quanta 200FEG SEM. Samples for cross-section were fractured with liquid nitrogen. SEM samples were sputtered with iridium (thickness of coating 3 nm) under vacuum before the analysis. X-ray diffraction (XRD) patterns were carried out with a diffractometer Bruker D8 Advance, Cu radiation (40kV, 40 mA scan range 10 to 40 degree).

Permeation tests: Single gas permeation tests were performed using an apparatus with constant feed pressure at room temperature. The volume of the permeating gas and the time needed to permeate this volume was measured by soap film flowmeter (10 mL) and stopwatch, respectively. From the known membrane A, transmembrane partial pressure difference Δp_i , the volume of permeating gas V_i and time t the permeance was calculated:

$$J_i = \frac{V_i}{A \Delta p_i t} \quad (3.1)$$

Each experimental value of the volume and time for a particular gas was measured after reaching steady-state. The ideal selectivity α_{ij} of two gasses (i and j) was calculated as the ratio of their permeances

$$\alpha_{ij} = \frac{J_i}{J_j} \quad (3.2)$$

3.4 Results and discussion

Two preparation methods were followed. Both methods have the same first step which is the deposition of zinc oxide layer on the PAN substrate, and they differ in the second phase of conducting the ZIF-8 growth (Fig. 3.1). A thin (~90 nm) layer of zinc oxide was applied by magnetron sputtering technique; Fig. 3.2 depicts the cross-section of zinc oxide layer deposited on PAN.

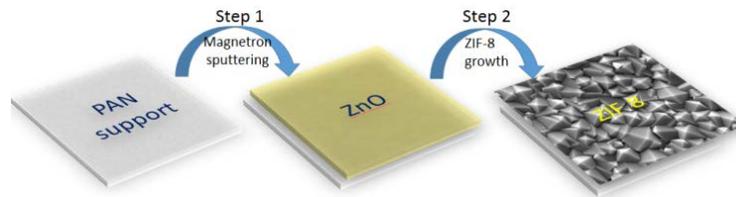


Fig. 3.1 Schematic illustration of the ZIF-8 membrane preparation on PAN support with sputtered zinc oxide layer.

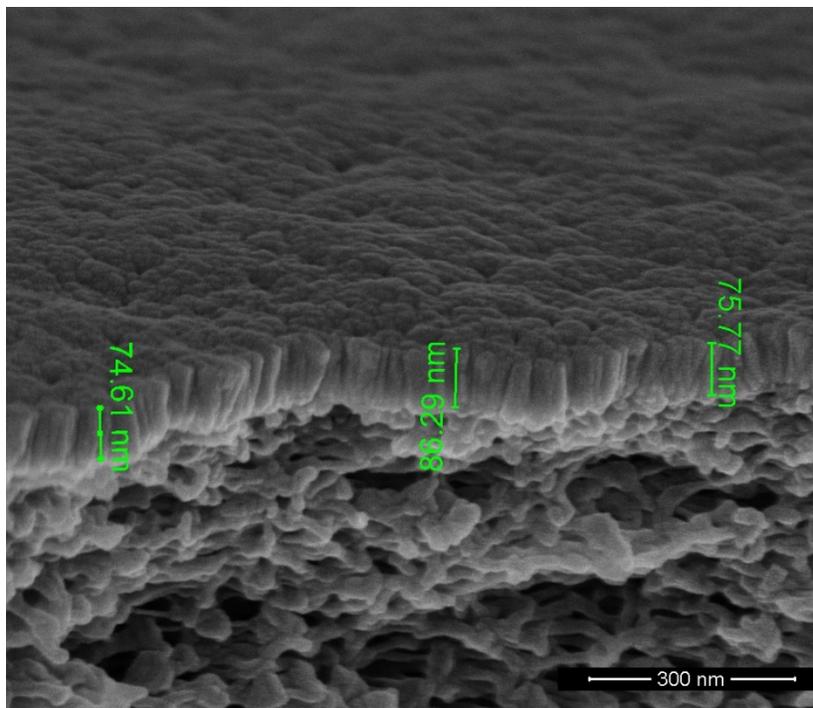


Fig. 3.2 SEM cross-section image of the PAN-ZnO membrane support.

Method A consists of direct immersing of PAN-ZnO support into pure 2-methylimidazole solution. This approach was also used by Drobek et al. [37] for the preparation of ZIF-8 membranes on zinc oxide layers deposited on alumina supports. This method is convenient since it is a straightforward and fast *in-situ* process and it does not require the addition of zinc salt in the growth solution. However, the ZIF-8 membranes prepared by method A did not show expected high selectivity. The SEM image of the top-view of the membrane is shown in Fig. 3.3. It can be seen that the zinc oxide layer was transformed into a ZIF-8 crystal layer. However, this layer was not dense enough, and the crystals were not inter-grown sufficiently. The permeation tests of this membrane also showed very high hydrogen permeance of $1.5 \times 10^{-5} \text{ mol m}^{-2}\text{sec}^{-1}\text{Pa}^{-1}$ which was about hundred times more than the average permeance of ZIF-8 membranes reported

previously [41]. Moreover, the obtained hydrogen/propane ideal selectivity for the ZIF-8 membrane prepared by the method A was 4.02 which is below Knudsen selectivity (4.7). These results led us to alter the preparation method as follows.

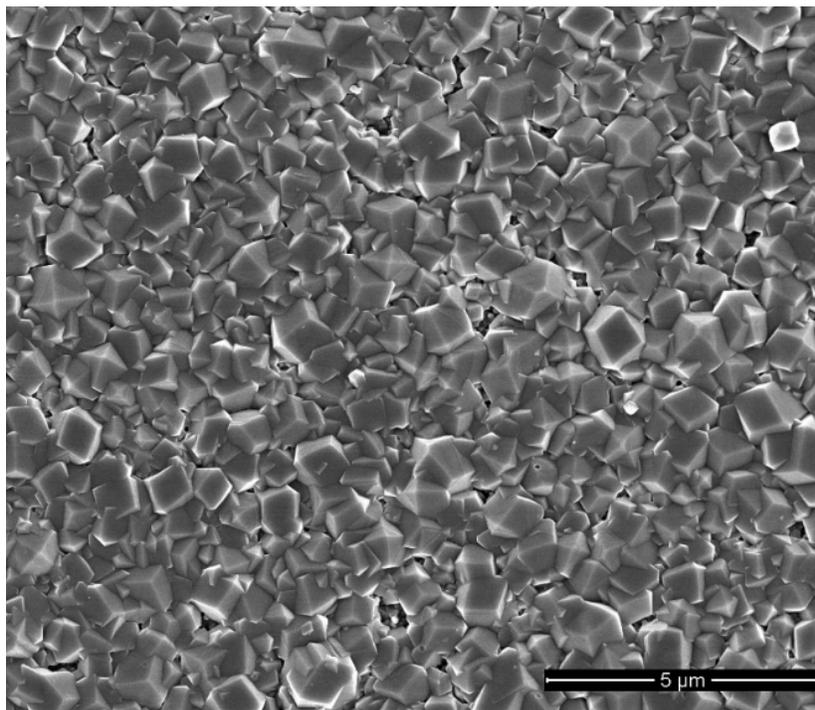


Fig. 3.3 SEM top-view image of the ZIF-8 membrane prepared by the Method A.

Method B has two additional steps compared to the previous method, and it belongs to the group of secondary growth methods. First, the sputtered PAN-ZnO support was dip coated in 2-methylimidazole solution so that the seed layer of ZIF-8 was formed by reaction of ZnO on the support and imidazole from the solution. Then it was dip coated in zinc nitrate solution and finally immersed in the mixture of 2-methylimidazole and zinc nitrate for secondary growth to allow ZIF-8 crystal grains to be intergrown. Top-view and cross-section of the ZIF-8 membrane obtained

using method B is shown in Fig. 3.4. The pictures declare that the ZIF-8 layer is relatively dense and crystal grains are small and well-intergrown. The ZIF-8 layer is around 900 nm thick which is to the best of our knowledge the thinnest ZIF-8 membrane on polymer support reported so far. Shekhah *et al.* [7] prepared ~500 nm thick ZIF-8 membranes on alumina support by the liquid phase epitaxy (layer-by-layer) method, which allows the control of thickness simply by a number of cycles.

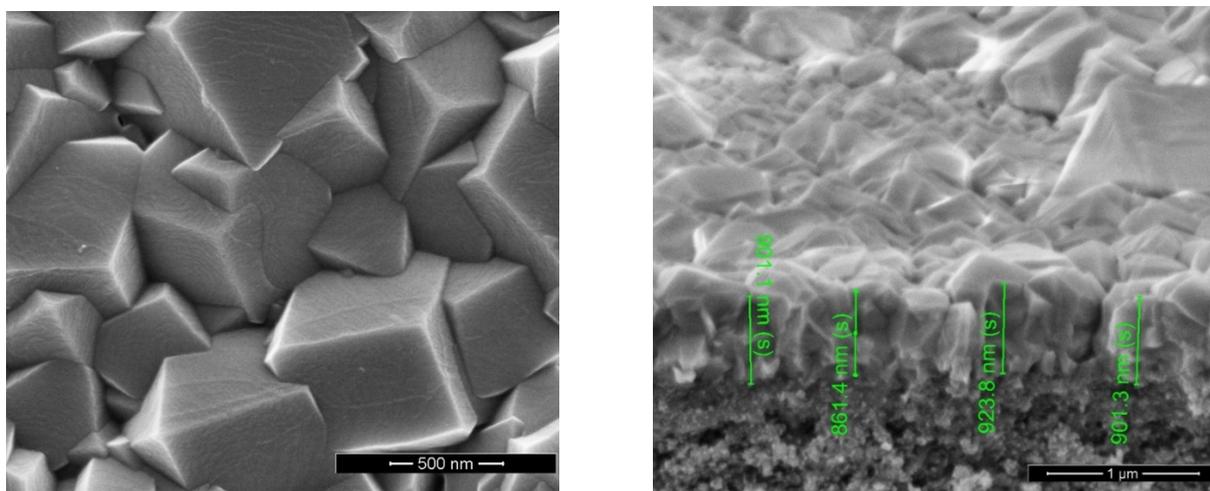


Fig. 3.4 SEM top-view and cross-section images of the ZIF-8 membrane prepared by the Method B.

The XRD spectra of as prepared ZIF-8 membrane and substrate are shown in Fig. 3.5. The positions of the peaks of ZIF-8 membrane are in agreement with previously reported ZIF-8 XRD spectra [42] and thus confirm the formation of the ZIF-8 crystals.

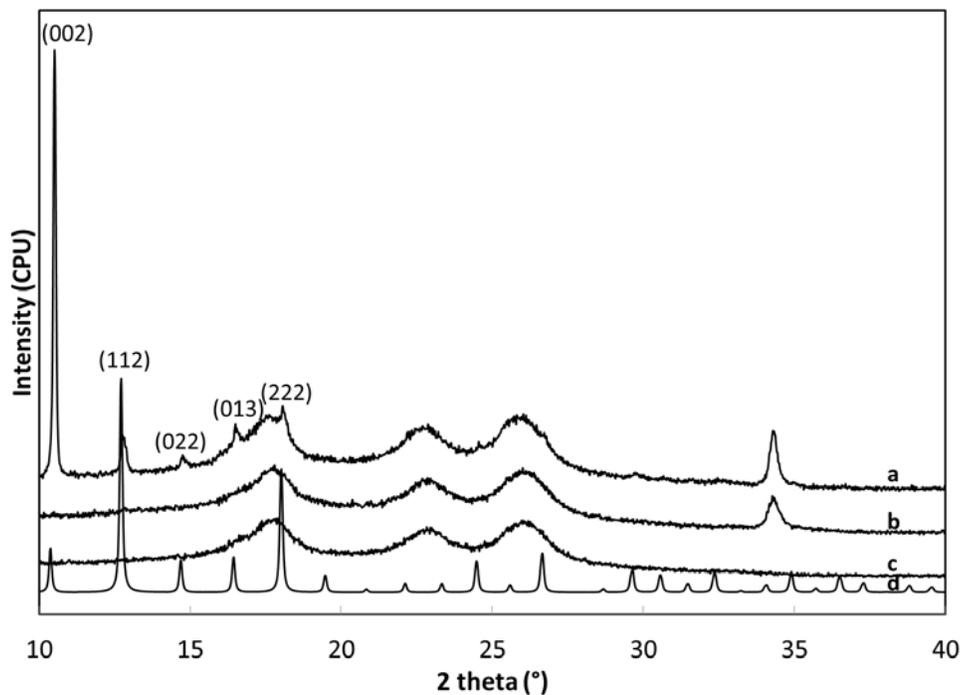


Fig. 3.5 X-ray diffractogram of PAN-ZnO-ZIF-8 membrane (a), PAN-ZnO (b), PAN support (c) and ZIF-8 (simulated) (d).

To examine the quality of the prepared ZIF-8 membrane, single gas permeation of hydrogen and propane was tested, and the ideal selectivity was calculated. Tab. 3.1 summarizes the results of permeation tests of neat PAN, PAN- ZnO, and PAN-ZnO-ZIF-8 membranes. The deposited zinc oxide layer decreases the flux of gasses roughly ten times comparing to the pristine PAN substrate with no influence on selectivity. The obtained hydrogen permeance of $1.23 \times 10^{-7} \text{ mol m}^{-2} \text{ sec}^{-1} \text{ Pa}^{-1}$ is comparable to the earlier literature reports of ZIF-8 layers on inorganic substrates [41] and [14], what indicates that our ZIF-8 layer is compact with no defects. The obtained selectivity of 26 for hydrogen/propane gasses is five times higher than the Knudsen selectivity. Looking at the literature, so far we can generalize that the ZIF-8 inorganic supported membranes

offer better separation performance for hydrogen/propane than the polymer supported ones. Caro's research group [14] observed for ZIF-8 membranes grown on α -alumina support separation factors for hydrogen/propane above 300; moreover, the ZIF-8 membrane grown on polydopamine-modified alumina support [43] achieved separation factor above 700. The inorganic substrate allows ZIF-8 synthesis at high temperature, and thus their ZIF-8 layers are relatively thick (more than 10 μm). Thanks to the non-flexible nature of inorganic support the risk of cracks' formation during handling is low. However, it should be noted that their testing method (Wicke–Kallenbach technique) for permeation is different because an equal pressure is maintained on both the sides of the permeation cell.

Because of the flexible nature of polymer supports, it is important to handle the membrane very carefully to avoid the formation of cracks in the ZIF-8 layer. We assume that this could be the main reason for having certain reproducibility issues in permeance and selectivity of the prepared ZIF-8 membranes. A control experiment was done using Method B for the pure PAN support (without ZnO layer). Such prepared ZIF-8/PAN membrane showed permeation and selectivity performance similar to the pristine PAN support because the ZIF-8 layer contained defects. That suggests that the zinc oxide layer deposited on the support is beneficial for obtaining defect-free well-intergrown ZIF-8 layer.

Tab. 3.1 Permeation results of the preprated ZIF-8 membrane and its support

Membrane	$P^*(\text{H}_2) / 10^{-7} \text{ mol m}^{-2} \text{ sec}^{-1} \text{ Pa}^{-1}$	$P^*(\text{C}_3\text{H}_8)$	α ($\text{H}_2/\text{C}_3\text{H}_8$)
PAN	505	138	3.7

PAN-ZnO	42.3	10.8	3.9
PAN-ZnO-ZIF-8	1.23	0.047	26

The ZIF-8 membrane prepared by method B was further tested by the time-lag permeation technique. From the obtained results (Tab. 3.2) it is seen that this membrane showed selectivity of 12 for propylene/propane when the feed pressure was 2 bars. With increasing feed pressure, the selectivity decreased, but the overall performance is comparable to the propylene/propane selectivities obtained by Brown *et al.* [8]

Tab. 3.2 Permeation results for the propylene/propane separation obtained by the time-lag measurement.

$p_{\text{feed}} / \text{bar}$	$P(\text{C}_3\text{H}_6) / \text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$	$\alpha(\text{C}_3\text{H}_6 / \text{C}_3\text{H}_8)$
2	1.3×10^{-8}	10
3	1.2×10^{-8}	8.5
4	1.2×10^{-8}	7.2

Tab. 3.3 shows the summary of several reported polymer-supported MOF membranes with their permeation results. It can be seen that our membrane's performance is comparable or better

than most of the other membranes. It should be noted that the reported [8] very high separation factor (318) for hydrogen/propane was also measured by the Wicke-Kallenbach permeation apparatus which does not apply a pressure difference on the membrane.

Tab. 3.3 Summary of literature reports of MOF membranes supported by polymers.

MOF	MOF thickness / μm	Support	$P(\text{H}_2) / 10^{-7} \text{ mol m}^{-2} \text{ sec}^{-1} \text{ Pa}^{-1}$	Selectivities	Ref
ZIF-8	0.9	Polyacrylonitrile	1.23	26* $\text{H}_2/\text{C}_3\text{H}_8$ 10* $\text{C}_3\text{H}_6 / \text{C}_3\text{H}_8$	This work
ZIF-8	16	Nylon	19.7	4.3* H_2/N_2	[20]
ZIF-8	2.5	Nylon	11.3	4.6* H_2/N_2	[21]
ZIF-90	5	Torlon	1.92	1.8 H_2/CO_2 3.5 CO_2/N_2 1.5 CO_2/CH_4	[24]
ZIF-8	7.2	Polyethersulfone	4	9.7 H_2/Ar 10.8 H_2/O_2 9.9 H_2/N_2 10.7 H_2/CH_4	[25]
ZIF-8	24.5	Polysulfone	3.97	3.8* $\text{H}_2/\text{C}_3\text{H}_8$ 3.8* H_2/CO_2	[22]
HKUST-1	9	Polysulfone	0.787	5.7* $\text{H}_2/\text{C}_3\text{H}_8$	[22]

				7.2* H ₂ /CO ₂	
HKUST-1	6.5	Polyvinylidene fluoride	20.1* 19.7	5.4 (2.5*) H ₂ /CH ₄ 6.5 (3.3*) H ₂ /N ₂ 3.4* H ₂ /O ₂ 8.1 (4.2*) H ₂ /CO ₂	[30]
ZIF-8	1.5	Polyetherimide/ ZnO	16	22.4* H ₂ /C ₃ H ₈	[36]
ZIF-8	35	Polysulfone	2	10.4 H ₂ /CH ₄ 12.4 H ₂ /N ₂	[44]
HKUST-1	13	Polyacrylonitrile	705	5* H ₂ /N ₂ 5.1* H ₂ /O ₂ 7.05* H ₂ /CO ₂	[45]
ZIF-8	9	Torlon	3.12	318 H ₂ /C ₃ H ₈ 14.5 C ₃ H ₆ /C ₃ H ₈	[8]
HKUST-1	10	Polysulfone	4.85	21.03* H ₂ /CO ₂ 7.23* N ₂ /CO ₂	[28]
ZIF-7	2.4	Polysulfone	0.0215	34.6 H ₂ /CH ₄ 35.1 H ₂ /N ₂ 2.4 H ₂ /CO ₂ 13.5 CO ₂ /CH ₄	[26]

				13.6 CO ₂ /N ₂	
ZIF-8	3.6	Polysulfone	0.0482	17.2 H ₂ /CH ₄ 18.3 H ₂ /N ₂ 2.6 H ₂ /CO ₂ 6.1 CO ₂ /CH ₄ 7.1 CO ₂ /N ₂	[26]

*single gas permeation measurement, selectivity calculated as Eq. (3.2)

3.5 Conclusion

In conclusion, ZIF-8 membranes were prepared by a double-zinc-source method on porous PAN support. This approach employs deposition of zinc oxide by magnetron sputtering before ZIF-8 growth. We could demonstrate that magnetron sputtering of zinc oxide is a promising tool for enhancing the ZIF-8 growth on a polymer substrate. We were able to develop a defect-free thin ZIF-8 layer with relatively high permeance for hydrogen and a reasonable selectivity for hydrogen/propane and propylene/propane separations.

3.6 Acknowledgment

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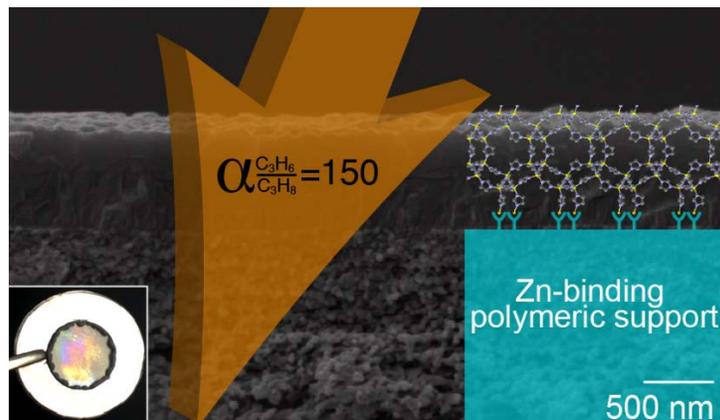
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4 Chapter: Defect-Free Metal-Organic Framework Membrane Prepared On Metal Chelating Porous Polymeric Support by Contra-Diffusion Technique*



4.1 Abstract

Since the discovery of size-selective metal-organic frameworks (MOFs), researchers have tried to manufacture them into gas separation membranes. Impressive gas selectivities were found, but these MOF membranes were mostly made on inorganic supports, which are generally too bulky and expensive for industrial gas separation. Forming MOF layers on porous polymer supports is industrially attractive but technically challenging. In this work we introduce two features to overcome these problems. We use a metal chelating support polymer to bind the MOF layer, and we control MOF crystal growth by contra-diffusion, aiming at a very thin nano-crystalline MOF

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layer. Using a metal chelating polythiosemicarbazide (PTSC) support and adjusting the metal and organic ligand concentrations carefully, a very compact ZIF-8 layer was produced that displayed interference colors due to its smooth surface and extreme thinness – within in the range of visible light. High performance in terms of hydrogen/propane (8358) and propylene/propane (150) selectivity were measured.

4.2 Introduction

Use of Metal Organic Frameworks (MOF) in membranes has been researched for a decade. MOFs have been incorporated as fillers in mixed-matrix membranes, and have been grown as continuous, dense layers on top of porous supports. Comprehensive reviews of MOF membrane synthesis and applications were recently provided by Li *et al.* [1] and Zhang *et al.* [2] A subclass of MOF called zeolitic imidazolate frameworks (ZIF) are a group of materials topologically isomorphic with zeolites and composed of tetrahedrally coordinated transition metal ions (e.g. Fe, Co, Cu, Zn) bridged by imidazolate linkers.

Among them, ZIF-8 is particularly attractive because of its easy synthesis, good chemical and thermal stability, relevant pore size and recent commercial availability [3]. More than 70 % of the published work on the topic of ZIF-enabled membranes deals with ZIF-8 [2]. And, thanks to its promising performance in terms of permeance and selectivity for hydrogen separation and propylene/propane separation [4], ZIF-8 membranes have gained even greater attention. Since 2009, numerous reports have been presented describing the preparation of continuous ZIF-8 layers on inorganic supports. The results show promise, however the high cost and processing

difficulties of inorganic supports have motivated efforts to prepare ZIF-8 layers on polymeric porous supports—a low-cost and easily processable alternative. If such layers can be manufactured inexpensively, the benefits to the chemical industry would be great.

ZIF-8 layers have been successfully grown on Nylon [5], PAN [6,7], PEI [8], PES [9], PVDF [10] and other polymeric materials [11,12]. In order to obtain a continuous, dense, thin, selective ZIF-8 layer, both the properties of the support and the synthesis method are important. The main synthesis methods used for obtaining ZIF-8 layers on polymer supports can be classified as follows: i) in-situ [9], ii) secondary seeded growth [6,8], iii) contra-diffusion [5,11], iv) interfacial synthesis [12,13] and v) layer-by-layer [14]. It has been shown that modification of the polymer support prior to ZIF-8 growth may enhance final membrane performance [11,15]. The modification may be physical or chemical and its key purpose is to create a more attractive surface for ZIF-8 crystal attachment and growth.

We expected that a polymer with the ability to bind zinc metal would provide a favorable support for growing a ZIF-8 layer. Poly-thiosemicarbazide (Fig. 4.1) belongs to the group of thiosemicarbazide materials that have been recognized for their ability to form stable chelates with a wide variety of metals. PTSC was first introduced in 1962 by Campbell *et al.* [16,17], who showed that this polymer forms stable chemical complexes with iron, nickel, silver, copper, mercury, and lead. Our group reported the first preparation of PTSC membranes [18,19]. Villalobos *et al.* exploited PTSC's ability to form complexes with several metal ions to develop a new membrane fabrication process [21], to prepare palladium- and gold-rich catalytic membranes [21,22] and to make membrane adsorbers for recovery of precious metals [19]. In

this project, we further explore PTSC's affinity for zinc ions and its performance as a support for ZIF-8 growth.

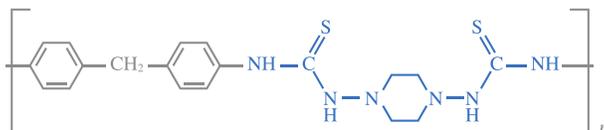


Fig. 4.1 Chemical structure of poly-thiosemicarbazide.

Ultrathin, dense ZIF-8 layers were prepared by a contra-diffusion method on a porous PTSC polymer support prepared in-house. ZIF-8 crystals form when zinc reacts with 2-methylimidazole (HMIM). In the contra-diffusion method two solutions, with the same solvent and each containing one reactant, are introduced to opposite sides of the support. The reactants diffuse in opposite directions through the porous support, forming ZIF-8 crystals where they meet. Under the right conditions, subsequent diffusion occurs through the gaps between existing crystals, filling them and forming a thin, dense, planar layer.

4.3 Experimental details

Materials: Polyester nonwoven support (PE05TH-100) was purchased from HIROSE. Dimethyl sulfoxide (DMSO), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) ($\geq 99.0\%$) and 2-methylimidazole (HMIM) (99 %) were supplied by Sigma-Aldrich. Methanol (99.80 %) was supplied by Fluka Analytical. N,N'-diaminopiperazine was supplied by Ramidus AB. Poly(trimethylsilyl)propyne

(PTMSP) was purchased from ABCR GmbH & Co. KG and cyclohexane was supplied by Honeywell Burdick & Jackson. The polyacrylonitrile (PAN) support membrane was obtained from GMT Membrantechnik GmbH (Rheinfelden). All chemicals were used as received without further purification.

Synthesis of PTSC polymer: Poly-thiosemicarbazide was synthesized according to literature [17] by the reaction of N,N'-diaminopiperazine and methylenebis(4-phenylisothiocyanate) in dimethyl sulfoxide (DMSO). Equimolar quantities of both monomers were dissolved in DMSO at 50 °C and allowed to react for 48 hours. The resulting viscous solution was poured into hot water to precipitate the polymer. The polymer was then washed two times with Milli-Q water and dried in a vacuum oven at 60 °C for two days.

Preparation of the PTSC support membrane: PTSC membranes were prepared by non-solvent induced phase separation. First a solution of 15 wt. % PTSC, 10 wt. % 1,4-dioxane and 75 wt. % DMSO was stirred for 5 h at 60 °C and allowed to rest for another 5 h until air bubbles had escaped. Then a 250- μm -thick polymer solution film was cast on a polyester nonwoven support fixed on a glass plate. The cast film was then immersed in a non-solvent bath (water) at room temperature for at least 12 h. The resulting PTSC membranes were dried and stored at room temperature. PTSC support was further used as support for ZIF-8 and ZIF-67 layers. Details about ZIF-67 experiments are provided in the Appendix of this dissertation.

Contra-diffusion ZIF-8 layer synthesis: PTSC membranes were cut into coupons with diameter of 1.5 cm and fixed between rings of aluminum tape (Nashua Aluminum Waterproofing Repair Foil Tape, 11 mil Thick) with outer diameter of 2.4 cm and inner diameter of 0.95 cm. For contra-diffusion experiments we used a Side-Bi-Side cell with orifice diameter of 14 mm supplied by PermeGear® (Fig. 4.2).



Fig. 4.2 Side-Bi-Side PermeGear® cell used for the preparation of ZIF-8 membrane.

The volume of each cell half is 5 mL. The cell halves are equipped with jackets which allow control of the synthesis temperature. In this work, all experiments were conducted at room temperature, the active side of the PTSC membrane generally facing the zinc source solution. After a membrane was placed between the cell halves, the cell clamp was fixed. The adjusting knob was then gently tightened to hold the glass halves and membrane together. Two separate methanol solutions of HMIM and Zinc nitrate hexahydrate were prepared. The concentrations and codes of the membranes obtained from these reactants' solutions are summarized in Tab. 4.1.

Tab. 4.1 Labeling of PTSC/ZIF-8 membranes prepared from different ZIF-8 reactant concentrations.

ZIF-8/PTSC Membrane	HMIM concentration in methanol	Zn(NO ₃) ₂ .6 H ₂ O concentration in methanol
M1	65 g/L	15 g/L
M2	13 g/L	3 g/L
M3	6.5 g/L	1.5 g/L
M4	3.5 g/L	0.75 g/L

After 48 hours of ZIF-8 layer growth the membrane was carefully withdrawn from the cell and dried at 50 °C in a vacuum oven for at least 1 day.

PTMSP sealing solution: The ZIF-8 membranes were coated with PTMSP solution (0.5 wt. %), which was prepared by dissolving PTMSP powder in cyclohexane under stirring at room temperature overnight. The full area coating was done by spreading a drop of the PTMSP solution on the ZIF-8 surface from a pipette and letting it to dry under a warm stream of air for about 2 minutes. The only-edges coating was done using a fine paint brush.

Characterization: Scanning electron microscopy (SEM) images of the surfaces and cross-sections of membranes were carried out with a FEI Quanta 200 FEG SEM. Samples for cross-section were

fractured after being immersed for at least two minutes in liquid nitrogen. Samples were sputtered with iridium (approximately 3 nm) under vacuum before analysis.

X-ray diffraction (XRD) patterns were measured with a Bruker D8 Advance diffractometer, Cu radiation (40 kV, 40 mA scan range 5–40°).

The adsorption capacity of the PTSC support was measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The ICP-OES machine was calibrated with 1 ppm, 10 ppm and 100 ppm standard solution before analysis. The deviation was less than 10 % for the standard samples.

Permeation test: Permeance of hydrogen, propane and propylene was tested by the Wicke-Kallenbach technique using an in-house-built apparatus (Fig. 4.3).

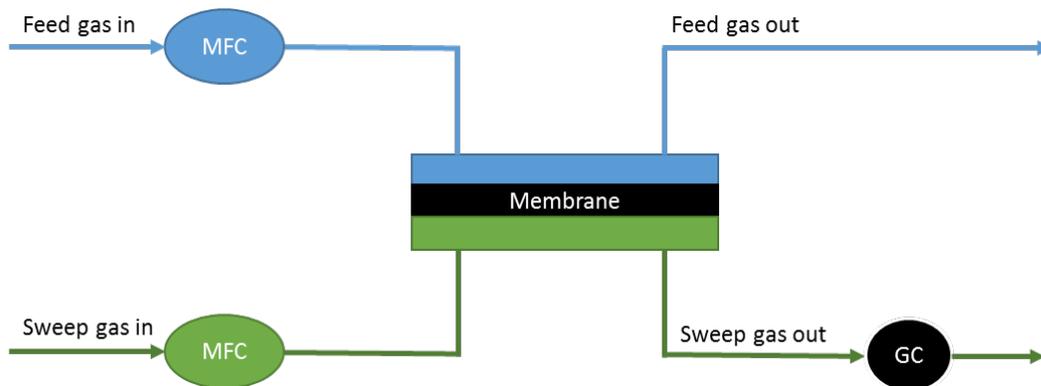


Fig. 4.3 Wicke-Kallenbach setup with mass flow controllers (MFC) for feed and sweep gas and gas chromatograph (GC) analyzing the permeate.

Flow rates \dot{V} of feed gas and sweep gas (nitrogen) were kept at 30 mL/min by mass flow controllers. Permeate stream composition was analyzed by a gas chromatograph (Agilent 490 Micro GC) and the fraction of the studied gas x_i in the sweep gas was determined using a calibration curve. The permeance of the studied gas J_i was then calculated from the following equation:

$$J_i = \frac{x_i \dot{V}}{A \Delta p_i} \quad (4.1)$$

where A is active membrane area and Δp_i is the transmembrane partial pressure difference of the studied gas. The ideal selectivity α_{ij} of the two gases (i and j , where i is the faster permeating gas) was then calculated from the ratio of their permeances:

$$\alpha_{ij} = \frac{J_i}{J_j} \quad (4.2)$$

4.4 Results and discussion

PTSC polymer was obtained from the reaction of 4-phenylisothiocyanate and N,N'-diaminopiperazine in dimethyl sulfoxide (DMSO) solvent as described elsewhere [17,19]. The PTSC solution in DMSO was cast on a non-woven polyester (Hirose HT 100) and the asymmetric membrane was then fabricated by non-solvent induced phase separation using water as a non-solvent bath. The membrane is porous with skin layer thickness between 10 to 20 nm and is chemically stable under ZIF-8 synthesis conditions. PTSC membranes adsorbed approximately 2 wt. % of zinc ions at equilibrium over the range of Zn concentrations used to prepare the ZIF-8

layers. The zinc binding ability of PTSC provides a higher density of zinc source at the support surface, and insures adhesion between the support and the ZIF-8 layer.

To prevent damage of the ZIF-8 layer during permeation testing, we mounted the PTSC support between rings of aluminium tape (Fig. 4.3 a) prior to ZIF-8 layer synthesis.

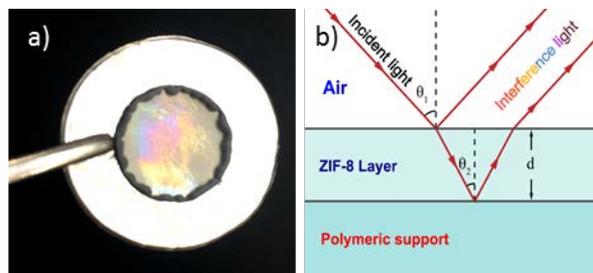


Fig. 4.4 (a) Digital photograph of ZIF-8/PTSC M3 membrane; (b) illustration of the thin film interference phenomenon in ZIF-8/PTSC membrane.

Fig. 4.2 shows the type of glass contra-diffusion cell used. The support was placed between the two chambers, which were then filled with solutions of zinc nitrate and HMIM in methanol. Experiments performed with zinc solution facing the PTSC surface produced ZIF-8 crystal layers on this surface, with no zinc detected elsewhere in the membrane (Fig. 4.4). Tests with the solutions reversed, i.e. with HMIM solution facing PTSC, produced ZIF-8 particles throughout the support's internal structure. When zinc solution faces PTSC, The PTSC surface skin traps zinc, preventing it from diffusing into the support and leaving it available to react with HMIM at the surface. Thus the zinc-complexing support material and the asymmetric pore morphology work in combination to produce ZIF-8 crystals in only the desired location.

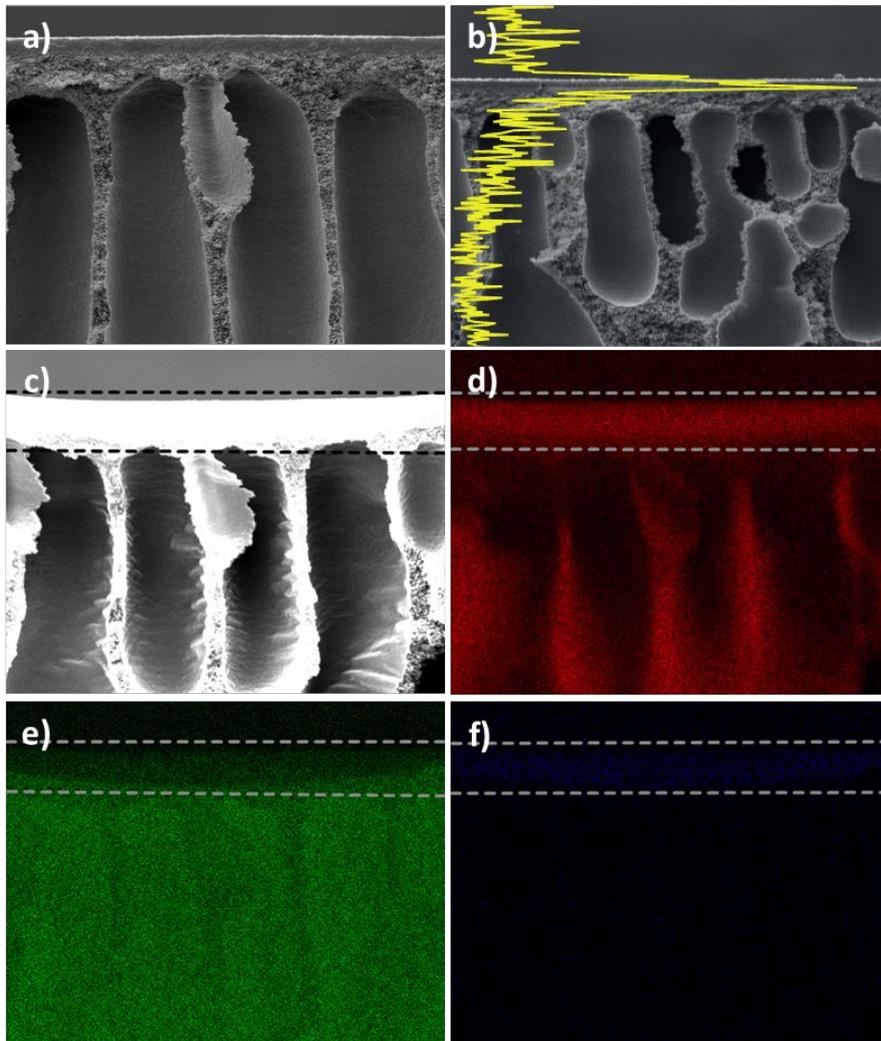


Fig. 4.5 Cross-section scanning electron microscope images and energy-dispersive X-ray (EDX) analysis of the ZIF-8/PTSC M3 membrane: (a) Secondary electron image, 5keV; (b) EDX vertical line scan for Zn; (c) Secondary electron image of the mapped area, 10 keV; (d) C map; (e) S map; (f) Zn map.

A control experiment with commercial polyacrylonitrile (PAN) support and zinc solution facing the dense PAN surface was also conducted. It produced a nonselective membrane with ZIF-8 crystals present throughout its entire internal structure (see Fig. 4.5 and Tab. 4.3).

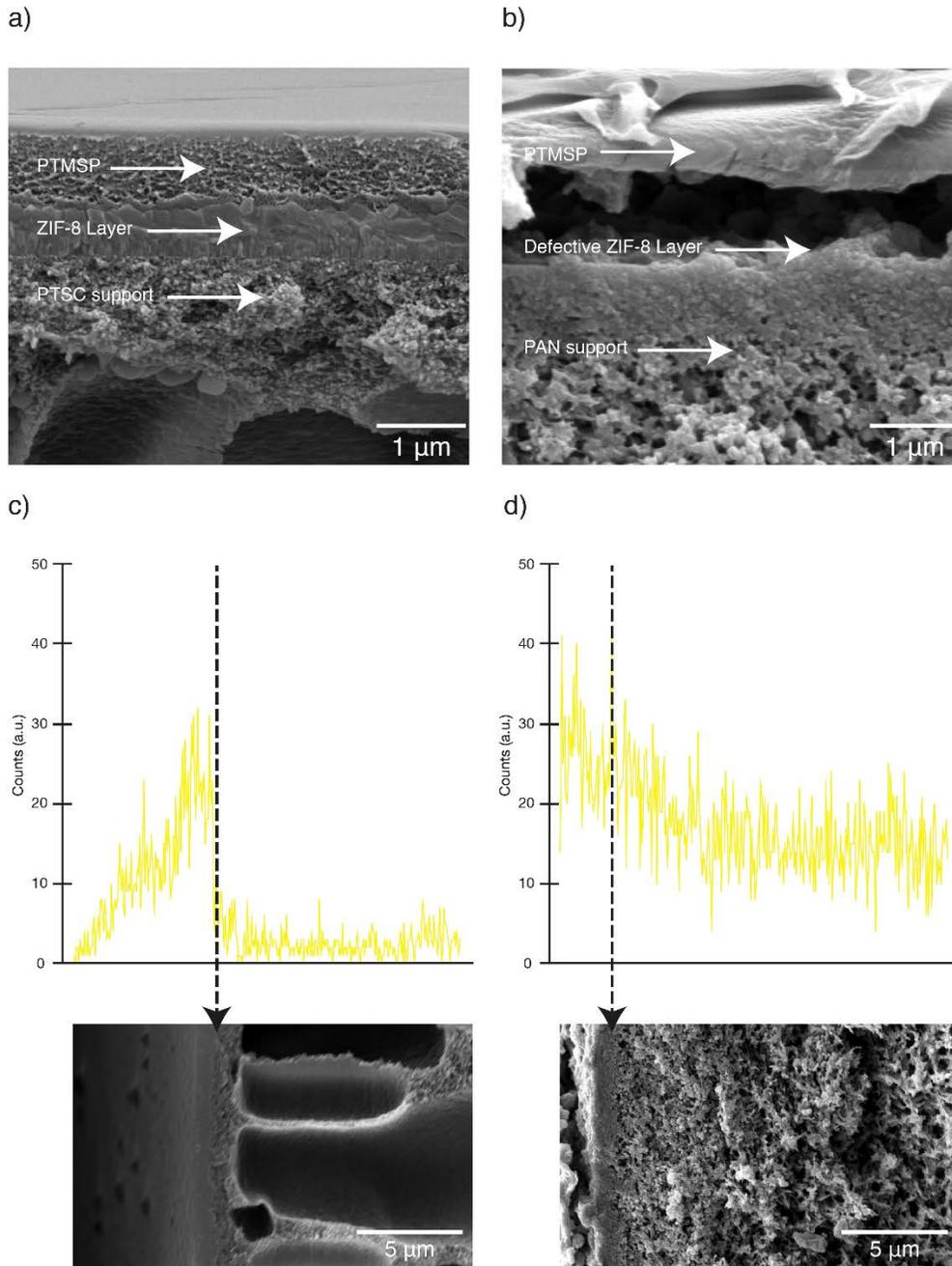


Fig. 4.6 Cross-section scanning electron microscope images and energy-dispersive X-ray (EDX) analysis of ZIF-8 membranes over PTSC (M3) and over commercial PAN after PTMSP coating: (a) Secondary electron image of sample M3; (b) Secondary electron image of a ZIF-8 layer grown.

Reactant concentrations dramatically affected the structure of the ZIF-8 layer and the performance of the final ZIF-8 membrane. In initial experiments, we followed a similar recipe to that proposed by Yao *et al.* [5] with $c(\text{HMIM}) = 65 \text{ g/L}$ and $c(\text{zinc salt}) = 15 \text{ g/L}$ (membrane noted as M1). It can be seen (Fig. 4.6 a) that the ZIF-8 layer obtained did not form the desired compact and intergrown film and was quite thick ($7 \mu\text{m}$; Fig. 4.7 a). When the concentration of reactants was reduced by five times (membrane noted as M2), the ZIF-8 crystals on the membrane's surface formed a more compact layer (Fig. 4.6 b and Fig. 4.7 b). When we decreased the concentration of reactants by ten times ($c(\text{HMIM}) = 6.5 \text{ g/L}$, $c(\text{zinc salt}) = 1.5 \text{ g/L}$), we observed a surprisingly different ZIF-8 layer—nicely intergrown crystals and superior performance (membrane noted as M3). After the ZIF-8 membrane was removed from the contra-diffusion cell and dried, we immediately noticed an unusually shiny membrane surface reflecting several colors (Fig. 4.3 a). SEM images (Fig. 4.6 c and Fig. 4.7 c) show a layer of tightly inter-grown ZIF-8 crystals with rhombic dodecahedron morphology. With a thickness of 620 nm, our ZIF-8/PTSC membrane is among the thinnest ZIF-8 layers on polymeric support reported. The thickness of this transparent ZIF-8 layer falls in the range of visible light's wavelengths and thus displays the thin film interference phenomenon (as illustrated in Fig. 4.3 b). Formation of ZIF-8 crystals was confirmed by X-ray element map and X-ray diffraction analysis (Fig. 4.4 and Fig. 4.8). A further decrease in reactant concentrations ($c(\text{HMIM}) = 3.5 \text{ g/L}$, $c(\text{zinc salt}) = 0.75 \text{ g/L}$) produced a layer of large crystals with insufficient density (membrane noted as M4, Fig. 4.6 d and Fig. 4.7 d).

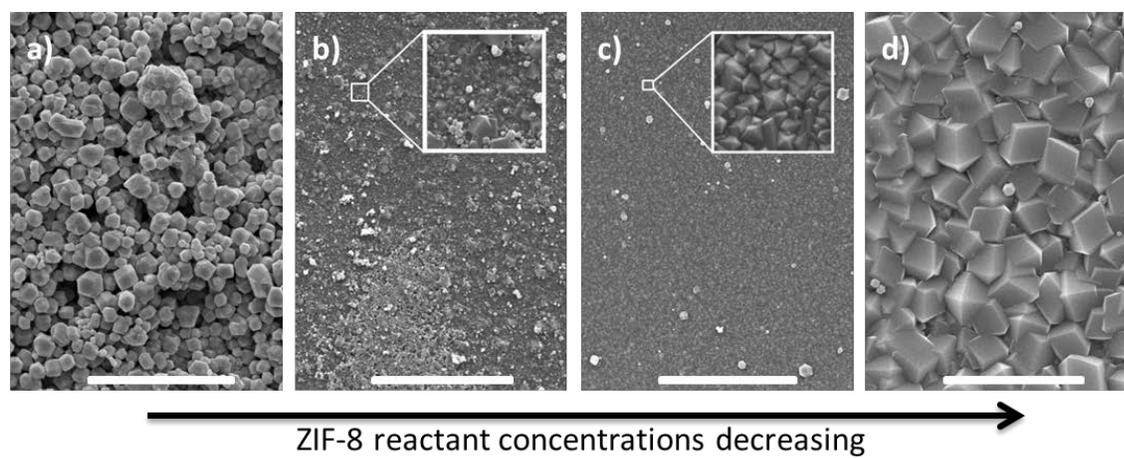


Fig. 4.7 SEM surface images of ZIF-8/PTSC membranes prepared with different reactant concentrations: (a) M1; (b) M2; (c) M3; (d) M4. Scale bar: 10 μm .

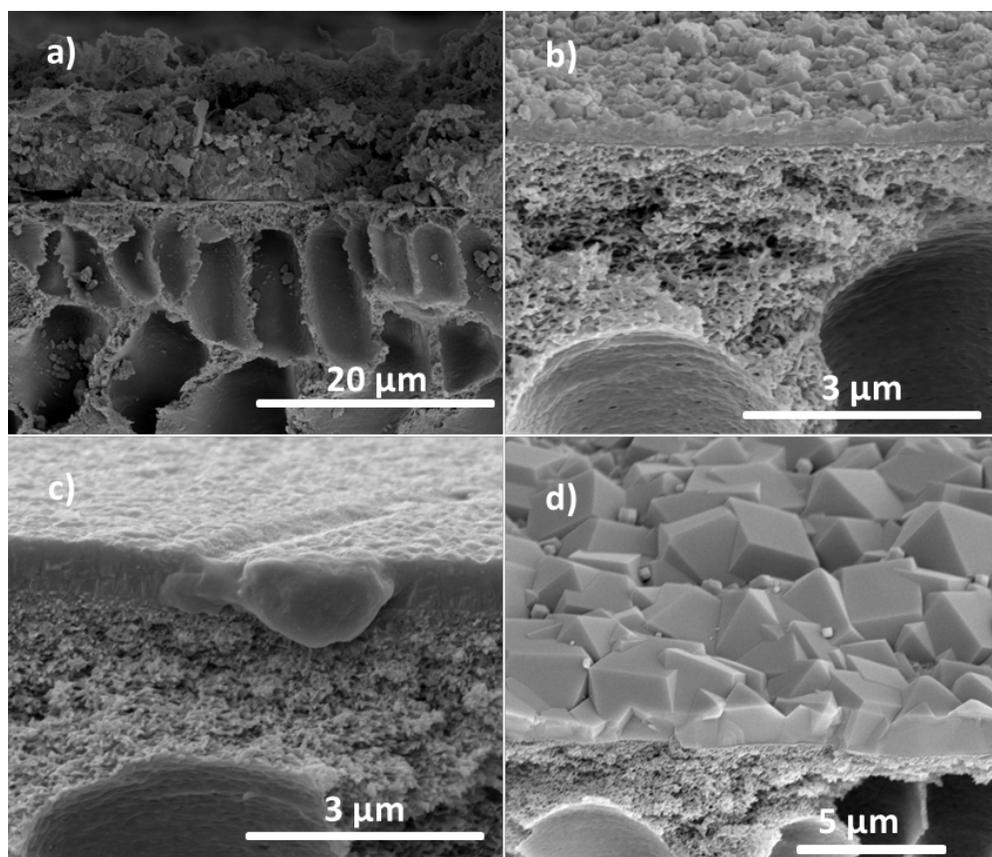


Fig. 4.8 SEM images of the cross-sections of ZIF-8/PTSC: (a) M1; (b) M2; (c) M3 and (d) M4 membranes.

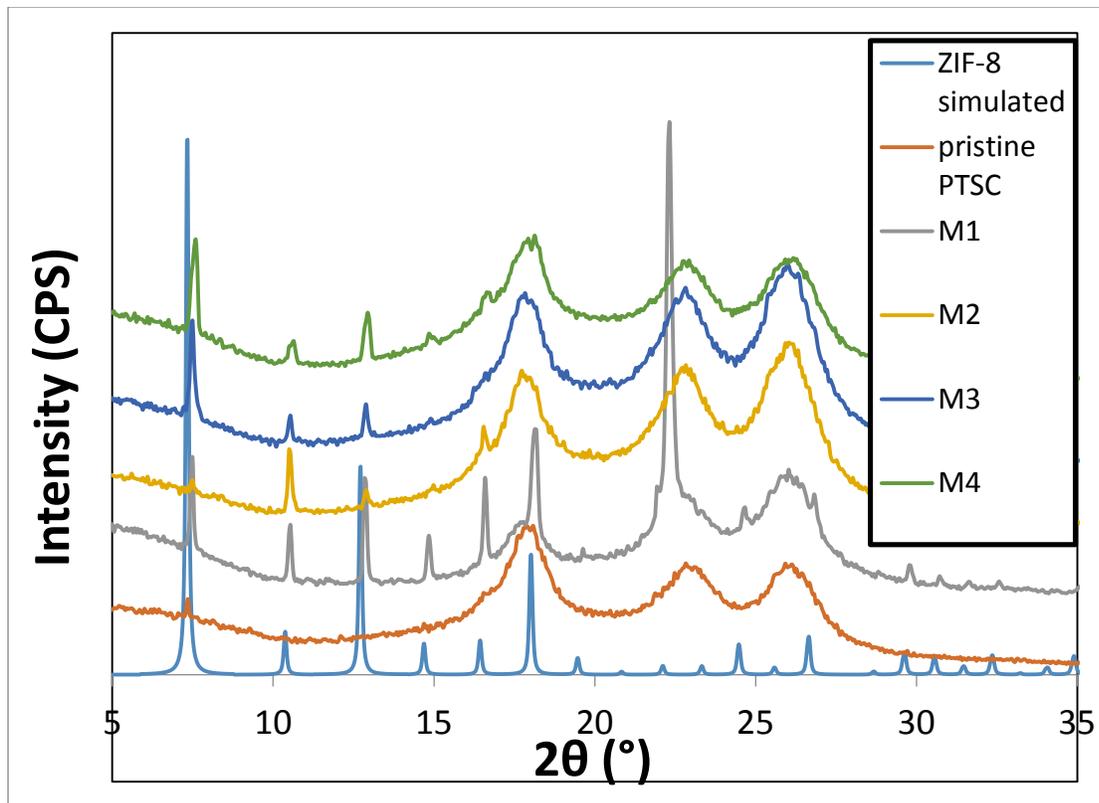


Fig. 4.9 X-ray diffractogram of ZIF-8 simulated (blue); pristine PTSC (red); ZIF-8/PTSC M1 (green); ZIF-8/PTSC M2 (purple); ZIF-8/PTSC M3 (light blue) and ZIF-8/PTSC M4 (orange).

The SEM images shown in Fig. 4.6 and Fig. 4.7 reveal the strong influence of reactant concentrations on MOF layer morphology. Crystal growth depends on the relative reactant diffusion rates through the membrane pores, but also on the pore size and metal binding capacity of the support. In general, crystal size decreases with metal and ligand concentration (Fig. 4.6 a-c), but we observed that below a certain threshold, crystal size increases again (M4, Fig. 4.6 d). Presumably these crystals are not well inter-grown, and gaps between them allow diffusion of the ligand into the zinc solution, permitting additional growth at the membrane surface. At moderately low concentrations (Fig. 4.7 c) the surface pores of the support are quickly blocked

by forming ZIF-8 crystals and further growth then takes place in a confined space, leading to a more compact, defect-free MOF layer. Wang's group introduced contra-diffusion [5] for MOF growth in 2011 and studied the effect of synthesis conditions on the properties of the forming ZIF-8 layer on a nylon support. They used relatively high reactant concentrations and obtained relatively thick layers on both sides of the support. However, in their later report [23] they used much lower reactant concentrations and obtained much thinner ZIF-8 layers with improved performance, in line with our observations.

Gas permeation through the ZIF-8/PTSC composite membranes was tested by the Wicke-Kallenbach technique where the total pressure difference across the membrane is maintained at zero. The feed gas flushes the ZIF-8 side of the membrane while nitrogen flows past the permeate side, and then to a gas chromatograph to measure feed gas that has permeated through the membrane. Flow rates of both feed gas and sweep gas were set to 30 ml/min. Hydrogen and propane permeances were measured and ideal selectivity was calculated as their ratio (Eq. 4.1 and Eq. 4.2). As could be expected from the SEM images of M1, M2 and M4 ZIF-8/PTSC membranes, they did not show good performance, offering selectivities only in the range of Knudsen selectivity. Thus, we will discuss only the M3 membrane's results. The best of the seven M3 coupons made gave selectivity of 25.5 for propylene/propane and 1737 for hydrogen/propane separation with hydrogen permeance of $2.1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. This high performance positions our membrane among the best ZIF-8 membranes prepared on polymeric or inorganic supports. Large performance differences between M3 coupons were observed (Tab. 4.2).

Tab. 4.2 Permeation results for M3 membrane obtained by Wicke-Kallenbach measurement

Membrane				After Only-Edges-PTMSP- Painting			After Full-Area-PTMSP Coating		
	$P_{H_2} / \text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$	$\alpha (H_2/C_3H_8)$	$\alpha (C_3H_6/C_3H_8)$	$P_{H_2} / \text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$	$\alpha (H_2/C_3H_8)$	$\alpha (C_3H_6/C_3H_8)$	$P_{H_2} / \text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$	$\alpha (H_2/C_3H_8)$	$\alpha (C_3H_6/C_3H_8)$
M3 coupon 1	2.3×10^{-7}	167							
M3 coupon 2	4.35×10^{-8}	523							
M3 coupon 3	8.1×10^{-8}	18	1.4				4.1×10^{-8}	596	22.6
M3 coupon 4	3.5×10^{-7}	172	3				1.0×10^{-7}	931	37.5
M3 coupon 5	2.1×10^{-7}	1737	25.5	2.1×10^{-7}	6268	86	1.1×10^{-7}	4076	106
M3 coupon 6	3.2×10^{-7}	1218	22	3.2×10^{-7}	8358	150	1.2×10^{-7}	2126	94
M3 coupon 7	6.5×10^{-8}	21	1.6	5.4×10^{-8}	90.5	4.1	4.5×10^{-8}	1653	82
PAN-ZIF-8	3.9×10^{-7}	4.4	1.1				2.7×10^{-9}	25	1.4

SEMs and rainbow effect indicate a thin, tight layer on all coupons. We hypothesized that these performance variations were caused by occasional defects in the MOF layer – defects so rare that their number in different coupons varies considerably. We further hypothesized that these defects tend to occur at the edges of the coupon, as a result of the lab-scale fabrication technique. Specifically, the interface between the adhesive-lined aluminium tape holder and the support may be a source of defects (Fig. 4.9).

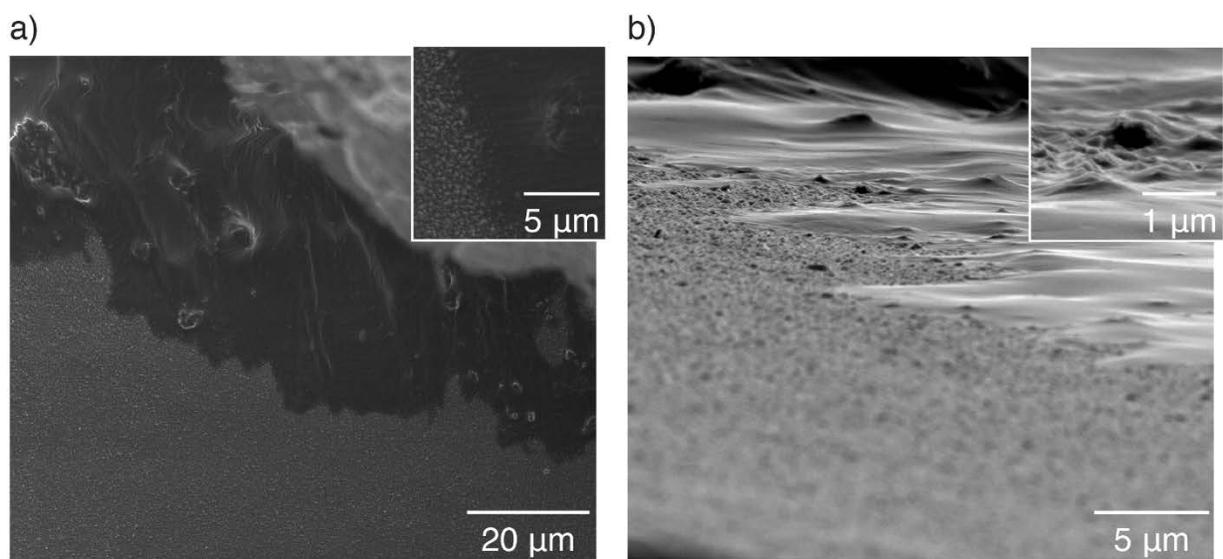


Fig. 4.10 SEM images of the interface between the butyl rubber adhesive from the aluminum tape and the ZIF-8 layer. The insets show possible defects.

To test the first hypothesis, coupons were coated with 0.5 wt. % PTMSP solution. As can be seen in Tab. 4.2 the selectivity always improved, indicating that the coating reduced nonselective flow through defects. As expected, permeance decreased, because the PTMSP layer adds a resistance. To test the second hypothesis, we coated only the edges of the coupons with the PTMSP solution.

Selectivity increased dramatically – to the highest levels ever reported. We measured a hydrogen/propane selectivity of 8358 and a propylene/propane selectivity of 150 for the best M3 coupon coated with PTMSP only in the edges. It should be mentioned that the PTMSP itself does not contribute to the increase in selectivity. As a highly permeable high free-volume polymer it has a reverse selectivity; large organic molecules such as butane and propane permeate faster than hydrogen. [24] Also, the propene/propane selectivity of PTMSP is negligible.

A simple bending test was conducted in order to evaluate the mechanical stability of our membrane. Coupon 4 coated with PTMSP was removed from the permeation cell and bent approximately 5 degrees, and the performance was checked again. The selectivity and permeance values were recorded to be the same as before bending. Bending the membrane more than 5 degrees resulted in a substantial loss in the selectivity, without a change in the H₂ permeance.

Different measurement techniques (i.e., Wicke-Kallenbach, constant volume, constant pressure) and conditions (i.e., temperature, pressure, tested gases) make it difficult to compare ZIF membranes directly. Previously, the ZIF-8/polymer composite membrane with perhaps the best reported combination of permeance and selectivity ($P(\text{H}_2) = 7.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and H₂/C₃H₈ selectivity = 833 with thickness of 2 μm) is the one prepared by Shamsaei *et al.*[11]. It was synthesized by contra-diffusion on a polymeric support previously subjected to a post-treatment to functionalize its surface with amine groups. They explained the importance of the support modification to improve ZIF-8 layer growth and bonding to the support. Hou *et al.* [15]

recently introduced preparation of ZIF-8 on APTES-functionalized titania-PVDF support by a direct growth method. They obtained a very fast membrane ($P(\text{H}_2) = 2.01 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and H_2/CO_2 selectivity = 7) with thickness of around 1 μm . In both cases the abundant amine groups present at the support's surface served as connection links between growing ZIF-8 and the substrate.

4.5 Conclusions

We have demonstrated that it is possible to guide the growth of the ZIF-8 layer so it forms exclusively at the surface of the membrane without the need for additional surface modification steps. Future experiments will identify other combinations of metal binding supports and metal-organic frameworks. Contra-diffusion has been established as an effective method to control MOF crystal morphology and layer location. Here we have shown that when using this method, the fortuitous combination of metal-complexing polymer with standard, asymmetrically skinned support morphology is all that is required to spur formation of highly selective and permeable MOF/polymer composite membranes. The propylene/propane selectivity and the propylene permeance reported here are in a commercially attractive region. [25] Future studies are required to determine whether these MOF composite membranes can be operated under real-world conditions.

Harnessing the industrial separation potential of MOFs requires facing and addressing their limitations. The molecular structure of ZIF-8 is ideally suited to separating propylene from

propane, but growing and supporting its brittle crystals to produce useful, economical membranes demands new techniques. This research demonstrates a step in that direction.

4.6 Acknowledgment

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5 Chapter: ZIF Membranes Synthesis on Modified Polyetherimide Porous Support by Contra-Diffusion Method

5.1 Abstract

We present two surface modifications of a polyetherimide (PEI) support to introduce functional groups able to enhance the adhesion between the support and the growing ZIF layer. The in-house-cast PEI membranes were reacted with ethylenediamine (EDA) and histamine (His), and such modified supports were used as supports for ZIF-8 growth by the contra-diffusion method. The effect of parameters such as short synthesis time (less than 3 hours) and the temperature lower than room temperature on the final membrane's performance was investigated while aiming to obtain the thinnest possible yet selective ZIF-8 layer.

5.2 Introduction

The advantages of choosing a polymer support instead of an inorganic support for growing MOF membrane were several times highlighted in literature as well as in this dissertation, mainly in the Literature review part and in the introduction parts of previous chapters. Among them, there is the option of chemical modification of the polymer support surface with functional groups, which can serve as affinity enhancers between the support and the growing MOF layer. The modification of the support before the ZIF growth has been reported previously by several authors. Shamsaei *et al.* [1, 2] treated the polymer support with the vapors of ethylenediamine

to obtain a surface with abundant amine groups, which played the role of links between the support and the MOF layer during the contra-diffusion growth. Li *et al.* [3] reacted polyvinylidene fluoride (PVDF) support with two primary amines which produced -NH_2 groups on the support surface. The functional groups can complex metal ions that would subsequently react with the ligand and thus form nucleation centers for further MOF layer growth. Li *et al.* [4] synthesized the $\text{Cu}_3(\text{BTC})_2$ and ZIF-8 layers on PAN hollow fibers which were in the first step hydrolyzed and the obtained deprotonated carboxyl group served as binding sites for the copper or zinc ion. Moreover, the stiffness and compression strength of the PAN fibers have been improved by the reaction.

In this work, we choose porous polymer support made of polyetherimide, which is a commercial and relatively cheap polymer (Ultem 1000, Sabic). This polymer support was modified by two different reagents: ethylenediamine and histamine. The reactions with the chosen modifiers were conveniently conducted at relatively low temperatures and short reaction times.

The ZIF-8 membranes were fabricated on the modified PEI supports by a contra-diffusion method. This method was introduced by Yao *et al.* [5] in 2011, who also studied the effects of reactant concentrations, reaction time (16-72h) and orientation of the membrane on the MOF layer properties and performance. The contra-diffusion experiments were mostly conducted at room or somewhat higher than room temperature.

Herein, we reduced the synthesis temperature below room temperature. To the best of our knowledge, this is the first report about cooled ZIF-8 synthesis. Moreover, we have also

shortened the synthesis times to less than 1 hour to observe how thin yet still selective ZIF-8 layer could be obtained.

5.3 Experimental details

Materials: Polyester nonwoven support (PE05TH-100) was purchased from HIROSE. Polyetherimide (Ultem®1000) was purchased from Sabic. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) ($\geq 99.0\%$), 2-methylimidazole (HMIM) (99%), histamine and ethylenediamine were supplied by Sigma-Aldrich. Methanol (99.80%) was supplied by Fluka Analytical. Poly(trimethylsilyl)propyne (PTMSP) was purchased from ABCR GmbH & Co. KG and cyclohexane was supplied by Honeywell Burdick & Jackson. All chemicals were used as received without further purification.

PEI support preparation: PEI membranes were prepared by non-solvent induced phase separation. First, a solution of 22 wt. % PEI in DMAc was stirred for six hours at 60 °C and allowed to rest for another five hours until air bubbles had escaped. Then a 200- μm -thick polymer solution film was cast on a polyester nonwoven support fixed on a glass plate. The cast film was then immersed in a water bath at room temperature for at least 24 h. The resulting PEI membranes were dried and stored at room temperature until use.

Modification of the PEI support membrane with histamine: PEI membranes were immersed into 2.5 wt. % solution of histamine in methanol at 50 °C for 2 h. The modified membrane was washed with excess of methanol to remove the traces of histamine.

Modification of the PEI support membrane with ethylene diamine: The dried PEI membrane was immersed into 5 wt. % EDA solution in methanol for 1 hour at room temperature under constant stirring. The modified membrane was washed with excess of methanol to remove the traces of EDA.

Contra-diffusion synthesis of the ZIF-8 membrane: The PermeGear® contra-diffusion cell and the developed recipe in the previous work have been applied for the ZIF-8 contra-diffusion synthesis. The EDA-PEI and His-PEI modified membranes were cut into coupons with a diameter of 1.5 cm and fixed between rings of aluminum tape with an outer diameter of 2.4 cm and inner diameter of 0.95 cm. The zinc source solution was prepared by dissolving 0.046 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 30 ml methanol, and the ligand source solution was prepared by dissolving 0.196 g of 2-methylimidazole in 30 ml methanol. The experiments were conducted at a temperature range from 5 to 22 °C with synthesis time varying from 5 min to 6 hours. The active side of the modified PEI membrane was facing the zinc source solution. After the growth, the membranes were rinsed with methanol and dried in vacuum oven at 50 °C for at least 24 hours before they were tested for permeation of gases.

PTMSP sealing solution: The ZIF-8 membranes were coated with a PTMSP solution (0.5 wt. %), which was prepared by dissolving PTMSP powder in cyclohexane under stirring at room temperature overnight. The full-area coating was done by spreading a drop of the PTMSP solution on the ZIF-8 surface from a pipette and letting it dry under a warm stream of air for about 2 minutes. The only-edges coating was done using a fine paint brush.

Characterization: Scanning electron microscopy (SEM) images of the surfaces and cross-sections of membranes were carried out with a FEI Quanta 200 FEG SEM. Samples for cross-section were fractured after being immersed for at least two minutes in liquid nitrogen. Samples were sputtered with iridium (approximately 3 nm) under vacuum before analysis. The adsorption capacity of the PEI and modified PEI support was measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The ICP-OES machine was calibrated with 1 ppm, 10 ppm and 100 ppm standard solution before analysis. The deviation was less than 10 % for the standard samples.

Permeation test: The permeance of hydrogen, propane and propylene was tested by the Wicke-Kallenbach technique using an in-house-built apparatus. Flow rates \dot{V} of feed gas and sweep gas (nitrogen) were kept at 30 mL/min by mass flow controllers. Permeate stream composition was analyzed by a gas chromatograph (Agilent 490 Micro GC) and the fraction of the studied gas x_i in the sweep gas was determined using a calibration curve. The permeance of the studied gas J_i was then calculated from the following equation:

$$J_i = \frac{x_i \dot{V}}{A \Delta p_i} \quad (5.1)$$

where A is the active membrane area and Δp_i is the transmembrane partial pressure difference of the studied gas. The ideal selectivity α_{ij} of the two gases (i and j , where i is the faster permeating gas) was then calculated from the ratio of their permeances:

$$\alpha_{ij} = \frac{J_i}{J_j} \quad (5.2)$$

5.4 Results and Discussion

5.4.1 ZIF-8/His-PEI membrane

Initially, the PEI membrane was modified with the histamine. To the best of our knowledge, this is the first time when histamine is being proposed for modification of polymer support to improve its affinity to MOF layer. The capacity of histamine to bind metals such as copper, cobalt or zinc has been reported in the past [6-10]. Moreover, the histamine molecule consists of an imidazole ring just like the ligand of ZIF-8, 2-methylimidazole. These assumptions led us to consider histamine as a promising candidate for modifying PEI support. The formation of histamine bond to PEI chains has been confirmed by FTIR analysis (Fig. 5.1).

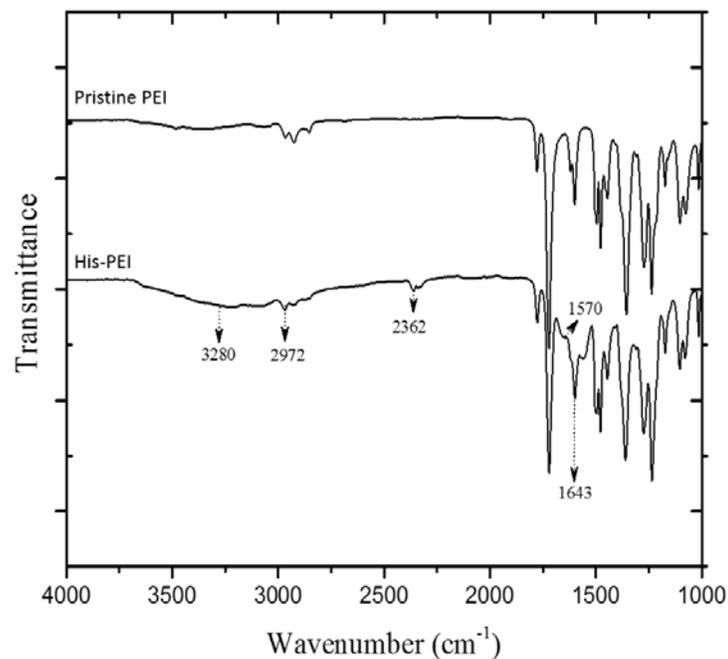


Fig. 5.1 ATR-FTIR spectrum for pristine and histamine modified PEI membrane.

The broad band at 3280 cm^{-1} is caused by the stretching vibration of -OH and secondary amine groups present in the modified membrane. The absorption bands observed at 2962 cm^{-1} is attributed to the stretching vibrations of $-\text{CH}_2$ groups. The two new absorption bands at 1643 and 1570 cm^{-1} are associated with stretching vibration of $\text{C}=\text{O}$ (amide I) and $\text{N}-\text{H}$ (amide II). However, the characteristic peaks for $\text{C}=\text{N}$ and $\text{N}-\text{H}$ groups of imidazole moieties are overlapped due to the similar stretching vibration of other functional groups existed in PEI membrane. These results validate the modification of PEI membrane with histamine via a ring opening reaction at $50\text{ }^\circ\text{C}$ for 2 h as shown in Fig. 5.2.

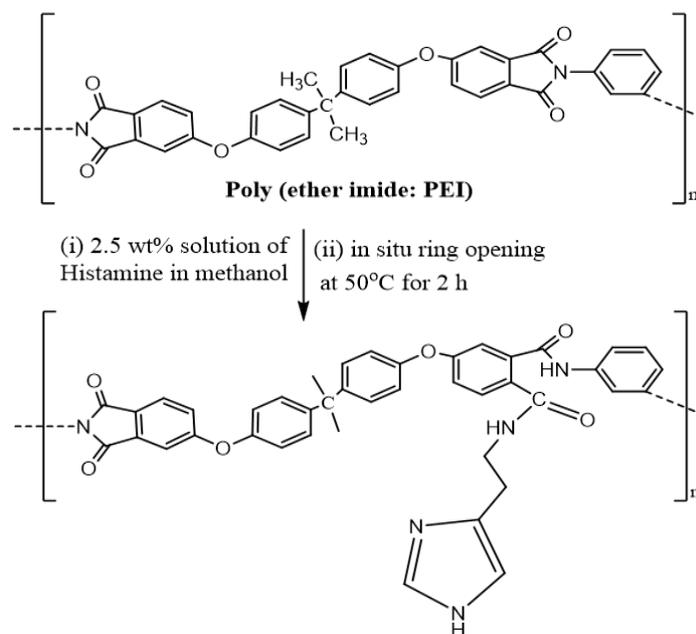


Fig. 5.2 The reaction route to prepare the His-PEI via a ring opening reaction with histamine.

The His-PEI substrate was used as support for the ZIF-8 layer by contra-diffusion growth following our previously reported recipe [11]. SEM images in Fig. 5.3 show that after 48 hours of growth, there were large crystals attached to the support top surface, but they do not form a continuous

layer. Additionally, when zooming inside the finger-like pores, we can see that the ZIF-8 did form a layer inside the pores of the support membrane, however this is not desired.

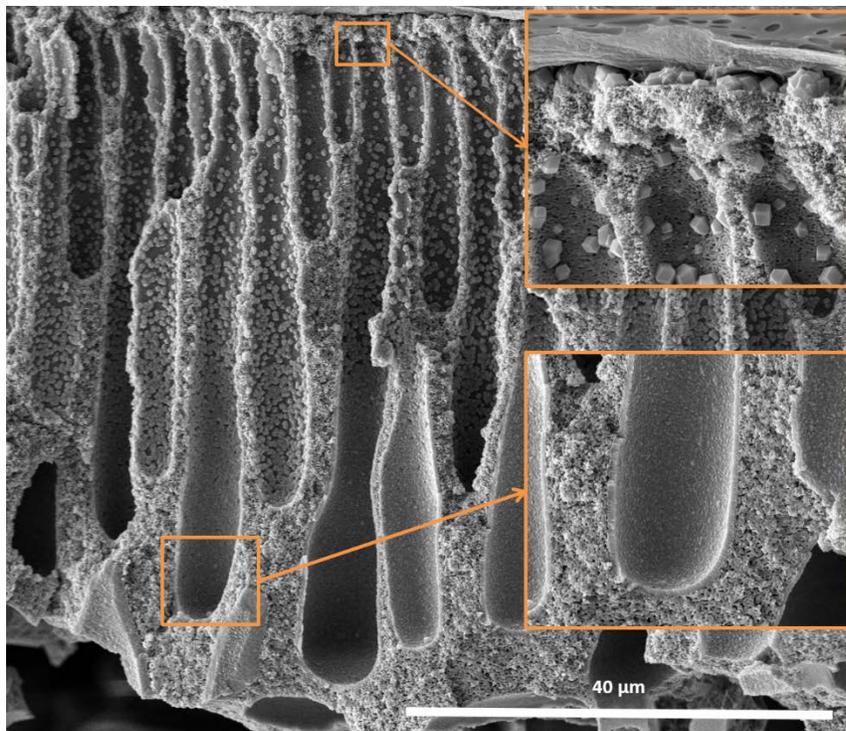


Fig. 5.3 SEM image of the cross-section of ZIF-8/His-PEI membrane prepared by the contra-diffusion method for 48 hours at room temperature.

We assumed that if the growth time was shorter, we could obtain a layer only on the surface and not inside the pores. Fig. 5.4 shows cross-section of the ZIF-8/His-PEI membrane obtained after four hours of the contra-diffusion reaction.

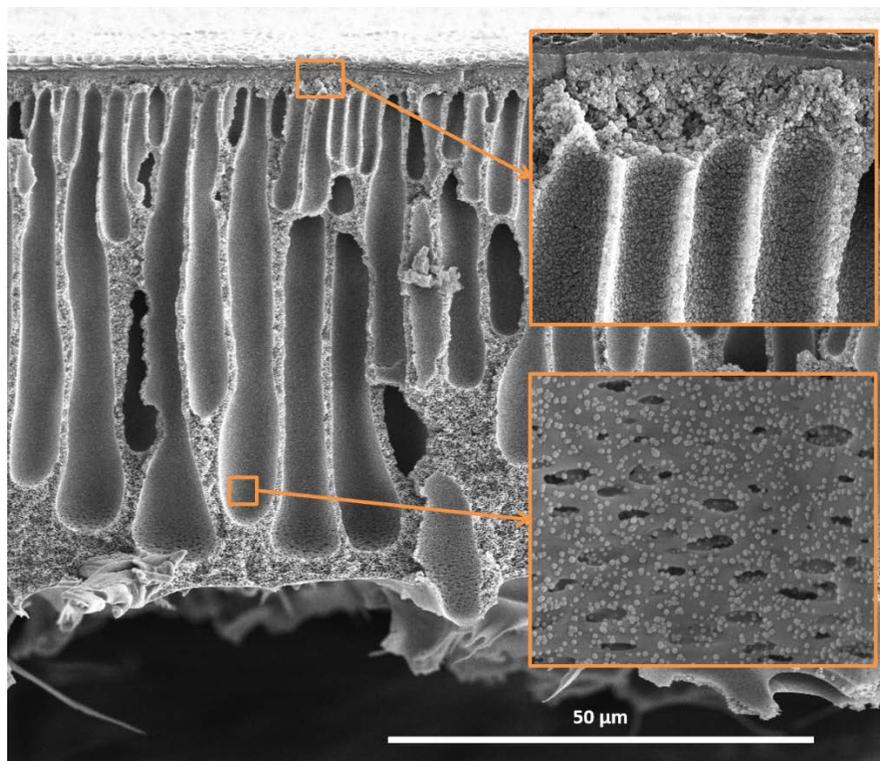


Fig. 5.4 SEM image of the cross-section of ZIF-8/His-PEI membrane prepared by the contra-diffusion method for 4 hours at room temperature.

It is obvious that the amount of the crystals inside the pores is less and that they did not form a layer like in the previous case. However, this membrane also does not possess the desired continuous ZIF-8 layer on the support surface. This unsatisfactory results led us to change the orientation of the support and turn its active side to face the imidazole source solution.

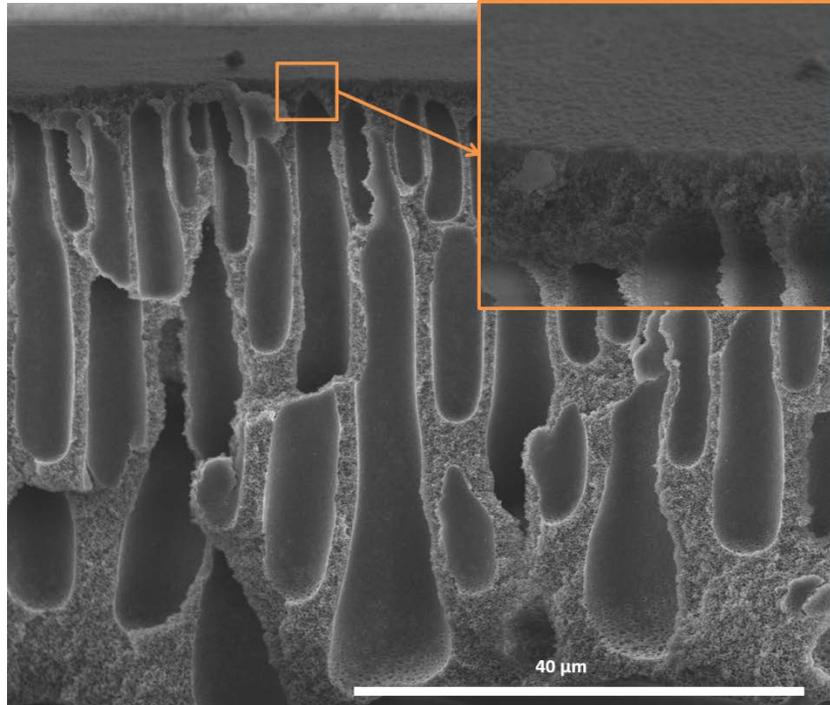


Fig. 5.5 SEM image of the cross-section of ZIF-8/His-PEI membrane prepared by the contra-diffusion method with active membrane side facing the imidazole source solution.

The SEM analysis showed that this membrane did not contain ZIF-8 crystals inside the pores however the layer, which was on the top-surface was not sufficiently compact. All prepared ZIF-8/His-PEI membrane were tested for gas permeation. However, they did not offer any significant hydrogen/propane or propylene/propane selectivity performance even after applying the PTMSP coating.

5.4.2 ZIF-8/EDA-PEI membrane

Ethylenediamine has been used as modifier previously by Shamsaei *et al.* [2] when they exposed the polymer support to EDA vapors, which has to be conducted at a higher temperature and in a

closed vessel with a special arrangement. We conveniently performed the modification reaction at room temperature for one hour by direct immersing of the support into a low concentration methanolic solution of EDA. The modification was confirmed by FTIR analysis (Fig. 5.6).

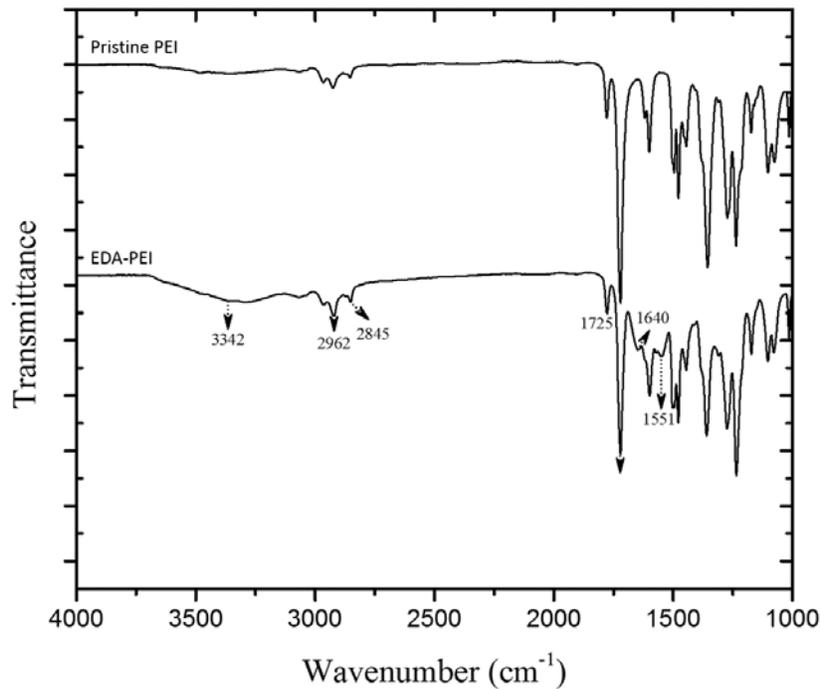


Fig. 5.6 ATR-FTIR spectrum for pristine and ethylenediamine modified PEI membrane.

The absorption bands observed at 2962 and 2845 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of aliphatic $-\text{CH}_2$ and C-H groups. The absorption band at 1725 cm^{-1} is ascribed to the stretching vibrations of imide C=O . The characteristic broad peak at 3342 cm^{-1} appeared due to the presence of $-\text{OH}$ and secondary amine ($-\text{NH}$) in the modified PEI membrane. The two new absorption bands are visible at 1640 and 1551 cm^{-1} , which are associated with stretching vibration of C=O (amide I) and N-H (amide II). These results confirm the modification of PEI with EDA by a ring opening reaction at room temperature (Fig. 5.7).

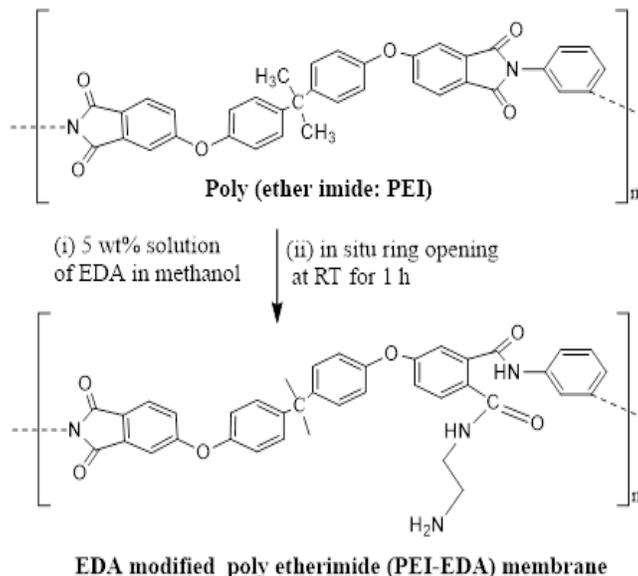


Fig. 5.7 Reaction route for preparation of the histamine modified PEI membrane.

Zinc binding ability test showed that EDA-modified PEI could bind almost 2 mg/cm^2 of zinc ions while the pristine PEI possesses zero binding ability of zinc. Binding of zinc can be regarded as a promising feature of a polymer support to serve as support for growing ZIF-8.

The contra-diffusion method offers many parameters to be varied and studied how they affect the final MOF membrane properties and thus also its performance. Shamsaei *et al.* [2] studied the synthesis time range of 30 – 60 min which resulted in very thin (200 nm) layers. In our previous work [11], we examined the effect of different reactant concentrations on the ZIF-8 layer. However, so far there are no reports about using synthesis temperatures below room temperature.

Initially, we followed the recipe proposed in our previous work with the synthesis time of 48 hours at room temperature. We connected the contra-diffusion cell to a chiller and conducted the ZIF-8 growth at 10 and 15 °C. The SEM images in Fig. 5.8 show how the thickness of the ZIF-8 layer was influenced by these low temperatures.

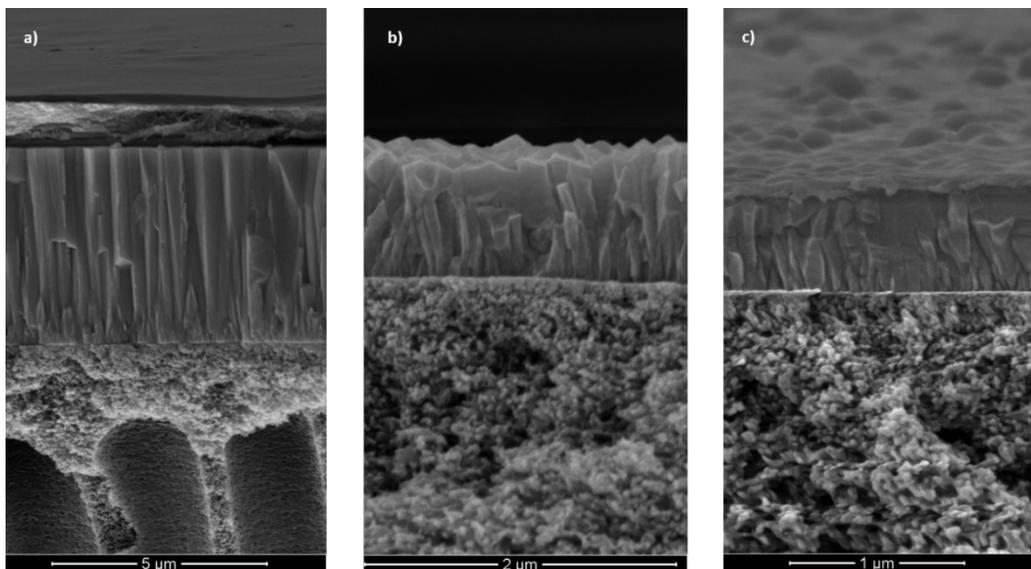


Fig. 5.8 ZIF-8 membrane on EDA-PEI support prepared at a) room temperature, b) 15 °C and c) 10 °C.

The ZIF-8 growth on EDA-PEI at room temperature results in a relatively thick 5 μm layer. It is worthy to notice that this layer is much thicker compared to our previous work with ZIF-8 on PTSC support (620 nm). The PEI support has bigger pores and higher porosity compared to PTSC, and thus although applying the same contra-diffusion reaction conditions, we obtain a different ZIF-8 layers thickness.

The Fig. 5.8 b) reveals that by lowering the temperature just by six degrees, the ZIF-8 layer's thickness decreased more than seven times, to about 700 nm. If the temperature is decreased to 10 °C (Fig. 5.8 c), a ZIF-8 layer with a thickness of less than 500 nm can be obtained.

These results suggest that besides lowering the reactant concentrations and shortening the reaction time, there is a way to reach very thin MOF layers also by choosing cooled synthesis.

The ZIF-8/EDA-PEI membranes were further tested for gas permeation of hydrogen, propylene, and propane by the Wicke-Kallenbach technique; the results are summarized in Tab. 5.1. (The empty cells in the table mean that the propylene gas was not tested for the given membrane because it did not show promising separation performance for hydrogen and propane.)

The edge area of the interface between the membrane and the alumina tape was painted by PTMSP solution as proposed in our previous work [11] where we showed that most of the defects are located in this area.

Each membrane was then fully-coated with PTMSP solution and measured again. It can be seen that the ZIF-8 membrane prepared at 15 °C reached high-performance already before the PTMSP coating. The selectivity propylene/propane was almost 50, and it was doubled after the PTMSP sealing layer was applied.

Tab. 5.1 Permeation results for ZIF-8 membrane prepared at different synthesis temperatures for 48 hours of reaction time.

T / °C	P H ₂ / mol m ⁻² s ⁻¹ Pa ⁻¹	α (H ₂ /C ₃ H ₈)	α (C ₃ H ₆ /C ₃ H ₈)	After PTMSP (0.5%) coating		
				P H ₂ / mol m ⁻² s ⁻¹ Pa ⁻¹	α (H ₂ /C ₃ H ₈)	α (C ₃ H ₆ /C ₃ H ₈)
22 (RT)	3.79 x 10 ⁻⁸	31.5	1.7	1.98 x 10 ⁻⁸	492	17
15	3.96 x 10 ⁻⁷	1816	49	3.15 x 10 ⁻⁷	3591	114
10	1.65 x 10 ⁻⁷	7.7		4.86 x 10 ⁻⁸	1108	45

In the next step, we reduce the reaction time from 48 hours to 3 hours, 1 hour and 5 minutes while maintaining the room temperature condition.

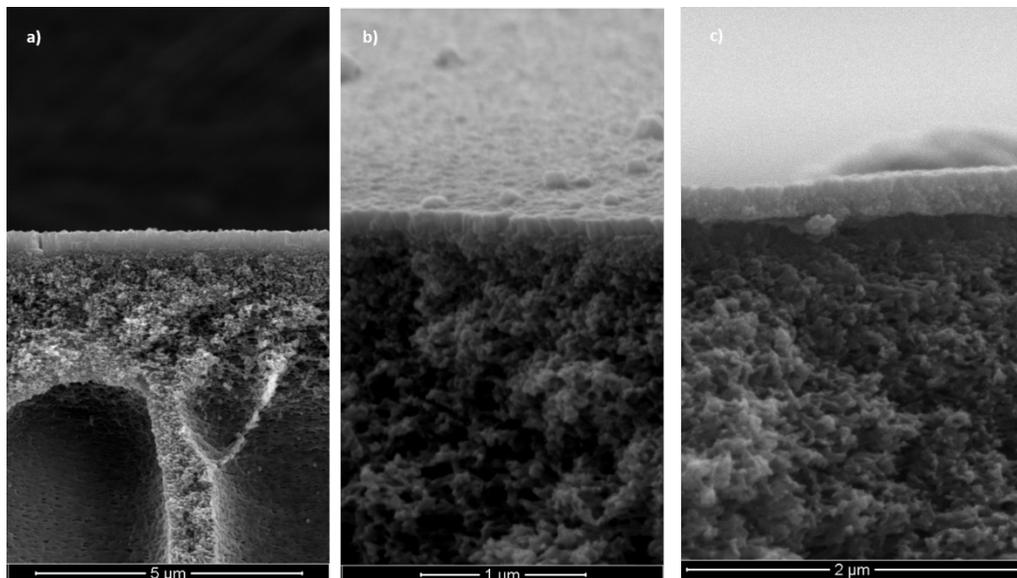


Fig. 5.9 SEM images of cross-section of ZIF-8 membranes prepared on EDA-PEI for reaction time of a) 3 hours; b) 1 hour; and c) 5 minutes.

Fig. 5.9 offers a comparison among ZIF-8 layers prepared at the different reaction times. After 3 hours, the ZIF-8 layer reached a thickness of 400 nm, which is 12 times less than the thickness obtained after 48 hours. When the synthesis time is even shorter (1 hour), we observe a ZIF-8 layer with a thickness of around 300 nm. Interestingly, a layer of around 200 nm is obtained already after 5 minutes after the contra-diffusion growth starts.

Membranes were coated with PTMSP in the same manner as the previous set of membranes and as well tested for gas permeation showing results concised in Tab. 5.2.

Tab. 5.2 Permeation results for ZIF-8 membrane prepared at different synthesis times at room temperature.

Time	P H ₂ / mol m ⁻² s ⁻¹ Pa ⁻¹	α (H ₂ /C ₃ H ₈)	α (C ₃ H ₆ /C ₃ H ₈)	After PTMSP (0.5%) coating		
				P H ₂ / mol m ⁻² s ⁻¹ Pa ⁻¹	α (H ₂ /C ₃ H ₈)	α (C ₃ H ₆ /C ₃ H ₈)
3 h	2.2 x 10 ⁻⁷	5.6		1.1 x 10 ⁻⁷	1380	75
2 h	1.4 x 10 ⁻⁷	18.3		3.1 x 10 ⁻⁸	177	
1 h	1.9 x 10 ⁻⁷	73.2	3.4	1.5 x 10 ⁻⁷	323	16
5 min	1.7 x 10 ⁻⁷	23		5.9 x 10 ⁻⁸	162	

The permeation results show that membrane obtained after only 5 minutes reaction time can offer some hydrogen selectivity after it was coated with PTMSP. The membrane prepared after 1 hour showed better performance, however, the best one was the 3 hour-reaction-time-membrane with an ideal selectivity of 75 for propylene/propane after PTMSP coating. Our approach is to prepare ultrathin ZIF-8 membrane under the most convenient conditions and simply coat it with a very permeable polymer, which can seal potential defects and at the same time serve as a protective layer for the ZIF-8 membrane.

If we consider lowering the temperature or shortening the time as variable parameters, reducing the time is more attractive because cooling requires additional energy. However, only out of

curiosity, we tried also the combination of low temperature and short reaction time to observe how thin a ZIF-8 layer could be obtained.

Fig. 5.10 shows a SEM image of the ZIF-8 membrane prepared for 15 minutes at 15 °C. One can notice that the thickness of this layer is only around 120 nm. This is comparable to the ZIF-8 films prepared by chemical vapor deposition method proposed by Stassen *et al.* [12] They sputtered 6 nm thin layer of zinc oxide which was exposed to 2-methylimidazole vapors and transformed to 104 nm thin film of ZIF-8.

The permeation tests of this sample brought unsatisfactory results with no significant hydrogen nor propylene selectivity over propane even after PTMSP coating.

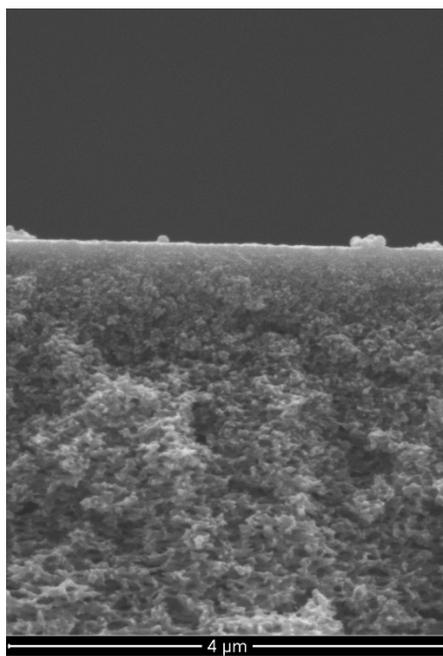


Fig. 5.10 SEM image of the cross-section of the ZIF-8 membrane prepared at 15 °C for 15 minutes.

5.5 Conclusions

The growth of ZIF-8 layers by contra-diffusion method has been studied on two modified polymer supports. Porous polymer support made of polyetherimide was modified by ethylenediamine and histamine to introduce functional amine groups which bind metal ions and thus may improve the affinity between the support and the ZIF-8 film.

The synthesis temperatures lower than room temperature have been used for the contra-diffusion growth of ZIF-8 layer. Additionally, a short synthesis time less than 1 hour has been tried. Zif-8 layers thinner than 500 nm have been obtained and showed high gas separation performance which can be boosted by applying a final PTMSP sealing coating.

5.6 Acknowledgement

We thank Rahul Shevate for measuring the zinc binding capacity of PEI and EDA-PEI membranes. We are also grateful to Mahendra Kumar who conducted chemical modification reactions of PEI membranes and their FTIR analysis.

5.7 References

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6 Chapter

6.1 The dissertation conclusions

This dissertation presented four approaches how to enhance the growth of ZIF layers on polymer supports. Each project aimed to use a convenient MOF growth method combined with physical or chemical modification of the polymer support.

The first two projects described in Chapter 2&3 are both, although in different ways, employing the double-zinc-source method. During the MOF growth, the source of metal does not come only from the crystallization solution but also from the support itself. Nucleation centers are thus formed on the support, and the further MOF layer growth is boosted.

The presence of zinc oxide inside the support and on the surface of the support proved to be helpful for the development of ZIF-8 membrane by secondary seeded growth. ZIF-8 membranes on common polymers (PAN and PEI) with thickness around 1 μm were obtained and tested for gas permeation by the constant-pressure-variable-volume method and by the time-lag measurement. Additionally, the sealing silicon rubber coating was introduced as a protective and pin-holes sealing film for ZIF-8 crystal layer.

The third and fourth project focus on the chemical properties of the polymer support used. In Chapter 4, the poly thiosemicarbazide (PTSC) support was chosen because of its metal chelating ability. Similarly, in Chapter 5 we conducted modification of PEI membranes with histamine and ethylenediamine to functionalize the surface with groups which can bind metal ions. The support attracts the metal ions, which serve as nucleation centers of growing MOF layer.

From the gained experience, the contra-diffusion method showed to be a more efficient growth method for obtaining thin (less than 1 μm) ZIF layers. The conditions of the contra-diffusion experiment such as reaction time, temperature, reactant concentrations and orientation of the support have been studied, and their effect on the final membrane properties was evaluated. A highly permeable high-free-volume polymer, PTMSP, have been used as a coating for the ZIF membrane and its boosting effect on selectivity by sealing the defects in ZIF layers has been tested. The gas permeation through synthesized ZIF membranes was measured by Wicke-Kallenbach technique and one of the highest performances for the propylene/propane separation reported so far was reached.

6.2 Recommendations for the future work

Synthesis of other MOF membranes on polymer supports

My first recommendation is to conduct research on other MOFs such as ZIF-7, ZIF-90 or MOF-5, *etc.* using the methods proposed in this thesis. We have tried to prepare ZIF-67 membranes on PTSC polymer by the contra-diffusion method (obtained results are summarized in the Appendix). However, the synthesis conditions have to be further optimized to obtain a selective membrane. If a compact dense layer were not obtained I would recommend the mixed-metal strategy. First, the ZIF-8 membrane can be prepared as described in Chapter 4 and then it should be immersed in a cobalt solution to observe if the ions can be subsidized. Then the properties of the mother ZIF-8 membrane and the cobalt-subsidized membrane can be compared.

Vapor chemical deposition (VCD)

The next recommendation is the application of the reported VCD [1] method for MOF membranes synthesis. I had tried a few experiments when I exposed a polymer support with a sputtered layer of zinc oxide to the vapors of 2-methylimidazole, but the first results did not show the desired formation of a compact ZIF-8 layer. However, I believe this approach is promising and brings the option of extremely fast MOF layers synthesis.

Ultrathin MOF layers

We have tried to prepare the thinnest yet selective possible ZIF-8 membrane, and we reached a sample of around 200 nm thickness. To the best of our knowledge, there are no reports which

present MOF membranes with a thickness less than 100 nm. However, I believe that the future is in ultrathin MOF layers – in the range of 10 to 50 nm. These layers would be to a certain extent also flexible, and thus the argument that MOF layers break on flexible polymer support wouldn't be valid anymore. Ultrathin layers would also offer higher fluxes. How to prepare such thin layers? Perhaps, the already mentioned VDC technique could offer a way. Also, the contra-diffusion method combined with interfacial synthesis can be an option.

During the few years spent in the laboratory, I have tried several unusual growth approaches, some of them are not mentioned in this dissertation, because their results did not show a potential. However, I am sure that further development of new methods for growing MOF layers is still needed. The often used methods as the *in-situ*, secondary seeded growth or the contra-diffusion could be further optimized. Convenient methods which will be fast, simple and cheap are what further research should aim for.

Hollow fibers

The last recommendation is to scale the contra-diffusion method to preparation of MOF films on hollow fibers made of the polymers suggested in the dissertation (PTSC and modified PEI).

6.2.1 References

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7 Appendix: ZIF-67 membrane synthesis on PTSC polymer support by contra-diffusion method

ZIF-67 is MOF structure composed of cobalt ions connected by 2-methylimidazole linkers (Fig. A1). It has sodalite like topology and the theoretical pore aperture of 3.4 Å which is in the same range as ZIF-8. Therefore it has also been recognized as a potentially good candidate for gas separation.

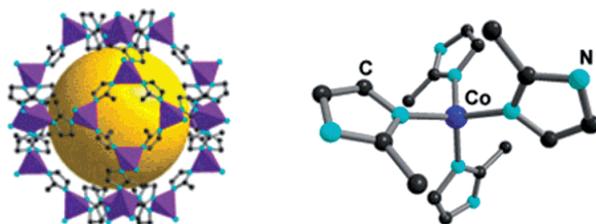


Fig. 7.1 Schematic illustration of the ZIF-67 framework structure (adopted from [1]).

Kwon *et al.* [2] have recently reported preparation of ZIF-67 membrane grown on ZIF-8 seeds by secondary growth method. They observed enhanced separation performance for propylene/propane. Wang *et al.* [3] prepared ZIF-67 membrane by secondary seeded growth method using relatively low temperature (30 °C) and water as the solvent. However, they did not reach desired separation performance until the cobalt ions were subsidized with zinc. Krokidas *et al.* [4] compared the potential of the ZIF-67 with a ZIF-8 framework for the propylene/propane

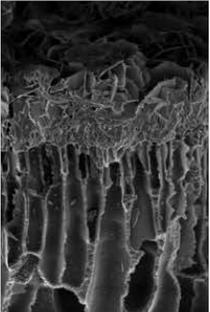
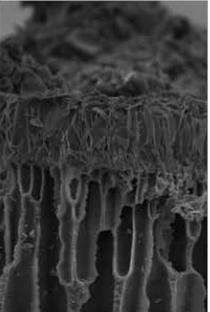
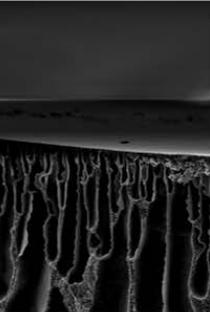
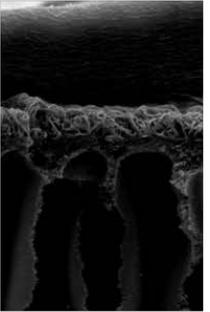
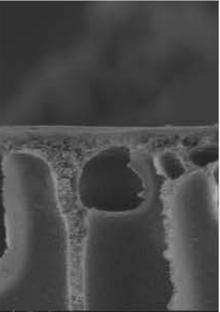
separation using the computational techniques. They concluded that ZIF-67 had offered higher selectivity for this industrially important separation.

To the best of our knowledge, there are no reports about ZIF-67 membrane being prepared by the contra-diffusion method. We have used the metal-chelating polymer PTSC discussed in Chapter 4 as the support for the ZIF-67 membrane.

Initially, six different recipes have been used, and the obtained results are summarized in Tab. A1. The membrane marked as M1 was prepared according to the recipe provided by Osama Sheikhan who used this recipe for growing ZIF-67 membrane via the layer-by-layer method. They have used the addition of triethylenediamine (TEA) to the imidazole solution to deprotonate the ligand molecule and thus increase its reactivity with cobalt ion. The cross-section of the M1 membrane showed very thick (more than 15 μm) flower-like growth of ZIF-67 layer which was peeling off from the support. That led us to decrease the reactant concentrations to half (M2). However, the layer of M2 looked similar to M1.

The next membrane M3 was prepared by replacing the water with methanol and excluding the TEA. The membrane turned brown, and we assume that PTSC crosslinked with the cobalt ions, but there is no desired growth of ZIF-67 layer.

Tab. 7.1 Summary of M1-M6 membranes obtained from different synthesis recipes.

Membrane	M1	M2	M3	M4	M5	M6
Co(NO₃)₂·6H₂O (facing membrane)	0.14g + 10ml H ₂ O	0.07g + 10ml H ₂ O	0.07g + 10ml MeOH	0.008g + 30ml H ₂ O	0.004g + 30ml H ₂ O	0.003g + 15ml H ₂ O + 0.011 HMIM
HMIM (facing support)	0.33g + 10ml H ₂ O + 0.4g TEA	0.16g + 10ml H ₂ O + 0.2g TEA	0.16g + 50ml MeOH	0.02 g + 30ml H ₂ O + 0.02 g TEA	0.01g + 30ml H ₂ O + 0.01 g TEA	0.008g TEA + 15ml H ₂ O
Photography						
SEM cross-section						
Thickness	15+ μm	12 μm	-	1.5 μm	900 nm	-

The results of M1 and M2 have led us to decrease the reactant concentrations even more – 50 times (M4) and 100 times (M5). We reached thinner layers (1.5 μm and 900 nm, respectively). However, the problem of not obtaining a compact layer maintained.

The SEM image in Fig. A2 depicts the surface of the M5 membrane with flower-like structured crystals which do not form a dense layer.

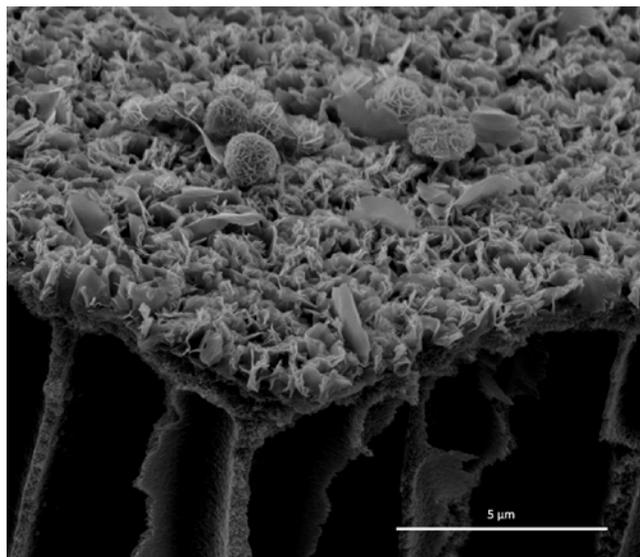


Fig. 7.2 SEM image of the M5 membrane's surface.

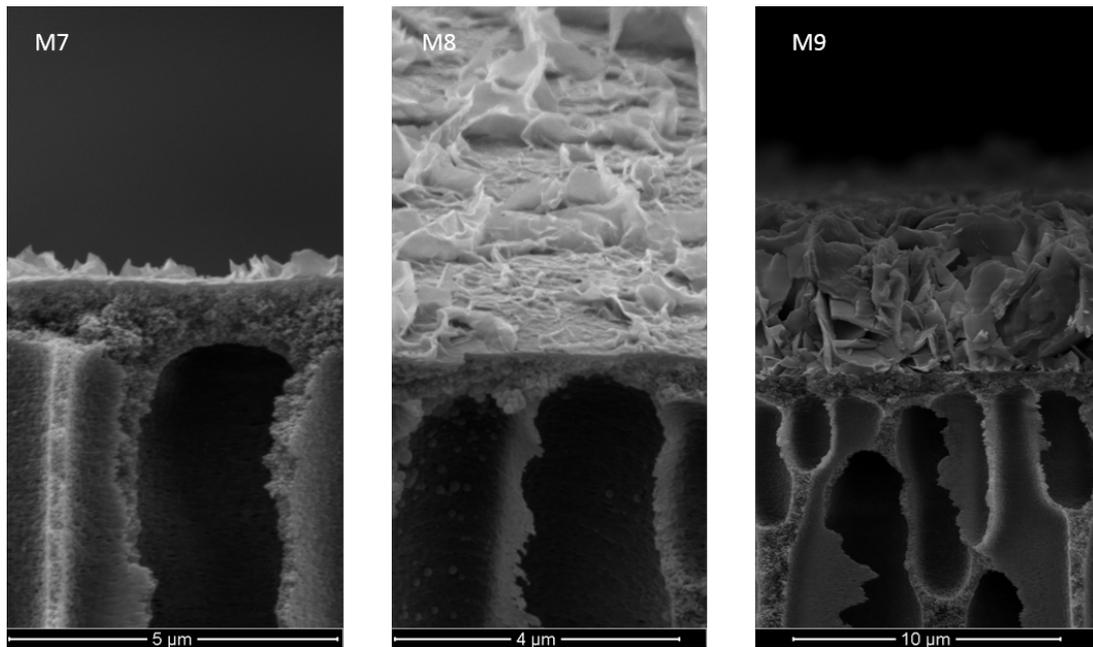
The prepared membranes (M1 – M6) were also tested for propylene and propane permeation. However, very high fluxes of both gasses with selectivity less than two were obtained which confirmed the poor quality of ZIF-67 films.

In the next set of experiments, we followed selected reports [2, 3, 5-7] about the preparation of ZIF-67 in bulk or as a film and modified them partially. Following reactant concentrations were prepared (Tab. A2).

Tab. 7.2 The weights of reactants used for preparation of M7-M9 membranes.

Membrane	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	HMIM
M7	0.012 g + 2.5 ml MEOH + 17.5 ml H_2O	0.23 g + 2.5 ml MEOH + 17.5 ml H_2O
M8	0.032 g + 20 ml MEOH	0.17 g + 20 ml MEOH
M9	0.015 g + 20 ml MEOH	0.56 g + 20 ml MEOH

The contra-diffusion reaction were conducted for 24 hours at room temperatures. Fig. A3 provides comparison of M7-M9 cross-section SEM images.

**Fig. 7.3** SEM images of the cross-section of M7-M9 membranes.

M7-M9 membranes possessed similar flake-like structures of the crystals which are not sufficiently intergrown and do not form a compact layer. Fig. A3 shows a closer look at the surface of the M9 membrane. Membranes M7-M9 were as well tested for gas permeation. However, no significant selectivities were observed.

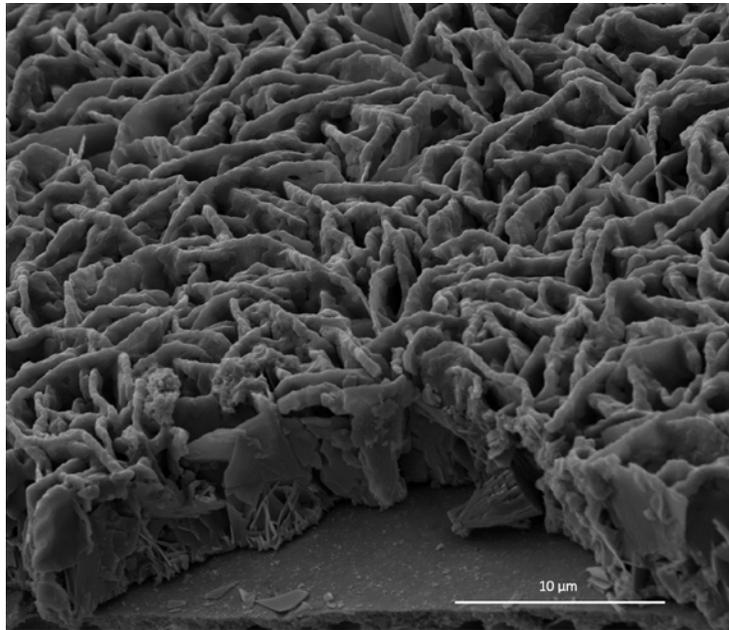


Fig. 7.4 SEM image of the M9 membrane's surface.

In conclusion, we have studied the effect of various reactant concentrations on the growth of ZIF-67 membrane on PTSC support via the contra-diffusion method at room temperature. We were able to reach very thin layers (1 μm) however we with flower-like or flake-like crystal structures. Further optimization of the synthesis conditions is required to obtain a compact membrane with high gas permeation and selectivity performance.

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