Polymer supported ZIF-8 membranes prepared via an interfacial synthesis method

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Porous polymer supported continuous ZIF-8 membranes were prepared via an interfacial synthesis method. Membranes with only one synthesis cycle showed excellent performance in the nanofiltration range.

MOF films have attracted a lot of interest over the past decade. With applications in luminescence, QCM-based sensors, optoelectronics, membrane separations and catalysis. MOF films can be formed on different supporting materials, varying from inorganic substrates, such as silica, alumina, to organic substrates, such as polymer films and porous polymeric membranes. Different synthesis schemes have been developed for the fabrication of thin MOF films, such as: (A) the direct growth/deposition from solvothermal mother solutions, (B) the stepwise layer-by-layer growth of crystals onto the substrate, and (C) the counter-diffusion method. ZIF-8 has a theoretical accessible window aperture of 0.34 nm and a relatively large cavity of 1.11 nm in diameter, with great potential in both liquid and gas phase separations. There are increasing reports on ZIF-8 membranes for gas separation, but fewer on liquid separations, especially on continuously ZIF-8 membranes. For ZIF-8 membrane fabrication, methods A and B are the most commonly used methods. ZIF-8 films on inorganic supports have been prepared via method A for gas separations. The first continuous ZIF-8 film was prepared on a tubular z-alumina support by secondary seed growth for CO2/CH4 separation. A z-alumina support rubbed with ZIF-8 seeds was immersed in a mother solution and then hydrothermally treated. The formed 8-layered membrane showed a CO2/CH4 selectivity of 7. Later on, a ZIF-8 film prepared on porous polyethersulfone (PES) membrane for hydrogen separations. Using method B, a polysulfone (Ps) membrane was dipped into a zinc nitrate solution in methanol for 12 h. The zinc nitrate saturated Psf membrane was then immersed in a 2-methylimidazole solution for 12 h, followed by drying. After several cycles, the ZIF-8-Psf composite membrane was formed. Using a similar approach, some of the thinnest membranes ever reported were prepared on porous alumina supports, with at least 100 times lower gas permeance than the results reported in literature, indicating high quality membranes with negligible defects and gaps, in conjunction with clear time-lag behaviour. In the counter-diffusion synthesis (method C), zinc and ligand solutions were separated by a porous substrate. After crossing the substrate and meeting each other, the crystallization occurs simultaneously until the entire pores are plugged by ZIF-8 crystals. The ZIF-8 membranes with thickness of 16 μm (methanol as solvent) and 2.5 μm (water as solvent) showed H2/N2 ideal selectivity of 4.3 and 4.6 respectively. The counter-diffusion method was further modified by combining with the solvothermal method. The ZIF-8 membranes exhibited high separation performance toward propylene over propane.

The preparation method is highly critical for the fabrication of defect-free ZIF-8 membranes. However, due to the complex ZIF nucleation and growth processes, it is hard to correlate directly the preparation method with the membrane properties. Growing polycrystalline ZIF-8 films via method A makes the control of the growth process very difficult. Particularly, the high probability of growing undesired large crystals and thick MOF layers often results in very poor film-reproducibility. Another major problem is the supports. The difference in thermal expansion between the MOF layer and the support, which can cause cracks during heating–cooling operations. For the counter-diffusion method, the diffusion rates of metal ion solution and imidazolate solution can be different because of their different interactions with the substrate. Therefore, the reaction zone is within the substrates, and the resulting membranes are either thick or with defects. In addition, this method is also time-consuming. MOF-5, Cu3(BTC)2 and ZIF-8 have been synthesized at the interface between two immiscible liquids at which metal...
ions and ligand molecules meet and react.\textsuperscript{20,21} Inspired by the well-established thin film composite membrane preparation method of interfacial polymerization,\textsuperscript{22,23} an interfacial synthesis method is proposed here for the synthesis of ZIF-8 films. Considering flexible polymeric supports have favourable interactions with organic ligands of MOFs,\textsuperscript{24} polyethersulfone (PES) based porous membranes were used as supports. The synthesized PES supported ZIF-8 membranes were characterized in detail and the performance of these membranes was investigated.

When a zinc nitrate aqueous solution was brought in contact with a hexane based 2-methylimidazole solution in presence of a small amount of ethanol as co-solvent, the ligand and the zinc\textsuperscript{2+} reacted at the water/organic interface, leading to a white layer at the interface after a certain time (Fig. 1a). White powder was obtained after removal of the liquid phase by centrifuge, followed by steps of washing and drying. The SEM image of this powder shows an aggregated morphology rather than uniform crystals (Fig. 1c). The XRD pattern of this white powder is identical with that of ZIF-8 crystals conventionally prepared in DMF as a solvent (Fig. 1d, ZIF-8-REF), confirming the ZIF-8 formation.

A PES membrane prepared by phase inversion (ESI\textsuperscript{†}) was impregnated with a zinc nitrate aqueous (15 g L\textsuperscript{-1}) overnight. After removal of the excess aqueous solution from the support surface using a rubber wiper, 2-methylimidazole in hexane (16.24 g L\textsuperscript{-1}), using a small amount of ethanol as co-solvent (see ESI\textsuperscript{†} details), was gently poured on the surface. The solution was drained off after a 1 h reaction time. The membranes were finally post-treated overnight at 100 °C. The PES support has a very broad peak reflecting the amorphous character of this type of polymer. Weak peaks appear on the XRD pattern of the PES supported ZIF-8 membrane (ZIF-8/PES membrane). These peaks match well with the peaks of ZIF-8 crystals (Fig. 1d). Combined with the ATR-IR spectrum of the ZIF-8/PES membrane (ESI\textsuperscript{†} Fig. S2), this confirms that a ZIF-8 layer was formed on the PES support. SEM images (ESI\textsuperscript{†} Fig. S3) show the different surface morphologies between the ZIF-8/PES membranes. The surface of the ZIF-8/PES is also homogenous but with some particle-like and shell-like spots. This indicates that a continuous ZIF-8 layer was formed on the porous support. This difference is more obvious in the AFM images. A much rougher surface is observed for the ZIF-8/PES membranes, due to the formation of the ZIF-8 layer on the support (ESI\textsuperscript{†} Table S1). The contact angle measurements show that the PES supported ZIF-8 membranes have larger contact angle than the PES membranes (ESI\textsuperscript{†} Fig. S7), indicating more hydrophobic surfaces. However, there is no obvious interface between the ZIF-8 layer and the selective layer of PES support, as seen from the cross-section images (ESI\textsuperscript{†} Fig. S4). This is because ZIF-8 starts to grow from the open pores of the PES support. Once the ZIF-8 crystals form in the pores, they grow and fill the pores of the selective layer of the PES support, serving as roots. Afterwards, a continuous thin layer formed on the surface of the PES support. This hypothesis was confirmed by the TEM images (Fig. 2b, and ESI\textsuperscript{†} Fig. S5). For the ZIF-8/PES membranes, the white spots, homogeneously distributed in the selective layer of the supporting membrane compared to the reference membrane, can be assigned to the ZIF-8 nuclei formed in the pores of the support during the interfacial reaction. These nuclei grow and fill the pores as the reagents diffuse from the aqueous and organic phases to the interface.

By varying the interfacial reaction time and the polymer concentration of the support casting solution, similar surface, cross-section morphologies and even similar contact angles were observed (ESI\textsuperscript{†} Fig. S5–S7 and Table S1). The ZIF-8 layer is smoother and denser when the polymer concentration is higher and the reaction time is longer, which is evidenced by the ZIF-8 membrane surface images (ESI\textsuperscript{†} Fig. S6), the surface roughness (ESI\textsuperscript{†} Table S1) and the SRNF
results (Table 1). However this variation in surface morphology is not significant, which leads to little change in contact angle. However, the dye removal performance in typical solvent resistant nanofiltration (SRNF) experiments was significantly influenced by these parameters (Table S1 and Fig. S7 in the ESI†). A 1 h reaction time was found to be optimal, as both the permeances and the rose bengal (RB) rejections did not change much for longer reaction times. Shorter reaction times did not favour for the formation of defect-free dense thin ZIF-8 layer, as indicated by the RB filtration results (ESI† Fig. S8). For the different supports, the SRNF data show that the RB rejection of the support increases with the polymer concentration, but the performance is very poor even for the support prepared with 22% polymer concentration (PES-22%). After formation of the ZIF-8 layer on these supports, the RB rejection significantly improves with a sharp drop in permeance (Table 1). For instance, the RB rejection from water for PES-16% is only 15.7%, where the RB rejection of that same PES support coated with a ZIF-8 layer (ZIF-8(1 h)/PES-16%) is improved to 92.5%. The RB rejection is even higher for ZIF-8 membranes with a support prepared from a higher polymer concentration: 98.9% from water for ZIF-8(1 h)/PES-22%. The water permeances drop in around 10–30 times compared to the supports. The same trend was found in ethanol and isopropanol (IPA). These results thus prove that a dense ZIF-8 layer is formed on the porous PES supports by the simple interfacial synthesis method. For ethanol and IPA, slightly lower RB rejections than from water were observed. The permeance for the PES supports is in the trend (water > ethanol > IPA), which can be explained by the molar volume effect.5 For the supported ZIF-8 membranes, the permeance trend changes to ethanol ~ water > IPA. ZIF-8 has a very flexible pore structure and very hydrophobic pore walls. This can explain why the ethanol permeances are close to the water permeances for the PES supported ZIF-8 membranes. The molecular size of IPA (0.49 nm) is larger than the pore size of ZIF-8 (0.34 nm) compared to ethanol (0.45 nm). Although IPA can enter the pores, the transfer resistance will be larger, even if there is a pore opening effect.

In summary, continuous thin ZIF-8 membranes were successfully prepared on porous polymeric supports via a simple interfacial synthesis method. Although these membranes were prepared in just one synthesis cycle, these membranes showed excellent Rose Bengal removal performances from different solvents. Compared to the solvo-thermal synthesis method, the present method is easy to up-scale and could thus be used to prepare MOF membranes with larger surface area on different porous supports. Future work will focus on screening suitable solvents for the imidazole ligand and using modulation ligands to control the ZIF-8 morphology. In addition, this method will be extended to other types of MOFs and the membrane applications will be extended to other membrane separation processes.

The authors gratefully acknowledge Belgian government (IAP-PAI networking), Flemish government (long-term Methusalem) and KU Leuven (OT/11/061 projects) Yanbo Li acknowledges the KU Leuven for a PDM postdoctoral fellowship. Lik H. Gee thanks the FWO-Vlaanderen for a postdoctoral research fellowship.

### Notes and references


### Table 1

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