Accepted Manuscript

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PII: S1387-1811(15)00478-3

DOI: [10.1016/j.micromeso.2015.08.038](https://doi.org/10.1016/j.micromeso.2015.08.038)

Reference: MICMAT 7283

To appear in: *Microporous and Mesoporous Materials*

Received Date: 27 July 2015

Revised Date: 30 August 2015

Accepted Date: 31 August 2015

Please cite this article as: P. Neelakanda, E. Barankova, K.-V. Peinemann, Polymer supported ZIF-8 membranes by conversion of sputtered zinc oxide layers, *Microporous and Mesoporous Materials* (2015), doi: 10.1016/j.micromeso.2015.08.038.

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Polymer supported ZIF-8 membranes by conversion of sputtered zinc oxide layers

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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) and defect free 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 5 times higher than the Knudsen selectivity. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis were done to characterize the membranes.

KEYWORDS

ZIF-8 membrane; Magnetron deposition; ZnO conversion; Hydrogen; Propane

1. 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. Recently two detailed reviews were published dealing especially with MOF/ceramic composites and their applications [12, 13] ; however, polymer substrates could be 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 4 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 method 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 acted also 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 advantages are: the use of water as a solvent, room temperature synthesis and relatively short synthesis time.

2. EXPERIMENTAL METHODS

2.1. 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.

2.2. ZnO deposition: PAN membranes were fixed on the metal pallet in the sputter instrument with two-side 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.

2.3. Synthesis of 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.

- 2.4. 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).
- 2.5. 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 , volume of permeating gas V_i and time t the permeance was calculated:

$$J_i = \frac{V_i}{A \Delta p_i t} \quad (1)$$

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

$$\alpha_{ij} = \frac{J_i}{J_j} \quad (2)$$

3. RESULTS AND DISCUSSION

Two preparation methods were followed. Both the methods have the same first step which is the deposition of zinc oxide layer on the PAN substrate and they differ in the second step of conducting the ZIF-8 growth (Scheme 1). A thin (~90 nm) layer of zinc oxide was applied by magnetron sputtering technique; Fig. 1 depicts the cross-section of zinc oxide layer deposited on PAN.

Scheme 1. General ZIF-8 membrane preparation

Fig. 1. SEM cross-section image of PAN-ZnO membrane support

The method A consists of direct immersing of PAN-ZnO support into pure 2-methylimidazole solution. This method was used also by Drobek *et al.* [37] for preparation

of ZIF-8 membranes on zinc oxide layers deposited on alumina supports. This approach is convenient since it is a simple and fast *in-situ* method and it does not require 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. 2. It can be seen that the zinc oxide layer was transformed into 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. 2. SEM top-view image of ZIF-8 membrane prepared by Method A

Method B has two additional steps comparing 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 intergrown. Top-view and cross-section of the ZIF-8 membrane obtained using method B is shown in Fig. 3. 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 number of cycles.

Fig. 3. SEM top-view and cross-section images of ZIF-8 membrane prepared by Method B

The XRD spectra of as prepared ZIF-8 membrane and substrate are shown in Fig. 4. 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. 4. X-ray diffractogram of PAN-ZnO-ZIF-8 membrane (a), PAN-ZnO (b), PAN support (c) and ZIF-8 (simulated) (d).

To check the quality of the prepared ZIF-8 membrane, single gas permeation of hydrogen and propane was tested and the ideal selectivity was calculated. Tab. 1 summarizes 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 10 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 layer 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 gases is 5 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 [14] research group 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. So presently it is difficult to decide to which extent the large differences in selectivity are based on the different measurement techniques or on differences in the quality of the ZIF layer.

Because of the flexible nature of polymer support it is important to handle the membrane very carefully to avoid formation of cracks in the ZIF-8 layer. In spite of careful handling we were not able to achieve a satisfying reproducibility for the PAN-ZnO-ZIF-8 membranes. The hydrogen/propane selectivity of 26 given in Table 1 is the best value we could obtain. All other membranes had selectivities below 15. The reason for these low selectivities is very likely the presence of tiny pinholes or cracks, which were not visible in the SEM images. We are currently examining possibilities to repair these defects by a suitable polymer coating.

Tab. 1. Permeation results of prepared ZIF-8 and support membranes

Tab. 2 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. 2. Summary of literature reports of MOF membranes supported by polymers**4. CONCLUSION**

In conclusion, ZIF-8 membranes were prepared by a double-zinc-source method on porous PAN support. This method employs deposition of zinc oxide by magnetron sputtering prior to 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 gases which was 5 times higher than the Knudsen selectivity.

5. ACKNOWLEDGMENT

We thank Ali Behzad and Ohoud Mohammed Eid Alharbi for assisting with SEM analysis. The authors gratefully acknowledge the financial support from King Abdullah University of Science and Technology (KAUST).

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Table 1. Permeation results of prepared ZIF-8 and support membranes

	P* (H ₂)	P*(C ₃ H ₈)	α (H ₂ /C ₃ H ₈)
PAN	505	138	3.7
PAN-ZnO	42.3	10.8	3.9
PAN-ZnO-ZIF-8	1.23	0.047	26 (best value)

*/ 10⁻⁷ mol m⁻² sec⁻¹ Pa⁻¹

Table 2. Summary of literature reports of MOF membranes supported by polymers

MOF	MOF thickness / μm	Support	P (H ₂) / 10 ⁻⁷ mol m ⁻² sec ⁻¹ Pa ⁻¹	Selectivities	Ref
ZIF-8	0.9	Polyacrylonitrile	1.23	26* H ₂ /C ₃ 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* H ₂ /C ₃ H ₈ 3.8* H ₂ /CO ₂	[22]
HKUST-1	9	Polysulfone	0.787	5.7* H ₂ /C ₃ H ₈ 7.2* H ₂ /CO ₂	[22]
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 13.6 CO ₂ /N ₂	[26]
ZIF-8	3.6	Polysulfone	0.0482	17.2 H ₂ /CH ₄ 18.3 H ₂ /N ₂	[26]

				2.6 H ₂ /CO ₂ 6.1 CO ₂ /CH ₄ 7.1 CO ₂ /N ₂	
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*single gas permeation measurement, selectivity calculated as Eq. (2)

FIGURE CAPTIONS

Scheme 1. General ZIF-8 membrane preparation

Fig. 1. SEM cross-section image of PAN-ZnO membrane support

Fig. 2. SEM top-view image of ZIF-8 membrane prepared by Method A

Fig. 3. SEM top-view and cross-section images of ZIF-8 membrane prepared by Method B

Fig. 4. X-ray diffractogram of PAN-ZnO-ZIF-8 membrane (a), PAN-ZnO (b), PAN support (c) and ZIF-8 (simulated) (d).

FIGURES

Scheme 1

Fig.1

Fig. 2.

Fig. 3.

Fig. 4.

- Very thin (900nm) ZIF-8 membranes were synthesized on polyacrylonitrile PAN support by a double-zinc-source method.
- Thin zinc oxide layer was deposited on PAN support by magnetron sputtering.
- Conversion of zinc oxide to ZIF-8 was proposed as a beneficial step during growth of ZIF-8 continuous layer.
- Prepared ZIF-8 membrane showed good performance for hydrogen-propane separation.