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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} mol m^{-2} sec^{-1} 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.

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 Ni_2(L-asp)$_2$(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

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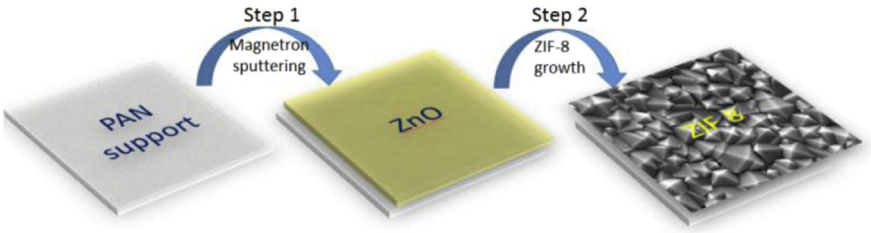

Scheme 1. General ZIF-8 membrane preparation.

good H_2/C_3H_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 ($Zn(NO_3)_2.6H_2O$) (≥99.0%), sodium hydroxide (NaOH) (≥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 100 mTorr. The thickness of deposited layer can be adjusted by the length of the deposition time. In our experiments the deposition duration of 1 h 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 h. Method B: PAN-ZnO support was dip-coated for 10 s in 2-methylimidazole solution (3.2 g in 23 mL DI water (pH = 9.5)). Then the membrane was dip-coated for 10 s in zinc nitrate solution (0.25 g of $Zn(NO_3)_2.6H_2O$ 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: $Zn(NO_3)_2.6H_2O$ (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 h 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

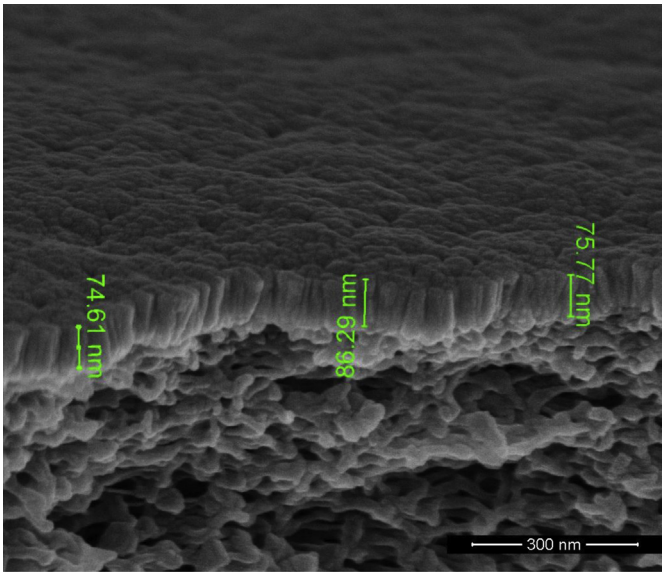

Fig. 1. SEM cross-section image of PAN-ZnO membrane support.

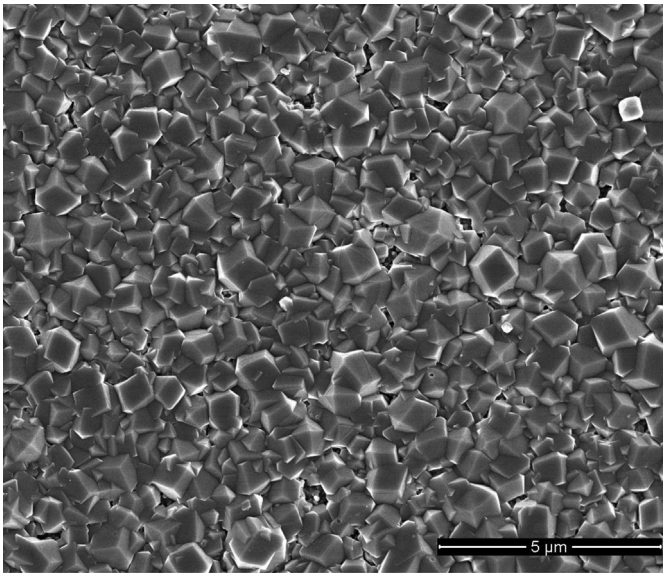

Fig. 2. SEM top-view image of ZIF-8 membrane prepared by Method A.