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Direct spraying approach for synthesis of ZIF-7 membranes by electrospray deposition

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ABSTRACT

Zeolitic imidazolate frameworks (ZIFs) are promising materials for advanced membrane applications due to their desirable properties, which enable them to recognize specific target molecules based on the molecular sieving mechanism and/or adsorption affinity. However, their large scale commercial applications still remain a challenge because of the absence of a synthesis method that offers reproducibility, scalability, and cost-effectiveness. To this end, here we report our work of synthesizing supported zeolitic imidazolate framework ZIF-7 films and membranes in a facile and time-efficient manner at ambient pressure using a simple electrospray deposition technique. A governing parameter which dominantly affected the microstructures and crystal integrity of the membranes was deposition temperature while precursor flow rate and applied voltage to the precursor solution were important variables to obtain a stable spraying mode which is essential to have a uniform coating. Our method, which is an electrostatic force-assisted coating approach, has the following attractive advantages over conventional synthetic routes such as *in situ* and secondary growth methods: (1) dramatic reduction in synthesis time and precursor consumption, (2) simplification in the activation process, and (3) potential scalability. Furthermore, the membranes obtained under optimized conditions outperformed previously reported ZIF-7 membranes for H_2/CO_2 separation while showing rather noticeable improvement in H_2 permeance which is roughly 4–10 times higher than the previous counterparts.

1. Introduction

Metal organic frameworks (MOFs) are a relatively new class of hybrid organic–inorganic materials consisting of metal ions or their clusters linked to organic ligands [1]. The great variety of possible combinations between metal atoms and organic linkers and their coordination bonding nature allows these materials to rather easily be fine-tuned on their physical/chemical properties as compared to other types of materials (*e.g.*, zeolite, and metal oxide) [2,3]. Due to these outstanding features, they have the chance to be applied to advanced fields, for instance, gas storage, adsorption, catalysis, and membranes [3–6].

Zeolitic-imidazolate frameworks (ZIFs), a sub-branch of MOFs, have metal nodes (usually zinc or cobalt) and imidazolate (or imidazolate derivative) ligands as constituents [7–9]. They share crystal structures with zeolites due to the bond angle resemblance between metal–linker–metal bond angle (*ca.* 145°) in ZIFs and Si–O–Si bond angle found in many zeolites [9]. ZIFs have been noted for their exceptional thermal and chemical stabilities coupled with ultra-microporosity [3,9]. Due to these properties, ZIFs have been considered to be excellent candidates for the advanced membrane applications.

The preparation of ZIF membranes can be conducted generally either by *in-situ* method [10–15] or by secondary growth method [16–21]. The *in-situ* method is attractive due to its simplicity in which the synthesis starts with bare supports [13,15,22] or chemically modified ones [14,23,24] for enhancing heterogeneous nucleation and growth. However, the membranes, prepared from the *in-situ* method, are usually thick, require long synthesis time, and more importantly result in poor grain boundary structures. Many endeavors have been made to improve the *in-situ* method. For example, the noticeable reduction in synthesis time for ZIF-8 membranes was accomplished by using microwave heating instead of conventional oven heating while chemical surface modification approaches have been widely proven to be effective for enhancing heterogeneous nucleation and growth for a series of ZIF membranes such as ZIF-8 [13–15], ZIF-22 [25], ZIF-90 [26], and so on. In addition, a few research groups used a counter diffusion concept to prepare ZIF-8 membranes where ligand and metal sources were supplied in the opposite direction [15,22,24], limiting the formation of the membranes only at an interface. This limited crystallization resulted in the formation of thinner membranes with improved microstructure. As opposed to the *in-situ* method, the secondary growth method begins with implanting seeds on

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supports which will be grown into continuous membranes in a separated growth step. However, in spite of its complexity in the synthesis stemming from the additional seeding step, it generally gives better control over membrane microstructures than the *in-situ* method does due to the benefit of having seeds at the beginning of growth. So far, much attention has been paid to improving seeding techniques. The seeding techniques have evolved from the most widely used dip-coating [18,27–32] and slip-coating [33,34] methods at present to electrospinning [35] and microwave-assisted methods [20] to obtain high-quality and reproducible seed layers, which is directly reflected in their final membrane performance. For instance, Kwon et al. [20] could synthesize propylene-selective ZIF-8 membranes in a reproducible manner from the seed layers prepared from their microwave-assisted seeding technique. In addition, the electrospinning-based seeding technique also proved itself to be promising by producing ZIF-8 membranes with molecular sieving effect [35].

In spite of the above-described advancement in synthesis technology for ZIF membrane synthesis, the current approaches still retain a series of drawbacks which hinders potential of large-scale commercial application of the ZIF membranes: (1) slow batch process, (2) large consumption of expensive precursors and environmentally harmful organic solvent, and (3) scale-up issue. To suggest a potential solution for these obstacles, we report, here, a novel direct spraying approach for the synthesis of well-intergrown ZIF membranes in a facile and time-efficient manner at ambient pressure. Our synthesis method is based on the electrostatic force-assisted spraying method that generates extremely fine liquid droplets through electrostatic charging. Due to the nature of electrospraying, this new method offers dramatic reduction in synthesis time and precursor consumption, easy control of the membrane thickness as well as simplification in the activation process. ZIF-7, which is composed of zinc cations interconnected with benzimidazolate (bim) anions, forming the sodalite (SOD) structure with a pore size of about 0.3 nm, was selected as a model ZIF structure to demonstrate our new approach. The effect of electrospray conditions was systematically investigated, and the fabricated ZIF-7 membranes were characterized by XRD, FE-SEM, TGA and binary gas permeation tests for H_2/CO_2 mixture.

2. Experimental details

2.1. Synthesis of ZIF-7 membranes by electrospray deposition

A precursor solution for electrospray deposition was prepared by modifying the procedure in the literature [14]. In brief, 6.12 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, Sigma-Aldrich) was dissolved in 80 mL of dimethylformamide ($HCON(CH_3)_2$, 99.8%, Sigma-Aldrich; DMF) by stirring for 30 min. At the same time, 0.6 g of sodium formate (HCOONa, 99%, Sigma-Aldrich) and 3.24 g of benzimidazole ($C_7H_6N_2$, 98%, Sigma-Aldrich) were dissolved in 80 mL of DMF by stirring for 30 min. After 30 min of mixing the two solutions, the mixture was immediately used for electrospray deposition. The mixture remained clear without crystal formation during the experimental period. The molar ratio of the final precursor solution was Zn^{2+}/bim/sodium formate/DMF = 1:1.33:0.5:101.

A schematic illustration of the experimental set-up is shown in Fig. 1. Prior to the onset of electrospray deposition, a disk-shaped α-alumina substrate (diameter: 20 mm, thickness: 2 mm, pore diameter: 0.12 μm, porosity: 40%) was heated to a designated temperature from 160 °C to 200 °C. The precursor solution was supplied into a metal capillary (22 G, internal diameter = 0.413 mm), which was held at high electrical potential, by a syringe pump at a flow rate from 0.5 to 2 mL/h. The voltage applied to the capillary was changed from 5 kV to 12 kV. The distance between the capillary tip and the substrate was 4 cm so that the spraying area completely covered the substrate surface. A sprayed volume of the precursor solution was varied from 0.05 to 0.5 mL to control the thickness of the membranes.

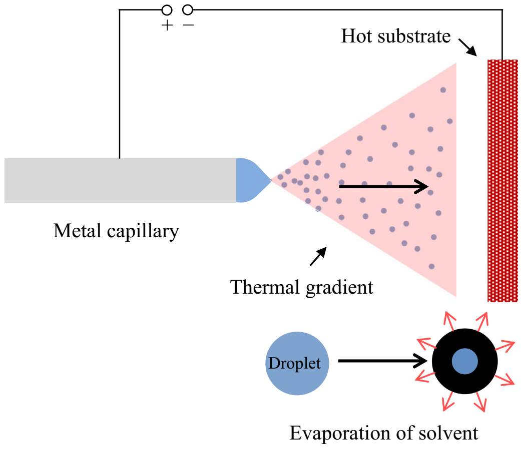

Fig. 1. Schematic diagram of electrospray deposition for synthesizing ZIF-7 membranes.

After the deposition, the membrane was cooled to room temperature at a cooling rate of 1 °C/min in order to reduce the thermal stress, which is responsible for crack formation due to the difference in the thermal expansion coefficients between the α-alumina support and the ZIF-7 membrane.

The as-synthesized ZIF-7 membranes were solvent-exchanged by immersing them in methanol for 1 h in order to remove bulky DMF molecules occluded inside the cavity of the ZIF-7 framework. Afterwards, the membranes were slowly dried at 45 °C overnight under humid conditions [36].

2.2. Characterization

The XRD (M18XHF-SRA, Mac Science, Japan) was used to identify the crystal phases. The morphology and thickness of the membranes were observed by a field-emission scanning electron microscope (Leo-Supra 55, Carl Zeiss STM, Germany). To assure the full activation of the membranes, the scratched powder from the membrane surface was examined using TGA (Q50, TA Instrument, USA). H_2/CO_2 gas permeation tests were conducted to evaluate the membrane quality as a molecular sieve at varied temperature using the Wicke–Kallenbach technique. An equimolar H_2/CO_2 mixture (50 mL/min each) was supplied to a feed side while 80 mL/min of N_2 was fed to a permeate side for sweeping transported gas mixture to gas chromatography (M6000D, Younglin, Korea) for composition analysis.

3. Results and discussion

Electrospraying, a versatile coating technique, can generate uniformly distributed fine droplets out of an ionic solution on the basis of balancing an electrostatic force applied on a relatively large droplet at the tip of a capillary and the surface tension forces of the droplet. Depending on the fluid properties (*e.g.* electric conductivity, dielectric constant, viscosity) and other parameters (*e.g.* electric potential applied on the capillary, capillary geometry, solution flow rate), various spraying modes can be obtained, which can be broadly classified into dripping, cone-jet, and multi-jet modes [37]. Among these modes, the cone-jet mode is preferred for coating purposes since it can enable complete coverage on a