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Short communication

High performance ZIF-8 molecular sieve membrane on hollow ceramic fiber via crystallizing-rubbing seed deposition

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HIGHLIGHTS

- ▶ Hollow fiber alumina tube was used as membrane support.
- ▶ A novel crystallizing-rubbing seeding method was developed.
- ▶ High quality ZIF-8 membrane was obtained by secondary growth.
- ▶ High permeance of hydrogen was achieved.
- ▶ Excellent H_2 separation performance was reached.

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ABSTRACT

In this report, a continuous well-intergrown ZIF-8 membrane on hollow ceramic fiber tube was successfully synthesized by a novel crystallizing-rubbing seed deposition. It is shown that the obtained ZIF-8 membrane was compact and defect-free, with a thickness of about 5 μm. The obtained membrane displayed high H_2 molecular sieve separation performance. Specifically, the H_2 permeance reached an excellent value of 1.1×10^{-6} mol m^{-2} s^{-1} Pa^{-1}, and the ideal separation factors for H_2/CO_2, H_2/N_2 and H_2/CH_4 were calculated to be 5.2, 7.3 and 6.8 at room temperature, respectively. We show that the fine seeds generated by crystallizing-rubbing play the key role for enhancing the heterogeneous nucleation of ZIF-8 crystals, which thus result in a high quality ZIF-8 membrane.

1. Introduction

Metal–organic frameworks (MOFs) are a new class of porous inorganic–organic hybrid materials [1]. The tailorability of pore size, adsorption affinity and extreme surface area make them attractive for gas storage, catalysis and membrane separation [2–4]. Particularly, zeolitic imidazolate frameworks (ZIFs) [5], a subclass of MOFs that exhibits outstanding thermal and chemical stability and similar molecular sieving properties with zeolites, have emerged as ideal candidates for separation membrane development [6,7]. However, the preparation of a continuous and dense MOFs membrane is still very challenging because the heterogeneous nucleation density of most MOFs crystal on supports is quite low [8]. To tackle this challenge, different strategies including seeded growth [9], support modification [10] and contra-diffusion [11] have been proposed. For example, MOF membranes exhibiting better separation performance have been successfully obtained via seeded growth very recently [12].

Compared with in situ growth, seeded growth method can enable better manipulation of membrane microstructure by controlling the relevant properties of seed layer. The seeding on the support is deemed as the key factor to achieve high quality membrane. However, it is necessary to overcome the issue of weak interaction of MOF seed on the support in seeded growth [13]. Many seeding approaches including thermal seeding [14], reactive seeding [14], rubbing [7] and pre-coating of a polymer binder [15] have been proposed to enhance the bonding between MOF crystal and the supports. An alternative way to improve this interaction is to employ an appropriate polymeric support owing to the high affinity between MOF and polymer. In this manner, continuous ZIF-90 membrane has been successfully fabricated on polymeric hollow fiber recently [16]. Although those strategies are efficient in some ways, robust synthesis strategies for the facile synthesis of high performance MOF membrane are still desired.

Recently, Wang et al. [17] proposed a novel dipcoating-wiping seed method to prepare defect-free LTA membrane. This method

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can produce a uniform seed layer on the support, which then provides heterogeneous nucleation sites for growth of a high quality membrane. Inspired by this method, in this work, we prepared high performance ZIF-8 membrane on hollow ceramic fiber tube (HCT) via crystallizing-rubbing seed deposition. Here we chose ZIF-8 membrane because ZIF-8 has a sodalite structure with a pore aperture of 0.34 nm, which is larger than the kinetic diameter of H_2 (0.289 nm), but smaller than others such as N_2 (0.364 nm) and CH_4 (0.38 nm). Clearly, it implies a promising application in H_2 separation [6,10,18–20]. HCT was chosen as the support, because of its chemical and mechanical stability, as well as high packing density and area/volume ratio [17,21]. Therefore, the module size and cost could be reduced in practical application. However, successful demonstrations of well intergrown MOF membranes on HCT have been rarely reported [16,22–24], because the adhesion strength between MOF crystals and HCT is rather weak and the highly curved surface of HCT makes the fabrication of membrane on the surface even more challenging, compared to the disk support.

In this work, the ZIF-8 membrane was prepared via three steps: (1) we first used in situ solvent thermal crystallization to deposit ZIF-8 crystals on the HTC support. (2) Subsequently, the surface pore of support covered with a compact seed layer was achieved by rubbing the support after solvent thermal crystallization. (3) Finally, the secondary growth method was applied to form the continuous and defect free ZIF-8 membrane on the seed loaded support. We will show that the synthesized membrane exhibited a very high permeance of H_2 and excellent molecular sieve performance for separating H_2 from CH_4, N_2 and CO_2.

2. Experimental

2.1. Synthesis of defect-free ZIF-8 membrane

In the present study, HCT support (α-Al_2O_3: i.d.: 2.5 mm, o.d.: 3.5 mm, pore size: 100 nm, porosity: 30–40%, Hyflux membrane company) was seeded by crystallizing-rubbing seed deposition. The seeded support was then subjected to secondary solvent thermal growth.

2.1.1. In situ solvent thermal crystallization

0.330 g of Hmim and 0.212 g of $HCOONa{\cdot}2H_2O$ were dissolved in 30 ml methanol. A solution consisting of 0.281 g $ZnCl_2{\cdot}6H_2O$ and 20 ml of methanol was added to the above solution and sonicated for 5 min. A HCT was mounted on a home-made Teflon holder and placed vertically in Teflon lined stainless steel autoclave filled with synthesis solution. The in situ crystallization was carried out at 383 K for 4 h.

2.1.2. Seeding by rubbing method

The poorly intergrown ZIF-8 crystals deposited on HCT obtained after in situ crystallization was then carefully rubbed manually by fine sandpaper (1500#). The procedure is similar to Ref. [17]. The seeded support was dried at 50 °C overnight.

2.1.3. Secondary growth of defect free ZIF-8 membrane

The seeded support was underwent a secondary growth. The synthesis condition is same as the in situ growth. After the crystallization, the membrane was washed thoroughly with methanol and soaked in methanol for 12 h. Then, the membrane was dried at a vacuum oven at 100 °C for 12 h.

2.2. Characterization techniques

XRD patterns were collected on a Bruker AXS D8 Advance diffractometer using Cu Kα (λ = 1.5406 Å) radiation at a voltage of 40 kV and 40 mA. Scanning electron microscopy (SEM) images were obtained from a field emission scanning electron microscope (FESEM, Hitachi S-4800).

2.3. Gas permeation test

Single gas permeation experiments were undertaken in a home-made permeation apparatus at a pressure drop of 0.1 MPa. The single H_2, N_2, CH_4 and CO_2 gas permeances were determined by five runs of test from at least two membranes synthesized at the same conditions. Before each test, the permeation module was purged for at least 1 h.

3. Results and discussion

3.1. Synthesis and characterization of HCT supported ZIF-8 membrane

Schematic diagram of ZIF-8 membrane fabrication by crystallizing-rubbing seeding method followed by secondary growth is presented in Fig. 1. Due to the lack of strong bonding between the support and ZIF-8 crystals, poorly intergrown ZIF-8 crystals with defects and gaps were inevitably generated by in situ solvent thermal synthesis, making the support covered with ZIF-8 in some zones, while uncovered in other zones. Therefore, we then rubbed the loosely intergrown ZIF-8 crystals and crushed them to small ones, leaving a uniform distribution of small ZIF-8 crystals throughout the support including the previous defect and gap area. This compact and uniform seed layer would promote the nucleation and intergrowth of ZIF-8 crystals on the HCT support surface. As a result, a dense and defect free ZIF-8 membrane was formed and expected to show molecular sieving selectivity for H_2 separation. In the present study, a modified recipe [20] with increased Hmim/Zn^{2+} ratio was adopted for the synthesis solution in the secondary growth. After the solvent thermal synthesis, the membrane was washed thoroughly with excessive methanol followed by drying at room temperature for 24 h.

XRD patterns of the seed layer generated after rubbing and the membrane on HCT after secondary growth are shown in Fig. 2. It

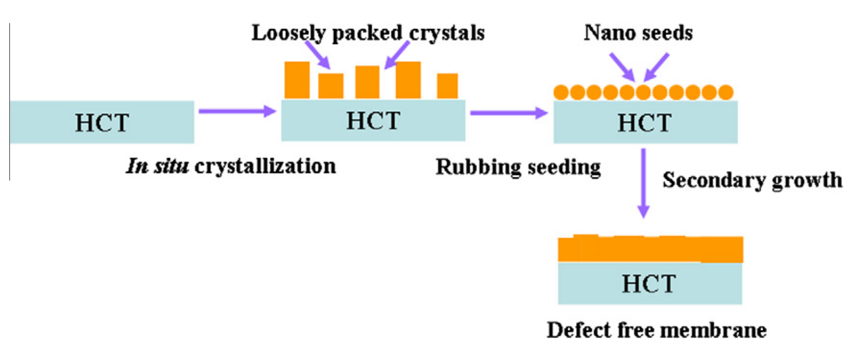

Fig. 1. Schematic representation of ZIF-8 membrane fabrication by rubbing seeding method followed by secondary growth (HCT: hollow ceramic fiber tube).