



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 H₂ 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 H₂ molecular sieve separation performance. Specifically, the H₂ permeance reached an excellent value of $1.1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and the ideal separation factors for H₂/CO₂, H₂/N₂ and H₂/CH₄ 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.

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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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