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Improved H_2/CO_2 separation performance on mixed-linker ZIF-7 polycrystalline membranes

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HIGHLIGHTS

- The ZIF-7-NH_2 polycrystalline membranes were first prepared.
- The coating of Pebax®1657 layer effectively control the microstructure of membrane.
- Improved separation performance for H_2/CO_2 mixture on ZIF-7 membrane was reported.
- ZIF-7-NH_2 crystals exhibit higher hydrothermal stability than mono-ligand ZIF-7.

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ABSTRACT

Membrane-based hydrogen purification has been considered to be a promising alternative because of its low energy consumption, ease of operation, and cost effectiveness. Amino-functionalized ZIF-7 (ZIF-7-NH_2) is an attractive candidate for membrane gas separation due to the maintenance of pore-opening structure after total removal of guest molecules (DMF). In this work, ZIF-7-NH_2 membrane with improved both H_2 permeance and H_2/CO_2 selectivity than reported mono-ligand ZIF-7 membrane was first prepared. Several activation process for ZIF-7-NH_2 membranes to opening the pores were investigated. It was found that the coating of a Pebax®1657 layer on the surface of ZIF-7-NH_2 membrane is crucial for preventing the formation of cracks during pore-activation procedure. The permeance of H_2 and separation factor for H_2/CO_2 binary mixtures were improved to $\sim 1 \times 10^{-7}$ mol/m^2 s Pa and ~19, respectively. The separation performance was very close to the upper bound for inorganic microporous membranes. Furthermore, the improved hydrothermal stability on ZIF-7-NH_2 materials endows the membrane is highly potential for hydrogen purification.

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1. Introduction

Hydrogen has been proposed as a promising renewable energy resource due to its elemental abundance and no air pollution (Gibson, 2017; Qiu et al., 2014; Yuan et al., 2017). The most commonly used route for obtaining hydrogen is the purification and recovery of H_2/CO_2 mixture, which are produced via the steam-methane reforming followed by water-gas shift process (Nikolaidis and Poullikkas, 2017; Rostrup-Nielsen and Rostrup-Nielsen, 2002; Voldsund et al., 2016). In comparison with the conventional separation methods like pressure swing adsorption (PSA), membrane-based separation has been considered to be the most promising alternative because of its low energy consumption, ease of operation, and cost effectiveness (Al-Mufachi et al., 2015; Peng et al., 2017). However, there are no membrane materials that a combination of high selectivity, permeability and stability during operation. Organic polymer membranes always suffer from instability problems in contact with solvents or at high temperatures. Even though inorganic membranes (Pd-based metal membranes, microporous silica membranes, carbon membranes, and zeolite membranes) are more promising under harsh separation conditions, they are also limited by some key drawbacks (Battersby et al., 2009; Braun et al., 2014; Ismail and David, 2001; Rangnekar et al., 2015). For example, both Pd-based metal membranes and silica membranes display superior H_2/CO_2 separation performance, but they suffer from instability if traces of impurity (e.g. CO or H_2S) are present. Carbon membranes are too fragile to be used in practice. Zeolite membranes usually exhibit low selectivity for H_2/CO_2 mixture, due to relatively large pore sizes and uncontrollable inter-crystalline defects.

Zeolitic imidazolate frameworks (ZIFs), as a subset of metal-organic frameworks (MOFs), have emerged as candidates for fabricating novel molecular sieve membranes owing to their

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zeolite-like permanent porosity, uniform pore size, and exceptional thermal and chemical stability (Cai et al., 2014; Eum et al., 2016a, b, 2017; Huang et al., 2010b; Pan and Lai, 2011; Wang and Wang, 2016). For the H_2/CO_2 separation, ZIF-7 constructed from benzimidazolate (BIm) anions and zinc cations is considered as a promising molecular-sieving membrane materials due to its desired aperture size (0.3 nm), just between the kinetic diameter of H_2 (0.29 nm) and CO_2 (0.33 nm). As demonstrated by Li and coworkers, ZIF-7 polycrystalline membranes exhibit a high selectivity (~12) for H_2 over CO_2 (Li et al., 2010b). However, the gas-permeance is not enough high, and the separation performance is not technically attractive for industrial application. The mostly possible reason for lower H_2 permeance ($\sim 0.4 \times 10^{-7}$ mol/m^2 s Pa) through ZIF-7 membrane is the existence of certain amount of solvent DMF inside the framework, because the total removal of DMF molecules inside the ZIF-7 framework can lead to a phase transition to from ZIF-7-I to ZIF-7-II, a non-porous materials without penetration of any gas (Zhao et al., 2014b).

More recently, we found that the partial substitution of BIm with amino-functionalized BIm in ZIF-7 framework can effectively prohibit the flexibility of framework and thus control the gate-opening effect (Xiang et al., 2017). This implies that the total removal of DMF molecules inside the amino-functionalized ZIF-7 (ZIF-7-NH_2) framework can still sustain its original ZIF-7-I structure (SOD topology), prohibiting the phase transition to nonporous ZIF-7-II framework. To this end, ZIF-7-NH_2 membrane would present an improved gas-permeation ability due to the total removal of embedded DMF molecules, which would partially block the window of ZIF-7 structure.

In this study, ZIF-7-NH_2 polycrystalline membranes were first synthesized through the seeded-secondary growth method. Compared with mono-ligand ZIF-7 materials, the amino-functionalized counterparts have a higher hydrothermal stability, which is a desired feature for MOFs materials in practical applicability. It was found that the covering of a rubbery polymeric (Pebax®1657) coating on the as-synthesized ZIF-7-NH_2 membrane is a crucial step for pore-activation process to fabricate high-quality membranes. The separation performance for H_2/CO_2 separation on the ZIF-7-NH_2 polycrystalline membrane is very close to the upper bound for inorganic microporous membranes (Li et al., 2010b). The permeance of H_2 and separation factor for H_2/CO_2 mixtures were $\sim 1 \times 10^{-7}$ mol/m^2 s Pa and ~19, respectively. Therefore, the developed ZIF-7-NH_2 polycrystalline membrane with improved separation performance and hydrothermal stability is attractive for potential application in hydrogen purification.

2. Experimental

2.1. Preparation of ZIF-7-NH_2 nanocrystals

All chemicals were purchased from Sigma-Aldrich and used as received. ZIF-7-NH_2 nanocrystals were synthesized followed our previous reports (Xiang et al., 2017). In a typical synthesis, the ligand solution was firstly prepared by mixing benzimidazole (5 mmol) and 2-aminobenzimidazole (BIm-NH_2, 5 mmol) in 50 mL of methanol. A separate metal solution containing 5 mmol Zn $(NO_3)_2$ $6H_2O$ in 50 mL of DMF was also prepared, and then was rapidly poured into the above ligand solution with stirring at room temperature (~25 °C). The mixture slowly became turbid and continued stirred for 6 h, followed by the centrifugal collection (10,000 rpm, 10 min) and washing with fresh methanol (5 mL × 3). Some ZIF-7-NH_2 nanocrystals were re-dispersed in fresh methanol to prepare the seeding solution (0.1% solid content), and other precipitates were vacuum-dried (150 °C, 24 h) for further characterization.

2.2. Measurement of hydrothermal stability for nanocrystals

For comparison of the hydrothermal stability between mono-ligand ZIF-7 and ZIF-7-NH_2 nanocrystals, mono-ligand ZIF-7 nanocrystals were firstly synthesized following the above synthesis procedures using pure BIm ligand. The experimental examination of their hydrothermal stability were performed by separately suspending nanocrystals in aqueous solution (~3 wt%) at 50 and 80 °C for certain times. Subsequently, the solids were centrifuged and dried (100 °C, 24 h) for further characterization. The resulting sample was denoted as ZIF-7-x-y (x = 50 or 80 °C), where y indicates the duration of immersion in water.

2.3. Preparation of ZIF-7-NH_2 polycrystalline membrane

The seeded secondary-growth method (Li et al., 2010a; Pan et al., 2012) was used to prepare ZIF-7-NH_2 polycrystalline membrane. The seeding procedure was implemented by slip-coating of one side of home-made α-alumina discs in the above seeding solution. The seeding step was repeated for two times to obtain the satisfied covering of seeds. Subsequently, the seeded supports were exposed to the secondary synthesis solution for further secondary growth at 150 °C for 3 h. The secondary synthesis solution was prepared by mixing 0.2 g BIm, 0.2 g BIm-NH_2 and 0.77 g Zn $(NO_3)_2$ $6H_2O$ in 40 mL DMF. After synthesis, the as-synthesized membranes were carefully washed with methanol.

2.4. Coating of a Pebax®1657 layer on ZIF-7-NH_2 membrane

Pebax®1657 coating solution (8 wt%) was prepared by dissolving Pebax®1657 pellets (Arkema Inc., France) in a mixture of ethanol/water (70/30 wt%) at 80 °C under reflux and mild stirring for 3–4 h. A few drops of Pebax®1657 solution was spread on the surface of above as-synthesized ZIF-7-NH_2 polycrystalline membrane using a pipette, followed by vacuum-drying at 100 °C for 24 h. The resulting composite membrane was denoted as Pebax®1657/ZIF-7-NH_2 composite membrane.

2.5. Characterization

X-ray diffraction (XRD) patterns of all ZIF-7 nanocrystals and membrane samples were collected on a Rigaku Smartlab TM 9 KW powder diffractometer at 40 kV, 40 mA. Morphologies of the as-prepared samples were all characterized by scanning electron microscope (SEM, S4800, Hitachi, Japan). Prior to the SEM observations, all samples were coated with gold in vacuum to increase their conductivity. Fourier transform infrared spectra (FTIR) of samples were scanned (4000–400 cm^{-1}) using a Nicolet iS10 FTIR spectrometer with a horizontal attenuated transmission accessory. Nitrogen adsorption-desorption isotherms of mono-ligand ZIF-7 and ZIF-7-NH_2 nanoparticles were measured at 77 K using a BELSORP-max machine. Prior to the measurements, all samples were vacuum-treated at 150 °C for 24 h to totally remove the guest molecules (DMF).

2.6. Gas permeation

All permeation measurements were performed using the Wicke–Kallenbach technique (Sabetghadam et al., 2016). The compositions of the feed and the permeate streams were measured online by a gas chromatograph (Agilent 7890A). For the single gas measurements, flow rates of both feeding gas and sweep gas (N_2) were set as 35 mL/min. The pressures at both sides were constant (1 bar). For the mixed gas measurements, feed flow rate was constant with a total volumetric flow rate of 70 mL/min with each gas of 35 mL/min (1:1 mixture). The sweep gas was N_2, and the flow

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