Electronic Supporting Information

Continuous polycrystalline ZIF-8 membranes supported on Polyethersulfone (PES)-ZIF-8 mixed matrix membranes for CO₂/CH₄ Separation

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1. Experimental Details

Chemicals

2-methylimidazole (Hmim, 99%), zinc nitrate hexahydrate (98%), sodium formate (99%) zinc chloride (98%), methanol (99.6%), 1-Methyl-2-pyrrolidinone (NMP, 99%) were obtained from Sigma Aldrich. Ultrapure de-ionized (DI) water (18 MΩ cm) was used for all samples preparation. All chemicals were used as purchase directly without further purification.

Preparation of ZIF-8 crystals

The preparation of ZIF-8 crystals was carried out in an excess of 2-methylimidazole in order to attain the rapid coordination reaction, though the stoichiometric proportion of the reaction (\([\text{Hmim}]:[\text{Zn}^{2+}]\)) is 2:1. The aqueous solution was prepared by reacting 1.50 g zinc nitrate hexahydrate and 20 g 2-methylimidazole in 90 mL de-ionized water. The resulting solution was stirred at room temperature for 30 minutes followed by centrifugation at 8000 rpm for 15 minutes to recover the ZIF-8 solids. These solids were washed with de-ionized water three times via centrifugation followed by drying at 80 °C.

Preparation of ZIF-8-PES mixed matrix supports

The ZIF-8-PES mixed matrix supports were prepared in a phase inversion induced by immersion precipitation technique. The weight ratio of the PES:NMP was set to be 1:3 and the weight percentage of the ZIF-8 fillers was added simultaneously to form 5, 10, and 20 wt% ZIF-8 loadings in the PES:NMP casting solution. After the PES beads were added to the NMP solvent, the corresponding weight percentages of ZIF-8 crystals were added to the PES:NMP solutions. The solutions were continuously stirred for 24 hours at 60 °C to evenly disperse the ZIF-8 crystals in the solution. The resulting solutions were further subjected to alternating stirring and sonications to remove any trapped air bubbles. Subsequently, the casting solutions were poured onto the glass plate and spread evenly using a 100 µm casting blade. The films formed on the glass plate were dried under room temperature followed by detachment of films from the glass plate. Finally, the casted membranes were kept in distilled water for 24 hours and dried at room temperature for 24 hours followed by 120°C for another 24 hours to obtain the final membranes.

Preparation of ZIF-8 membranes on mixed matrix supports

A combined rubbing and dip coating seeding step was performed. Initially, a ZIF-8 paste with ZIF-8 seeds:DI water = 1:10 was prepared. The mixed matrix membranes were rub coated on one side with ZIF-8 paste along its axis direction for 3 times and dried for 2 hours at 40 °C. This is followed by dip coating in 1 wt% seed suspension and drying at room temperature overnight. The preparation of precursor for secondary seeded growth of top ZIF-8 layers was done by dissolving 1.5 g of zinc chloride, 5.2 g of 2-methylimidazol, and 3.0 g of sodium formate in 80 mL of methanol. The seeded mixed matrix membrane was sent for solvothermal synthesis at 80 °C for 6 hours in a pressurized autoclave filled with the
precursor solution. The collected membranes were soaked in methanol overnight prior to drying.

2. Characterizations

X-ray diffraction (XRD) patterns were acquired using Bruker D8 Discover with the samples measured from $2\theta = 5^\circ$ to $90^\circ$ in $1^\circ$/min steps. To investigate the morphology of the membranes, field emission scanning electron microscope (FESEM) images were collected on a Hitachi SU8010. The cross sectional membranes for FESEM imaging were prepared by freeze fracture of the samples after immersion in liquid nitrogen. These samples were subsequently coated with platinum using a sputter coater prior to imaging to mitigate charging. Single gas permeation measurements were carried out at pressure drop of 1-2 bar at 25°C. The mixed matrix supports and mixed matrix supported ZIF-8 membranes were mounted on the stainless steel holder with rubber o rings used as sealing material between the membrane and the module. This is followed by measurement of the permeate flow rates with a soap film bubble flow meter. The single CO$_2$ and CH$_4$ gas permeances were determined as a function of permeation time. On the other hand, binary gas permeation was performed with 1:1 CO$_2$:CH$_4$ mixtures with transmembrane pressure of 1 bar. The permeation module was purged for at least 1 hour prior to testing and the permeates composition were analyzed by gas chromatograph (Agilent 7890A).