Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Growth of ZIF-8 membrane on the inner-surface of ceramic hollow fiber via cycling precursors

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1. Experimental details

1.1 Fabrication of ceramic hollow fiber

The ceramic hollow fiber supports were prepared according to the method reported in previous literature [1]. Aluminum powder, polyvinylpyrrolidone (PVP) and N-methyl-2-pyrrolidone (NMP) were taken in a stainless bottle. To ensure that the aluminum powders were dispersed evenly in the suspended solution, a stirrer at a given speed was used. After that, polyethersulfone (PES) was added into the suspension solution slowly. The result polymer solution was degassed at room temperature. Then the spinning dope was extruded by a variable flow pump through the spinneret into water with the air gap of 150 mm. Finally, the prepared precursor was dried at 373 K for 12 h and then calcined to form the ceramic hollow fiber. The pore size distribution of ceramic hollow fiber was measured by a bubble-point method. The pore size of the ceramic hollow fiber is 650~700 nm. Their outer diameter and inner diameter were approximately 1.3 mm and 1.0 mm, respectively. Fig. S1 shows the microstructures of the alpha-Al_2O_3 ceramic hollow fiber.

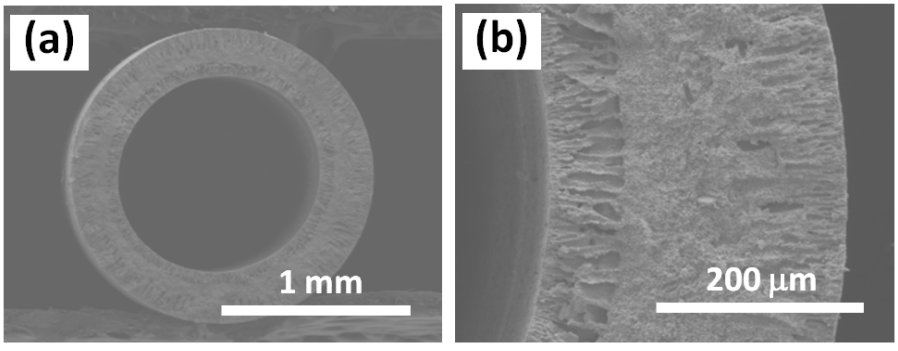

Fig. S1 SEM images of (a) a ceramic hollow fiber, (b) an enlarged cross-section of a ceramic hollow fiber.

1.2 Growth of the inner-side hollow fiber ZIF-8 membrane

The inner-side hollow fiber ZIF-8 membrane is fabricated via cycling precursors by a continuous flow system (see Fig. S2). All procedures, including modification, seeding step, and secondary growth, are carried out in this setup by changing different synthetic solutions. The typical growth procedure is described as follows.

Before seeding procedure, in order to deposit an APTES monolayer on the inner surface, the alpha-Al_2O_3 ceramic hollow fiber was treated with APTES (2 mL in 100 mL ethanol) via the continuous flow system at 30 ^oC for 2 h. Then, the lumen of the ceramic hollow fiber was washed with vast ethanol to decrease the effect of the physically deposited APTES and dried at 50 ^oC for 2 h. After that, the seeding synthesis solution, prepared by mixing 0.275 g $Zn(NO_3)_2 \cdot 6H_2O$ and 5.675 g 2-methylimidazole with 100 mL DI water, continuously flowed through the lumen of APTES modified alpha-Al_2O_3 ceramic hollow fiber using the above setup (typical synthesis condition: 30 ^oC for 0.5 h). Then, the lumen of the ceramic hollow fiber was washed with vast methanol to sweep away the uncombined ZIF-8 crystals and dried at 50 ^oC for 2 h. Finally, the secondary growth process was carried out by the similar way. The synthesis solution, prepared by mixing 0.275 g $Zn(NO_3)_2 \cdot 6H_2O$ and 5.675 g 2-methylimidazole with 100 mL DI water, continuously flowed through the seed layer using the same setup (typical synthesis condition: 30 ^oC for 6 h). The membrane was also washed with vast methanol and dried at 50 °C for 24 h. In this work, the flow rate was fixed at 2.5 mL min^{-1} for all steps.

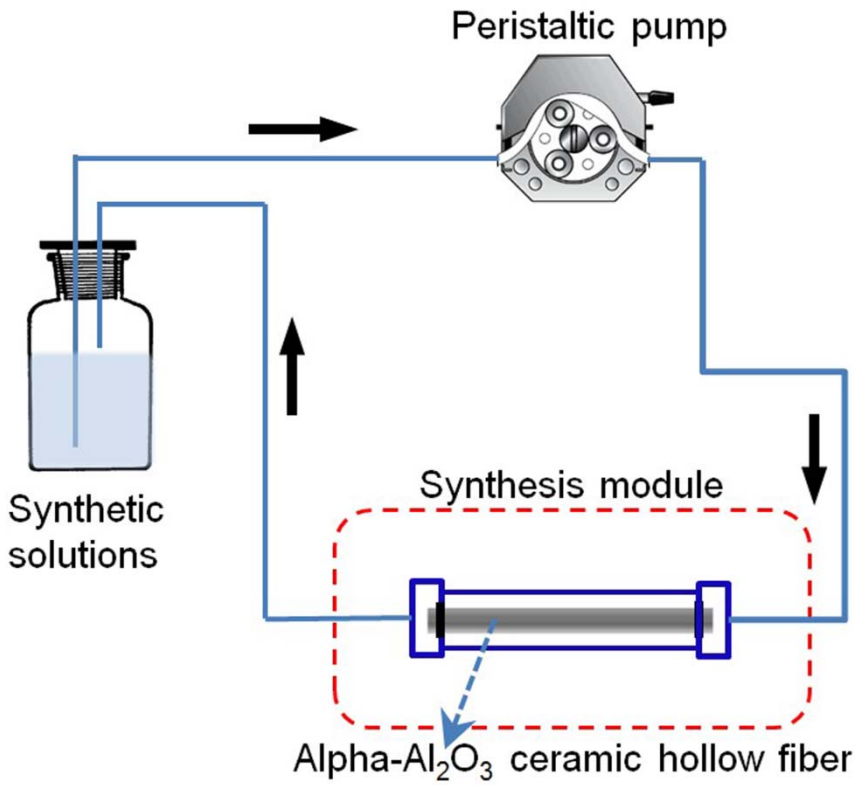

Fig. S2 Schematic diagram of the cycling precursors method used for preparing inner-side hollow fiber ZIF-8 membranes

1.3 Characterizations

The morphologies of membrane and support were examined by scanning electron microscopy (SEM) (Quanta-200, Philips FEI). The working parameters are: high voltage (HV) 20-30 kV, work distance (WD) 8-10 mm and spot 2.0-3.0. The crystal phases of samples were determined by X-ray diffraction (XRD) with Cu Ka radiation (Bruker, model D8 Advance). Diffraction patterns were collected at room temperature in the range of $5^{o} \leq 2\theta \leq 50°$ with a step width of 0.05° and scan rate of 0.2 $s \cdot step^{-1}$. Fourier transform infrared spectroscopy (FT-IR) spectra were separately

recorded in a FT-IR spectrophotometer (AVATAR-FT-IR-360, Thermo Nicolet, USA) with the range 3000-500 cm^{-1}.

1.4 Quartz crystal microbalance measurement

Quartz crystal microbalance technique (QCM200 Quartz Crystal Microbalance, Stanford research systems, Inc.) was used to monitor the ZIF-8 crystal growth process. A typical experiment was described as follows.

A bare gold substrate (mounted on a standard holder) was immersed in APTES solution (2 mL in 100 mL ethanol) at 30 ^{o}C for 2 h to deposit an APTES monolayer on the gold substrate, and then dried at room temperature. After that, The modified gold substrate (mounted on a standard holder) was immersed in the synthetic solution (prepared by mixing 0.275 g $Zn(NO_3)_2 \cdot 6H_2O$ and 5.675 g 2-methylimidazole with 100 mL DI water). Simultaneously, the corresponding results were recorded as a function of the test time.

1.5 Gas separation

Gas permeation experiments were performed on the permeation setup as reported in our previous work. [2, 3] All the measurements were performed using the Wicke–Kallenbach technique with an on-line gas chromatography (Agilent Technologies 7820A). In this work, the sealing was a critical challenge because the gas molecules would leak out from the section of the ceramic hollow fiber. In order to address this problem, a quartz tube was inserted to the lumen of the support, and then sealed by

silicone rubber. After that, the permeation module and the quartz tube were sealed. Fig. S3 shows the schematic of the permeation module and the sealing method.

For the single gas measurements, the feed flow rates were set to 50 mL·min^{-1}. For the binary mixed gas, the feed side was fed at a total volumetric flow rate of 100 mL·min^{-1} with each gas of 50 mL·min^{-1}. In all measurements, helium was used as sweep gas at a flow rate of 50 mL·min^{-1}. Atmosphere pressure was applied to both sides of the permeation cell.

The membrane permeance (Fi) is defined as:

$$F_i = \frac{N_i}{\Delta P_i \cdot A} \qquad (1)$$

Where N_i is the permeate rate of component i (mol·s^{-1}), ΔP_i is the transmembrane pressure difference of i (pa), and A is the membrane area (m^2).

The ideal selectivity is calculated by the ratio of single gas permeances.

The separation factor was calculated as:

$$\alpha_{i,j} = \frac{y_i / y_j}{x_i / x_j} \qquad (2)$$

Where x and y are the molar fractions of the one component in the feed and permeate, respectively.

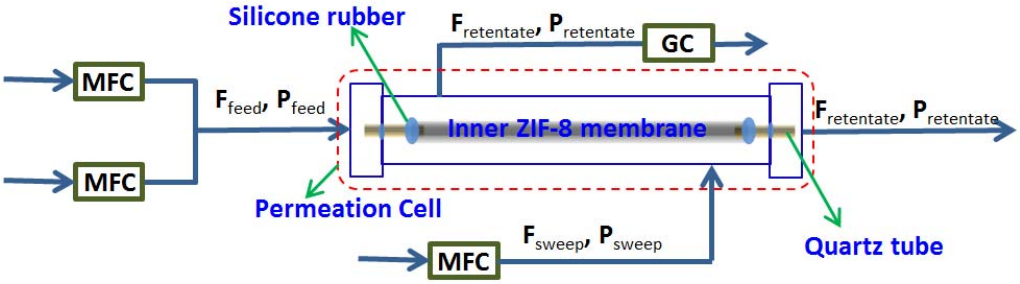

Fig. S3. Schematic diagram of permeation equipment for the gas separation. "MFC" and "GC" are mass flow controller and gas chromatography (Agilent Technologies 7820A), respectively. "F" and "P" are the flow rate and pressure, respectively.

Reference

1. Lie Meng, Hongze Guo, Ziye Dong, Hong Jiang, Weihong Xing, Wanqin Jin. Ceramic hollow fiber membrane distributor for heterogeneous catalysis: Effects of membrane structure and operating conditions, *Chem. Eng. J.*, 2013, **223**, 356.

2. Xueliang Dong, Kang Huang, Sainan Liu, Rufei Ren, Wanqin Jin, Y. S. Lin. Synthesis of zeolitic imidazolate framework-78 molecular-sieve membrane: defect formation and elimination, *J. Mater. Chem.*, 2012, **22**, 19222.

3. Jiangpu Nan, Xueliang Dong, Wenjin Wang, Wanqin Jin, Nanping Xu, Step-by-Step seeding procedure for preparing HKUST-1 membrane on porous r-alumina support, *Langmuir*, 2011, **27**, 4309.

2. XRD patterns

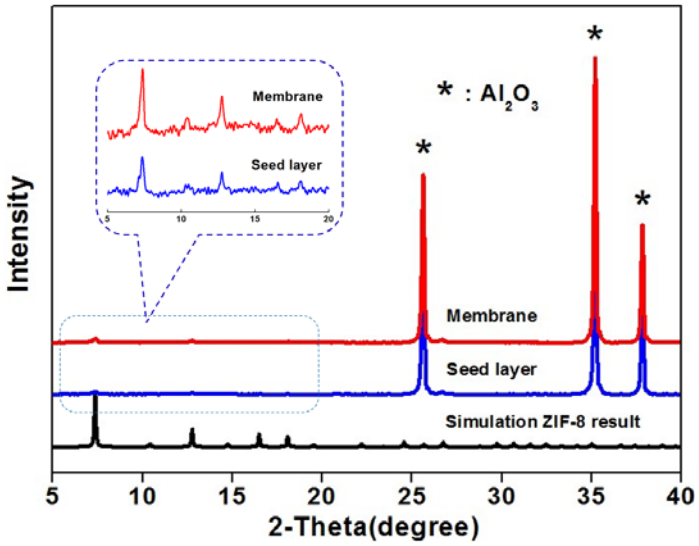

Fig. S4 XRD patterns of the inner-side hollow fiber ZIF-8 seed layer, the as-synthesized ZIF-8 membrane, and the simulated ZIF-8 structure. The patterns from 5^{o} to 20^{o} are enlarged as the insert.

3. SEM image of the ZIF-8 seed layer using unmodified alpha-Al_2O_3 ceramic hollow fiber

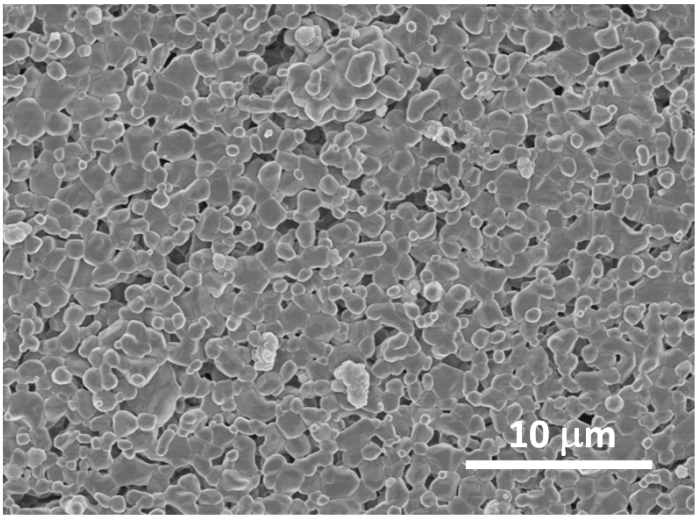

Fig. S5 SEM image of the ZIF-8 seed layer using unmodified alpha-Al_2O_3 ceramic hollow fiber

4. SEM image, XRD pattern, and IR spectra of ZIF-8 crystals collected from the feed tank after the secondary growth process

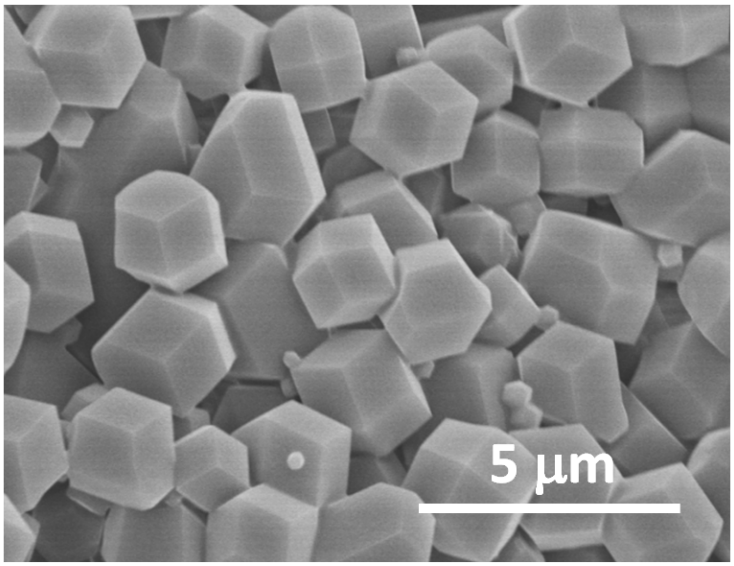

Fig. S6 SEM image of ZIF-8 crystals

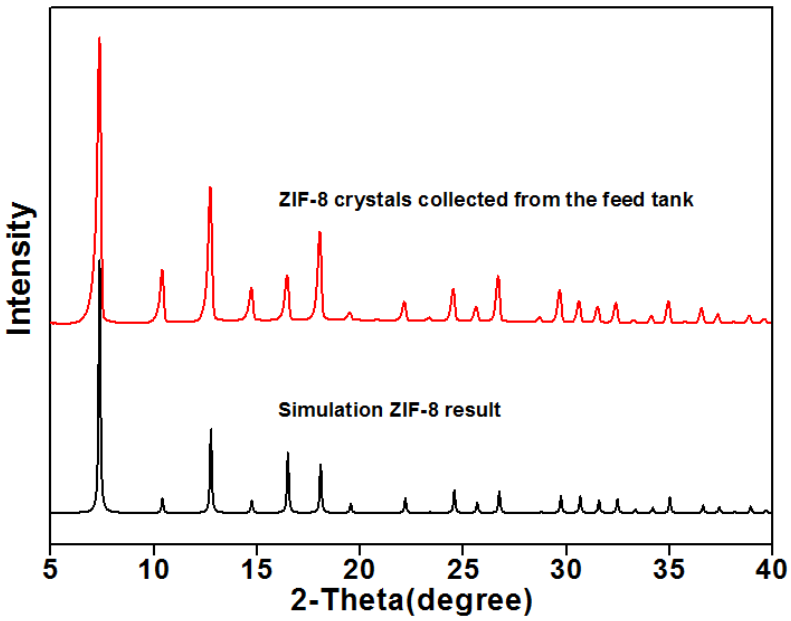

Fig. S7 XRD pattern of ZIF-8 crystals

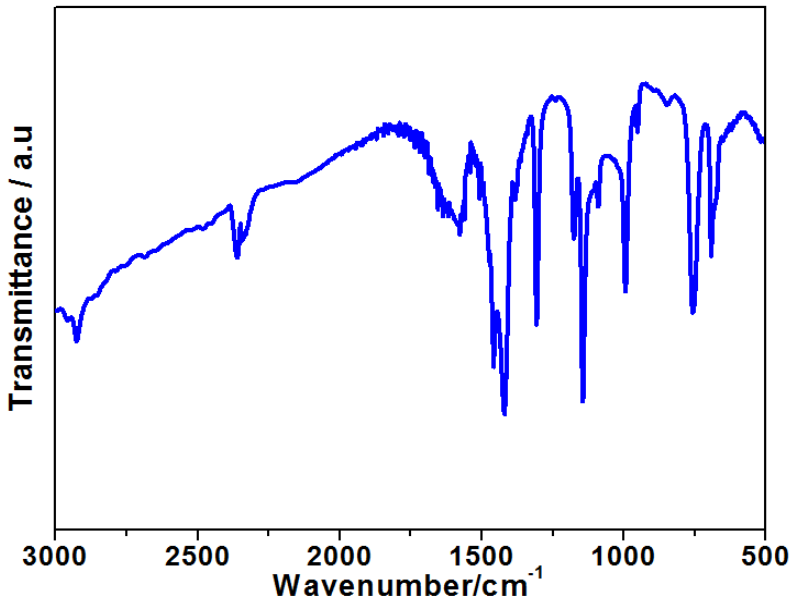

Fig. S8 IR spectra of ZIF-8 crystals

5. Single gas permeances

Table S1 Permeances and H_2 ideal selectivities from single gas.

	Kinetic diameter (nm)	Permeance (X 10^{-7} $mol^{-2}s^{-1}Pa^{-1}$)	H_2 ideal selectivity	Knudsen separation factors
H_2	0.289	4.324	----	----
CO_2	0.330	1.220	3.54	4.7
N_2	0.364	0.352	12.28	3.7
CH_4	0.380	0.322	13.41	2.8