



Journal Name

COMMUNICATION

High selectivity ZIF-93 hollow fiber membranes for gas separation

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Electronic Supporting Information

P84 hollow fiber fabrication procedure

HFs with an asymmetric morphology were spun using the dry jet, wet quench method.¹ Through a spinning process, a polymer solution (polymer, solvents, non-solvents, additives) was co-extruded with the bore fluid (a solvent-rich mixture of solvent and non-solvent) through a spinneret. When the extruded solution passed through the air gap, a skin layer formed due to the vaporization of the solvent with a high vapor pressure. Then the fiber reached the quench bath and a rapid phase separation occurred. A porous substructure was formed while the fiber travelled through the quench bath. After the quench bath, the fiber was wound onto a take-up drum and kept in the drum for further rinsing for 15-20 min. The fibers were removed from the drum, kept in DI water for four days for cleaning. Then they were solvent exchanged by means of three 30 min successive methanol baths followed by three 30 min hexane baths.² The last solvent (hexane) was removed by drying at 70 °C under vacuum overnight. The dope composition and fiber spinning conditions used in this work are shown in Table S1, comprising NMP (anhydrous N-methylpyrrolidone, Sigma-Aldrich, 99.5%) and EtOH (anhydrous ethanol, Prolabo). Copolyimide P84 was generously supplied by HP Polymer GmbH. The parameters of the spinning process are given in Table S2. Additional details regarding the spinning process and principles can be found elsewhere.^{2,3}

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Table S1 Composition of the dope and the bore solutions used in the P84 HF spinning process.

	Polymer solution [wt%]	Bore fluid [wt%]
P84 (HP Polymer GmbH)	28.5	-
NMP	62.4	89.9
DI water	-	10.1
EtOH	9.1	-

Table S2 Working conditions used in the P84 HF spinning process.

Dope flow	Dope pressure	Bore flow	Bore fluid pressure	Spinneret T	Quench bath T	Air gap	Take up rate	Room T	Humidity
mL/h	atm	mL/h	atm	°C	°C	cm	m/min	°C	%
180	10.9	60	0.1	35	25	10	25	24	69

Microfluidic membrane fabrication – ZIF-93@P84 crystallization

The MOF-supported membranes were fabricated in a microfluidic system consisting of three syringe pumps (NE-300, New Era Pump Systems) for the reagent solutions and the solvent. These solutions were stored in 20–30 mL polypropylene syringes, as explained in our previous work.⁴ The solutions were pumped through PTFE tubing (0.04 in ID, 1/16 in OD) and then, just after the mixing of the reagents, into a 20 cm long copolyimide P84 HF (202 mm ID, 356 mm OD). A PTFE-special glue (Ceys®) was used to seal the membrane to the PTFE tube. Experimental details about P84 HF fabrication procedure can be found in the Supporting Information.

For the fabrication of ZIF-93 membranes (ZIF-93@P84), the P84 HF was first washed with 2 mL of distilled water for 40 min at 50 mL/min. Then the metal and ligand solution were pumped in the lumen of the HF support. A 0.15 mol·L⁻¹ zinc nitrate hexahydrate solution (Zn(NO₃)₂·6H₂O, Sigma-Aldrich, 98%) in water was mixed together with a 0.30 mol·L⁻¹ 4-methyl-5-imidazolecarboxaldehyde (C₅H₆N₂O, Sigma-Aldrich, 99%) and 0.30 mol·L⁻¹ sodium formate (NaCOOH, Sigma-Aldrich, >99%) solution in methanol (Scharlab, 99.9%) as metal and ligand solutions, respectively.

The ZIF-93 membrane syntheses lasted 80 min at a total flow rate of 50 mL/min, a total volume of 4 mL of the reagent solution being pumped. The total reagent used for the ZIF-93 membrane fabrication was 89.2 mg Zn(NO₃)₂·6H₂O, 66.0 mg organic ligand (4-methyl-5-imidazolecarboxaldehyde) and 40.8 mg NaCOOH. Finally, another 2 mL (for 40 min at 50 mL/min) of distilled water was pumped for washing. These conditions gave rise to a laminar flow within the P84 HF: dissolved reagent transfer was enhanced through the boundary layers towards the HF wall. A residence time (τ) of 7.7 s was calculated for the flow inside the fiber. The solution leaving the microfluidic system was collected, centrifuged at 10000 rpm for 15 min and dried at 100 °C overnight. The collected ZIF-93 crystals were used for characterization, while the fabricated membrane was dried at room temperature overnight.

Annealing treatments were applied to the fabricated MOF (ZIF-93) membranes. These were carried out at 175 °C for 24 h with

slow 25 °C·h⁻¹ rates of heating and cooling (6 h each plus 12 h plateau at maximum temperature), *in situ* before the permeation tests with a H₂/CH₄/Ar atmosphere until an steady-state was accomplished.

Characterization

Activated MOF membranes as well as the pure P84 supports were tested in gas separations at 35 and 100 °C. Equimolar H₂/CH₄ or CO₂/CH₄ 10 cm³(STP)/min mixtures were fed inside the HF membrane lumen. Sweep Ar (H₂/CH₄) or He (CO₂/CH₄) from 1 to 20 cm³(STP)/min streams created a driving force for the gases to permeate through the membranes. The permeate flows were then analyzed in a micro-gas chromatograph (Agilent 3000A). A total pressure of 1.25 bar was applied on both sides of the membrane, the total pressure gradient being null. The P84 HF membranes were sealed in 1/8 in stainless steel tubing using epoxy resin glue (Fig. S2). The length between the seals was 13 cm, giving rise to an effective permeable area of 0.825 cm². Permeance values (mol·m⁻²·s⁻¹·Pa⁻¹) were calculated using the log-mean partial pressure difference along the HF once steady state was reached, whereas the separation selectivities corresponded to the ratios of permeances.

XRD (X-ray diffraction) patterns of the MOF membranes and powders were obtained using a D-Max Rigaku X-ray diffractometer (40 kV, 80 mA) with a Cu K α (λ =0.1542 nm) rotating anode from 4 to 36° (2 θ) with a 0.025°·s⁻¹ step. TGA (thermo gravimetric analyses) were carried out with a Mettler Toledo TGA/DSC SF/755, oxidizing the samples in an air atmosphere from 25 to 850 °C at a rate of 10 °C·min⁻¹. ATR-FTIR (attenuated total reflection-Fourier transform infrared spectroscopy) spectra were obtained using a Bruker Vertex 70, accumulating 40 scans from 4000 to 600 cm⁻¹ with 4 cm⁻¹ resolution. Cross-section SEM (scanning electron microscopy) images of the membranes were obtained using an FEI™INSPECT-F and a FEI™Nova200 with a cryo-transfer chamber, both operated at 10 kV. With the latter device, the MOF-polymer interface was brought to light by cryo-focused ion beam (FIB) technique, using Ga atoms for etching. EDS (energy dispersive spectroscopy) analyses of the main elements were obtained with an INCA PentaFET x3 (Oxford Instruments).

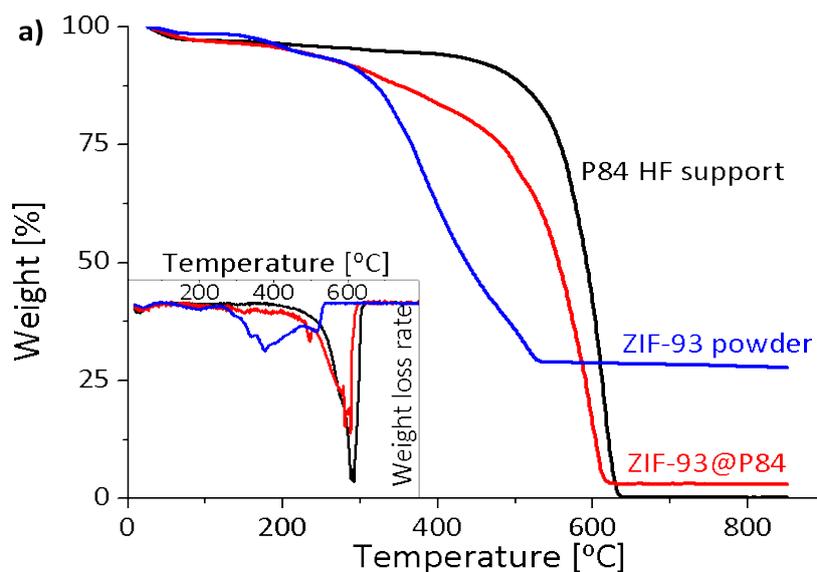


Fig. S1 Weight loss curves in air atmosphere of ZIF-93 membranes compared with the pure P84 hollow fiber support and pure MOF powder.

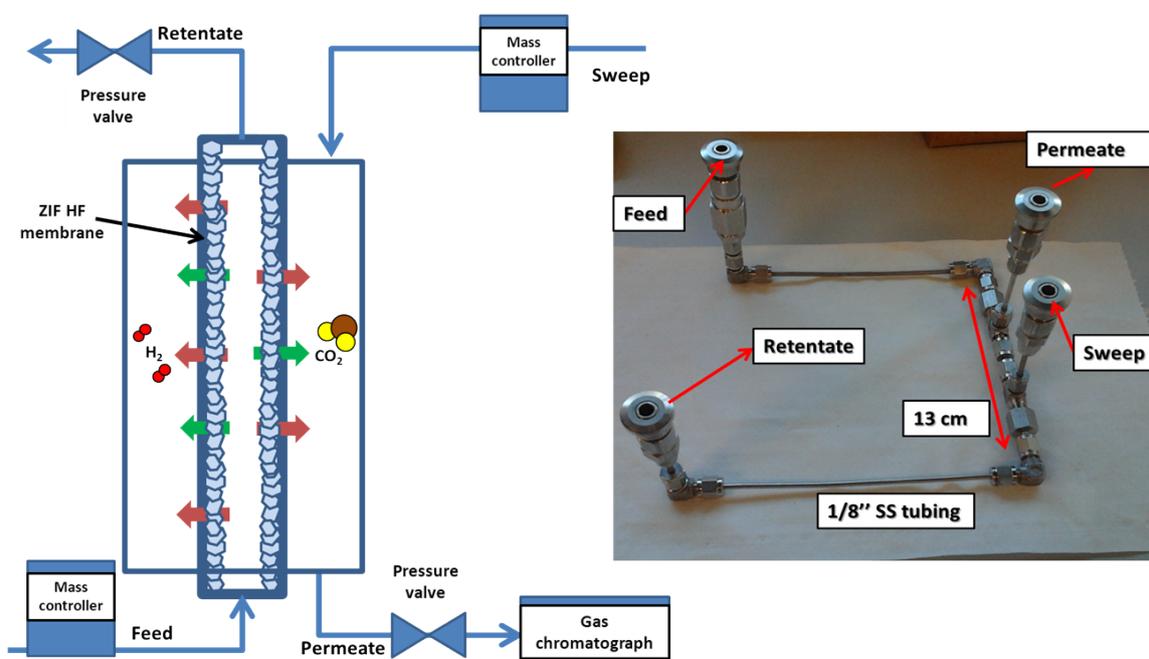


Fig. S2 Gas plant scheme and experimental stainless-steel module used for HF membrane permeation tests. A 13 cm long HF is sealed with epoxy resin where an equimolar gas mixture to be separated is fed inside the fiber. The permeate stream is swept crosscurrent.

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