Supporting Information for

A step-by-step seeding procedure for preparing HKUST-1 membrane on porous α-alumina support

Jiangpu Nan, Xueliang Dong, Wenjin Wang, Wanqin Jin*, and Nanping Xu

State Key Laboratory of Materials-Oriented Chemical Engineering,

Nanjing University of Technology

5 Xinmofan Road, Nanjing 210009, P. R. China

Tel.: (+86) 25-83172266

E-mail:wqjin@njut.edu.cn

1. Gas permeation

Before gas permeation measurements, the membranes were sealed in modules with silicone O-rings and swept using H_2 at the feed side. Meanwhile, the modules were heated from room temperature to 100 °C at a rate of 20 °C·h^{-1} and held for 0.5 h, then cooled to room temperature at the same rate. After that, the activated HKUST-1 membrane was tested by gas permeation experiments. For the single component permeation, the permeate side was contacted with the atmosphere (~0.1 MPa), and the feed side pressure was controlled with exactitude manometers. For the mixture permeation, the permeate side was also contacted with the atmosphere (~0.1 MPa), and the feed side pressure was kept at 0.15 to 0.2 MPa. During the mixture permeation, the pressure of single component at the feed side or permeate side depends on its partial pressure. Exactitude manometers and temperature transducers controlled the test pressure and temperature, respectively. The effective membrane area was about 3.8 cm^2. The single gas permeation of H_2, CO_2, N_2, and CH_4 were performed, the permeated gases were recorded using the bubble flower. Ideal selectivity was calculated as the ratio of permeances. For mixture permeation, Wicke-Kallenbach mode connecting an on-line gas chromatography was used. Feed gas and sweep gas rate is 100 ml/min (1:1) and 50 ml/min, respectively, the Ar was used as sweep gas. The permeation apparatus was shown in Figure S1.

At steady state, the permeance of component *a* was calculated as

$$F_a = \frac{N_a}{P_a \times A}$$

Where N_a is the permeate rate of component *a* (mol/s), P_a the tranmembrane pressure difference of component a (Pa), and A is the effective membrane area (m^2).

The separation factor was calculated as

$$\alpha_{a/b} = \frac{(y_a / y_b)}{(x_a / x_b)}$$

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

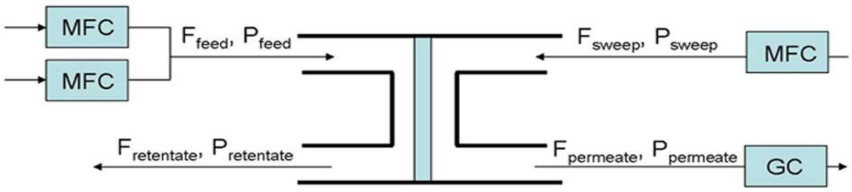

Figure S1. Permeation equipment for the gas separation.

“MFC” and “GC” are mass flow controller and gas chromatography (Shimadzu GC-2014), respectively. “F” and “P” are the flow rate and pressure, respectively.

2. Digital photo of seeded alumina support.

The alumina support surface after step-by-step seeding for four cycles was recorded with a digital camera (Nikon, D90); a digital photo of the bare support was also provided for comparison.

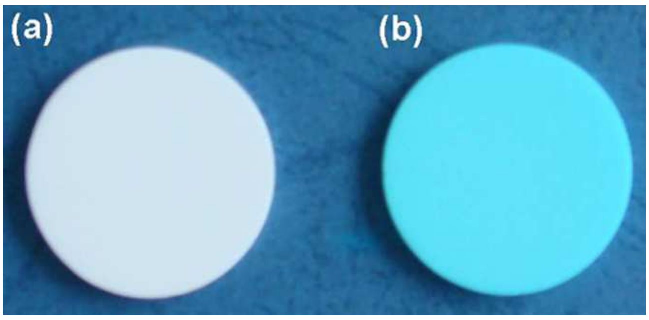

Figure S2. Digital photos: (a) bare support, (b) seeded alumina support after four cycles.

3. XRD patterns of seeded alumina supports

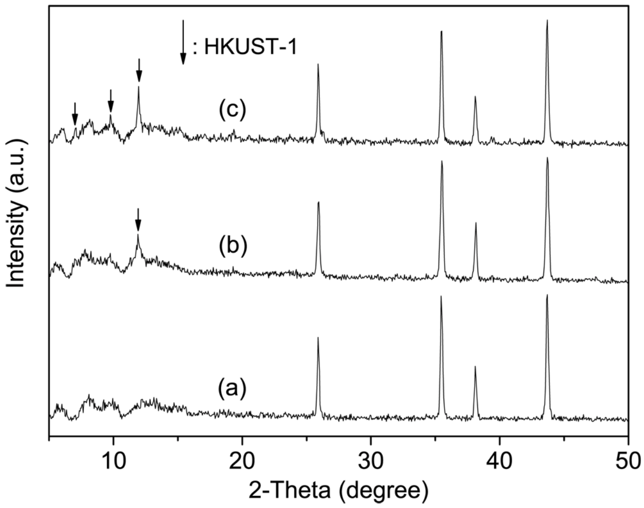

Figure S3. X-ray diffraction patterns: (a) bare α-alumina support; seeded α-alumina support after (b) 15 and (c) 40 cycles.

4. XRD patterns of HKUST-1 membranes prepared on the seeded α-alumina support.

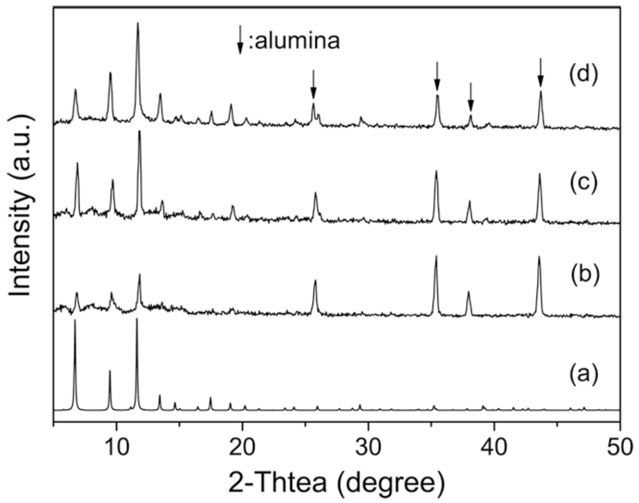

Figure S4. X-ray diffraction patterns: (a) HKUST-1 crystalline powder; (b), (c), and (d) HKUST-1 membranes prepared with synthesis solutions (I), (II), and (III), respectively.

4. XRD pattern and SEM images of HKUST-1 membrane prepared by the *in situ* growth.

We also prepared a HKUST-1 membrane on the alumina support using the *in situ* growth with synthesis solution (III). The characterization results of XRD and SEM are shown in Figure S3 and Figure S4, respectively.

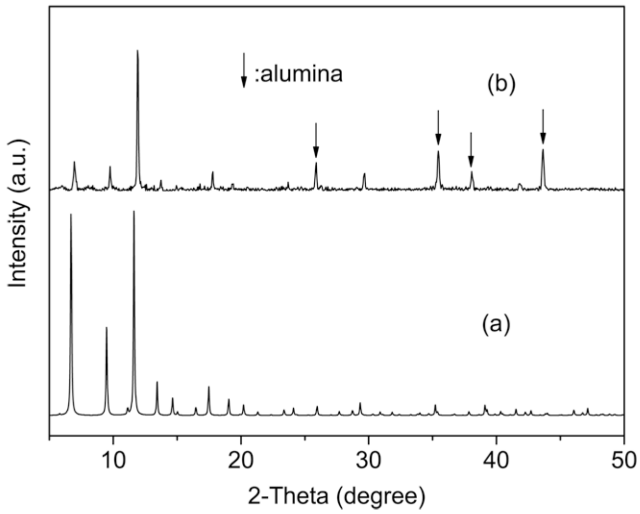

Figure S5. X-ray diffraction patterns of (a) HKUST-1 crystalline powder, and (b) HKUST-1 membrane prepared on the alumina support with synthesis solution (III) by the *in situ* growth.

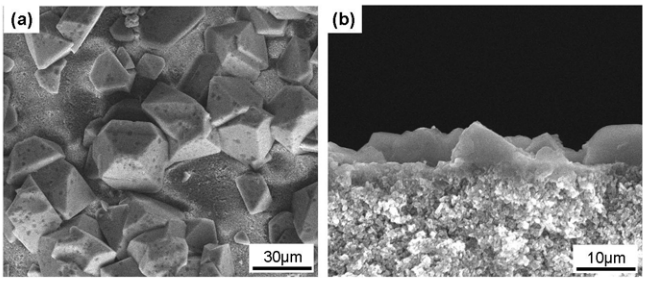

Figure S6. Scanning electron micrographs: (a) surface and (b) cross-section of HKUST-1 membrane synthesized on the alumina support with synthesis solution (III) by the *in situ* growth.

5. The gas permeation performance of HKUST-1 membrane.

Table S1. Single and mixture component permeances and H_2 ideal selectivity and binary separation factor of HKUST-1 membrane at 25 ºC.

	Gas	Permeances ($\times 10^{-7} mol m^{-2} s^{-1} Pa^{-1}$)	H_2 ideal selectivity	H_2 separation factor
Single gas	H_2	7.48		
	CH_4	2.57	2.9	
	N_2	2.00	3.7	
	CO_2	1.48	5.1	
Mixture gas	H_2	5.16		3
	CH_4	1.68		
	H_2	4.79		3.7
	N_2	1.25		
	H_2	6.74		4.6
	CO_2	1.40		