Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for

Deposition of chemical modified α-Al_2O_3 particles for high performance ZIF-8 membrane on a macroporous tube

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1.Experimental details:

Materials:

Chemicals were used as received: zinc nitrate hexahydrate (>99%, Sinopharm Chemical Reagent Co., Ltd), 2-methylimidazole (Hmim, >99%, Rizhao Leadersh chemical Co., LT), 3-aminopropyl-triethoxysilane (APTES, 98%, J&K Scientific Ltd.), α-Al_2O_3 particles (0.5um, Dalian Luminglight Co., Ltd.). Porous α-Al_2O_3 tubes (Foshan Ceramics Research Institute of China: 13mm o.d., 9mm i.d., a nominal pore size of 3μm and porosity of 30–40%) were used as supports.

APTES modification on the α-Al_2O_3 particle surface:

5g α-Al_2O_3 particles having a particle size ranging from 0.5μm to 0.6μm were treated with 4ml APTES in 150ml toluene at 120°C for 24h under N_2 conditions, leading to APTES monolayer deposited on the α-Al_2O_3 particle surface.

Deposition of APTES-modified α-Al_2O_3 particles onto the tubular support:

Water suspension containing 3wt.% *APTES*-modified α-Al_2O_3 particles or *APTES*- free α-Al_2O_3 particles was used as coating solution respectively for the deposition of α-Al_2O_3 particle onto the support. Before hot dip-coating, the supports were calcined at 550^{o}C for 6h and cooled down to room temperature for use with controlled heating and cooling rates of 2^{o}C/min respectively. The hot dip-coating[1s] of α-Al_2O_3 particles onto the outer surface of the support was carried out by directly dipped the preheated support at 150°C oven into the coating solution for 20s followed by drying at 50^{o}C overnight.

Counter diffusion synthesis of ZIF-8 membrane: (Fig. 1S)

0.146g of 2-methylimidazole (Hmim) solution dissolved in 25ml of methanol (solution A) and was supplied from the outer volume of the support, 0.066g of $Zn(NO_3)_2{\cdot}6H_2O$ dissolved in 4ml of methanol (solution B) was supplied from the inner volume of the support. The pre-treated support with one end sealed by Teflon cap was put vertically into a Teflon lined stainless steel autoclave along the wall followed by filling with solution A (about 18ml), the level of solution A should not exceed the top of the support at this moment. Immediately, solution B was filled into the inner volume of the support from the unsealed end, followed by sealing this end with Teflon cap and adding the rest A solution (about 7 mL) again to exceed the top of the support.[2s] The crystallization reaction was carried out at 150^{o}C for 5h and the membrane was washed with pure methanol then dried in vacuum oven.

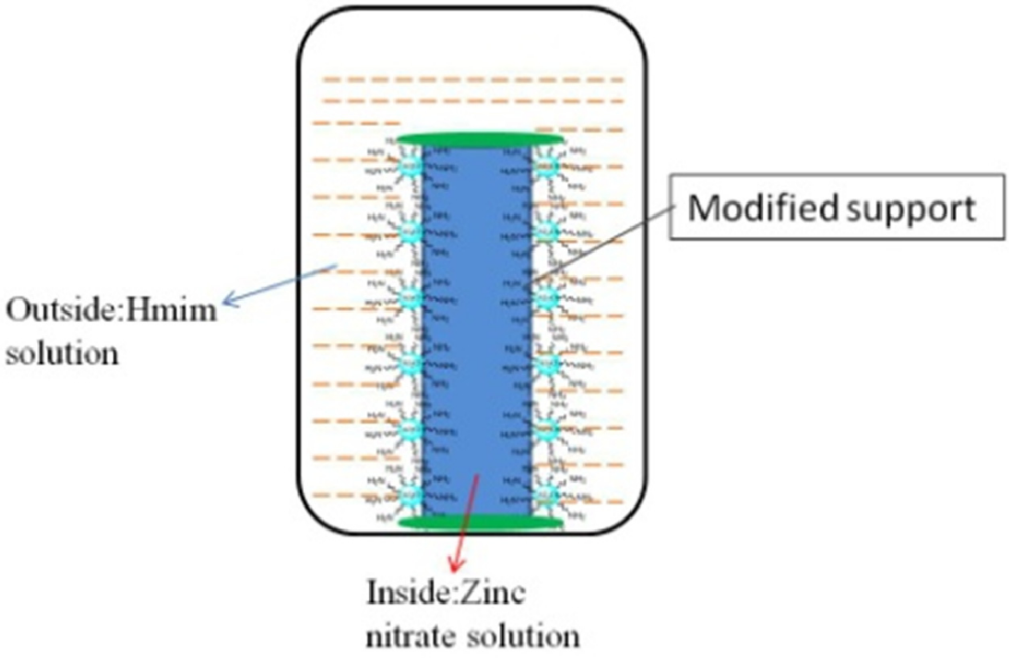


Figure 1S Schematic diagram of diffusion cell for ZIF-8 membrane preparation

2. Characterization

Scanning electron microscopy (SEM) images of the surfaces of membranes were taken with a KYKY2800B microscope at an acceleration voltage of 15 kV and a working distance of 10 mm after gold coating.. X-ray diffraction (XRD) patterns were collected on a Philips Analytical X-ray diffractometer using Cu Kα radiation (30 mA and 40 kV).

The gas permeation properties of the ZIF-8 membranes was investigated using single gases of H_2 (0.289 nm), CO_2(0.33 nm) and N_2 (0.364 nm) in a permeation set up as shown in Figure 2S.[3s] The values in brackets are the kinetic diameters of the various gases, respectively. The membrane was placed in a home-made stainless steel module with a cylindrical geometry. Rubber gaskets were used as sealing between the membrane and the module. The feed stream was pressurized, while downstream pressure was maintained at atmospheric pressure. The pressure difference through the membrane was maintained at 0.05MPa in the single gas permeation test. Before the measurement of each gas species, the permeation apparatus was purged with the respective gas to avoid the disturbance from previous gas permeation during measurements. The permeance P_i for the permeating gas i is defined as:

$$P_i = \frac{N_i}{\Delta P_i A} \;,$$

Where N_i is the permeating flux of component i (mol/s), ΔP_i is the transmembrane pressure difference of component i (Pa), and A is the membrane area (m^2). The separation factor $a_{i,j}$ is defined as the ratio of the permeance P_i and P_j:

$$a_i = \frac{P_i}{P_j} \;.$$

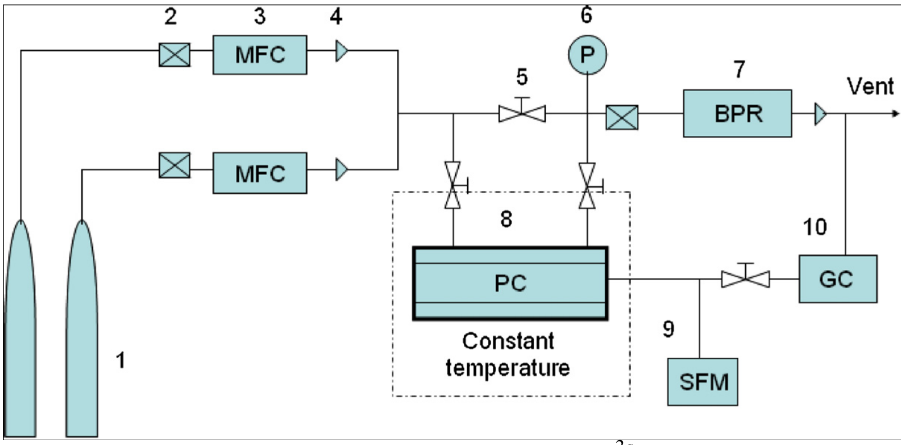
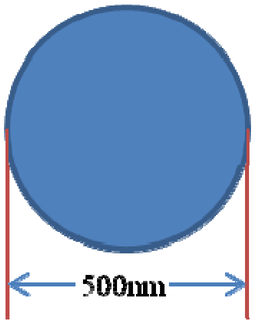


Figure 2S Schematic diagram of the gas permeation apparatus[3s]. (1) Feed gas cylinder, (2) filter, (3) mass flow controller, (4) non-return valve, (5) shut-down valve, (6) pressure gauge, (7) back pressure regulator, (8) permeation cell, (9) soap bubble film flow meter and (10) gas chromatograph.

3. Results and Discussions

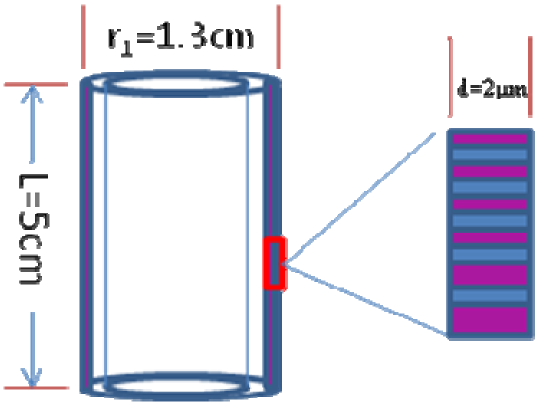
3.1 Caculation of the surface areas of the Al_2O_3 particles deposited on the support and the corresponding tubular support covered by Al_2O_3 particles:

Models:

Al_2O_3 particle :  ,

Model assumes the particle geometry is sphere.Weight of the Deposited Al_2O_3 particle: particle radium, r=250nm, m=0.007g, the density of the $\rho=3.9g\cdot cm^{-3}$.

$$S_1 = \frac{3m}{\rho r} = \frac{3\times 0.007g}{3.9g\cdot cm^{-3}\times 2.5\times 10^{-5}} = 215.38cm^2$$



the tubular support:

Model assumes the pore is sphere. Aperture :r=1×10-4. m=9.521g, ε=0.35.

$$S_2 = \frac{2\varepsilon\pi l[(\frac{r_1}{2})^2-(\frac{r_1}{2}-d)^2]}{mr}$$

$$= \frac{2\times 0.3\times 3.14\times 5cm\times [(\frac{1.3cm}{2})^2-(\frac{1.3cm}{2}-0.0002cm)^2]}{1\times 10^{-4}cm}$$

$$= 28.56cm^2$$

3.2 SEM images of the Al_2O_3 support and ZIF-8 membranes on the bare support or the pretreated Al_2O_3 support by deposition of APTES-free Al_2O_3 particles:

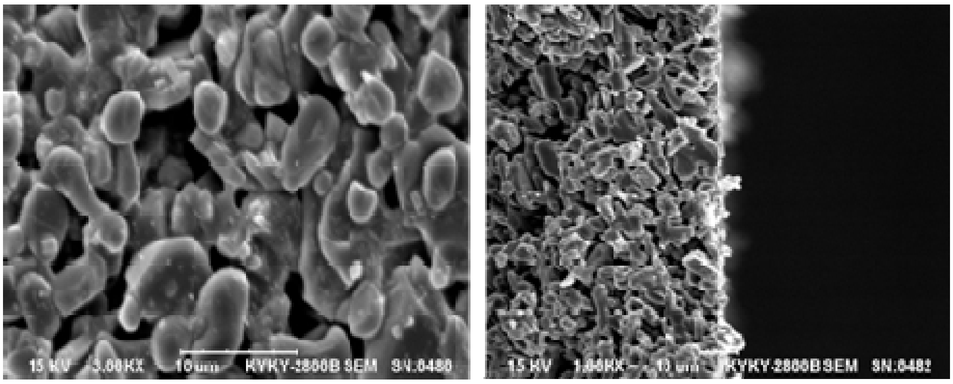


Figure 3S. SEM images of a tubular porous Al_2O_3 support without any modification.(left: surface view; right: cross section)

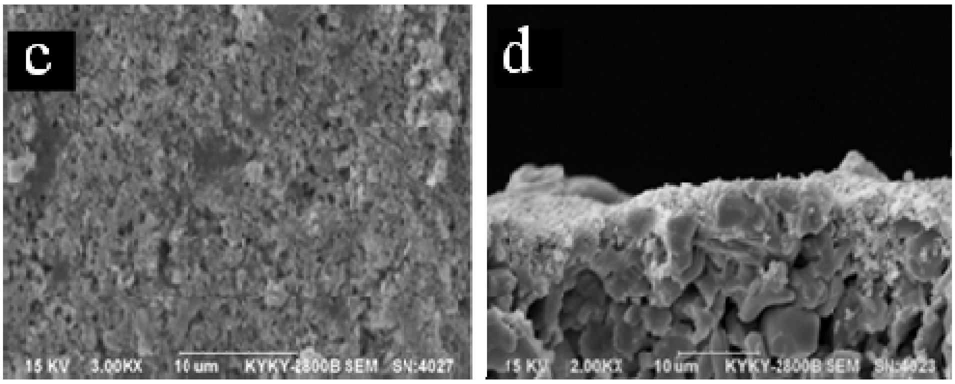


Figure 4S. SEM images of ZIF-8 membrane on the pretreated support by deposition of APTES-free Al_2O_3 particles (left: surface view; right: cross section)

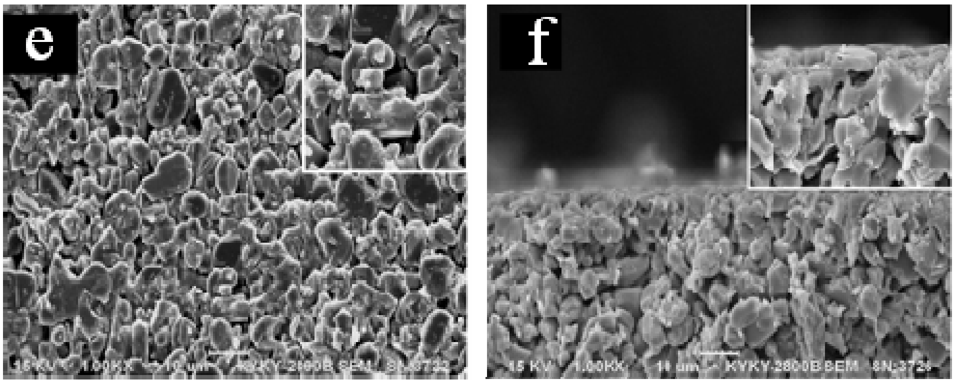


Figure 5S. SEM images of ZIF-8 membrane on the bare Al_2O_3 support without any modification (left: surface view; right: cross section)

3.3 Table S1: Comparison of separation performance of the obtained ZIF-8 membrane in this study for H_2/N_2 and H_2/CO_2 systems with other porous H_2 separation membranes reported

Membrane	**Pore size (nm)**	**Gas separation performance selectivity**		**H_2 permeance [$mol m^{-2} s^{-1} Pa^{-1}$]**	**reference**	**Separation index [c] π**	
		H_2/CO_2	**H_2/N_2**			**H_2/CO_2**	**H_2/N_2**
Zeolite X	0.74	4.5	-	1.4×10^{-7}	[4s]	4.9×10^{-6}	-
Silicate-1	0.55	1.84	1.23	7.9×10^{-6}	[5s]	0.66	0.182
ZSM-5	0.55	-	15.5	9.3×10^{-13}	[6s]	-	1.35×10^{-6}
Matrix AlPO4	-	9.7	-	1.1×10^{-7}	[7s]	0.00096	-
SAPO-34	0.38	1.3	25	3.0×10^{-8}	[8s]	0.0012	0.095
LTA AlPO4	0.4	7.6	-	$2.1–2.5\times10^{-7}$	[9s]	0.1386	-
NaA	0.4	5.3	4.2	$2.5–3.6\times10^{-7}$	[10s]	0.1075	0.008
SSZ-13	0.38	1.6	5.0	3.1×10^{-7}	[11s]	0.0158	0.105
Hybrid silica	-	-	10[a]	2.0×10^{-5}	[16]	-	14.4
Silica	0.38-0.55	7.5[a]	64[a]	2×10^{-6}	[12s]	1.3	12.6
Silica	-	-	100[a]	$2.23\text{-}4.46\times10^{-7}$	[13s]	-	0.442-0.883
Silica (CVD)	--	--	1000	3.0×10^{-7}	[14s]	-	6.0×10^{-4}
CMS	--	--	45	2.0×10^{-6}	[15s]	-	9
Pd	-	-	∞	3.33×10^{-6}	[16s]	-	∞
Pd	-		>70000	8.4×10^{-6}	[17s]	-	>39070
HKUST-1	0.9×0.9	6.8	7.0	2.14×10^{-6}	[4]	6.20	6.42
ZIF-8	0.34	4.5[a]	11.6[a]	5.1×10^{-8}	[5a]	0.018	0.054
ZIF-7	0.3	6.5	7.7	$7.7–8.0\times10^{-8}$	[6d]	0.044	0.054
ZIF-22	0.3	7.2	6.4	$1.6–1.9\times10^{-7}$	[7a]	0.12	0.103
ZIF-90	0.35	7.2	12.6	2.50×10^{-7}	[7b]	0.16	0.29
ZIF-8	0.34	17.05*[a]*	15.44*[a]*	5.73×10^{-5}	This work	91.96	82.74

[a] Ideal separation factor. [b] Knudsen diffusion. [c]: $\pi=(P_{H2}\times(\text{selectivity}-1)\times$ permeate pressure

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