Supplementary Information

Fabrication of Sandwiched Silicalite-1 Membrane at 2D Confined Space for Enhanced Alcohol/Water Separation

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1. Experimental

1.1. Chemicals

Tetrapropylammonium hydroxide (TPAOH, 2.0 M in water), ammonium fluoride (NH₄F, 98%), sodium sulfate (Na₂SO₄, 99%) and ammonia solution (28% ~ 30%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tetraethyl orthosilicate (TEOS, 96%), 1-bromodocosane ($C_{22}H_{45}Br$,>98%), 1-bromohexane ($C_{6}H_{13}Br$, >98%), *N*,*N*,*N*',*N*'-tetramethyl-1,6-diaminohexane ($C_{10}H_{24}N_2$, > 98%) and tetraethylammonium hydroxide (TEAOH, 35% w/w) were purchased from Tokyo Chemical Industry Co., Ltd. Sodium hydroxide (NaOH, 99%) was purchased from Adama Reagent Co., Ltd. Absolute ethanol (AR), acetonitrile (AR), butanol (AR), toluene (AR) and sodium silicate (Na₂SiO₃, 98%) were purchased from Tianjin Concord Technology Co., Ltd. Aqueous colloidal suspension of single layer graphene oxide (GO) was purchased from Suzhou TanFeng Graphene Technology Co., Ltd.

1.2. Preparation of silicalite-1 nanosheet seed

The synthetic process of 2D silicalite-1 using $C_{22}H_{45}$ -N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₆H₁₃ Br₂⁻ (abbreviated to C₂₂₋₆₋₆) as the organic structure-directing agent (OSDA) was developed according to our previous report.¹ In brief, a specified amount of OSDA was firstly dissolved in deionized water (DI water) at 70 °C. Then, the silica source (TEOS), basic solution and specific amounts of GO solutions were added into OSDA solution. And the final molar composition of the synthetic mixture was 7.5 C₂₂₋₆₋₆ : 100 SiO₂ : 10 NaOH : 25 Na₂SO₄ : 4000 H₂O : 10 GO. After aging at 60 °C for 6 h, the precursors were transferred into a HF-washed Teflon liner in stainless steel autoclave, heating at 150 °C and tumbling at 70 rpm under autogenous pressure. After specific time, the products were separated by centrifugation and washed with DI water for three times. After drying at 80 °C for 12 h, the powder sample was calcined at 550 °C for 8 h with a heating rate of 2 °C/min to remove the OSDA and GO. And then, the product was ground in an agate mortar for 15 minutes to obtain silicalite-1 nanosheet seed.

1.3. Preparation of porous SiO₂ support

1.3.1. Synthesis of Stöber silica particles

Stöber silica particles with sizes of 50 nm and 350 nm were synthesized according to classical procedures with modification to achieve a narrow particle size distribution.² TEOS, ammonia solution, DI water and ethanol were mixed in appropriate compositions as listed in the Table S1, called solution A and B, respectively.

For synthesizing 50 nm Stöber silica, solution B was added to the conical flask followed with approximately 10 min of stirring. And then, solution A was quickly added to solution B (in a conical flask) at once. This reaction continued for 2 h at room temperature under stirring at 400 rpm. After synthesis, particles were centrifuged out at 12,000 rpm for 15 min and washed with 40 mL ethanol for four times. Particles were dried at 70 °C overnight and then calcined at 400 °C for 4 h with a heating rate of 2 °C/min and cooling rate of 4 °C/min. The post-treatment of 350 nm Stöber silica

was the same as that of 50 nm Stöber silica except the calcination temperature was 700 °C.

1.3.2. Preparation of porous SiO₂ support (Stöber silica disk)

Stöber silica disks were prepared according to the method described by Pham *et al.*.³ In short, 1.0 mL aqueous solution of Na₂SiO₃ (0.5% in DI water) was added dropwise into 10 g of 350 nm Stöber silica particles and the particles were ground for 10 min in an agate mortar. Then, 1.6 g particles were compacted in a die at the pressure of 160 kgf/cm³ for 60 s. The compacted disks were calcined at 950 °C for 2 h with a heating rate of 100 °C/h. The diameter and thickness of the porous silica disk were about 22 mm and 2 mm, respectively. The porosity measured by a mercury porosimeter is 35% with an average pore size of 109 nm. After calcination, the disks were manually polished with SiC sandpaper (grit 1000 and 2000), and then 50 nm Stöber silica particles were manually rubbed on the disk. Finally, the supports were calcined at 550 °C for 8 h with a heating rate of 2 °C/min and cooling rate of 4 °C/min. The cycle of rubbing 50 nm Stöber silica and calcination may be repeated one more time to make the surface smoother.

1.3.3. Preparation of silicalite-1 membrane

Silicalite-1 nanosheet seeds were firstly rubbed by hand with powder-free nitrile gloves on the surface of porous SiO₂ supports and then sprayed with a suspension of 0.5 wt% seed in *n*-butanol to bridge the gap between the seeds. Prior to secondary growth, the MFI-coated substrates were calcined at 550 °C for 6 h under air flow with a heating rate of 1 °C/min and cooling rate of 2 °C/min to enhance the connectivity between template-free seed and support. Then, the seeded supports were soaked in an aqueous NH₄F solution (0.2 M) for 5 h to remove unfixed seeds, washed by DI water, and then dried at room temperature overnight.

Similar to the work of Pham *et al.*,³ in order to achieve a loading of 200 µL of structure directing agent (SDA) solution on the seeded support, the MFI-coated supports were dip-coated with 0.025 M TPAOH/TEAOH (0.05 M TPAOH : 0.05 M TEAOH = 1:1, vol : vol) aqueous solution, where the seeded-side was impregnated with the SDA solution for 40 s. Then, two MFI-coated substrates were loaded face-to-face horizontally on a Teflon holder in a 50 mL HF-washed Teflon-liner stainless steel autoclave (The placement mode is showed in Figure S1). A SDA solution (0.2 M, 200 µL) was added into the bottom of the liner placed in a sealed autoclave, then heated at 150 °C for 8 ~ 40 h under static condition. The as-synthesized silicalite-1 membranes were removed after cooling to ambient temperature and dried in a vacuum oven at 80 °C overnight. Finally, they were preserved in a desiccator until pervaporation test.

1.3.4. Pervaporation test

Pervaporation performance of the zeolite membranes was evaluated by a home-made equipment (Figure S2 and Figure S3)⁴ where the ethanol solution in water (5 wt%) was heated to 60 °C, and the n-butanol/water (2 wt%) was heated to 70 °C, respectively. The permeate was collected in a cold trap at 60 ~ 120 min intervals (Figure S3). The total flux (*J*) and separation factor

(α) are defined as follows:

$$J = W / (A \times t) \tag{1}$$

$$\alpha_{ethanol/water} = (y_{ethanol} / y_{water}) / (x_{ethanol} / x_{water})$$
⁽²⁾

where *W* is the total weight of the permeate (kg), *A* is the separation area of zeolite membrane (m²), *t* is the collecting time (h), *x* and *y* are the weight fraction of components in the feed and permeate, respectively. The weight of permeate was calculated by measuring the mass increase of cold trap after collection, and the mass fraction of ethanol and water in the feed and permeate were analyzed by gas chromatography (Hongrui Technologies, SP-7890) equipped with a packed column (PQ, 2 m \times 4 mm) and a thermal conductivity detector (TCD).

The above-mentioned separation factor α can be divided into two terms (equation 3): α_{mem} represents the membrane intrinsic selectivity and α_{evap} can be obtained from the vapor-liquid equilibrium of feed mixture (equation 4).⁵

$$\alpha = \alpha_{mem} \times \alpha_{evap} \tag{3}$$

$$\alpha_{evap} = \frac{m_{ethanol,v} / m_{water,v}}{m_{ethanol,f} / m_{water,f}}$$
(4)

The $m_{i,v}$ and $m_{i,f}$ represent the mass fraction of component *i* in the vapor phase and feed mixture, respectively. α_{evap} can be calculated by non-random two-liquid (NRTL) model in Aspen Plus 9.0.⁶

1.3.5. Characterization

The morphology and thickness of the seed and membrane were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) operating at 3 kV. Transmission electron microscope (TEM) images of silicalite-1 nanosheet seeds were recorded on JEM-2100F (JEOS) with an accelerating voltage of 200 kV. The crystallinity of the as-prepared crystal seeds were determined by X-ray diffraction (XRD, Bruke AXS, D8-'A'-Ddvance) using CuK α radiation (40 kV, 15 mA); scans were done from 1 to 50° with a step size of 0.02° and dwelling time of 0.4 s.

2. Figures



Fig. S1 The placement mode of two Teflon supports and the sandwiched membrane.





Fig. S2 The structure of the permeation cell loaded with the sandwiched membrane.



Fig. S3 Schematic illustration of the home-made pervaporation equipment.



Fig. S4 Top (a, c) and cross-section (b, d) views of the separated surface (sandwiched membranes) by gel-free secondary growth for 8 h (a, b), 12 h (c, d) at 150 °C.



Fig. S5 XRD pattern of separated surface of the sandwiched membrane grown at 100 $^\circ$ C for 24 h.



Fig. S6 XRD pattern (a) and top-view image (b) of separated surface of the sandwiched membrane grown at 180 °C for 24 h.



Fig. S7 Comparison of the n-butanol/water separation factors of sandwiched membranes with previously reported different types of membranes.

3. Tables

	1	,
Particle size	Solution A	Solution B
50 nm (100 mL batch)	4.5 mL TEOS	19.3 mL DI water
	35.6 mL ethanol	0.6 mL NH ₄ OH(28-30 wt%)
350 nm (500 mL batch)	22.3 mL TEOS	96.6 g DI water
	178 mL ethanol	18.9 mL NH ₄ OH(28-30 wt%)
		16 mL ethanol

Table S1 Solution compositions for Stöber silica synthesis

	Synthesis	Synthesis	Pervaporation			Separation	Pof
Sunnort (Particle size um)	time	temperature	Tomporatura Food		– Flux		
	(h)	(°C)	(°C)	(wt%)	(kg.m ⁻² ·h ⁻¹)	factor	Rei
Stainless steel disc(0.5-2)	48	170	60	5	0.76	58	7
Stainless steel tube (0.1)	48	170	60	5	4	30	8
Stainless steel tube (1)	48	175	60	5	1	23	9
Stainless steel disk(10)	48	170	30	4 65	0.6	63	10
Stainless steel disk(10)	48-96	170	30	4 95	0.4	43	11
Stainless steel disk (0 5-2)	48	170	30	4	0.7	32	12
Stainless steel disk (2)	24-144	170	30	4	0.4	47	13
Stainless steel tube (0.5)	48	185	25	5	0.1	10	14
Stainless steel tube (0.2)	72	170	30	5	0.1	60	15
Stainless steel net	73	170	25	5	1.5	20	-
(300 mesh)	15	170	25	5	1.5	20	_
Stainless steel tube(0.5)	48	185	25	5	0.07	10	-
Stainless steel support	48	170	30	10	0.09	33	-
α -Al ₂ O ₂ monolith	Finished	Finished	76	16	19	30	16
u Mi203 mononui	product	product	70	10	1.9	57	10
α -Al ₂ O ₃ tube (0.2)	72	95	25	5	0.2	43	17
α -Al ₂ O ₃ tube (1-3)	4-20	175	60	5	1.2	88	18
α-Al2O3 tube (1-3)	96	170	60	5	1.2	88	-
α -Al ₂ O ₃ hollow fiber (0.1)	6-12	175	60	5	9.8	58	-
α -Al ₂ O ₃ hollow fiber (0.2)	6	175	60	5	7.6	51	-
Mullite tube (1)	16	175	60	5	0.93	106	-
Mullite tube (1)	8	175	60	10	2.55	72	-
Mullite tube (1)	48	170	60	5	1.8	62	19
Mullite tube (1)	20	180	60	5	1.91	66	18
Mullite tube (1)	16	180	60	5	7.4	47	20
Mullite tube (1.9)	24	170	60	3.7	0.7	36	21
Silica tube (0.3)	32	180	60	3	1.5	66	22
Porous silica disc	24.20	100	()	~	2.1	07	7
(quartz+ stöber)	24-30	180	00	5	2.1	85	6
Silica tube (0.3)	20-28	180	60	3	0.6	95	23
Silica tube (0.3)	22-32	180	80	3	1.35	69	-
Titania tube (34 nm)	-	180	60	5	1.8	81	24
YSZ hollow fiber (1-3)	8	180	60	5	7.4	47	20

Table S2 The 5 wt% ethanol/water pervaporation performance of MFI membranes reported in recent studies

Support (22mm	Synthesis	Synthosis	Pervapora	tion	Flux (kg.m ⁻² ·h ⁻¹)	Separation factor	α _{mem}
diameter)	time (h)	temperature(°C)	Temperature(°C)	Feed (wt%)			
Porous silica disc	8	185	60	5	53.2	2.4	0.2
Porous silica disc	10	185	60	5	58.7	3.1	0.3
Porous silica disc	12	150	60	5	77.9	8.4	0.8
Porous silica disc	18	185	60	5	40.1	9	0.8
Porous silica disc(M1)	24	150	60	5	2.3	136	12.6
Porous silica disc(M2)	24	150	60	5	3.5	121	11.2
Porous silica disc(M3)	24	150	60	5	4.6	106	9.8

Table S3 The Ethanol/Water separation performance for sandwiched silicalite-1 membranes in this work

 $Table \ S4 \ The \ Butanol/Water \ pervaporation \ performance \ of \ membranes$

Mamhrona	Feed	Temperature	Flux	Concretion factor	D - f	
Meniorane	(wt%)	$(^{\circ}C)$ (kg.m ⁻² ·h ⁻¹)		Separation factor	Kelefences	
PDMS/PVDF-Fe(II)	3% n-BuOH	30	0.34	42	25	
PDMS/PVDF membrane	3% n-BuOH	30	0.24	44	25	
PDMS membranes	1.5 % n-Butanol	55	0.88	29.56	26	
PDMS membranes	1 % n-Butanol	40	1.28	42.9	27	
polyhedral oligomeric silsesquioxanes/polyether block	3 % n-Butanol	40	1.33	27.2	28	
amide nano-hybrid membrane						
ZIF-8/PDMS Hybrid Membranes	5 % n-Butanol	80	2.8	52.81	29	
Silicalite-1 membranes	2% n-Butanol	70	0.11	150	30	
MFI membranes	5 % n-Butanol	140	40	16	31	
PTMSP/PDMSM (98/2) membrane	2 % n-Butanol	25	0.12	128	32	
PIM-1/PVDF membrane	5 % n-Butanol	65	9	18.5	33	
sandwiched silicalite-1 membrane	2% n-Butanol	70	2.2	113	4. 1	
sandwiched silicalite-1 membrane	whed silicalite-1 membrane 2% n-Butanol 70		3.8	102		

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