Electronic Supplementary Information (ESI):

Tuning aluminum spatial distribution of ZSM-5 membrane : a new strategy to fabricate stable and high performance zeolite membranes for dehydration of acetic acid

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1. Experimental details

Materials

Porous α -Al₂O₃ tubes with outside diameter of 13 mm, inside diameter of 9 mm, a nominal pore size of 2-3 µm and porosity of 30-40% were used as supports (XRD pattern and SEM images given in Fig. S1 and 2, respectively). There supports were purchased from Foshan Ceramics Research Institute (FCRI) of China. The micrometer-sized ZSM-5 crystal particles (Si/Al ratio = 30) assembled by nano ZSM-5 crystals of 50nm were supplied by Laboratory of Catalysis, Dalian University of Technology (DLUT), China. SiO₂ sol (SiO₂, 25wt.%, Qingdao Haiyang Chemical Co., Ltd), sodium hydroxide (NaOH, 96wt.%, Tianjin Kermel Chemical Reagent Co., Ltd), aluminum sulfate ocatadecahydrate (Al₂(SO₄)₃ 18H₂O, 99wt.%, Sinopharm Chemical Reagent Co., Ltd), sodium fluoride (NaF, 98wt.%, Sinopharm Chemical Reagent Co., Ltd) and tetra-propyl ammonium hydroxide (TPAOH, 1.0 M solution) were utilized as silica source, hydroxide source, aluminum source, fluoride source and organic structure-directing agent, respectively. All chemicals were used without further purification.



Fig. S1 XRD pattern of the Al₂O₃ support.



Fig. S2 Top view (left) and cross-section (right) SEM images of the Al₂O₃ support.

2. Synthesis and Characterizations.

ZSM-5 seeds and seeding process

The micrometer-sized ZSM-5 crystal particles (Fig. S3 and 4) assembled by the nano ZSM-5 crystals of 50nm were used as large ZSM-5 seeds. The small ZSM-5 crystals used as small seeds were prepared as follows: the nanocrystal-assembled ZSM-5 crystalline powders were grinded through ball milling, followed by dispersing in an ultrasonic bath with sufficiently deionized water for 30 minutes; then the water suspension containing small ZSM-5 crystals was kept at room temperature for overnight. The larger crystals were settled down to the bottom of the beaker while smaller crystals were dispersed in the upper part of the water suspension owing to the gravitational effect. The ZSM-5 crystals dispersed in the upper part of the water suspension were used for the small seeds in the present work. The use of the hierarchical ZSM-5 microparticles can not only provide plenty of nucleation sites for the growth of membrane but also prevent the ZSM-5 crystal penetrating into the depth of the support. The further deposition of small ZSM-5 seeds can further impact the ZSM-5seed layers. As a result, a thin seeds can further impact the ZSM-5 seed layers. As a result, a thin and dense and large pinhole-free ZSM-5 seed layer is obtained as revealed (Fig. S6).



Fig. S3 XRD pattern of hierarchical ZSM-5 microparticles as large ZSM-5 seeds.



Fig. S4 SEM image of the hierarchical ZSM-5 micro-particle seeds (A) and the surface of the seed layer (B).

The ZSM-5 aggregate particles were used as large seeds. A varying-temperature hot-dip coating (VTHDC) technique¹ was employed for seeding. The hot-dip coating (VTHDC) process is comprised of three steps:1) depositing the large ZSM-5 seeds 2) then wiping the superfluous and loose ZSM-5 crystals on the support surface 3) depositing the small seeds to further provide plenty of nucleation sites and smooth the surface. The process of VTHDC seeding is as follows: the supports with two ends sealed by Teflon cap were preheated at 448 K in an oven for 30 minute then were dipping into the water suspension containing 2.0 wt.% large ZSM-5 seeds for 25 s followed by drying for 3 h at 353 K. Subsequently, the outer surfaces of the dried supports was gently erased using absorbent cotton to remove the superfluous and loose ZSM-5 crystals; Then the erased support were preheated at 353 K in oven again for 2.0 h and then were rapidly dipping into the water suspension containing 0.5 wt.% small sized ZSM-5 crystals for 20 s followed by drying for 3 h at 353 K.

Membrane Synthesis

The seeded support with both ends sealed by Teflon cap was immersed vertically in stainless steel autoclave and filled with an organic template-free synthesis gel containing fluoride as co-mineralizing agent. The molar composition of the synthesis gel for M1 is 6 Na₂O: 1.8 Al₂O₃: 36 SiO₂: 1620 H₂O: 32.4 NaF. The synthesis gel for the M1was prepared as follows: the silicate was prepared by dissolving Si-sol and sodium hydroxide in deionized water under vigorously stirring for 16 h at 298 K, then aluminum sulfate ocatadecahydrate and sodium fluoride were added to the silicate solution and kept for 2 h at 298 K under vigorous stirring, in this way a milk like synthesis gel was obtained.

The autoclave containing synthesis gel and the seeded support was moved into a preheated oven for the hydrothermal reaction of the membrane at 448 K for 48 h. After the hydrothermal reaction, the membrane was collected and washed with boiling water until the PH is neutral then dried at 323 K for overnight.

For comparison, the membrane M2 and M3 was prepared using the same condition

with that of M1 except without NaF and with TPAOH in the gel respectively, the synthesis gel composition, and the membrane M4 and M5 prepared was obtained from the gel containing with and without TPAOH by tuning the alkalinity and amount of Al source, respectively. The synthesis gel composition for the membrane M1-M5 is given in Table S1.

No.	Molar composition of the synthesis gel	Crystallization	
	Wolar composition of the synthesis ger	temperature (K)	time (h)
M1	6Na ₂ O:1.8Al ₂ O ₃ :36SiO ₂ :1620H ₂ O:32.4NaF	448	48
M2	6Na2O:1.8Al2O3:36SiO2:1620H2O	448	48
M4	$7.2 Na_2 O: 1.0 Al_2 O_3: 36 SiO_2: 1620 H_2 O: 32.4 NaF: 7.2 TPAOH$	448	48
M5	$7.2 Na_2 O: 0.9 Al_2 O_3: 36 SiO_2: 1620 H_2 O: 32.4 Na F$	448	48
M3	$6Na_2O\!:\!1.8Al_2O_3\!:\!36SiO_2\!:\!1620H_2O\!:\!32.4NaF\!:\!7.2TPAOH$	448	48

Table S1 Conditions of the fabricated membranes.

Characterizations

The morphology of the ZSM-5 membranes was observed by scanning electron microscopy (SEM) using a QUANTA 450 at an acceleration voltage of 30 kV after a layer of gold coating. The data of X-ray diffraction (XRD) patterns were collected from a Philips Analytical X-ray diffractometer using Cu Kα radiation (30 mA and 40 kV). A series of X-ray photoelectron spectroscopy (XPS) spectra were collected on a Thermo ESCALAB 250Xi in order to obtain Si/Al ratios of ZSM-5 membrane surface at randomly detected spots, and, the Si/Al ratio of the membrane was also determined by Energy Dispersive Spectrometer (EDS) using the same microscope equipped with an X-MAX 20 mm²/50 mm². For the membrane M1, EDS analysis was first carried out at an acceleration voltage of 30 kV. In order to improve the spatial resolution, EDS analysis by decreasing the voltage from 30 kV to 5 kV was further carried out. Water vapor adsorption measurements of the ZSM-5 powder scratched from the ZSM-5 membrane M1 were carried out using a Micromeritics 3Flex surface characterization analyzer (Micromeritics Instrument (Shanghai) Ltd.) at 298 K. Each gas permeation data was taken for three times, and the average value of these three data was used.

Permporosimetry

permporosimetry was used to measure membrane quality and the pore size distribution of the related membranes. It is well-known that the n-hexane or benzene

was used as a condensable vapor for the measurement. However, the adsorption of n-hexane expands the MFI crystals, which in turn shrinks the defects². Hence, in the work, benzene which has little effect on the MFI crystals² was used as condensable vapor with N_2 as a non-condensable carrier gas for the measurements which was carried out at 303.15 K. The transmembrane pressure was kept constant (100 kPa), and the permeate side was kept at atmospheric pressure.

Pervaporation measurement and acid resistance tests

The separation performance of the ZSM-5 membrane was evaluated by pervaporation separation for aqueous solution of acetic acid using a laboratory-scale batch PV experimental apparatus as shown in Fig. S5. The feed solution was vigorously stirred to reduce the effect of concentration polarization. And the temperature of the feed was controlled constant by thermostat oil bath. The inside of the membranes was evacuated by a vacuum pump and the permeate fraction was collected by a cold trap cooled by liquid nitrogen. The pressure on the permeate side was keep less than 400 Pa. The concentrations of the feed and permeate were measured on a gas chromatograph (GC) using a GC7890T. The separation performance of membranes was evaluated by the permeation flux (Q; kg/m²h) and the separation factor (S.F.; α). The permeation flux was calculated by the mass of the permeate in a given time interval. The S.F. was defined in the following:

$$\alpha_{A/B} = (Y_A/Y_B) / (X_A/X_B)$$
(**)

where X_A and X_B denote the mass fraction of components A and B respectively in the feed, respectively; Y_A and Y_B the mass fractions of components A and B permeate, respectively; A and B represent for water and acetic acid, respectively.

The pervaporation experiments were performed at a specified feed acetic acid concentration at 353 K for the investigation of pervaporation characteristics change with the elapsed time for the time-dependent measurements of the fresh membranes M1 and for the acid resistance measurements of the steady membrane respectively. And then the dependency of separation performance on the AcOH concentration were done in a wide concentration range from 75.00 wt.% to 96.50 wt% at 353 K.



Fig. S5 Experimental apparatus for pervaporation unit: (a) magnetic stirring apparatus, (b) thermostat oil bath, (c) membrane tube, (d) acid-resisting membrane modules, (e) stock bottle, (f) cold trap, (g) liquid nitrogen, (h) silicone vacuum tube, (i) vacuum buffer tank, (j) iron stand, (k) vacuum manometer, and (l) vacuum pump.

3. Results and Discussions



Fig. S6 Top view (left) and cross-section (right) SEM images of the final seed layer.



Fig. S7 The photograph of the membrane sample used for XPS surface analysis (A) and cross-section SEM images of the membrane M1 (B); XPS Si 2p (C) and Al 2p (D) spectra recorded on three random location of the M1 surface; The EDS line analysis of Si (E) and Al (F) element of the M1 cross section with voltage of 5 kV (from the bottom of the M1 to the top surface).



Fig. S8 The separation performance of the ZSM-5 membrane M1at 83.00 wt.% AcOH-H₂O and 353 K as a function of immersion period in a 83.00 wt.% AcOH-H₂O mixture.



Fig. S9 The separation performance of the ZSM-5 membrane M1after immersion experiment at 83.00 wt.% AcOH-H₂O mixture at 353 K as a function elapsed time.



Fig. S10 Water vapor adsorption isotherm on the ZSM-5 powder collected from the membrane M1 at 298 K.



Fig. S11 The ZSM-5 membrane M2 prepared from the same synthesis gels except without the addition of NaF with that of the membrane M1 while keeping other synthesis conditions unchanged.



Fig. S12 XRD pattern of the membrane M3.



Fig. S13 SEM images of M3 surface (A) and cross section (B); The Al (C) and Si (E) element EDS mapping of the M3 surface; The EDS line analysis of Al (D) and Si (F) element of the M3 cross-section (from the bottom of the M3 to the top surface).



Fig. S14 XRD pattern of the membrane M4.



Fig. S15 SEM images of M4 surface (A) and cross section (B); The Al (C) and Si (E) element EDS mapping of the M4 surface; The EDS line analysis of Al (D) and Si (F) element of the M4 cross-section (from the bottom of the M4 to the top surface).



Fig. S16 XRD pattern of the membrane M5.



Fig. S17 SEM images of M5 surface (A) and cross section (B); The Al (C) and Si (E) element EDS mapping of the M5 surface; The EDS line analysis of Al (D) and Si (F) element of the M5 cross-section (from the bottom of the M5 to the top surface).

as-synthesized memoranes.								
	Si/Al ratio	Permeance $(\times 10^{-7} \text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$		Ideal sep. factor		PV performances [#]		
Sample	of							
No.	membranes	TT	NT	0E			Sep. factor	Flux
	layer*	H_2	1_2 \mathbf{N}_2	3F ₆	$\alpha_{\rm H2/N2}$	$\alpha_{\rm H2/SF6}$	(—)	$(\text{mol } \text{m}^{-2} \text{ s}^{-1})$
M1	10.0	1.50	0.41	0.12	3.66	12.50	∞	2.20
M2			—	—			—	—
M4	12.9	5.01	1.32	0.15	3.80	33.40	28.5	0.35
M5	14.3	3.61	0.96	0.20	3.76	18.05	∞	1.16
M3	17.5	32.94	10.52	4.16	3.13	7.92	7	6.30

Table S2 The single-gas permeation data (at 298 K, 0.1 MPa) and PV performances of as-synthesized membranes.

* Determined by EDS.

[#] PV performances of synthesized membranes for dehydrating 83 wt.% AcOH aqueous solution at 353 K.



Fig. S18 Permporosimetry polts using N₂/benzene and corresponding pore size distributions (kelvin diameter) for the membranes M1 (a), M4 (b), and M5 (c), respectively.



Fig. S19 XRD pattern of the membrane M1 after dehydration of acetic acid by pervaporation.



Fig. S20 SEM images of M1 surface (A) and cross section (B); the Al (C) and Si (E) element EDS mapping of the membrane surface; and the EDS line analysis of Al (D) and Si (F) element of the membrane cross section after processing water acetic acid separation (from the bottom of the M1 to the top surface).

Membrane	Feed conc.	Temp.	Sep. factor	Flux	Reference
	(water wt.%)	(K)	(—)	$(\mathrm{kg}\ \mathrm{m}^{-2}\ \mathrm{h}^{-1})$	
Mordenite	50	353	299	0.614	(3)
Mordenite	10	353	50	< 0.05	(3)
Mordenite	50	348	∞	0.98	(4)
Zeolite ZSM-5	10	348	1670	0.60	(4)
Zeolite T	50	348	182	1.46	(5)
Silica	10	373	525	5.9	(6)
Silica-titania	10	373	2050	2.16	(6)
Mordenite	6	353	∞	0.107	(7)
Mordenite	6	353	œ	0.136	(8)
Mordenite	17	353	∞	0.36	(9)
Zeolite ZSM-5	17	353	œ	2.20	
Zeolite ZSM-5	10	353	œ	1.90	This work
Zeolite ZSM-5	3.5	353	∞	1.10	

Table S3 Reported separation performance of various membranes for dehydration of acetic acid by pervaporation

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