

Electronic Supplementary Information for

Template-Free Synthesis of Beta Zeolite Membranes on Porous α -Al₂O₃ Supports

Yanting Tang, Xiufeng Liu, Shifeng Nai & Baoquan Zhang *

State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. E-mail: bqzhang@tju.edu.cn

Experimental details:

Materials. Beta zeolite membranes were prepared on the porous α -Al₂O₃ supports with a thickness of 2 mm and a diameter of 2 cm^{11, 25}. The following raw materials were used as provided: Fumed silica (99.98% SiO₂, Evonik), sodium hydroxide (NaOH, 96%, Tianjin Guangfu Chemical Co. Ltd), and sodium aluminate (NaAlO₂, 98%, Tianjin Guangfu Chemical Co. Ltd) were utilized as silica source, hydroxide source, and aluminum source for the template-free route, respectively. Tetraethylammonium hydroxide (TEAOH, 25%, Tianjin Guangfu Chemical Co. Ltd), tetraethylorthosilicate (TEOS, 98%, Tianjin Kewei Chemical Co. Ltd), and aluminium isopropoxide (AIP, 98%, Sigma-Aldrich) were used as template, silica source and aluminum source for the synthesis of beta seeds, respectively. 1,3,5-triisopropylbenzene (TIPB, 96%, Sinopharm Chemical Reagent Co., Ltd), methanol (MT, 99.9%), ethanol (EA, 99.7%), n-butanol (NBA, 99.5%), and methyl tertiary butyl ether (MTBE, 99%) supplied by Tianjin Guangfu Chemical Co. Ltd were used for the pervaporation experiments. All of the water used was obtained from a water purifier (Ulupure-II-10 T, Chengdu Ultrapure Technology Co., Ltd.) with a resistivity of 18.25 M Ω cm.

Synthesis

Beta-OTF zeolite membranes were prepared on the porous α -Al₂O₃ supports by the static hydrothermal synthesis. The seed layer on the α -Al₂O₃ substrate was prepared by using a spin-coater (KW-4A, Microelectric Institute of Chinese Academy of Sciences) with 0.5 wt % zeolite beta (Si/Al=15) suspension, followed by drying and calcinations at 450 °C for 10 h (Figure S1c, heating/cooling rate: 0.5 °C min⁻¹). The molar composition of precursor synthesis solution for the zeolite beta was 100 SiO₂: Al₂O₃: 18 TEA₂O: 1200 H₂O. The corresponding temperature and crystallization time were 100 °C and 7 d, respectively. The precursor synthesis suspension of beta zeolite membranes was prepared as follows. Amounts of NaOH and NaAlO₂ were dissolved in water under vigorously stirring for half an hour, and then the fumed silica was slowly added into the above solution at 80 °C. The synthesis suspension was stirred for 3 h, and the molar composition of the precursor suspension was 30 SiO₂: Al₂O₃: 10 Na₂O: 900 H₂O. Thereafter, the synthesis suspension was transferred into the stainless steel autoclave, in which the seeded α -Al₂O₃ support was placed horizontal downwards. The static hydrothermal synthesis was carried out at 140 °C for 5 d. After crystallization, as-synthesized membranes were rinsed by water, and then dipped in

1M of ammonia with ultrasonic treatment for 20 minute, followed by rinsed thoroughly with water and dried in 60 °C oven overnight.

Characterization

Beta zeolite membranes and crystals were characterized by X-ray diffraction (XRD, Rigaku D/max 2500v/pc diffractometer) using Cu K α radiation ($\lambda_1=0.1541$ nm and $\lambda_2=0.1544$ nm at 40 kV and 200 mA). These spectra were scanned in the range of $2\theta = 5\sim 40^\circ$ at a scanning rate of $4^\circ/\text{min}$. Morphology of the membranes was observed with field emission scanning electron microscopy (FE-SEM, FEI Nanosem 430) at an acceleration voltage range of 10~15 kV. The Si/Na ratios of beta zeolite membranes were confirmed by EDAX (FEI Nanosem 430) at an acceleration voltage of 20 kV. The zeolite beta size was determined by Malvern Zetasizer (NANO-ZS90) at 25 °C. The Si/Al ratio of the zeolite beta was confirmed by inductively coupled plasma optical emission spectrometer (ICP-OES, Vista MPX ICP). The functional groups of beta zeolite membranes and the $\alpha\text{-Al}_2\text{O}_3$ disk were detected by diffuse-reflectance FT-IR (DR-FT-IR, Nicolet 6700). The stability and thermal behavior of zeolite beta were investigated on a thermogravimetric analysis instrument (NETZSCH STA 449F3) with a heating ramp of 5°C min^{-1} under air flow.

Pervaporation test

Pervaporation experiments were carried out with a batch system as described elsewhere¹. After being stabilized for 2 h, the permeate vapor was collected by using two cold traps filled with liquid nitrogen for 4 h. The effective membrane area was ca. 1.8 cm^2 . The compositions of the feed and permeate were analyzed by a gas chromatograph (GC, Agilent Technologies 6890N) equipped with a 30 m column (catalog 19091J-413). Separation performance was evaluated in terms of mass flux, J ($\text{kg m}^{-2}\text{ h}^{-1}$), and separation factor, α .

$$J=m/(At) \quad (1)$$

where m , A , t denote the permeate mass, effective area of the membrane, and test time, respectively.

$$\alpha_{E/T}=(Y_E/Y_T)/(X_E/X_T) \quad (2)$$

where X_E (or X_T), and Y_E (or Y_T) are the mass fractions of ethanol (or TIPB) at the feed and permeate sides, respectively.

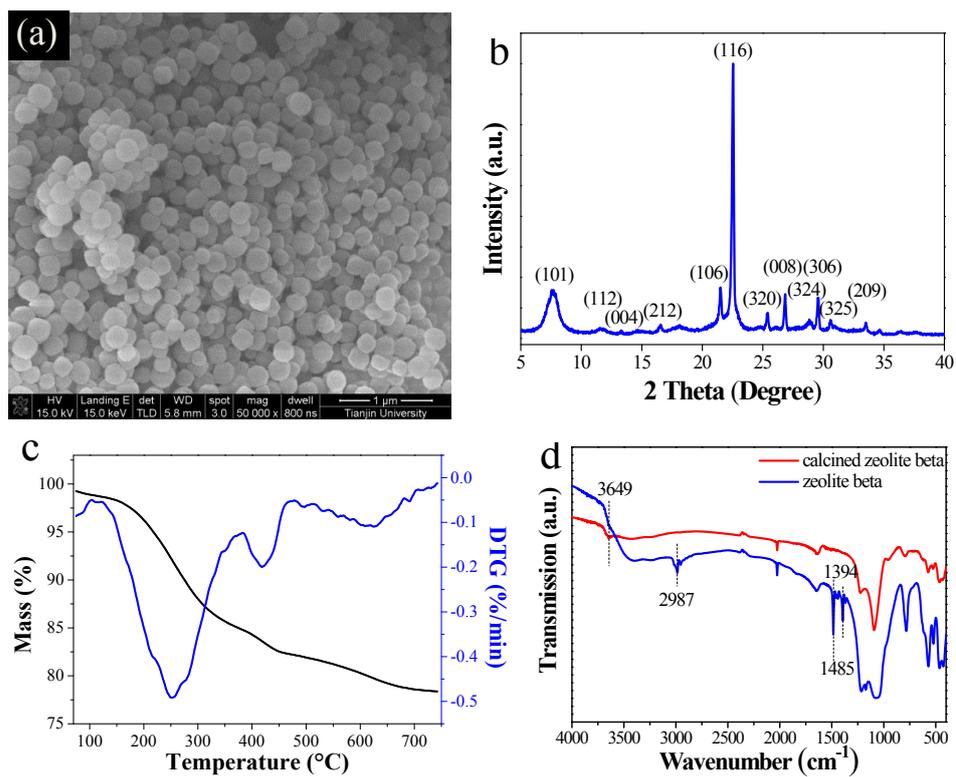


Fig. S1. SEM image (a), XRD pattern (b), TG analyses of zeolite beta in the air atmosphere (c), FT-IR spectra of zeolite beta before and after calcination (d).

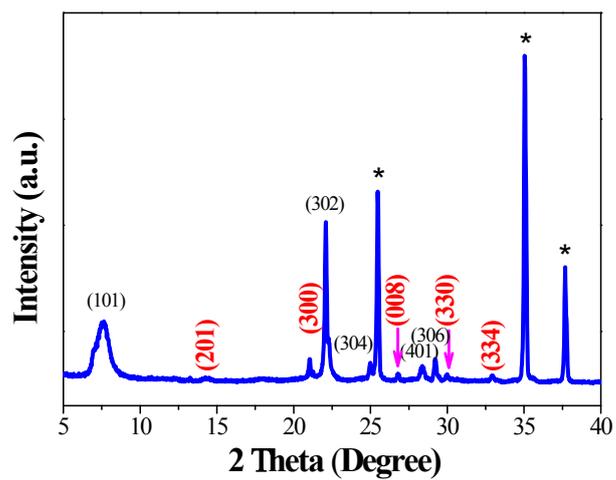


Fig. S2. XRD pattern of the beta-OTF zeolite membrane. The asterisk marks the peak originating from the α - Al_2O_3 support.

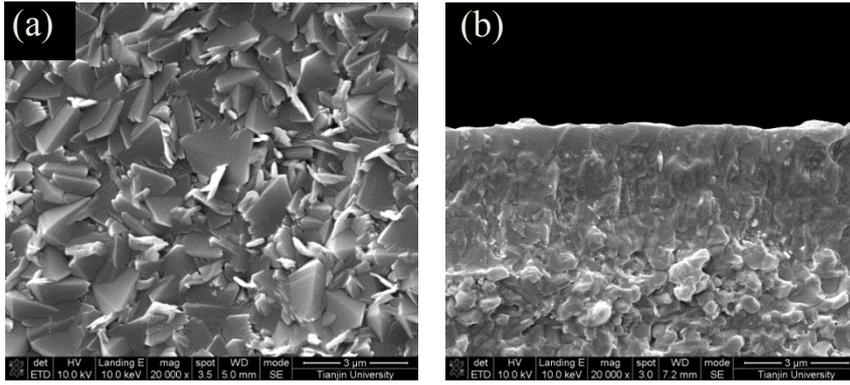


Fig. S3. Top view (a) and cross-section view (b) SEM images of the beta zeolite membrane prepared from the same condition except for using uncalcined seed layer.

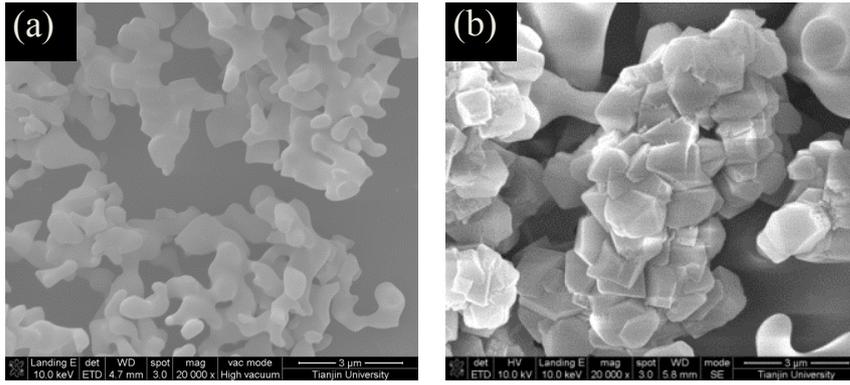


Fig. S4. SEM images of the product collected from the bottom of autoclave by using the uncalcined (a) or calcined (b) seed layer at different magnifications.

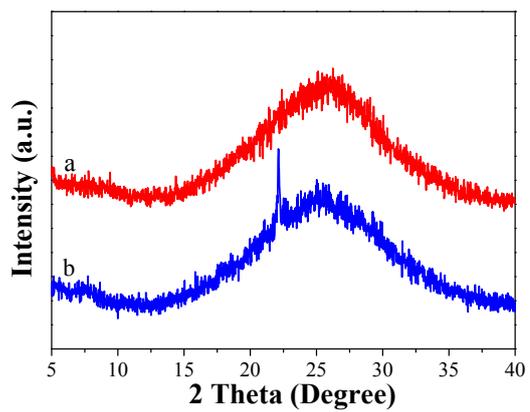


Fig. S5. XRD patterns of the product collected from the bottom of autoclave by using the uncalcined (a) or calcined (b) seed layer.

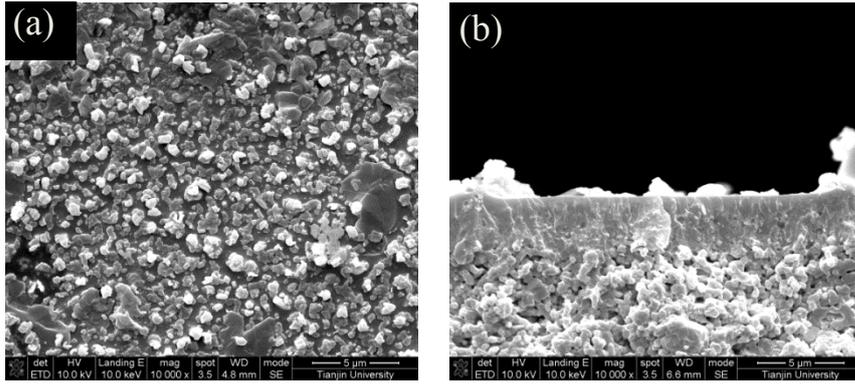


Fig. S6. Top view (a) and cross-section view (b) SEM images of the membrane obtained from the same hydrothermal synthesis condition when the support placed horizontal upwards.

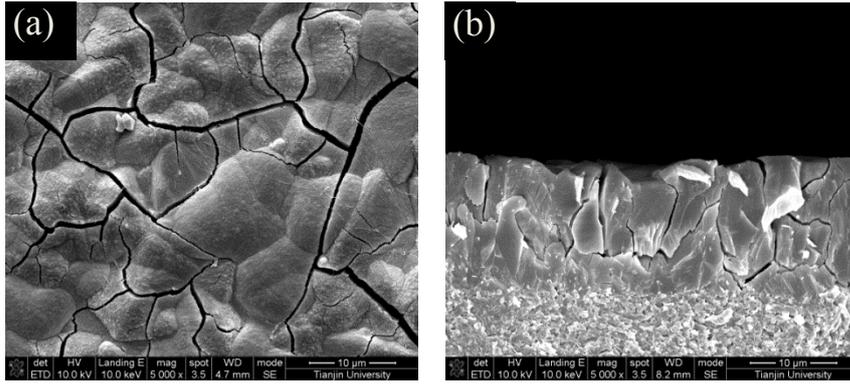


Fig. S7. Top view (a) and cross-section view (b) SEM images of the gel layer obtained from the same hydrothermal synthesis condition but without the beta seed layer.

References

1. W. S. Yang, B. Q. Zhang and X. F. Liu, *Microporous Mesoporous Mater.*, 2009, **117**, 391–394.