

Supplementary Information

Submicrometer-thick *b*-oriented Fe-silicalite-1 membranes:

Microwave-assisted fabrication and pervaporation performances

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Experimental

Materials

All the chemical reagents in the experiment were used without further purification. Tetraethyl orthosilicate (TEOS, 98.0%) was purchased from Tianjin Kewei Chemical Co., Ltd. Chitosan (medium molecular weight) was offered by Sigma-Aldrich company, USA. Tetrapropylammonium hydroxide (TPAOH, 20%), HF (40%), ethanol (99.7%), and Ferric nitrate ($\text{Fe}(\text{NO}_3)_3$, 98.5%) were supplied by Tianjin Guangfu Research Institute of Fine Chemicals. The deionized water (DI water) with a resistivity of 18.2 M Ω was produced by a water purifier (Ulupure-II-10 T, Chengdu Ultrapure Technology Co., Ltd.), and used throughout the study. The glass plate and porous α - Al_2O_3 disk (ϕ 20 mm \times 2 mm) were used as the membrane substrates. The manufacture and treatment of porous α - Al_2O_3 disk was reported previously.¹

Synthesis of Fe-silicalite-1 seed

The coffin-shape Fe-silicalite-1 crystal seeds ($0.6 \times 0.3 \times 0.06 \mu\text{m}^3$) were synthesized in fluoride media at near neutral pH, as similar with the described elsewhere.² The molar ratio of the solid clear gel was 1 SiO_2 : 0.5 TPAOH: 0.01 $\text{Fe}(\text{NO}_3)_3$: 0.5 HF: 60 H_2O . The synthesis gel was first prepared by mixing SiO_2 , TPAOH, $\text{Fe}(\text{NO}_3)_3$ and deionized water and stirring for 24 h. Then HF was quickly added to the synthesis mixtures under stirring. Finally, the obtained gel was transferred into a Teflon-lined autoclave, followed by the hydrothermal reaction with stirring at 180 °C for 5 d. The collected Fe-silicalite-1 crystals were thoroughly washed with a copious amount of deionized distilled water and dried at 120 °C overnight.

Synthesis of Fe-silicalite-1 seed layer and membrane

The manual assembly of Fe-silicalite-1 layers both on the glass plate and the porous α - Al_2O_3 disk supported chitosan films were performed according to our previous studies.^{3, 4} Before the secondary growth of Fe-silicalite-1 zeolite membranes, the seeded supports were calcined at 550 °C for 5 h with the heating and cooling rates of 0.5 °C min^{-1} to decompose the chitosan layer. Then the seed layer on the support was held by a self-made Teflon holder with the seed layer upwards in the synthesis solution with the molar composition of 1 TEOS: 0.2 TPAOH: 0.01 $\text{Fe}(\text{NO}_3)_3$: 800 H_2O . The hydrothermal synthesis was carried out in a microwave oven (MDS-6, Sineo Microwave Chemical Technology Co., Ltd) at 150 °C for 2 h. After synthesis, the membrane was washed with DI water and dried in vacuum at 95 °C. The templates were removed in a hydrogen atmosphere at 350 °C for 10 h with the heating and cooling rates of 0.5 °C min^{-1} according to our group previous publication.⁵

Characterization

Fe-silicalite-1 seed layers and membranes were characterized by field emission scanning electron microscopy (FE-SEM, FEI Nanosem 430) at an acceleration voltage range of 10~15 kV and X-ray diffraction (XRD, Rigaku D/max 2500v/pc diffractometer) using Cu K α radiation ($\lambda_1=0.1541 \text{ nm}$ and $\lambda_2=0.1544 \text{ nm}$ at 40 kV and 200 mA). Diffuse reflectance UV-visible spectra was measured in

a range of 200-600 nm on a Thermo Evolution 300 BB spectrophotometer to investigate the nature of the extra-framework iron species. The functional groups were detected by diffuse-reflectance FT-IR (DR-FT-IR, Nicolet 6700). The hydrophobicity of Fe-silicalite-1 zeolite membranes was studied by contact-angle measurements (CA, OCAH 20). The permoporometry method to measure the defect size distribution of the synthesized Fe-silicalite-1 membrane was obtained by the self-made zeolite membrane evaluation device, a detailed description of which has been given elsewhere.^{6,7}

N₂ permeation test and Pervaporation

The N₂ permeation test of the *b*-oriented Fe-silicalite-1 zeolite membrane was performed between 0.05 - 0.40 MPa and at 25 °C based on the concentration gradient method similar to that previously reported.^{8,9} The permeance is defined as $f = F/L = Q/S(P_h - P_l)$, where f is the permeance (mol m⁻² s⁻¹ Pa⁻¹), F the permeability (mol m m⁻² s⁻¹ Pa⁻¹), L the membrane thickness (m), Q the molar gas flow rate (mol s⁻¹), S the membrane area (m²), and P_h and P_l are the upstream and downstream pressure (Pa), respectively.

The pervaporation experiment was conducted with a batch system as described elsewhere.¹⁰ The permeation side was kept at vacuum (133 Pa). The flux was calculated by the weight of the condensed permeated species and the concentration: $J=W/At$, where W refers to the weight of permeate (kg), A is the membrane area (m²), t is the duration (h) of the sample collection. The feed and permeate concentrations of ethanol aqueous solution were measured by a gas chromatograph (GC, Varian CP-3380). The separation factor (α) was determined by the equation $\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$, where X_A , X_B and Y_A , Y_B are the weight fractions of ethanol (A) and water (B) in the feed and permeate sides, respectively.

Supplementary Figure

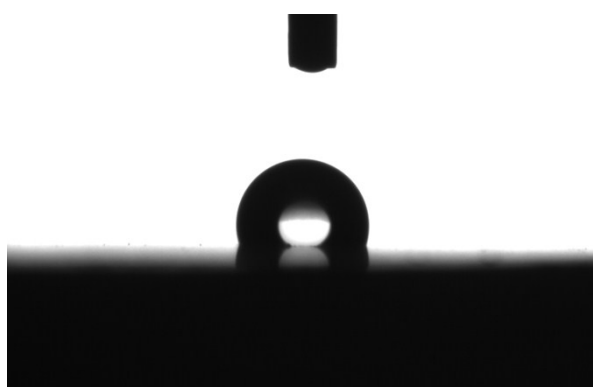


Fig. S1 The contact angle of the Fe-silicalite-1 membrane on α -Al₂O₃ after template removal

Notes and references

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