Supporting Information

Eco-friendly Fabrication of Hydrophilic ZSM-5 Membrane for Alcohol Upgrading

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Experimental Section

1. *Pretreatment of support*

A stainless-steel net (300 mesh) was used as the support. The net was cut into wafers of 30 mm in diameter, treated with liquid detergent solution for 30 minutes under ultrasonic condition. The net was washed with deionized water three times in ultrasonic bath and dried at 100 °C.

2. *Preparation of silicalite-1 seeds*

Silicalite-1 seeds with an average size of 300 nm were prepared from a synthesis solution with a molar composition of 4TPAOH: 10TEOS: 990H_2O under hydrothermal treatment at 140 °C for 10 h. The seeds were thoroughly washed with deionized water several times. The seed solution (20 g L^{-1}) was prepared by adjusting the pH value to 10 using aqueous NH_3 to avoid the seed aggregation. Then the seed solution was dropped onto the stainless-steel net and dried on a resistance furnace. The deposited seed layer was further calcined at 550 °C for 6 hours prior to secondary growth of ZSM-5 membrane.

3. *Preparation of ZSM-5 membrane*

The mother solution with molar composition of 9.5NaOH: 16.7SiO_2: 0.08$Al_2(SO_4)_3 \cdot 18H_2O$: 2310$H_2O$ was employed for the synthesis of ZSM-5 membranes. Typically, the seeded net was positioned vertically at the bottom of the

flask (250 mL) with 100mL precursor, followed by heating the flask at 100 °C under reflux for 45 days. After crystallization, membranes were taken out and repetitively washed with deionized water under ultrasonic vibration to remove physically attached crystals. The washed membranes were naturally dried (ambient condition) prior to further uses.

4. *Characterizations*

The crystalline structure of seeded layer and grown ZSM-5 membranes was confirmed by X-ray diffraction (XRD) using a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å) running at a voltage of 50 kV and a current of 200 mA. SEM images were collected using a JEOL JSM-6700F field emission scanning electron microscope. The Si/Al ratio of the membrane was determined by ICP-AES chemical analysis, and a series of XPS spectra were taken from the top membrane surface to the bottom net by beam-etching for 5 minutes each time (about 340 nm per minute) on a Scienta ESCA 200 spectrometer in order to obtain Si/Al ratios of ZSM-5 layer at different depths. Vapor adsorption-desorption measurements of water, ethanol and isopropanol on ZSM-5 material were carried out using an Autosorb iQ2 adsorptometer, Quantachrome Instruments. Prior to the tests, the collected ZSM-5 powder from the membrane were degassed under vacuum overnight at 150 °C. The measurements were carried out at 25 °C. Pervaporation experiments were carried out using a home-made pervaporation setup as schematically shown in Fig. S4. The permeation and retention solutions were analyzed by gas chromatography (GC-450, BRUKER).

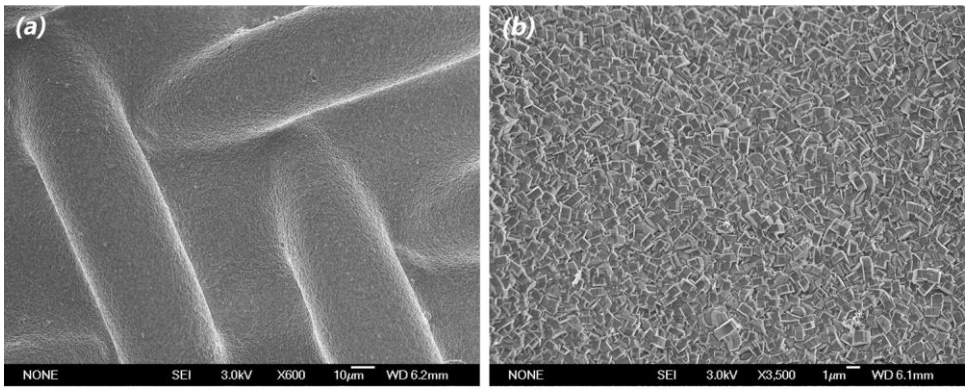

Fig. S1 Top views of SEM images of ZSM-5 membrane with low (a) and high (b) magnifications.

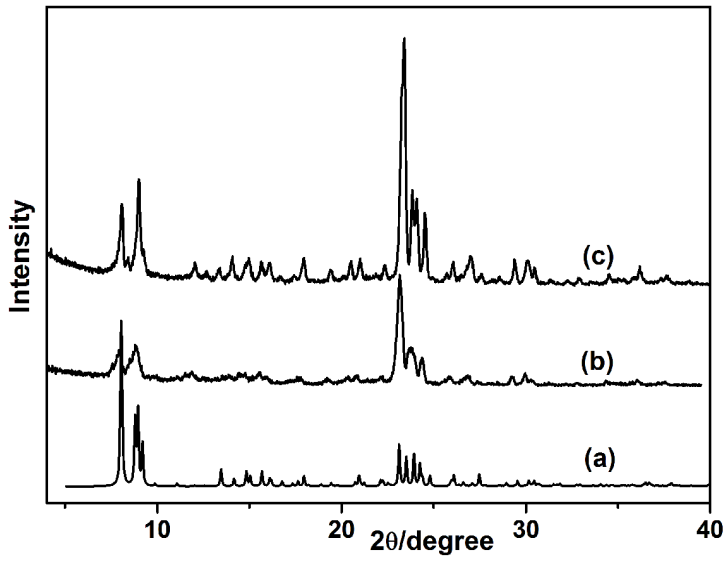

Fig. S2 XRD patterns of simulated MFI-type zeolite (a), seeded layer (b), and grown ZSM-5 membrane (c).

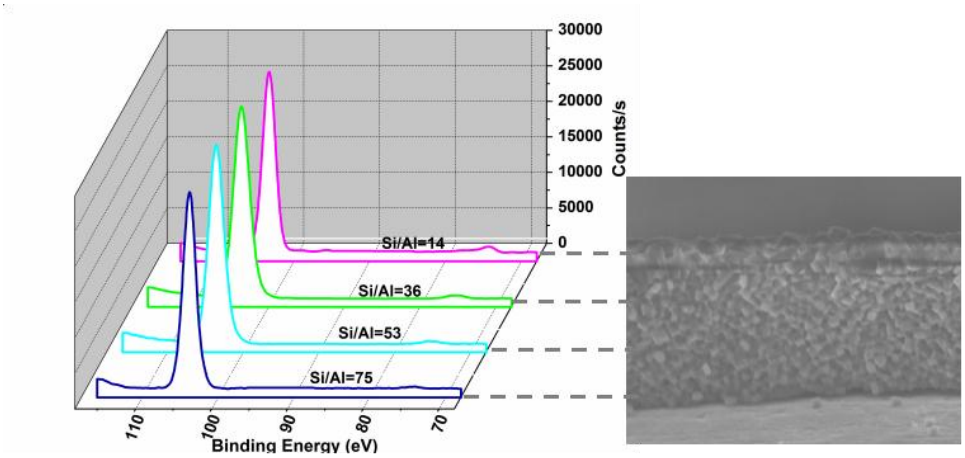

Fig. S3 XPS spectra of Si 2p (103.55 eV) and Al 2p (75.4 eV) signals at different depths of ZSM-5 membrane.

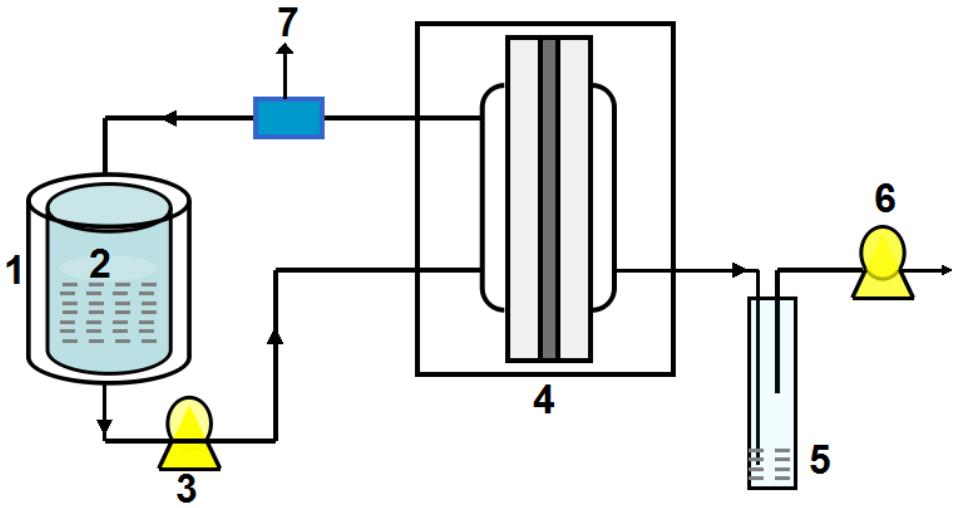

Fig. S4 Schematic presentation of the experimental apparatus for pervaporation tests; 1-heating equipment, 2-feed tank, 3-circulating pump, 4-membrane module, 5-permeate collector, 6-vacuum pump, 7- retentate sampling port.

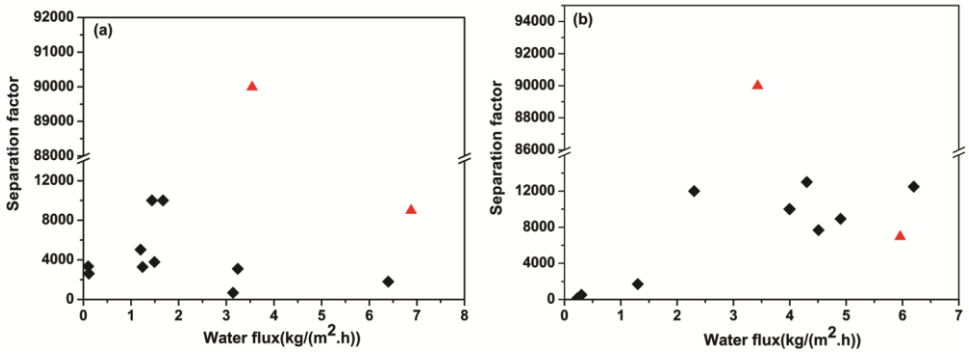

Fig. S5 A comparison of PV performances of IPA/H_2O (a) and EtOH/H_2O (b) using prepared ZSM-5 membranes (marked with red triangles) with other reported works.[1]

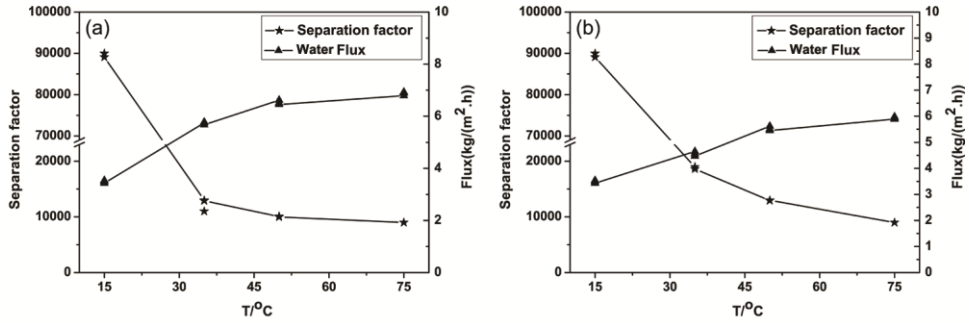

Fig. S6 PV results of IPA/H_2O with 90 wt.% IPA (a) and EtOH/H_2O with 95 wt.% EtOH (b) using ZSM-5 membrane at different temperatures.

1. (a) X. Lin, E. Kikuchi and M. Matsukata, *Chem. Commun.*, 2000, 957; (b) G. Li, E. Kikuchi and M. Matsukata, *Micropor. Mesopor. Mat.*, 2003, **62**, 211; (c) W. Y. Dong, X. W. Cheng, Y. F. Cheng and Y. C. Long, *Acta. Chim. Sinica.*, 2004, **62**, 1573; (d) A. S. Huang, Y. S. Lin and W. S. Yang, *J. Membr. Sci.*, 2004, **245**, 41; (e) A. A. Kittur, S. S. Kulkarni, M. I. Aralaguppi and M. Y. Kariduraganavar, *J. Membr. Sci.*, 2005, **247**, 75; (f) A. S. Huang and W. S. Yang, *Mater. Lett.*, 2007, **61**, 5129; (g) A. S. Huang and W. S. Yang, *Mater. Res. Bull.*, 2007, **42**, 657; (h) A. S. Huang, W. S. Yang and J. Liu, *Sep. Purif. Technol.*, 2007, **56**, 158; (i) K. Sato and T. Nakane, *J. Membr. Sci.*, 2007, **301**, 151; (j) A. Malekpour, M. R. Millani and M. Kheirkhah, *Desalination*, 2008, **225**, 199; (k) H. L. Sun, L. Y. Lu, X. Chen and Z. Y. Jiang, *Sep. Purif. Technol.*, 2008, **58**, 429; (l) Z. B. Wang, Q. Q. Ge, J. Shao and Y. S. Yan, *J. Am. Chem. Soc.*, 2009, **131**, 6910; (m) J. Zhang and W. Liu, *J. Membr. Sci.*, 2011, **371**, 197; (n) K. Sato, K. Sugimoto, T. Kyotani, N. Shimotsuma and T. Kurata, *Micropor. Mesopor. Mat.*, 2012, **160**, 85; (o) M. H. Zhu, Z. H. Lu, I. Kumakiri, K. Tanaka, X. S. Chen and H. Kita, *J. Membr. Sci.*, 2012, **415**, 57.