

Supplementary information

## Preparation of MFI zeolite membranes on coarse macropore stainless steel hollow fibers for the recovery of bioalcohols

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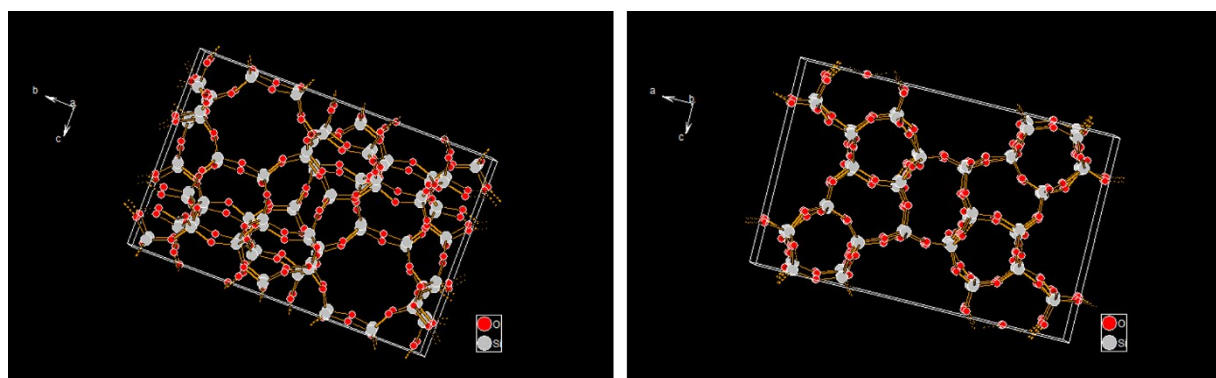


Fig. S1. Framework of a-oriented (left) MFI crystals with sinusoidal channels and b-oriented (right) MFI crystals with straight channels

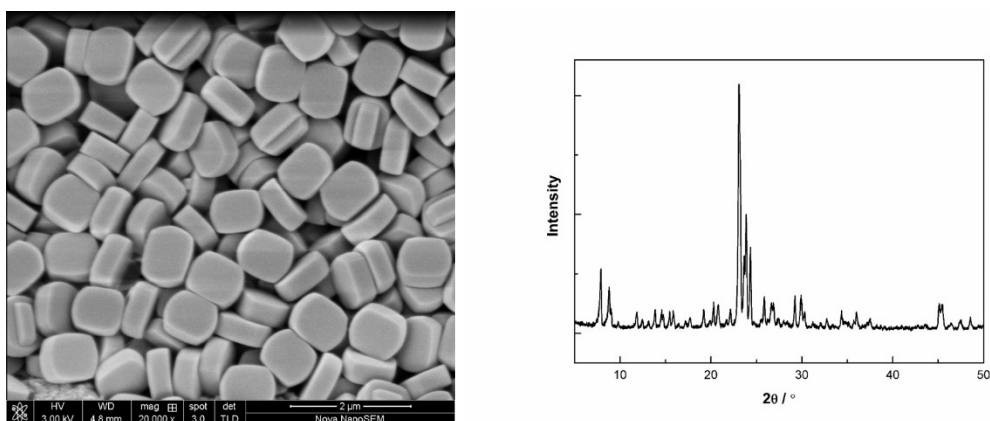


Fig. S2. SEM image and XRD pattern of MFI seeds

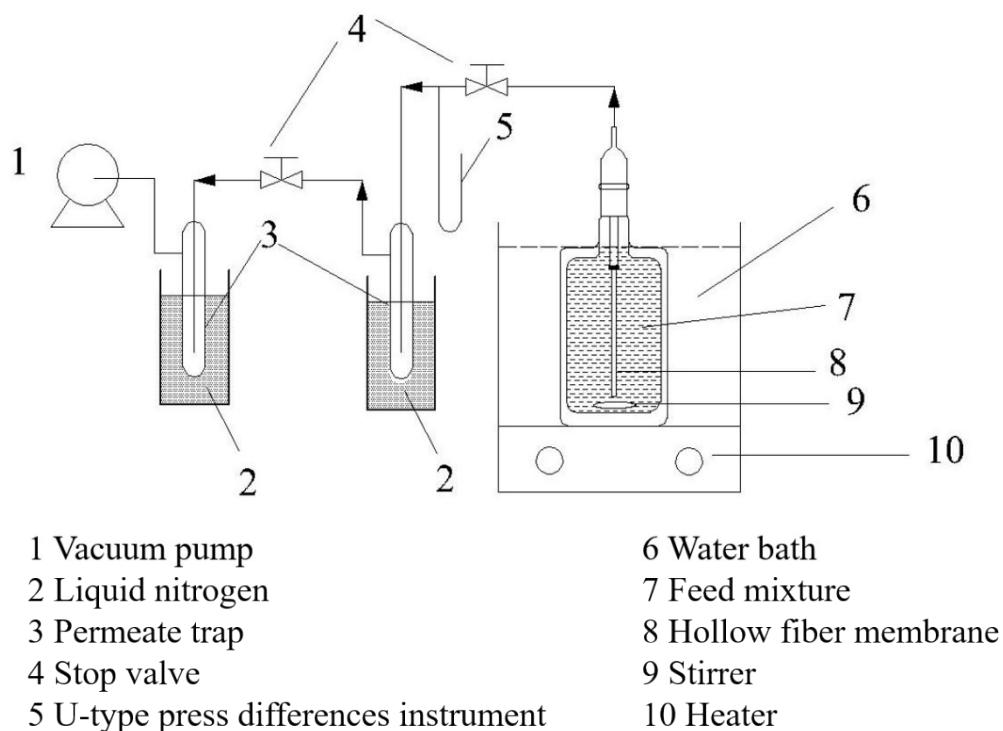


Fig. S3 Diagram of PV system

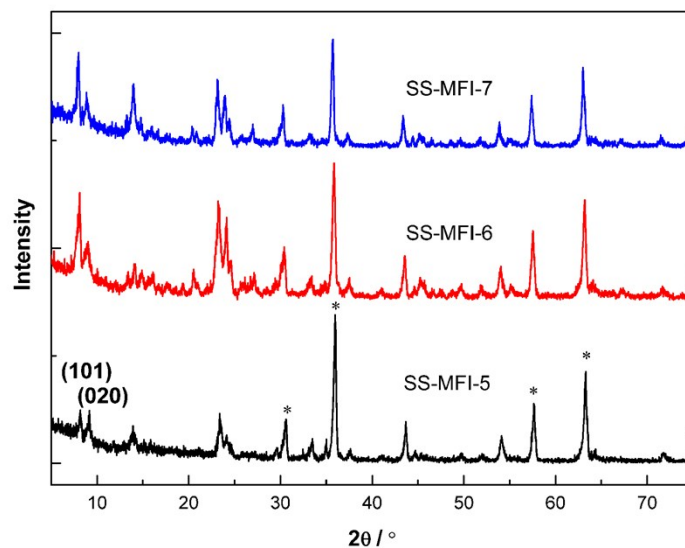


Fig. S4. XRD patterns of MFI membranes with different TEOS contents. Index (\*) represents the SS characteristic peak

XRD patterns of MFI membranes with different TEOS contents are shown in Fig. S4. With the increase of TEOS content, the intensity of MFI characteristic peaks enhanced, which meant that the resultant membranes became continuous and thick.

The resultant membranes also exhibited a high c-orientation degree due to the high ratio of  $[101]$  peak to  $[020]$  peak ( $I_{101}/I_{020}$ ).

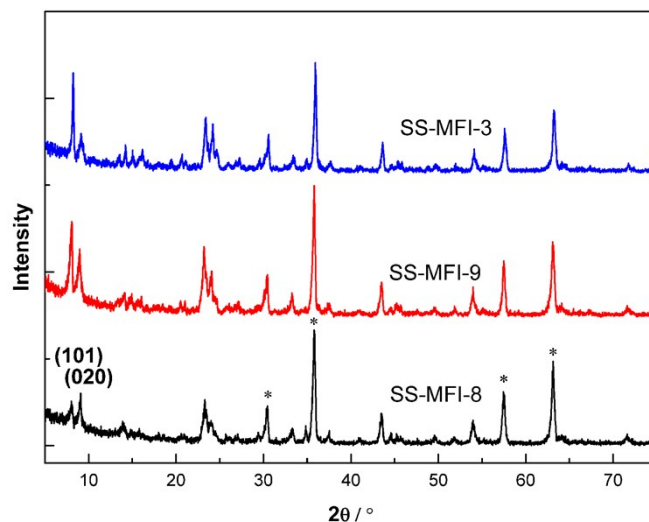


Fig. S5. XRD patterns of MFI membranes with different synthesis time at 175°C and 130°C. Index (\*) represents the SS characteristic peak

XRD patterns of MFI membranes with different synthesis time at different temperature are shown in Fig. S5. The thickness of membrane increased with the prolonging synthesis time. At low synthesis temperature and short time (Fig. S5 SS-MFI-8), the membrane exhibited random orientation. After long synthesis time, c-orientation crystals started to dominate the film. However, the degree of c-orientation at low synthesis temperature and long synthesis time (Fig. S5 SS-MFI-9) was not comparable to that at high synthesis temperature and short synthesis time Fig. (Fig. S5 SS-MFI-3). Therefore, high synthesis temperature with short time favored the preparation high orientation membrane in comparison with low synthesis temperature with long time.

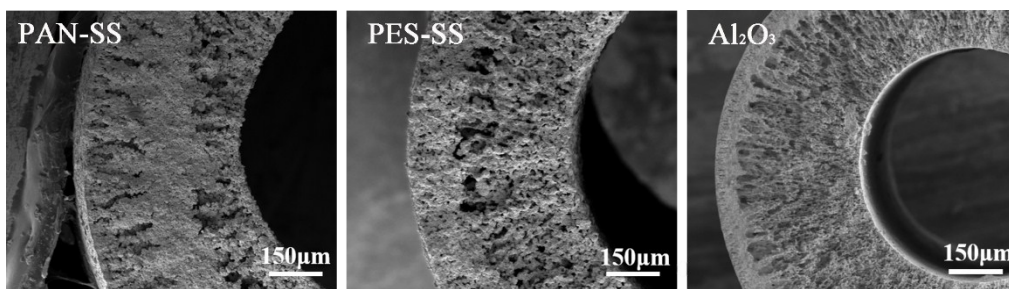


Fig. S6. Cross-section structures of different supports

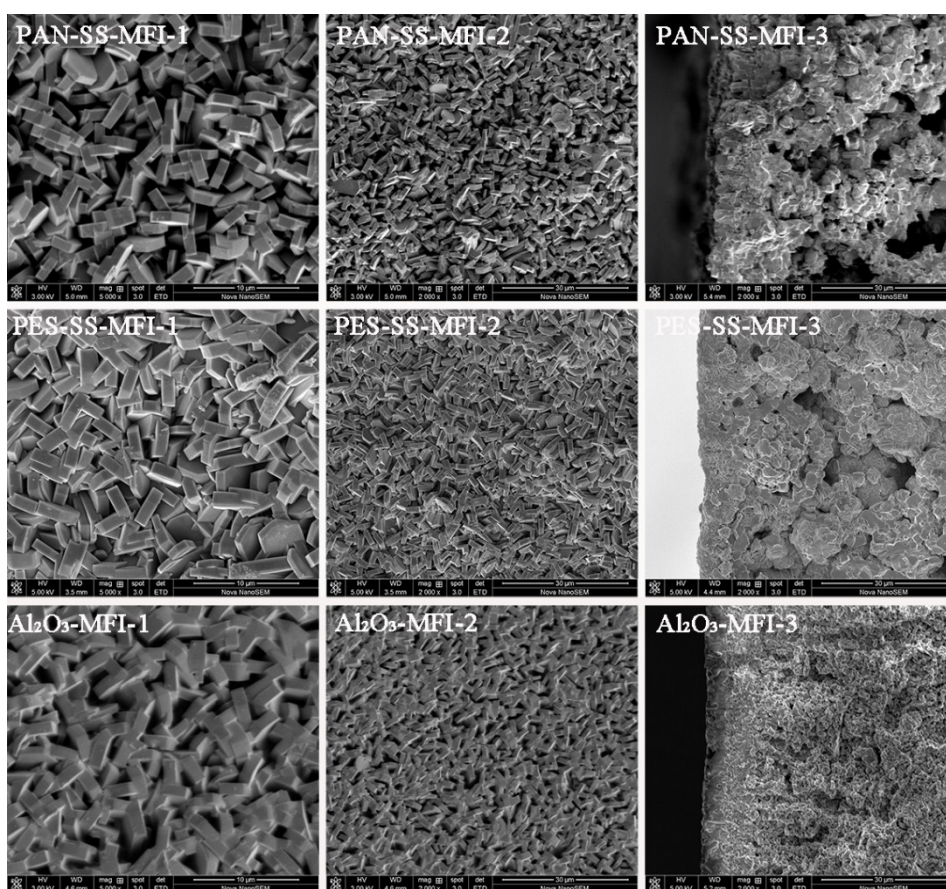


Fig. S7. SEM images of MFI membranes on different supports. 1-surfaces (5000×); 2-surfaces (2000×); 3-cross-sections (2000×)

Table S1 Effect of synthesis time on performance of MFI membranes synthesized at 130°C for ethanol/water PV

Membrane No.	Synthesis time (h)	Separation factor ( $\alpha$ )	Flux (kg/ (m <sup>2</sup> · h))
SS-MFI-8	8	49±4	1.58±0.02
SS-MFI-9	24	61±3	1.15±0.09

Table S1 shows the effect of synthesis time on performance of MFI membranes synthesized at 130°C for ethanol/water PV. With the increase of synthesis time, the separation factor increased while the flux decreased. The reason was that long synthesis time reduced the voids and increased the membrane thickness. By comparing PV performance of SS-MFI-8 with that of SS-MFI-3-2, it can also be concluded that high synthesis temperature with short time favored the preparation of high PV performance membranes.

Table S2 Effect of supports material on performance of MFI membranes for ethanol/water PV

Membrane No.	Support mean pore size ( $\mu\text{m}$ )	Support porosity (%)	Separation factor ( $\alpha$ )	Flux ( $\text{kg}/(\text{m}^2 \cdot \text{h})$ )
PAN-SS-MFI	1.75	48	65 $\pm$ 3	1.68 $\pm$ 0.16
PES-SS-MFI	1.35	38	63 $\pm$ 3	0.59 $\pm$ 0.05
Al <sub>2</sub> O <sub>3</sub> -MFI	0.33	65	16 $\pm$ 4	3.49 $\pm$ 0.31

Table S3 Performance of MFI membranes synthesized at 175°C for 6h for ethanol/water, isopropanol/water and butanol/water PV

Alcohols	Kinetic diameter (nm)	Separation factor ( $\alpha$ )	Flux ( $\text{kg}/(\text{m}^2 \cdot \text{h})$ )
Ethanol <sup>a</sup>	0.43	65 $\pm$ 3	1.68 $\pm$ 0.16
Isopropanol <sup>b</sup>	0.47	75 $\pm$ 3	0.38 $\pm$ 0.01
Butanol <sup>c</sup>	0.51	207 $\pm$ 11	0.22 $\pm$ 0.02

Operation conditions: <sup>a</sup> 5wt. % ethanol/water at 60°C, <sup>b</sup> 5wt. % isopropanol/water at 60°C, <sup>c</sup> 1.5wt. % butanol/water at 80°C.