Supporting information

Synthesis and Characterization of A Novel Type Mixed Matrix Membrane: Surface Sieving Membrane

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Experimental details

Synthesis of SAPO-34 crystals

The gel molar ratio was 1.0 Al_2O_3: 2.0 P_2O_5: 0.6 SiO_2: 4.0 TEAOH: 75 H_2O. In a typical synthesis, $Al(i\text{-}C_3H_7O)_3$ (98%), tetra-ethyl ammonium hydroxide (35 wt% aqueous solution) and DI H_2O were stirred for 3 h to form a clear solution. Then Ludox AS−40 colloidal silica (40 wt% SiO_2 suspensions in water) was added. After 3 h continuous stirring, H_3PO_4 (85 wt% aqueous solution) was added drop wise. The resulting solution was stirred overnight at room temperature. The solution was then placed in an autoclave and microwave heating (Milestone Ethos A advanced microwave system) was used to hold the solution at 453 K for 7 h. The solution was then cooled to room temperature and centrifuged at 6000 rpm for 30 min to separate the seeds, which were then washed with DI water. This centrifugation procedure was repeated three times, and the pellet was dried at 373 K overnight. After drying at 383K, the powder product was calcined at 873K for 6 h in air to remove the organic template. Detailed information can be found in J. Membr. Sci. 363 (2010), 29-35.

Membrane casting

Pure poly vinyl alcohol (PVA) membrane:

A 6 wt % PVA solution was obtained by dissolving PVA (99% hydrolyzed) in DMSO. Membranes were cast onto a glass substrate using a wire wound casting rod and the solvent was heated at 333K overnight to remove the solvent. The membrane thickness was determined using optical microscopy. Cross-sections were prepared by freeze-fracturing the membranes after several minutes of immersion in liquid N_2.

Surface sieving membrane:

The calcined SAPO-34 crystals were dispersed in anhydrous ethanol to make 0.1 ~ 1 wt% suspensions. Extensive sonication was used to disperse the SAPO-34 crystals. SAPO-34 crystals were attached to a glass substrate by dip coating method. A clean glass substrate was soaked in the suspension for 1 min, and then withdrawn vertically at a 1cm/min rate. The dip-coated glass substrate was dried at room temperature for 1 h. PVA membrane was cast on the dip-coated glass substrate using a wire wound casting rod and the casted membrane was heated at 333K overnight to remove the solvent. After peeling off the membrane from the glass substrate, a surface sieving membrane was obtained. It is worthy to point out that the surface covered by zeolite crystals is the feed side.

Pervaporation

Pervaporation experiments were performed using a laboratory pervaporation system. The membrane area was 12.6 cm^2. Membrane was sealed in a membrane module with viton o-rings and the membrane module was stored in oven with controlled temperature. A circulation pump fed the liquid mixture (methanol: dimethyl carbonate=90:10 wt%) to membrane and the pressure of feed side was at 1 atm for pervaporation separation mode. The permeate side was connected to a vacuum line and a liquid nitrogen trap was used to collect the permeated vapor. The pressure of permeate side was kept below 300 Pa.

The system was allowed to equilibrate for 2 h after reaching a test temperature. The permeate sample was collected for 2~6 h (depending on the membrane flux) and at least twice for each test condition. The weight of collected samples was recorded by a balance and the compositions of methanol-dimethyl carbonate mixtures were obtained by a gas chromatography (GC).

The pervaporation flux was calculated using the following equation:

Flux = W/At

where W (g) is the amount of the permeate collected during the experimental time interval t (h) at a steady state, A is the effective membrane area of 12.6 cm^2. The methnol/ dimethyl carbonate separation factor (α) for a membrane was calculated as follows:

$$\alpha = \frac{Y_{\mathrm{methanol}}/Y_{\mathrm{DMC}}}{X_{\mathrm{methanol}}/X_{\mathrm{DMC}}}$$

where Y and X are the weight fraction of either methanol or dimethyl carbonate in the permeate and feed, respectively.

The permeance/ selectivity of these membranes were also calculated in order to remove the effect of driving force and operation conditions. For a mixture, the permeance of component *i* is:

$$P_i = \frac{J_i}{\Delta p_i} \qquad (1)$$

where J_t (mol/(m^2·s)) is the steady-state flux of component *i* and Δp_i (Pa) is the partial pressures difference across the membrane. The separation selectivity, $\alpha_{i/j}^{sep}$, is the ratio of the permeances for mixtures.

Instrumentation

SEM images were acquired using JEOL JEM-2100 at 200 keV. X-ray diffraction (XRD) patterns were obtained with a Rigaku Ultima-III X-ray diffractometer using Cu Kα X-radiation. Thermal analyses were performed on a

Perkin-Elmer Pyris 1 differential scanning calorimetry (DSC), at a heating rate of 10 °C/min under nitrogen protection.

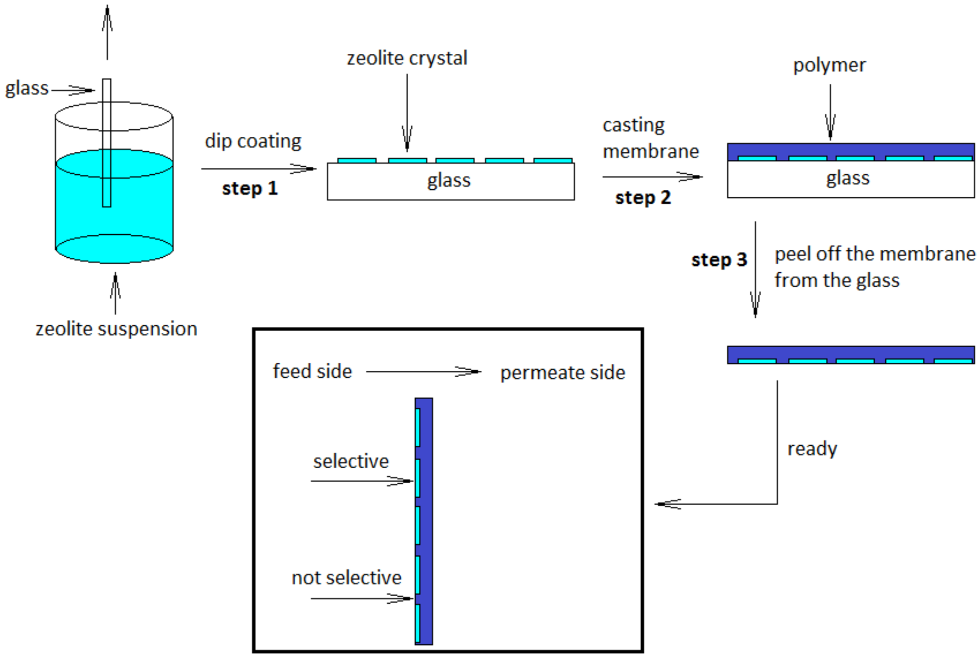


Fig S1. Preparation of surface sieving membrane.

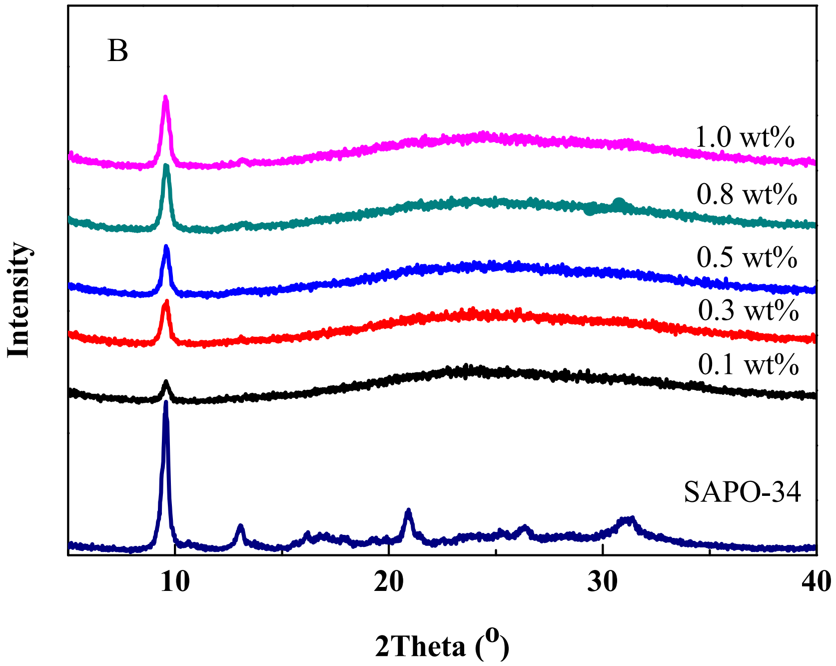
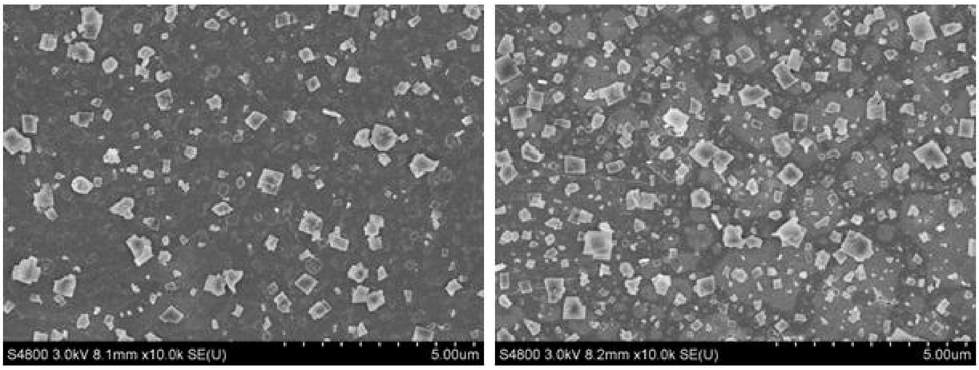
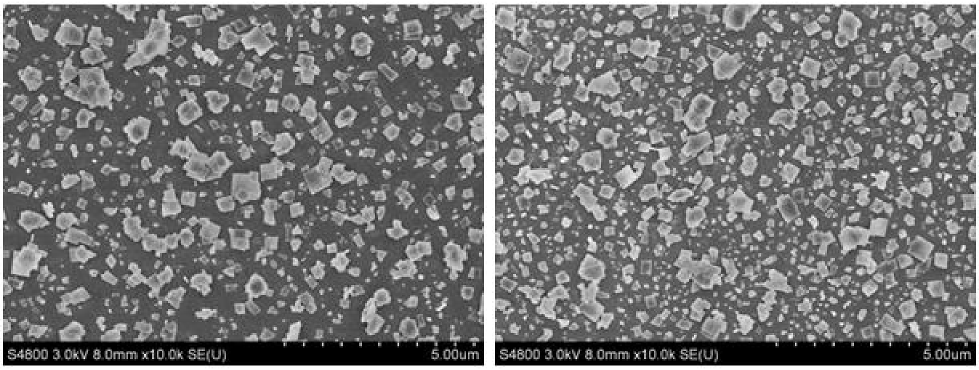


Fig S2. XRD patterns of glass substrates dip coated in SAPO-34 suspensions with different concentrations.



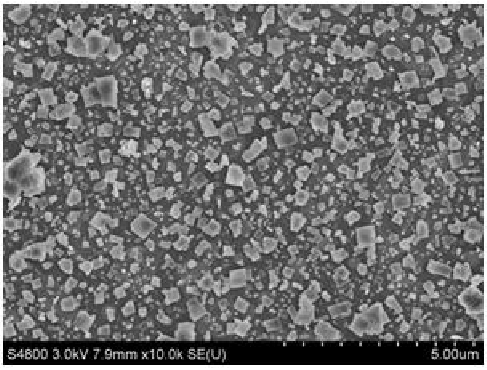
(a) 0.1 wt%

(b) 0.3 wt%



(c) 0.5 wt%

(d) 0.8 wt%



(e) 1.0 wt%

Fig S3. SEM images glass substrates dip coated in SAPO-34 suspensions with different concentrations.

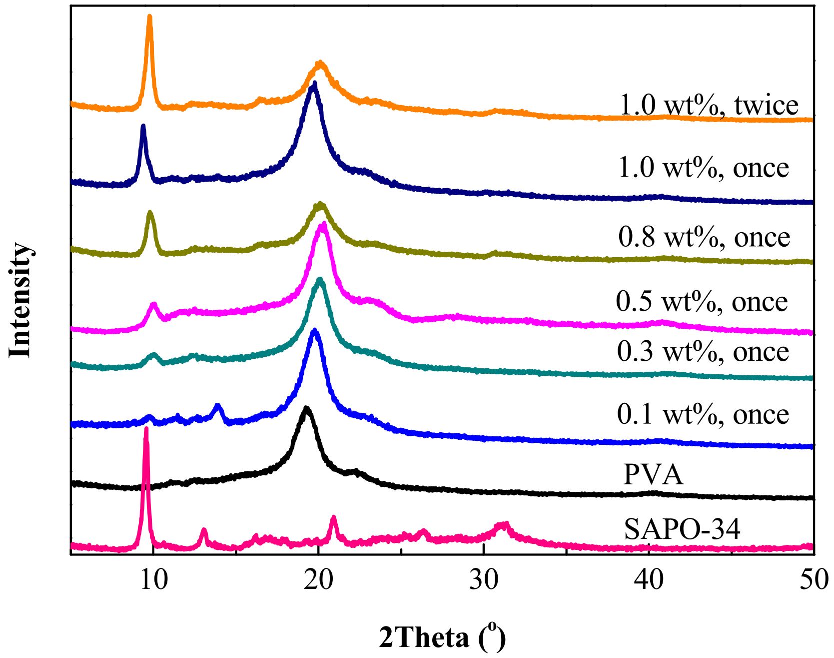
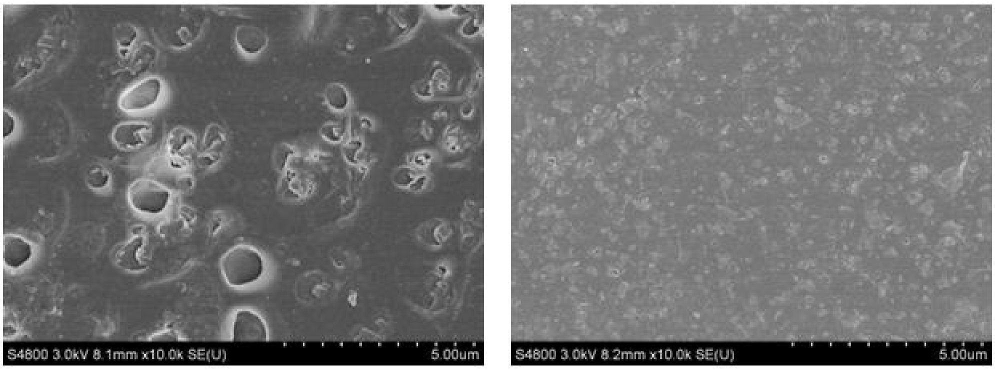
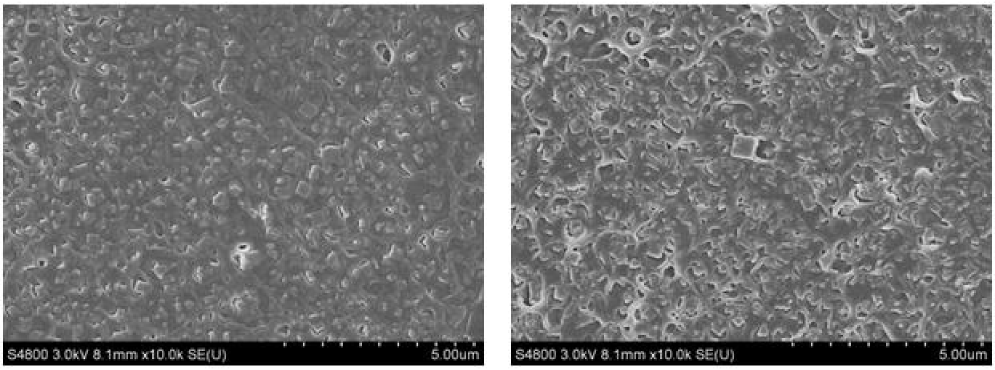


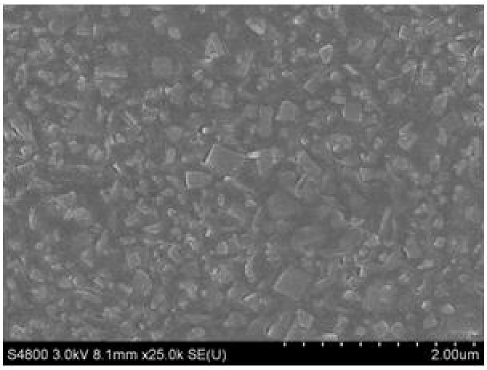
Fig S4. XRD patterns of surface sieving membranes prepared with different SAPO-34 loadings.



(a) 0.1 wt%　　(b) 0.3 wt%



(c) 0.5 wt%　　(d) 0.8 wt%



(e) 1.0 wt%

Fig S5. Top view SEM images of surface sieving membranes prepared with different SAPO-34 loadings.