Electronic Supplementary Information for

Preparation of preferentially oriented SAPO-34 membrane by secondary growth under microwave irradiation

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Experimental

Materials

All the chemical reagents were analytical grade and used without further purification. Fumed silica(Sigma-Aldrich), aluminum isopropoxide (AIP, 99%, Sigma-Aldrich), and orthophosphoric acid (H₃PO₄, 85%, Tianjin Guangfu Fine Chemical Research Institute) were utilized as silica source, aluminum source, and phosphorus source for the synthesis of SAPO-34 crystals and membranes, respectively. Tetraethylammonium hydroxide (TEAOH, 25%, Shanghai Cainorise Chemicals Co., Ltd) and dipropylamine (DPA, 99%, Tianjin Baishi Chemical Industry Co., Ltd) were used as templates. Deionized water used in all experiments was produced by a water purifier (Ulupure-II-10 T, Chengdu Ultrapure Technology Co., Ltd.) with a resistivity of 18.25 MΩ cm.

Synthesis of SAPO-34 crystals

SAPO-34 crystals were prepared by microwave heating method with a molar composition of 1.0 Al_2O_3 :1.0 P_2O_5 :0.3 SiO_2:1.2 TEAOH:0.5 DPA:52 H_2O . The synthesis gel was prepared by mixing AIP, fumed silica, TEAOH, DPA, H_3PO_4 and deionized water. After stirring at 321K for 72 h, the homogenous gel was placed in an autoclave and heated in a microwave oven (MDS-6, Sineo Microwave Chemical Technology Co., Ltd.) at 453 K for 2 h. After synthesis, the SAPO-34crystals were collected by centrifugation at 8000 rpm for 10 min. The crystals were then re-suspended with deionized water and centrifuged at 8000 rpm for 10 min to remove gel residues. This procedure was repeated five times and the resulting crystals were dried overnight at 333 K.

Synthesis of SAPO-34 membrane

SAPO-34 membrane was synthesized by secondary growth onto porous α -Al₂O₃ disk. Seed suspensions with a concentration of 0.5wt% in ethanol were coated onto the treated α -Al₂O₃ substrate by a spin-coating method. Continuous seed layer was prepared at a spinning rate of 1280 rpm for 40 s, and then dried overnight at 333 K. The coated support was placed in an autoclave and filled with synthesis gel. The gel composition for the secondary growth was 1.0 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:1.0 TEAOH:1.6 DPA:100 H₂O.The synthesis procedure is similar to that used for the crystals, except that the aging time was 24 h. The hydrothermal synthesis was carried out in a microwave oven at 453 K for 4 h. After synthesis, the membrane was washed with deionized water and dried at 378 K overnight. The templates were removed in flowing air at 663 K for 10 h with heating and cooling rates of 0.6 K/min and 0.9 K/min, respectively.

Characterizations

Scanning electron microscopy (SEM) was carried out on a Philips XL30ESEM. X-ray diffraction (XRD) measurements using K α radiation were carried out on a Rigaku D/max 2500 V/PC X-ray diffractometer. FT–IR spectrum was measured on the Thermo Nicolet 6700 spectrometer. The quality of the as-synthesized SAPO-34 membrane was checked by gas permeation based on the concentration gradient method similar to that previously reported.¹

The separation performance of SAPO-34 membrane was checked by separating CO_2/CH_4 binary gas mixture. In order to compare the separation properties of this SAPO-34 membrane and membranes reported in the literature,²⁻⁵ the same CO_2 feed concentration was used in the present work. Mixture permeations were measured at 302 K in a flow system. The membrane was mounted in a stainless steel module and sealed at each end with silicone o-rings. The zeolite layer of the membrane faced the feed side. Controlled using mass flow controllers, the CO_2/CH_4 streams were fed into the feed side at a flow rate of 80 mL min⁻¹, while the permeated gas on the permeate side was swept using N₂ at a flow rate of 10 mL min⁻¹. Permeate and retentate flow rates were monitored with bubble flowmeters. The feed and permeate pressures were 222 kPa and 84 kPa, respectively. Both feed and permeate pressures were controlled by back pressure regulators. After steady state was reached, the compositions of the feed, retentate, and permeate streams were measured using a Agilent Technologies 6890N gas chromatograph equipped with a thermal conductivity detector.

The separation selectivity, $\alpha_{i/i}$ is the ratio of the permeances for mixtures. The composition selectivity is

$$\alpha_{i/j} = \frac{x_{p,i}/x_{p,j}}{x_{f,i}/x_{f,j}}$$

where $x_{f,i}$ and $x_{p,i}$ are the mole fractions of component *i* in the feed and permeate, respectively.

Notes and references

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