Supporting Information

AlPO-18 Membranes for CO₂/CH₄ Separation

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Experimental

1. Synthesis of AlPO-18 seeds

In a typical synthesis, 6.2 g of aluminum isopropoxide (Al(i-C₃H₇O)₃, >99.99% metal basis, Aldrich), 23 g of deionized H₂O, and 40.2 g of tetraethylammonium hydroxide ((C₂H₅)₄NOH, 35 wt %, Sigma-Aldrich) were stirred for about 2 h to form a homogeneous solution. To this solution, 11 g of phosphoric acid (H₃PO₄, 85 wt %, Aldrich) was added dropwise, and the solution was aged for 24 hrs at room temperature under vigorous stirring. The solution was then placed in a sealed Teflon-lined autoclave (Parr Instrument Company) under autogenous pressure and treated hydrothermally at 473 K for 72 h in a conventional oven. After the solution was cooled to room temperature, the seeds were centrifuged at 4000 rpm for 15 min to separate the seeds and the seeds were washed with deionized water. Centrifugation-washing process was
repeated 3 times. The resultant precipitate was dried overnight at 343 K. The template was removed from the SAPO-34 framework by calcination at 773 K using flowing air in a computer-controlled muffle furnace, using a ramp procedure at heating and cooling rates of 1 K/min and 10 K/min respectively. The seed gel molar ratio was: 1Al₂O₃:3.15P₂O₅:6.3TEAOH:185H₂O. In addition, AlPO-18 seeds were prepared using aluminum tri-sec-butoxide (C₁₂H₂₇AlO₃, 97% Aldrich) as the aluminium source, and following the same procedure as above, and the same seed gel molar ratio.

2. AlPO-18 seeds characterization

The morphological features of AlPO-18 crystals were inspected with a FE-SEM (FEI Nova 600) with an acceleration voltage of 6 kV. The crystalline structure was analyzed by XRD patterns collected on a Bruker D8 Discover diffractometer at 40 kV, 40mA with Cu Kα radiation. The surface area and adsorption-desorption isotherm measurements were carried out on MicromeriticsTristar 3000 porosimeter at 77 K using liquid nitrogen as coolant. Prior to the nitrogen adsorption experiments, the samples were degassed at 573 K for 3 h.

3. Separation performance

The separation performance of the AlPO-18 membranes for equimolar CO₂/CH₄ gas mixtures was evaluated in flow separation system described elsewhere. The membranes were mounted in a stainless steel module with silicone O-rings as seals on both ends. The pressure on each side of the membrane was independently controlled. The driving force across the membrane was provided by pressure drop. In all separation experiments, the pressure drop was 138 KPa and the permeate pressure was 99.5 KPa (atmospheric pressure). The gas flux was measured by a soap
film bubble flow meter. The total feed flow rate was 100 mL/min. The compositions of the feed, retentate, and permeate streams were measured, after attaining the steady state, using a CARLE Series 400 gas chromatograph equipped with a thermal conductivity detector and HAYESEP-A column. The oven was kept at 60 °C. Because one component preferentially permeates through the membrane in the cross-flow configuration, the partial pressures in the feed and retentate are quite different. Therefore, a logarithm of the mean partial pressure drop was used to calculate the driving force. The separation selectivity was determined as the ratio of the permeances. The permeances were calculated as the fluxes divided by the partial pressure driving forces.

b) S.R. Venna, M.A.Carreon, *Journal of the American Chemical Society* 2010, **132**, 76.

*Figure S1.* XRD pattern of the ALPO-18 membrane (M1)