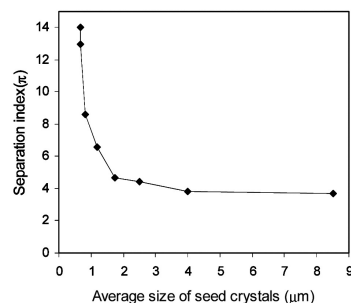
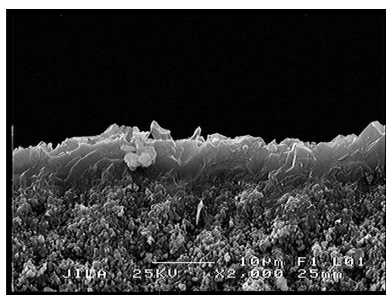


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## Alumina-Supported SAPO-34 Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation

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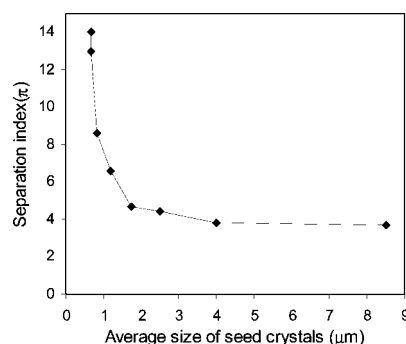
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Carbon dioxide is an impurity in many natural gas wells, and it must be removed because it reduces the energy content of the gas, and it is acidic and corrosive in the presence of water. Improved membranes for separating CO<sub>2</sub> from CH<sub>4</sub> would reduce the costs of natural gas purification.<sup>1</sup> Polymeric membranes can separate CO<sub>2</sub>/CH<sub>4</sub> mixtures, but high CO<sub>2</sub> pressures plasticize them and decrease their separation ability.<sup>2</sup> Lin et al.<sup>3</sup> reported that CO<sub>2</sub> pressures up to at least 1.7 MPa increased permeabilities and selectivities for highly branched, cross-linked poly(ethylene oxide) membranes, but natural gas well pressures can be 7 MPa and higher. Zeolite membranes have been used to separate CO<sub>2</sub> from CH<sub>4</sub> at these higher pressures. They are ideal for this separation because of their superior thermal, mechanical, and chemical stability, good erosion resistance, and stability at high CO<sub>2</sub> pressures. Zeolite T,<sup>4</sup> DDR,<sup>5</sup> silicalite-1,<sup>6</sup> and SAPO-34<sup>7–13</sup> have been reported for CO<sub>2</sub>/CH<sub>4</sub> separations. These small-pore zeolite membranes display high CO<sub>2</sub>/CH<sub>4</sub> selectivities due to a combination of differences in diffusivity and competitive adsorption.

We recently reported SAPO-34 membrane synthesis on porous stainless steel tubes using multiple structure-directing agents (SDAs).<sup>13</sup> These membranes displayed CO<sub>2</sub>/CH<sub>4</sub> separation selectivities as high as 227, with CO<sub>2</sub> permeances higher than  $3.6 \times 10^{-7}$  mol/m<sup>2</sup>·s·Pa at 295 K for a feed pressure of 224 kPa. In this paper, we report SAPO-34 membranes prepared using different pivotal crystallization templates and secondary structure-directing agents on porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports. The CO<sub>2</sub>/CH<sub>4</sub> separation performance depends on the sizes of the zeolite crystals used as seeds for membrane growth. Crystals smaller than 1  $\mu$ m yielded membranes that displayed unprecedented CO<sub>2</sub> permeances with high CO<sub>2</sub>/CH<sub>4</sub> selectivities. The membranes effectively separated CO<sub>2</sub>/CH<sub>4</sub> mixtures up to  $\sim$ 1.7 MPa, the highest pressure that could be used for a zeolite layer on the inside of the ceramic support.

The crystal size of the SAPO-34 seeds was controlled in the 0.7 to 8.5  $\mu$ m range by employing different SDAs.<sup>14</sup> The XRD patterns<sup>14</sup> indicated that all crystals have the chabazite structure of SAPO-34.<sup>15</sup> Figure 1 shows the CO<sub>2</sub>/CH<sub>4</sub> separation performance of SAPO-34 membranes as a function of average size of the seed crystals. Seeds less than 1  $\mu$ m produced membranes with superior separation performance. Smaller seeds, with a narrow size distribution, have the potential to close pack more homogeneously than larger crystals, so that the intercrystalline regions that need to intergrow are smaller, and thinner membranes can be prepared. Therefore, only seeds smaller than 1  $\mu$ m, with a narrow size distribution, were used for subsequent membrane preparation. The SAPO-34 membranes were prepared



**Figure 1.** Separation index  $\pi$  [(CO<sub>2</sub> permeance  $\times$  (selectivity - 1))  $\times$  permeate pressure] versus average size of SAPO-34 seed crystals.

**Table 1.** CO<sub>2</sub>/CH<sub>4</sub> Separation Properties for SAPO-34 Membranes (M) at a Permeate Pressure of 84 kPa and a Pressure Drop of 138 kPa.

M	seed size ( $\mu$ m)	$P_{\text{CO}_2}$ ( $\times 10^6$ ) <sup>a</sup>	$P_{\text{CH}_4}$ ( $\times 10^6$ ) <sup>a</sup>	CO <sub>2</sub> /CH <sub>4</sub> selectivity	$\pi$
A1	0.8 $\pm$ 0.1	1.0	1.2	86	7.4
A2	0.8 $\pm$ 0.1	1.0	1.1	99	8.6
A3	0.7 $\pm$ 0.1	1.2	0.9	131	13
A4	0.7 $\pm$ 0.1	2.0	2.3	86	14
A5	0.7 $\pm$ 0.1	1.8	1.0	171	25

<sup>a</sup> Permeance (mol/m<sup>2</sup>·s·Pa).

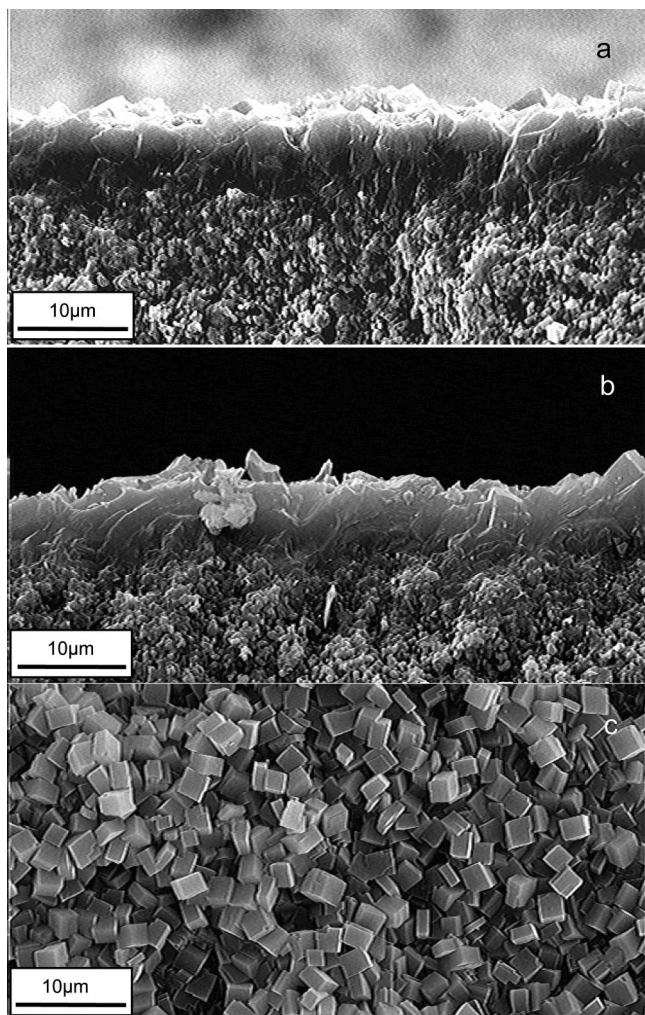
on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports by secondary seeded growth using two gel compositions and one or two synthesis steps.<sup>14</sup> Membrane secondary growth by seeds has been reported for LTA,<sup>16</sup> MFI,<sup>17</sup> and FAU<sup>18</sup> zeolites.

As shown in Table 1, the separation performance was highly dependent on the gel composition and the number of zeolite layers. Membranes prepared with one layer were about 6  $\mu$ m thick, whereas membranes prepared with two layers were  $\sim$ 7.5  $\mu$ m thick (Figure 2). The small difference in thicknesses suggests that the first layer partially dissolved during synthesis of the second layer. The second layer helped to decrease non-zeolite pores and thus increased the CO<sub>2</sub>/CH<sub>4</sub> selectivity (Membrane A5).

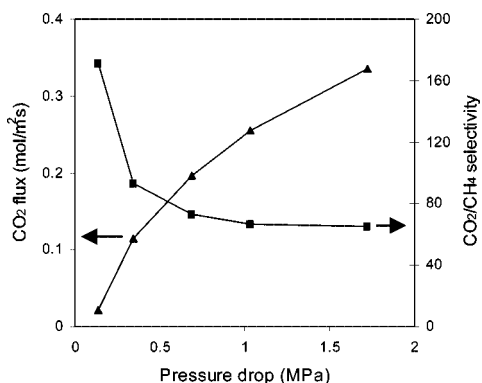
The membranes had CO<sub>2</sub>/CH<sub>4</sub> separation selectivities higher than 170, with CO<sub>2</sub> permeances as high as  $\sim 2 \times 10^{-6}$  mol/m<sup>2</sup>·s·Pa at 295 K and a feed pressure of 224 kPa. The size of the zeolite nanocrystal allowed the formation of thin membranes in which crystal inclusion in the pores of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports was minimum.<sup>14</sup> Also, as shown in Table 1, decreasing the seed crystal size from 0.8  $\pm$  0.1 to 0.7  $\pm$  0.1  $\mu$ m almost doubled the separation index. The addition of a second layer further improved the separation performance. The chemical compositions measured by ICP were similar to the synthesis gel composition (Si/Al = 0.15, P/Al = 1.0). For membranes prepared with a DPA/TEAOH ratio of 1.6, the ICP composition was Si/Al = 0.17 and P/Al = 1.07. For the membrane prepared

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**Figure 2.** SEM images of SAPO-34 membranes on  $\alpha$ - $\text{Al}_2\text{O}_3$  supports: cross section of membrane with (a) one synthesis layer, (b) two synthesis layers, and (c) top view of membrane with one synthesis layer.



**Figure 3.**  $\text{CO}_2$  flux and  $\text{CO}_2/\text{CH}_4$  selectivity for a 50:50  $\text{CO}_2/\text{CH}_4$  mixture at 295 K as a function of pressure drop for SAPO-34 Membrane A5. The permeate pressure was 84 kPa.

with a DPA/TEAOH ratio of 3.2, the ICP composition was Si/Al = 0.17 and P/Al = 1.04.

The high  $\text{CO}_2$  permeances observed in these membranes are not only due to the presence of small zeolite crystals with narrow size distributions, which lead to 6–7.5  $\mu\text{m}$  thin membranes, but also due to the interaction between the zeolite layer and the alumina support and the structural properties of the support. The  $\alpha$ - $\text{Al}_2\text{O}_3$  support is composed of two well-defined regions, an outer  $\sim 40$

$\mu\text{m}$  thick layer with 0.2  $\mu\text{m}$  average pore size, and a porous area with 0.8  $\mu\text{m}$  average pore size. The 0.2  $\mu\text{m}$  layer provides a smoother surface than on stainless steel supports, and this results in more uniform intergrowth between the zeolite crystals at the support interface, and thus high-quality zeolite membranes were formed. The 0.8  $\mu\text{m}$  average pore size region ( $\sim 35\%$  porosity versus  $\sim 17\%$  porosity on stainless steel supports<sup>13</sup>) results in higher fluxes. Zeolite/support microstructure correlates with isomer separation performance for MFI membranes.<sup>19–21</sup>

Membrane A5 was used to separate an equimolar  $\text{CO}_2/\text{CH}_4$  mixture at feed pressures up to 1.7 MPa. Higher pressures were not used to avoid breaking the alumina supports because the SAPO-34 layer was on the inside of the tube. These supports can withstand much larger pressure drops if the high pressure is on the outside of the support. Since carbon dioxide adsorbs more strongly than  $\text{CH}_4$ , it approached saturation at lower pressure than  $\text{CH}_4$ , so the  $\text{CO}_2/\text{CH}_4$  selectivity decreased as the pressure increased. At a pressure drop of 1.7 MPa, the  $\text{CO}_2$  permeance was  $0.58 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$  and the  $\text{CO}_2/\text{CH}_4$  selectivity was 65 (Figure 3).

In conclusion, reproducible SAPO-34 membranes (6–7.5  $\mu\text{m}$  thick) were synthesized by secondary seeded growth on  $\alpha$ - $\text{Al}_2\text{O}_3$  porous supports. Seeds smaller than 1  $\mu\text{m}$  displayed superior separation performance. The membranes had  $\text{CO}_2/\text{CH}_4$  separation selectivities higher than 170, with  $\text{CO}_2$  permeances as high as  $\sim 2.0 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$  at 295 K and a feed pressure of 224 kPa. The membranes effectively separated  $\text{CO}_2/\text{CH}_4$  mixtures up to 1.7 MPa.

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**Supporting Information Available:** Experimental methods. Synthesis conditions of Membranes A1–A5. SEM and XRD of SAPO-34 seeds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Lin, H.; Van Wagner, E.; Raharjo, R.; Freeman, B. D.; Roman, I. *Adv. Mater.* **2006**, *18*, 39–44.
- (2) Koros, W. J.; Majan, R. *J. Membr. Sci.* **2000**, *175*, 181–196.
- (3) Lin, H.; Van Wagner, E.; Freeman, B. D.; Toy, L. G.; Gupta, R. P. *Science* **2006**, *311*, 639–642.
- (4) Cui, Y.; Kita, H.; Okamoto, K.-I. *J. Mater. Chem.* **2004**, *14*, 924–932.
- (5) Tomita, T.; Nakayama, K.; Sakai, H. *Microporous Mesoporous Mater.* **2004**, *68*, 71–75.
- (6) Guo, H.; Zhu, G.; Li, H.; Zou, X.; Yin, X.; Yang, W.; Qiu, S.; Xu, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 7053–7056.
- (7) Poshusta, J. C.; Tuan, V. A.; Falconer, J. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **1998**, *37*, 3924–3929.
- (8) Poshusta, J. C.; Tuan, V. A.; Pape, E. A.; Noble, R. D.; Falconer, J. L. *AIChE J.* **2000**, *46*, 779–789.
- (9) Li, S.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **2004**, *241*, 121–135.
- (10) Li, S.; Martinek, J. G.; Falconer, J. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **2005**, *44*, 3220–3228.
- (11) Li, S.; Alvarado, G.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **2005**, *251*, 59–66.
- (12) Li, S.; Falconer, J. L.; Noble, R. D. *Adv. Mater.* **2006**, *18*, 2601–2603.
- (13) Carreon, M. A.; Li, S.; Falconer, J. L.; Noble, R. D. *Adv. Mater.* **2008**, *20*, 729–732.
- (14) See Supporting Information.
- (15) Thompson, R. W. In *Recent Advances in the Understanding of Zeolite Synthesis: Molecular Sieves*; Karge, H. G., Weitkamp, J., Eds.; Springer: Berlin, Heidelberg, 1998; Vol. 1.
- (16) Hedlund, J.; Schoeman, B.; Sterte, J. *Chem. Commun.* **1997**, *13*, 1193–1194.
- (17) Lovallo, M. C.; Gouzinis, A.; Tsapatsis, M. *AIChE J.* **1998**, *44*, 1903–1913.
- (18) Kusakabe, K.; Kuroda, T.; Morooka, S. *J. Membr. Sci.* **1998**, *148*, 13–23.
- (19) Hedlund, J.; Sterte, J.; Anthonis, M.; Bons, A.-J.; Carstensen, B.; Corcoran, N.; Cox, D.; Deckman, H.; Gijst, W.; Moor, P.-P.; Lai, F.; McHenry, J.; Mortier, W.; Reinoso, J.; Peters, J. *Microporous Mesoporous Mater.* **2002**, *52*, 179–189.
- (20) Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J. G.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. *Science* **2003**, *300*, 456–460.
- (21) Choi, J.; Ghosh, S.; King, L.; Tsapatsis, M. *Adsorption* **2006**, *12*, 339–360.

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