

## Molecular Sieving MFI-Type Zeolite Membranes for Pervaporation Separation of Xylene Isomers

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Zeolite membranes are a new class of membranes with distinct permeation/separation properties.<sup>1</sup> In the past few years, various research groups have reported synthesis of good quality zeolite membranes without meso- and macroporous defects. These zeolite membranes are of polycrystalline microstructure, consisting of the zeolitic pores with minimized gaps between the zeolite crystallites. Most of these zeolite membranes exhibit excellent vapor or liquid separation properties for molecules smaller than the zeolitic pores. The differences in the chemical affinities, rather than the shape or size with respect to the zeolite pore, for the permeating molecules often determine the separation properties of the zeolite membranes for these molecules.<sup>2</sup>

Separation of *p*-xylene (molecular size ~0.58 nm) from its bulkier *m*- and *o*-isomers (~0.68 nm) is of great importance in the petrochemical industry. Many research groups have studied silicalite ( $d_p \approx 0.6$  nm) membranes for xylene separation.<sup>3–7</sup> Recently, Tsapatsis and co-workers<sup>8</sup> reported the best results on MFI-type zeolite membranes for vapor permeation separation of xylene isomers. The b-channel-oriented zeolite membrane was obtained by a secondary growth method with a b-oriented seed layer and use of trimer-TPA as a template in the secondary growth step. The membrane offers *p*-xylene permeance of about  $2 \times 10^{-7}$  mol/m<sup>2</sup>·s·Pa with *p*- to *o*-xylene separation factor up to about 500.

Most studies on xylene separation by zeolite membranes, including the work of Tsapatsis and co-workers summarized above,<sup>8</sup> dealt with vapor permeation with xylene feed at very low partial pressure (low concentration) (e.g., 0.45 kPa, about 0.1% of its saturated vapor pressure at 200 °C). The separation factor decreases with increasing partial pressure of *p*-xylene.<sup>7,9</sup> For separation of a liquid mixture such as xylene isomers it is more desirable to operate the membrane process in the pervaporation mode in which the feed is a liquid and the permeate is a vapor. For separation of bulky molecules including xylene isomers by a zeolite membrane it is known that a membrane offering good separation properties for vapor permeation often exhibits poor separation properties for similar mixtures when operated in pervaporation mode.<sup>10</sup>

The objective of this communication is to report template-free synthesis of zeolite silicalite membranes with minimized intercrystalline pores and excellent performance of the zeolite membrane for pervaporation separation of xylene isomers. Vapor separation data of hydrocarbons and hydrogen by the zeolite membranes prepared by the template-free method are also reported, and the results are compared with silicalite membranes prepared by the well-established in situ method with a template.

Silicalite membrane prepared by in situ synthesis with an organic template shows excellent performance for separation of small gas molecules based on the difference in adsorption affinities of the permeating molecules with silicalite pores. These silicalite mem-

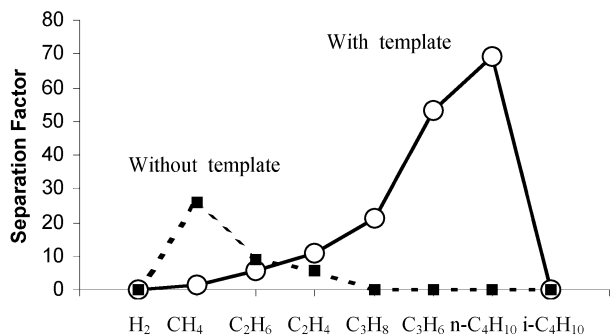
branes were synthesized through nucleation and growth of silicalite crystallites on  $\alpha$ -alumina support in a synthesis solution with composition of 20 g of silica (fumed silica, 99.98%, from Aldrich), 1.4 g of 1 M NaOH, and 100 mL of 1 M organic template (tetrapropylammonium hydroxide, TPAOH), at 185 °C for 4 h.<sup>2,3</sup> The dried silicalite membrane was gastight to helium, indicating good integrity of the silicalite film prepared. The silicalite membrane was calcined at about 400 °C to remove the template. Helium permeance measurement and XRD analyses were conducted on an as-synthesized silicalite membrane at different temperatures (starting from 20 to 450 °C). The results show that the membrane remains gastight until around 400 °C, at which time helium permeance increases sharply, and the silicalite crystals shrink due to removal of the template molecules from the silicalite pores. Silicalite crystals after template removal are smaller than the as-synthesized silicalite. These changes in the silicalite crystal volumes may create or enlarge intercrystalline gaps and impair other properties of zeolites.<sup>11</sup>

In this work, the template removal step was avoided by the following synthesis strategy and method. First, nanosized silicalite powder was prepared by hydrothermal synthesis of starting solution with a composition of 1 g of SiO<sub>2</sub>, 5 mL (1 M) of TPAOH, and 0.07 g of NaOH at 120 °C for 12 h. The silicalite crystals were purified by repeated centrifugation washes with deionized water, and a stable silicalite sol was then prepared from the silicalite powder with 0.5 wt % hydroxy propyl cellulose (HPC) (MW = 100 000 g/mol) solution and deionized water (solution composition: 1 g of silicalite, 0.14 g of HPC, and 94 mL of H<sub>2</sub>O). Second, a continuous zeolite layer consisting of mesopores (intercrystalline pores) and micropores (intracrystalline zeolitic pores) was coated on a porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support disk ( $d_p \approx 200$  nm) by dip-coating the support with the silicalite solution mentioned above (after adjusting the pH of the solution from about 10 to 3–4 by addition of HNO<sub>3</sub>), followed by drying and calcination at 450 °C to remove the template. Third, the supported mesoporous–microporous silicalite layer was brought in contact with a template-free silicalite synthesis solution with the composition of 0.16 g of NaOH, 1 g of SiO<sub>2</sub>, and 10.5 g of H<sub>2</sub>O at 180 °C for 4 h. This third step allowed intergrowth of the silicalite crystallites in the film formed by dip-coating in the second step. No template removal step was required for the silicalite membrane after the third step.

XRD analysis on the surface of the membranes prepared confirmed the formation of a zeolite layer of MFI structure on the  $\alpha$ -alumina support. Cross-sectional SEM analysis shows a silicalite layer thickness of about 3–5  $\mu$ m. The silicalite membranes were impermeable to 1,3,5-triisopropylbenzene (flux  $< 0.8 \times 10^{-3}$  kg/m<sup>2</sup>·h) as confirmed by pervaporation experiments with TIPB (97%, Aldrich) at 25 °C for 6 h. These silicalite membranes after TIPB pervaporation test were calcined at 350 °C (heating and cooling rate of 0.5 °C/min) to remove the adsorbed TIPB molecules before performing the gas separation and pervaporation experiments with

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**Figure 1.** Separation factor for various species in the eight-component gas mixture for silicalite membrane prepared, respectively, by the secondary growth method without template and in situ method with template (after template removal) at 25 °C.

**Table 1.** Pure Xylene Pervaporation Results for Two Silicalite Membranes Prepared by Template-Free Secondary Growth on One-Time Dip-Coated Supports

sample	flux ( $10^{-2}$ kg/m <sup>2</sup> ·hr)			separation factor	
	<i>p</i> -xylene	<i>o</i> -xylene	<i>m</i> -xylene	p/m	p/o
SS1	26.4	1.1	1.2	24	21
SS2	24.3	1.3	1.5	19	16

xylenes. Pure helium permeance for the silicalite membrane prepared without a template is about  $4 \times 10^{-7}$  mol/m<sup>2</sup>·s<sup>1</sup>·Pa<sup>1</sup> at room temperature, about 2 times smaller than the silicalite membrane of similar thickness prepared by the in situ method with a template.

Multicomponent gas permeation through the silicalite membrane with a gas mixture (a simulated refinery gas) of H<sub>2</sub> (mol % = 84.5), CH<sub>4</sub> (7.6), C<sub>2</sub>H<sub>6</sub> (2.5), C<sub>2</sub>H<sub>4</sub> (2.5), C<sub>3</sub>H<sub>8</sub> (0.75), C<sub>3</sub>H<sub>6</sub> (1.4), *n*-C<sub>4</sub>H<sub>10</sub> (0.4), and *i*-C<sub>4</sub>H<sub>10</sub> (0.3) as the feed at 1 atm and helium as the purge was measured for the template-free silicalite membrane in the separation setup described elsewhere.<sup>2</sup> The results of the separation factor, defined as the ratio of  $[Y_i/(1 - Y_i)]$  for species *i* in the permeate to that in the retentate, for the template-free silicalite membrane are compared in Figure 1, with the results for the silicalite membrane prepared by the in situ method with a template. The separation factor is indicative of permeability of various species for the silicalite membranes. For both membranes, *i*-C<sub>4</sub>H<sub>10</sub> and hydrogen are not permeable due to, respectively, the bulky molecule with slow mobility (*i*-C<sub>4</sub>H<sub>10</sub>) and blockage of other hydrocarbons filled in the membrane pores (H<sub>2</sub>). For other hydrocarbons, the permeability increases with increasing molecular weight (or adsorption affinity with hydrophobic silicalite) for the silicalite membrane prepared by the method with a template. This permeability versus the molecular weight relationship is reversed for the silicalite membrane prepared without a template.

Xylene pervaporation experiments were conducted with pure *o*-, *m*-, and *p*-xylene (purity: *o*-xylene: 98%, *m*-xylene: >99%, *p*-xylene: 99%, all from Aldrich) or a mixture of equal molar binary *o/p*-xylene and *m/p*-xylene as the feed (no dilution) at 1 atm and 50 °C by the same procedure reported previously.<sup>3</sup> Table 1 shows single permeation flux through silicalite membranes prepared by the secondary growth method without a template on one-time dip-coated silicalite membranes. As shown, the *p*-xylene to *o*- or *m*-xylene ideal separation factor of about 20 is obtained for both membrane samples. *o*-Xylene is slightly less permeable than *m*-xylene. Table 2 shows *p*-xylene and *o*-xylene permeation flux and their ideal and real separation factor on silicalite membrane samples prepared by the template-free method on two-time dip-coated mesoporous–microporous silicalite supports. As compared to Table 1, these samples listed in Table 2 offer better separation

**Table 2.** Pure and Binary Xylene Pervaporation Results for Two Silicalite Membranes Prepared by Template-Free Secondary Growth on Two-Time Dip-Coated Supports

parameter	with template		without template	
	pure	mixture	pure	mixture
flux for <i>p</i> -xylene <sup>a</sup>	34	15	28.2	13.7
flux for <i>o</i> -xylene	27	15	0.4	0.3
p/o separation factor	1.2	1	69	40

<sup>a</sup> Unit for flux ( $10^{-2}$ kg/m<sup>2</sup>·hr).

results than the silicalite membranes prepared on a one-time coated mesoporous–microporous silicalite layer. This indicates that the second time dip-coating repaired macroscopic defects on the one-time dip-coated silicalite layer. Thus, the secondary grown silicalite film on the two-time dip-coated samples has fewer macroscopic defects. Table 2 also compares the pervaporation flux and separation factor data on two template-free synthesized silicalite membranes with those of macroscopic defect-free silicalite membranes prepared by the in situ synthesis methods. As shown, the silicalite membranes prepared by the new method exhibit a slightly lower pervaporation flux but much higher separation factor (about 50–60). This is the best pervaporation separation result (in terms of both flux and selectivity) for xylene separation ever reported on any membrane.

Good quality silicalite membranes lack macroscopic or mesoscopic scale defects or pinholes. The silicalite membranes synthesized by the in situ method with a template contain microporous intercrystalline pores formed during the template removal step. The microporous intercrystalline pores may impair the molecule size-sensitive diffusivity offered by the silicalite intracrystalline pores. These membranes provide permselectivity based on the adsorption properties between the permeating molecules and silicalite. The silicalite membranes prepared by the secondary growth method without template contain much fewer or no intercrystalline pores (or intercrystalline gaps) and offer permselectivity based on the differences in the molecule size-sensitive intracrystalline (zeolitic) diffusivity. This explains why, for the C1–C4 hydrocarbons (excluding *i*-C<sub>4</sub>H<sub>10</sub>), the permeability decreases with increasing molecular size (or intracrystalline diffusivity) and increases with chain length (or adsorption affinity) for the membranes prepared without or with a template, respectively (Figure 1). In the case of xylene isomers, the bulky *o*- or *m*-xylenes are much slower to diffuse through the silicalite intracrystalline pores than *p*-xylene. As a result, the silicalite membranes prepared by the template-free method exhibit excellent molecular sieving properties for separation of liquid and gas (vapor) molecules of different sizes and structures.

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## References

- Lin, Y. S.; Kumakiri, I.; Nair, B. N.; Alsyouri, H. *Sep. Purif. Methods* **2002**, *32*, 229.
- Dong, J.; Liu, W.; Lin, Y. S. *AIChE J.* **2000**, *46*, 1957.
- Wegner, K.; Dong, J.; Lin, Y. S. *J. Membr. Sci.* **1999**, *158*, 17.
- Keizer, K.; Burggraaf, A. J.; Vroon, Z. A. E. P.; Verweij, H. *J. Membr. Sci.* **1998**, *147*, 159.
- Baertsch, C. D.; Funke, H. H.; Falconer, J. L.; Noble, R. D. *J. Phys. Chem.* **1996**, *100*, 7676.
- Sakai, H.; Tomita, T.; Takahashi, T. *Sep. Purif. Technol.* **2001**, *25*, 297.
- Xomeritakis, G.; Tsapatsis, M. *Chem. Mater.* **1999**, *11*, 875.
- Lai, Z. P.; 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.
- Xomeritakis, G.; Lai, Z. P.; Tsapatsis, M. *Ind. Eng. Chem. Res.* **2001**, *40*, 544.
- Flanders, C. L.; Tuan, V. A.; Noble, R. D.; Falconer, J. L. *J. Membr. Sci.* **2000**, *176*, 43.
- Lee, H.; Zones, S. I.; Davis, M. E. *Nature* **2003**, *425*, 385.

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