

A novel method for the synthesis of high performance silicalite membranes

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Silicalite membranes have been successfully synthesized onto mullite tubular supports by *in-situ* hydrothermal synthesis for only 8 h of crystallization, and showed high ethanol permselectivity for pervaporation of ethanol/water mixtures.

Zeolite membranes have strong potential applications for gas separation, pervaporation, and membrane reactors, especially MFI (silicalite and ZSM-5) membranes. On the other hand, less attention has been paid to pervaporation separation through zeolite membranes, even though zeolite A membranes are commercialized on a large scale by Mitsui Engineering Co. Ltd, in cooperation with Yamaguchi University, for dehydration of organic liquids. Silicalite membranes with hydrophobic properties exhibit preferentially selective permeation of organic components in contrast to zeolite A membranes. In 1994, Sano *et al.*¹ first reported that a separation factor of about 60 for ethanol (EtOH)/water mixtures was obtained for their silicalite membrane formed on a stainless steel disk with a crystal layer thickness of 400–500 μm , and further improved the separation factor up to 120 for 144 h crystallization in 1998.² They also prepared silicalite membranes on alumina disks, but their selectivity of 19 was much lower compared with that on the stainless steel support. Later, several groups tried to synthesize MFI membranes on tubular supports and made some progress. For example, separation factors of 11–44 were achieved.^{3–5} However, the pervaporation performance of these membranes reported in the literature is still not good enough for industrial applications. Furthermore, various strategies have been successfully developed for the production of good quality zeolite membranes on various porous supports,^{6–9} especially on flat discs. Considering practical applications, preparation of reproducible and high performance MFI zeolite membranes on cheaper porous tubular supports on a large scale, in which the cost greatly reduces, is still a challenge. In this paper, we report a simple and effective method to synthesize high performance silicalite membranes on mullite tubular supports for the shortest hydrothermal synthesis time among all the published papers.

A clear solution for the synthesis of silicalite membranes was prepared by mixing and stirring tetraethyl orthosilicate (TEOS, Aldrich), tetrapropylammonium hydroxide (TPAOH) and water at room temperature for 1 h. The resultant molar composition is $\text{SiO}_2:0.17\text{TPAOH}:120\text{H}_2\text{O}$. In such a Na-free medium, less gelation would affect the crystal growth onto the surface of a seeded support. A mullite porous tube with a pore size of 1 μm was chosen as the support because it is much cheaper than pure $\alpha\text{-Al}_2\text{O}_3$ tubes, especially at pore sizes of less than 1 μm . Before *in-situ* hydrothermal synthesis, mullite tubes were simply rubbed with a slurry of H-ZSM-5 ($\text{Si}/\text{Al} = \infty$, Tosho Comp.). This seeding method was first used for the synthesis of zeolite A membranes by Kita *et al.*¹⁰ which has been identified as an effective and reproducible seeding method.^{11,12} The seeded support was vertically immersed in the synthesis solution. Crystallization was carried out at 175 $^\circ\text{C}$ or 185 $^\circ\text{C}$ for 8 h. After crystallization, the sample was taken out, washed carefully with hot distilled water, dried at 100 $^\circ\text{C}$ for several hours, and then calcined at 400 $^\circ\text{C}$ for 20–40 h at a heating rate of 1 $^\circ\text{C min}^{-1}$.

The SEM surface view of the mullite support shown in Fig. 1 clearly indicates that the morphology is quite different from that of pure $\alpha\text{-Al}_2\text{O}_3$. After hydrothermal treatment for 8 h at 175 $^\circ\text{C}$, a well inter-grown silicalite crystal layer with a thickness of about 10 μm was formed on the seeded support, as shown in Fig. 2.

The pervaporation (PV) tests for EtOH/water mixtures were carried out at 60 $^\circ\text{C}$. The effective membrane area was about 10 cm^2 . The permeation side was kept under vacuum. The flux was calculated by weighing the condensed permeate. The separation factor was determined as $\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$, where X_A , X_B , Y_A , and Y_B denote the mass fractions of components A and B in the feed and permeate sides. The pervaporation results for the silicalite membranes synthesized at 175 $^\circ\text{C}$ and 185 $^\circ\text{C}$ for 8 h are listed in Table 1. Table 1 clearly shows that the pervaporation performance of our silicalite membranes was significantly improved compared with the previous results and also the membranes were prepared in a

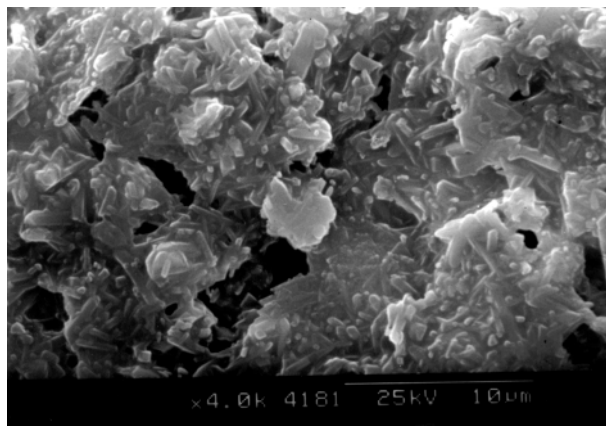


Fig. 1 SEM view of the surface of the mullite tube.

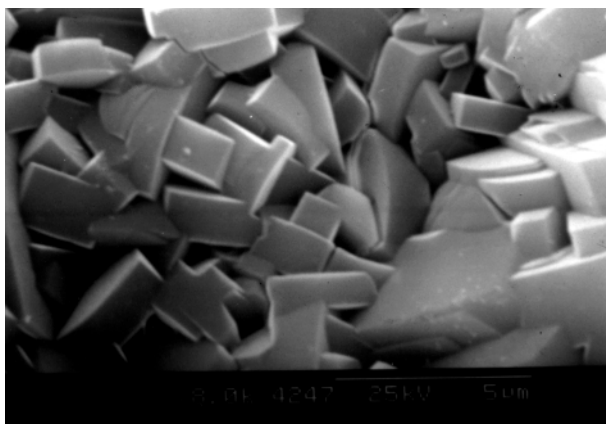


Fig. 2 SEM view of the surface of the silicalite membrane synthesized at 175 $^\circ\text{C}$ for 8 h.

Table 1 Pervaporation performance through the silicalite membranes for EtOH/H₂O mixtures at 60 °C

Member No	Synthesis conditions		EtOH/H ₂ O (10 wt% EtOH)	
	T/°C	t/h	Flux/kg m ⁻² h ⁻¹	Separation factor
Si-1	175	8	2.34	56
Si-2	175	8	2.55	72
Si-3	185	8	1.67	65
Si-4	185	8	1.58	64

highly reproducible manner. This suggests that silicalite membranes with both high flux and high separation factors can be prepared under suitable synthesis conditions, which has strong potential applications in the preferential separation of organic compounds from aqueous solutions. A systematic investigation of membrane preparation and membrane performance, including gas and vapor permeation, is under way.

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