doi:10.1246/cl.2010.388

Inexpensive Synthesis of Silicalite-1 Membranes with High Pervaporation Performance

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Good-intergrown silicalite-1 membranes with high ethanol permselectivity were prepared from a hyperdiluted solution with H_2O/SiO_2 ratio of 800 and an inexpensive template of tetrapropylammonium bromide (TPABr) on seeded mullite tubes.

Zeolite membranes have attracted considerable interest due to their potential applications for gas separation, pervaporation (PV) and membrane reactors in the past two decades. With the medium pore size of 0.53 nm × 0.56 nm and their hydrophobic properties, zeolite MFI (silicalite-1 and ZSM-5) membranes may be the most extensively researched for organics extraction from low concentration aqueous solutions by pervaporation.[1–4] Industrial applications of silicalite-1 membranes, however, have been so far hindered mainly by the prohibitive cost of membrane preparation or poor separation performance. In 1994, Sano et al.[1] reported the in situ preparation of silicalite-1 membranes on porous stainless steel and alumina discs from a clear solution with H_2O/SiO_2 ratio of 80; the membranes had a separation factor of 60 and 19 for a 5 wt % aqueous ethanol solution, respectively. Some groups tried to synthesize MFI membranes on porous tubular supports.[2–4] Membranes with a separation factor of 11–70 together with a flux of $0.1–0.9\,kg\,m^{-2}\,h^{-1}$ were reported on porous alumina, stainless steel, or silica tubes.[2–4] Recently, silicalite-1 membranes were prepared on multichannel monolith alumina supports.[5,6] Those membranes show low separation factor of 10–31 or low flux of $0.1–0.5\,kg\,m^{-2}\,h^{-1}$ toward aqueous ethanol solution.[5,6] In our previous work, silicalite-1 membranes with high selectivity were synthesized using tetrapropylammonium hydroxide (TPAOH) as template by in situ[7] and secondary growth.[8,9] In this paper, we present a simple preparation method of high-performance silicalite-1 membranes from very diluted solution with H_2O/SiO_2 ratio of 800 and an inexpensive template of tetrapropylammonium bromide (TPABr) on cheap mullite tubes, by which the total cost was greatly reduced.

Silicalite-1 membranes were prepared on 10-cm porous mullite tubes with average pore size of 1 µm and porosity of 43% (Nikkato Corp.). Clear aluminosilicate solutions were obtained by mixing tetraethyl orthosilicate (TEOS, 98 wt %, Aldrich), TPABr (99 wt %, Tokyo Kasei), NaOH (96 wt %, Aldrich) and deionized water under vigorous stirring for 1 h at room temperature. The mole compositions of resultant solutions were $1SiO_2{:}0.3TPABr{:}0.05Na_2O{:}120–800H_2O$. The $H_2O/SiO_2 = 800$ solution is referred to as a hyperdiluted solution in this study since it contains over 97 wt % water. For comparison, TPAOH (20–25 wt % in water, Tokyo Kasei) instead of TPABr is used to prepare a sodium-free solution with $TPAOH/TPABr = x/(0.3 - x)$, where $x = 0.2$ or 0.3. The tubes were polished with SiC sandpaper, washed, and dried at 100 °C for 6 h. Before hydrothermal synthesis, the tubes were seeded by dip-coating using an $8\,g\,L^{-1}$ aqueous silicalite-1 suspension for an immersed period of 30 s, and the seeding procedure was repeated again. The seeded tubes were then vertically placed in the synthesis solution. The crystallization was carried out at 180 °C for a given period. The seeds were prepared from a gel with a mole composition of $1SiO_2{:}0.25TPABr{:}0.15Na_2O{:}45H_2O$ at 130 °C for 20 h using colloidal silica (TM-40, 40 wt % in water, Aldrich) as silica source. After the synthesis, the samples were washed carefully with hot deionized water, dried, and then calcined at 500 °C for 15 h with a heating and cooling rate of $0.5\,°C\,min^{-1}$.

Zeolite membranes were verified by X-ray diffraction (XRD) (Advance D8, Bruker) with Cu K*a* radiation. The morphology and thickness of the membranes were characterized by field emission scanning electron microscopy (FE-SEM) (Quanta 200F, FEI). Elementary composition of membrane surface was analyzed by wavelength dispersive X-ray fluorescence (WDXRF) (S4 Pioneer, Bruker). PV tests toward an ethanol/water (5/95 wt %) mixture were carried out at 60 °C using a PV experimental apparatus described elsewhere.[7] The effective membrane area was ca. 27 cm² and the permeation side was kept under vacuum of 20 Pa.

Figure 1 shows the XRD patterns of the seeds, mullite tube, and silicalite-1 membrane. It can be seen that the pattern of zeolite membrane (S-3) prepared under hyperdiluted solution is consistent with the strong characteristic peaks of silicalite-1 seeds together with those of mullite tube, confirming that the outer surface of mullite tube is fully covered with a randomly oriented silicalite-1 layer.

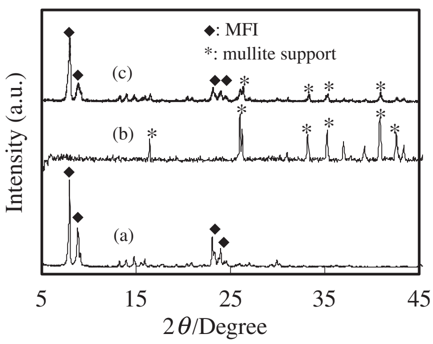

Figure 1. XRD patterns for (a) silicalite-1 seeds, (b) mullite tube, and (c) silicalite-1 membrane S-3.

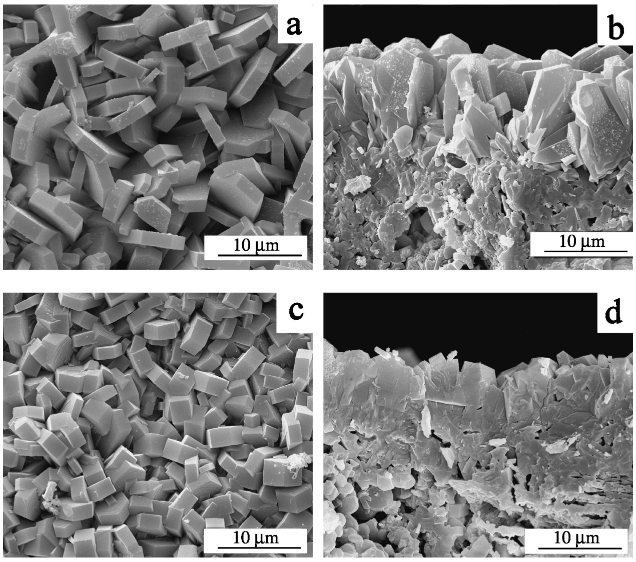

Figure 2. FE-SEM surface and cross-sectional photographs of (a) and (b) membrane S-1 and (c) and (d) membrane S-3, prepared by $H_2O/SiO_2 = 120$ and 800, respectivity.

Table 1. PV performance through silicalite-1 membranes toward an ethanol/water (5/95 wt %) mixture at 60 °C

No.	H_2O $/SiO_2$	Na_2O $/SiO_2$	TPAOH /TPABr[a]	t /h	Flux /$kg\,m^{-2}\,h^{-1}$	α
S-1	120	0.05	0	8	0.85	40
S-2	500	0.05	0	12	1.45	60
S-3	800	0.05	0	16	1.71	66
S-4	800	0	2	16	1.91	65
S-5	800	0	∞	16	1.42	80

[a] $TPA^+/SiO_2 = 0.3$

Figure 2 shows FE-SEM surface and cross-sectional photographs of silicalite-1 membranes prepared by H_2O/SiO_2 ratios of 120 and 800, respectivity. From the surface photographs (Figures 2a and 2c), it could be found that silicalite-1 membrane synthesized with hyperdiluted solution had an intergrown silicalite-1 layer with small and uniform particles. The cross-sectional photographs (Figures 2b and 2d) supported further that a more intergrown and thinner top zeolite layer with thickness of about 5 µm could be obtained by $H_2O/SiO_2 = 800$ than that of $H_2O/SiO_2 = 120$, as well as fewer silicalite-1 crystals entering support pore.

Table 1 shows the PV performance through silicalite-1 membranes prepared by H_2O/SiO_2 ratios from 120 to 800. Compared with the membranes S-1 and S-2, membrane S-3 prepared from hyperdiluted solution showed higher PV performance with a high flux of 1.71 $kg\,m^{-2}\,h^{-1}$ and a high separation factor (α) of 66 toward a feed of 5 wt % aqueous ethanol solution at 60 °C, which is the highest PV performance so far among the silicalite-1 membranes prepared with pure TPABr as template. High PV performance of membrane S-3 could mainly be attributed to the thin zeolite layer (shown in Figure 2d) and its hydrophobic property (Si/Al ratio large than 2000), since the hyperdiluted solution supplies the limited but probably appropriate "nutrition" and low alkalinity to avoid Al leaching from the support. On the other hand, membrane S-4 prepared from sodium-free solution with dual templates displayed the highest flux of 1.91 $kg\,m^{-2}\,h^{-1}$. Actually, a competition exists between TPA^+ and Na^+ incorporated into the channel when sodium-containing solution is used.[10] The incorporation of TPA^+ into the silicalite-1 structure is independent of hydroxide concentration, but the occlusion of Na^+ into the structure increases with increasing concentration of sodium hydroxide in the reaction batch.[10] The existence of Na^+ in the channel of zeolite layer is probably the reason that membrane S-3 had lower flux than membrane S-4 in our system. It could be also the other reason for higher flux of membranes prepared under more diluted sodium-containing solution, in which the lower concentration of sodium hydroxide would result in the lower density of sodium cation in silicalite-1 structure. Membrane S-5 synthesized using TPAOH displayed the higher selectivity of 80 but lower flux, indicating a compacter and thicker (SEM photograph not shown) forming on the substrate.

In our previous study, silicalite-1 membranes were prepared using TPAOH and H_2O/SiO_2 ratio of 120 on seeded mullite and α-Al_2O_3 tubes.[8] Compared with membranes prepared on mullite tubes in the literature, our membranes synthesized from hyperdiluted solution using cheaper TPABr had similar high PV performance. Higher separation performance could be obtained using α-Al_2O_3 tube with large average pore size of 2 µm, which indicates the support properties (i.e., pore size) take a great effect on the formation of zeolite layer.[8] However, high cost of the α-Al_2O_3 tube and synthesis solution containing TPAOH had held back its large-scale preparation. A detailed study of the crystallization of silicalite-1 membrane in hyperdiluted solution with TPABr as template is still under way.

In conclusion, we have shown a simple method to prepare high-performance silicalite-1 membranes from hyperdiluted solution using a cheep template of TPABr, which is suitable for industrial production due to its low cost. The membanes have potential applications in preferential separation of organics from aqueous solutions.

This work was supported by the Ministry of Science and Technology of the People's Republic of China (No. 2006DFB53070) and National Natural Science Foundations of the People's Republic of China (NSFC) (Nos. 20906042 and 20966003).

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