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Fabrication of SiO_2–ZrO_2 (50/50) membranes on the porous stainless steel-tube support for pervaporation

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ABSTRACT

The SiO_2–ZrO_2 membranes were fabricated with silica–zirconia sols on a porous stainless steel-tube support (O.D. = 10 mm, length = 20 mm, 316L SUS, Mott Corp. USA) by a dipping–rolling–freezing–fast drying (DRFF) and/or soaking–rolling–freezing–fast drying (SRFF) method. After coating of SiO_2–ZrO_2 sol, single gas permeation characteristics (He, H_2, and N_2) for SiO_2–ZrO_2 membranes were evaluated at room temperature, and the pervaporation experiments were performed at a specified feed isopropyl alcohol concentration of 90 wt% at 50˚C with silica–zirconia membranes. The morphology of surface and the cross sections of the membrane were investigated with FE-SEM analysis. Judging from FE-SEM analysis, the surface of silica–zirconia membrane on the PSS tube support was denser, and the number of surface defects considerably reduced than DRFF method, and the additional modification via the SRFF significantly diminished surface defects, which could not be avoided during the DRFF step. The membrane the silica–zirconia membrane showed hydrogen permeability under 10^{-7} mol m^{-2} s^{-1} Pa^{-1} and low water selectivity in the range of 10–23. The silica–zirconia membranes with a smooth surface on the stainless steel tube supports, was quite well prepared by the DRFF and SRFF method in this study.

Keywords: Porous stainless steel tube; DRFF–SRFF method; SiO_2–ZrO_2 membrane; Pervaporation

1. Introduction

Generally, distillation is used to separate multi-component liquid mixtures. However, distillation required large-scale equipment and a large amount of energy to separate mixtures with an azeotropic temperature, close boiling temperatures of the components, because the process based on differences of the boiling points of mixtures components. Pervaporation, which is one of membrane separation processes and based on the differences of solubility and/or diffusion rates of the permeants in the membrane, has been regarded as one of the most promising areas due to its providing a drastic opportunity for energy and cost savings. This process has been highly expected for separation of liquid mixtures of low molecular weights, especially azeotropic and close boiling

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mixtures. Dehydration of organic liquids is the most successful application of pervaporation with polymeric and inorganic membranes mainly because of a relatively large difference in molecular sizes between water and organic chemicals. Polymer membranes generally show high water permselectivity for organic solvents, such as alcohol, in the pervaporation process. But, some of polymeric membranes are not stable against organic solvents due to their swelling or dissolving, and show small pervaporation flux due to the low operating temperature limit [1–3].

Zeolite and silica membranes have attracted attention as inorganic membranes. A zeolite membranes with high selectivity and flux has been commercialized, but it is unstable in acid state [4]. Silica membranes, which were generally prepared with silica precursors, such as tetraethyl orthosilicate (TEOS) by sol–gel or chemical vapor deposition method, are not stable in aqueous solutions even at low rate water concentrations (i.e. around 10 wt%), especially in neutral and alkaline pHs [5–7]. However, silica membranes have a great advantage in terms of pore size controllability, and the incorporation of other components, such as zirconium, aluminum, nickel, and/or organic functional group into silica, and were also investigated for reverse osmosis, nanofiltration, hydrogen gas separation, and pervaporation [8–19].

The pore size control of such composite membranes is quite difficult, but silica–zirconia membranes by Hiroshima University have been developed for nanofiltration and for pervaporation [8–11]. M. Asaeda et al. developed SiO_2–ZrO_2 membranes, which were fabricated by improved sol–gel techniques on the α-Al_2O_3 supports, for pervaporation of aqueous organic solutions such as ethanol, isopropanol, 1-propanol, acetone, or tetrahydrofuran. And, a hybrid silica membrane with new type of organic–inorganic Si precursor, a bridged alkoxide, such as BTESE (≡Si–C-C–Si≡ unit) or BTESM (≡Si–C-Si≡ unit), were prepared on the α-Al_2O_3 supports for pervaporation [15–19], and found excellent hydrothermal and acid stability as well as high pervaporation performance for n-butane/water. Organic functional groups, such as methane and ethane, in bridged alkoxides reportedly contributed to increased hydrothermal stability of silica networks.

Although pore size-controlled SiO_2–ZrO_2 membranes or hybrid silica membranes on the porous α-Al_2O_3 supports showed sharp structure and high water flux, their utilization in industries was quite difficult. The mesoporous membranes on porous metal support are expected to be suitable for industrial application of membrane processes. D.W. Lee et al. at KRICT successfully prepared mesoporous silica membranes on a stainless steel disk support using colloidal silica sol with 100 nm-sized particles, via a dipping–rolling–freezing–fast drying (DRFF) and soaking–rolling–freezing–fast drying (SRFF) method [20,21]. In the previous study, we reported the possibility of preparation of silica–zirconia membranes prepared using colloidal silica–zirconia hybrid sols by the DRFF and SRFF method on porous stainless steel (PSS) tube support [22]. In this study, the optimization of silica–zirconia membrane by DRFF and SRFF method without large pinhole or crack were investigated with gas permeation and pervaporation of isopropyl alcohol (IPA)/water test.

2. Experiment details

2.1. Preparation of SiO_2–ZrO_2 sol and membranes

Silica colloidal sol and silica–zirconia (50/50) hybrid sols were prepared by the hydrolysis and condensation of TEOS and/or zirconium tetra-n-butoxide (ZrTB) precursors in acid catalyst system [20–22]. A PSS tube (O.D. = 10.0 mm, length = 20 mm, 316L SUS, Mott Corp. USA) was used as the support for membranes. In order to optimize, the silica–zirconia membranes were prepared by a DRFF and/or SRFF method as described in the following [20–22]. In the DRFF method, the support was dipped into solution for 30 s at first, and was rolled out with a urethane rolling sheet in order to eliminate cake layer formation on the substrate. Subsequently, the substrate was frozen in liquid nitrogen for 30 s, followed by fast drying of the substrate for 30 s on a hot plate heated to 250˚C. The DRFF process was repeated seven times to cover large pores, and then the substrate was then fired at 700˚C for 30 min in atmospheric air.

In order to minimize the number of defects on the membrane surface, the dipping step was replaced the soaking step in the SRFF method. One side of the membrane was sealed and opposite side of membrane was vacuumed by a rotary vacuum pump. The membrane was dipped into solution, and maintained for 30 s. The soaked substrate was rolled out with a urethane rolling pin. The substrate was subsequently frozen in liquid nitrogen for 30 s, followed by fast drying for 30 s on a hot plate heated to 250˚C. The SRFF process was also repeated seven times, and then the substrate was calcined at 700˚C for 30 min in the presence of atmospheric air. The silica–zirconia membranes prepared via various coating methods are listed in Table 1.

2.2. Characteristics of SiO_2–ZrO_2 membranes

The single gas permeation test was conducted after preparation of the silica–zirconia membranes. Single

Table 1
The SiO_2–ZrO_2 membranes prepared by various methods

Membrane	Intermediate layer		Separation layer	
M-1	–		SiO_2–ZrO_2 layer	DRFF–SRFF–SRFF–SRFF
M-2	–		SiO_2–ZrO_2 layer	DRFF–DRFF–DRFF–DRFF
M-3	SiO_2 layer	DRFF–SRFF	SiO_2–ZrO_2 layer	DRFF–DRFF

gas permeation characteristics (He, H_2, and N_2) for silica–zirconia membranes were evaluated at room temperature by using a soap-film flow meter [22]. Fig. 1 shows the schematic diagram of experimental apparatus required for the pervaporation measurement. The pervaporation experiments were performed at 90 wt% feed concentration of aqueous solution of IPA with silica–zirconia membranes at 50℃. The concentration in the feed and permeate mixtures were determined by a gas cromatograph (Agilent model GC-7890A, DB-1 column). After gas permeation and pervaporation test, the morphology of surface and the cross sections of the membrane were investigated using FE-SEM (Philips XL-30S, Tescan MIRA3) analysis.

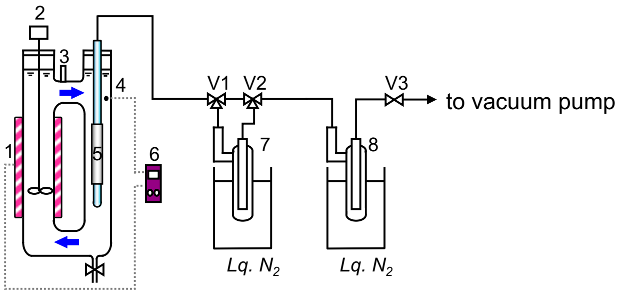

Fig. 1. A schematic diagram of pervaporation apparatus.

3. Results and discussion

3.1. Morphology of silica–zirconia membranes

The top layer of the membranes was coated with silica–zirconia hybrid sols on PSS tube supports or SiO_2 layer coated PSS tube support by means of the DRFF or SRFF method, as described in Table 1. Fig. 2 shows FE-SEM images of surface section of PSS substrates (a) and M-1 membrane ((b) and (c)). The PSS substrate has rough and large pores in the range of macropores as shown in Fig. 2(a). However, the surface morphology of the M-1 membrane was denser and contained a greatly reduced number of surface defects compared with substrate. Fig. 3 shows the morphology of cross ((a), (b), and (c)) and surface section ((d), (e), and (f)) of M-2 membrane, which was derived by only DRFF method with silica–zirconia hybrid sol. The M-2 membrane in cross and surface section was observed much more defects and pinholes at low magnification compared to the M-1 membrane in Fig. 2(b) and (c). Under high magnification (Fig. 3(c) and (f)), it was observed that the silica–zirconia hybrid sol were coated or aggregated only on the metal support. That is, the additional modification via the SRFF significantly diminished surface defects, which could not be avoided during the DRFF step [21]. The soaking process led to forced penetration of the coating materials into pores or defects via a vacuum in the opposite side of the membrane in comparison to the dipping process. And, the thickness of membrane was increased in soaking process.

In order to control the membrane thickness, which was correlated with the membrane performance, such as gas permeance and liquid flux, M-3 silica–zirconia membrane was prepared on the silica layer-coated PSS tube support. Fig. 4 exhibits the surface morphology of M-3 membrane. Compared to M-2 membrane, M-3 membrane was denser and reduced number of surface defects at low magnification, and relatively well covered with silica–zirconia hybrid sol at high magnification. On the basis of these results, it was concluded that synthetic route for M-3 silica–zirconia membrane relatively well coated on the PSS support.

3.2. Characterization of silica–zirconia membranes

Fig. 5 shows the hydrogen gas permeance measured at room temperature, and H_2/N_2 gas permselectivity of silica–zirconia membranes produced from various synthetic routes. The hydrogen gas permeation properties of M-1 membranes produced by means of the DRFF and SRFF method were under 10^{-8} $mol\,m^{-2}\,s^{-1}\,Pa^{-1}$ with H_2/N_2 permselectivity of 3.78. Although the membrane was prepared without defect, the membrane was denser and thicker during the SRFF process. As mentioned in Fig. 3, the surface of M-2 membrane was not covered without defects and pinhole. Therefore, high hydrogen gas permeance occurred from membrane defects. The value of H_2/N_2

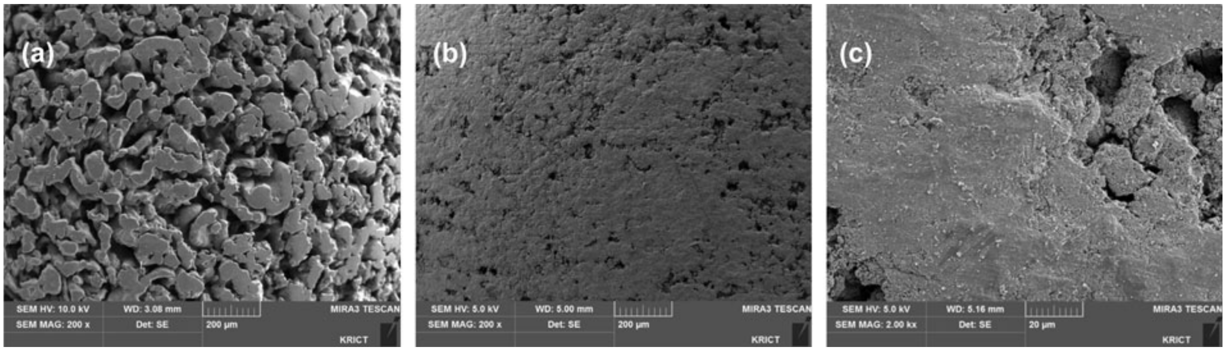

Fig. 2. FE-SEM images of surface section of PSS tube support (a) and M-1 membrane ((b), (c)).

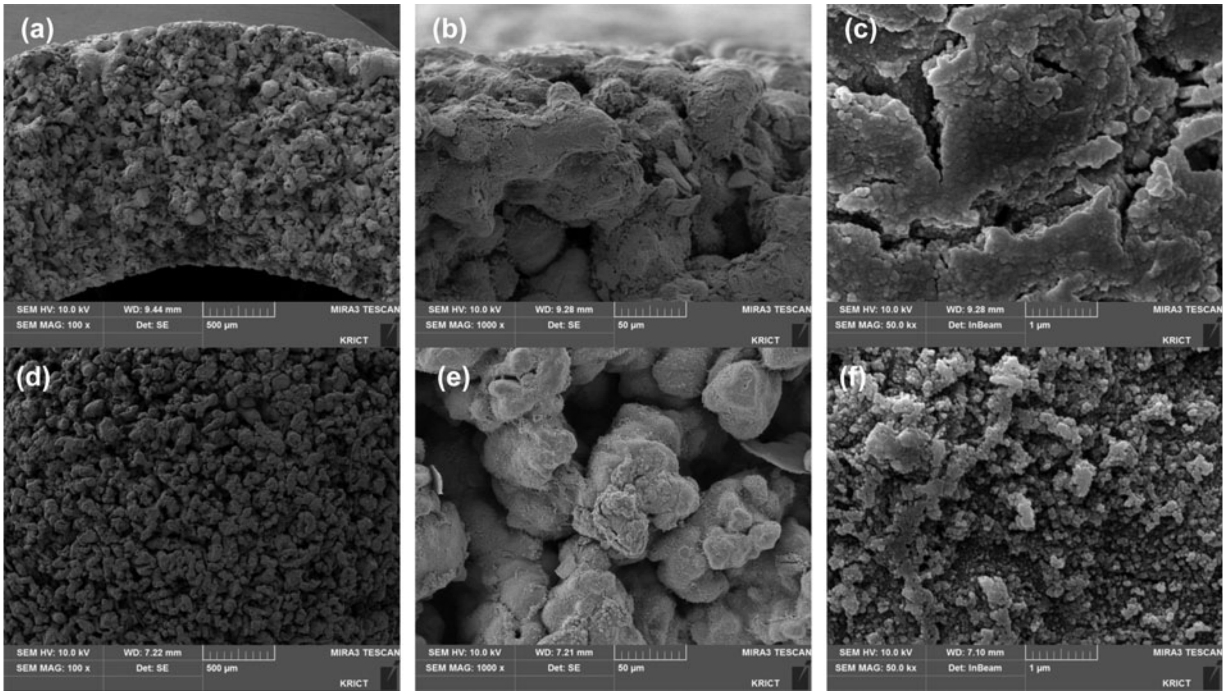

Fig. 3. FE-SEM images of M-2 membrane derive by DRFF method; ((a), (b), and (c)) cross section, ((d), (e), and (f)) surface section.

permselectivity for the M-3 membranes was distributed in the range of 2.3–3.5, and hydrogen gas permeation varied between M-1 and M-2 membrane. It means that silica particles reduced defects and made membrane surface smoother than without silica particle layer. In addition, the DRFF and SRFF method demonstrated the possibility of preparing silica–zirconia membranes with a smooth surface on the stainless steel tube supports.

Fig. 6 shows the correlation between total flux and water selectivity factor for 90 wt% of IPA feed concentration at 50˚C with (a) M-1 membrane and (b) M-3 membrane. Compared to M-1 membrane, the total flux of M-2 membrane increased and water selectivity slightly increased from 10 to 23. As mentioned in Fig. 5, M-1 and M-2 membranes varied in Knudsen diffusion and it means a lot of water molecules were permeated through large size of pores. Although the DRFF and SRFF method demonstrated the possibility of preparation silica–zirconia membranes on the PSS tube support, membrane performance was relatively low than expected and other researches [8–11]. Therefore, membrane performance would be developed with controlling membrane thickness and/or dipping with other solution in the nest study.

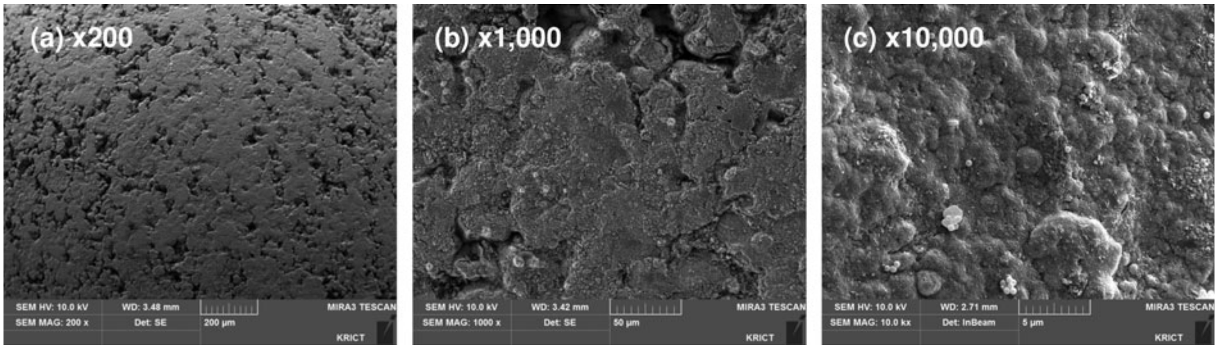

Fig. 4. FE-SEM images of the surface of M-3 membrane including intermediate layer with various magnification.

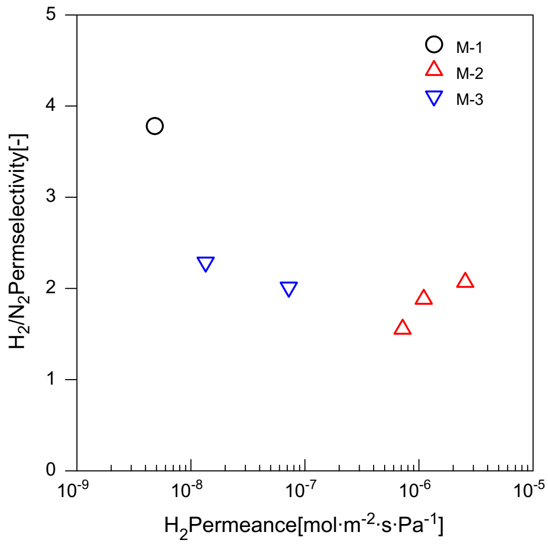

Fig. 5. Gas permeance of silica–zirconia membranes at room temperature.

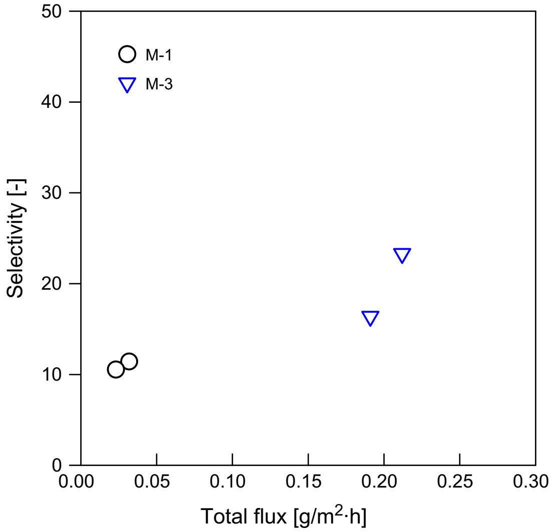

Fig. 6. Time dependence of pervaporation performance for IPA/water mixture at 50°C with (a) M-1 and (b) M-3 membrane.

4. Conclusion

The SiO_2–ZrO_2 membranes were fabricated with silica–zirconia hybrid sols on a PSS tube support (O.D. = 10 mm, length = 20 mm, 316L SUS, Mott Corp. USA) by a DRFF and/or SRFF method. Judging from FE-SEM analysis, the surface of these membranes prepared on the silica layer coated support was denser, and the number of surface defects was considerably reduced than only DRFF method. And, the additional modification via the SRFF significantly diminished surface defects, which could not be avoided during the DRFF step.

Although the DRFF and SRFF method demonstrated the possibility of preparing silica–zirconia membranes with a smooth surface on the stainless steel tube supports, the silica–zirconia membrane with hydrogen permeability under $10^{-7}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$ and H_2/N_2 permselectivity of in the range of 2.3–3.5 showed relatively low flux and water selectivity. Therefore, membrane performance would be developed with controlling membrane thickness and/or dipping with other solution in the nest study.

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