SiO₂-ZrO₂ nanofiltration membranes of different Si/Zr molar ratios: stability in hot water and acid/alkaline solutions

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Abstract

SiO₂-ZrO₂ nanofiltration membranes were fabricated by coating different molar ratios of SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7), and ZrO₂ sols onto α -alumina porous tubes and firing at 200 and 550 °C. The SiO₂ and SiO₂-ZrO₂ (9/1, 7/3, 5/5) membranes fired at 200 and 550 °C showed pore diameters ranging from 0.65-0.80 nm, while SiO₂-ZrO₂ (3/7) and ZrO₂ membranes fired at 550 °C showed larger pores than those fired at 200 °C due to the formation of crystalline structures in the ZrO₂.

SiO₂-ZrO₂ membranes with a zirconia content larger than 50 mol% showed high hydrothermal stability in hot water (90 °C). After treating SiO₂-ZrO₂ (5/5) membranes in hot water, the water permeability (L_p) increased dramatically while the rejection was unchanged. On the other hand, the L_p for SiO₂-ZrO₂ (3/7) membranes decreased while the rejection increased. This can be ascribed to the balance between the dissolution of Si and the generation of OH groups, which amounts to pore sizes and hydrophilicity. Moreover, SiO₂-ZrO₂ (5/5, 3/7) membranes showed stable water permeability and molecular weight cut-off values for as long as 4 weeks at pH values of 2 and 12, confirming a high level of chemical stability in strongly acid and alkaline solutions.

Keywords: SiO₂-ZrO₂ membrane, Si/Zr molar ratios, Nanofiltration, Hydrothermal stability, pH stability

1. Introduction

Nanofiltration (NF) membranes have a nominal pore size of approximately 1-2 nm and a molecular weight cut-off (MWCO) that range from 200 to 1000 [1]. According to their material properties, NF membranes can be typically classified into one of two major groups: polymeric and ceramic. Polymeric NF-membranes such as polysulfone, cellulose acetate, polyamide, etc., have been commercially available for many years and have been used for drinking water and wastewater treatment. The limitations of polymeric membranes include stability at high temperatures and corrosion resistance in strong acid and alkaline solutions [2]. In general, polymeric nanofiltration membranes are used at a maximum of 40-60 °C, and they are not resistant to some organic solvents [3-6]. On the other hand, ceramic membranes that are normally manufactured from inorganic materials such as alumina, titania, zirconia, silica, etc., have advantages compared with polymeric membranes: high mechanical strength, resistance to chemicals, and stability at high temperatures [7]. Depending on the types of membrane materials, some ceramic membranes can be used in highly specialized applications under extreme operating conditions such as exposure to high temperature and organic solvents.

Many researchers have focused on ceramic membranes with zirconia (ZrO₂), titania (TiO₂), alumina (Al₂O₃), and silica (SiO₂) top layers, which has become a hot topic in membrane research in nanofiltration, pervaporation and gas separation. Tsuru et al. [7, 8] reported successful preparation of TiO₂ nanofiltration membranes onto α -alumina capillary supports and studied nanofiltration performance at temperatures ranging from 30-80 °C. Voigt et al. [9] developed TiO₂ nanofiltration membranes on capillary supports with a molecular weight cut-off of 250 g/mol and a water permeability of $27.7 \times 10^{-12} \text{ m}^3 / (\text{m}^2 \text{ s Pa})$. Van Gestel et al. [10, 11] investigated the corrosion of γ -Al₂O₃, TiO₂ and ZrO₂ NF membranes in acid and alkaline solutions. The γ -Al₂O₃ membranes showed limited stability in aqueous media (pH 3-11), while the TiO₂ and ZrO₂ membranes demonstrated high stability at pH values ranging from 1 to 13. Schaep et al. [12] reported that γ -Al₂O₃ nanofiltration membranes were unstable at pH 2 or lower after an exposure time of 26 h. Moreover, SiO₂ membranes are known to be unstable in aqueous solution because they dissolve in

water at room and high temperature, particularly in neutral and alkaline solutions. However, these membranes impart a great advantage in terms of pore size controllability [13, 14].

Composites of silica with metal oxides such as zirconia, titania and aluminum have shown improved thermal and chemical stability. Many researchers have reported the use of $\text{SiO}_2\text{-ZrO}_2$ membranes for gas separation and pervaporation. Yoshida et al. [15] prepared $\text{SiO}_2\text{-ZrO}_2$ membranes with different ZrO_2 contents ($\text{Si/Zr} = 9/1, 7/3$ and $5/5$) by coating the sol onto porous supports in order to study the hydrothermal stability and permeation properties at 500°C by measuring the time courses of the permeance of pure N_2 and H_2 under water vapor. They found that the pores for N_2 permeation were decreased with increases in ZrO_2 content, suggesting the $\text{SiO}_2\text{-ZrO}_2$ matrix was densified by the increase in zirconia content. For hydrothermal stability, the N_2 and H_2 permeance of $\text{SiO}_2\text{-ZrO}_2$ ($9/1, 7/3$) membranes was decreased drastically due to densification of the silica by water vapor at high temperature. On the other hand, the N_2 and H_2 permeance of $\text{SiO}_2\text{-ZrO}_2$ ($5/5$) membranes was unchanged. Asaeda et al. [14, 16] reported that $\text{SiO}_2\text{-ZrO}_2$ membranes with zirconia content larger than 40 mol% were quite stable during the pervaporation performance of aqueous solutions that contained a low concentration of water.

A limited number of studies have reported $\text{SiO}_2\text{-ZrO}_2$ membrane performance for nanofiltration in an aqueous solution, although SiO_2 composites have a great advantage in pore-size controllability. Tsuru et al. [17] prepared $\text{SiO}_2\text{-ZrO}_2$ ($9/1$) membranes for nanofiltration in order to study their stability in an aqueous solution at 25°C . The water permeability of $\text{SiO}_2\text{-ZrO}_2$ ($9/1$) membranes decreased gradually during the initial two days and reached a stable value. The decreased water permeability was explained by hydration of the $\text{SiO}_2\text{-ZrO}_2$ surface in the water, which reduced the effective pore diameters for the permeation of water. We reported [18] the nanofiltration of $\text{SiO}_2\text{-ZrO}_2$ ($5/5$) membranes fired at 200, 300, 400, and 550°C . The water permeability of $\text{SiO}_2\text{-ZrO}_2$ ($5/5$) membranes decreased with an increase in the firing temperature due to chemical and physical changes. The water permeability of $\text{SiO}_2\text{-ZrO}_2$ ($5/5$) membranes decreased slightly during the initial 30 h, and then reached stable values. Moreover, $\text{SiO}_2\text{-ZrO}_2$ ($5/5$) membranes showed high hydrothermal stability in hot water [19], suggesting that doping zirconia

into silica sols improved the stability of SiO₂-ZrO₂ membranes in water. In order to develop SiO₂-ZrO₂ membranes with different Si/Zr molar ratios for nanofiltration, stability is crucial for membrane performance such as stability at high temperatures and under different pH values.

In the present study, SiO₂-ZrO₂ nanofiltration membranes with different molar ratios were prepared by coating SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7), and ZrO₂ sols onto cylindrical supports in order to clarify the hydrothermal and chemical stability of SiO₂-ZrO₂ membranes. Long-term stability tests for hydrothermal stability were carried out in water at 90 °C and in acid/alkaline solutions in order to examine the chemical stability.

2. Experimental

2.1 Preparation of SiO₂, SiO₂-ZrO₂ (9/1, 3/7, 5/5, 3/7), and ZrO₂ sols and powders

SiO₂, ZrO₂ and SiO₂-ZrO₂ composite colloidal sols with molar ratios of 9/1, 7/3, 5/5, and 3/7 were prepared via hydrolysis and condensation reactions of tetraethoxysilane (TEOS) and zirconium-tetra-butoxide solutions (80% ZrBT in 1-butanol). The compositions of the sols are shown in Table 1. TEOS was partially hydrolyzed in ethanol and hydrochloric acid for 3 h under a stirred cell, and then ZrBT was added drop-wise into the solution for co-condensation reactions. After 12 h, a large amount of water and hydrochloric acid (3-5 g) were added to the solution to control the pH (< 2) and then the solution was boiled for 8 h. The total amount (500 ml) was maintained by adding water during the boiling period. The colloidal sol sizes were measured via dynamic light scattering (DLS, Malvern, Zen3600) at 25 °C.

SiO₂, ZrO₂ and four types of SiO₂-ZrO₂ powders with molar ratios of 9/1, 7/3, 5/5, and 3/7 were prepared using a quick-drying method [14] at 180 °C, followed by calcinations under air at 200 and 550 °C. The powders were evaluated by X-ray diffraction (XRD, Rigaku, RINT2000, Japan) to detect the tetragonal and monoclinic phases of ZrO₂ in the mixed oxides SiO₂-ZrO₂ and by N₂ adsorption-desorption (BEL JAPAN INC., Bell Max Japan) at a liquid nitrogen temperature of -196 °C after powders were pretreated at 180 °C for 6 h under vacuum.

The solubility of the powders (100 mg) was tested in deionized water (20 ml) at 25 and 90

°C at pH 7 for 4 h. Then, the suspended solution was taken out and centrifuged at 5000 rpm for 15 min. Additional dissolution experiments were repeated at 90 °C by refilling with deionized water several times. The concentrations of Si and Zr ions in the solution were analyzed by inductively coupled plasma optical emission spectrometry (ICP, Seiko Instrument, SPS3000, Japan). The accuracy of ICP analysis is $\pm 5\%$. Corrosion tests of powders in aqueous solutions at pH 2 and 12 were performed at 25 °C for 7 days using SiO₂, SiO₂-ZrO₂ (5/5, 3/7) and ZrO₂ powders fired at 550 °C. The samples were centrifuged for quantitative analysis of dissolved Si and Zr. In a similar manner, the dissolution experiment was repeated by refilling solutions (pH 2 and 12) for several weeks. The pH measurements were carried out with a digital pH-meter (Asone; C-73, Japan).

Table1

Composition and average colloidal diameters of SiO₂-ZrO₂ sols

Composition [mol%]		TEOS [g]	ZrBT [g]	H ₂ O [g]	HCl (35%) [g]	C ₂ H ₅ OH [g]	Colloidal diameter* [nm]
SiO ₂	sol-A	10.1	-	3.5	3.0	110	21
	sol-B	5.1	-	1.7	3.0	110	10
SiO ₂ -ZrO ₂ (9/1)	sol-A	2.1	0.5	0.7	4.0	110	46
	sol-B	2.1	0.5	0.7	5.0	110	20
SiO ₂ -ZrO ₂ (7/3)	sol-A	2.8	2.7	1.0	4.0	110	33
	sol-B	2.8	2.7	1.0	5.0	110	20
SiO ₂ -ZrO ₂ (5/5)	sol-A	3.5	8.1	1.2	3.0	110	35
	sol-B	1.8	2.7	0.6	3.0	110	19
SiO ₂ -ZrO ₂ (3/7)	sol-A	1.9	10.1	0.7	3.0	110	60
	sol-B	0.9	5.1	0.3	3.0	110	24
ZrO ₂	sol-A	-	12.5	0.02	3.0	110	48
	sol-B	-	6.3	0.01	3.0	110	25

* Z-average size (mean size) by dynamic light scattering (DLS)

2.2 Fabrication of SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ membranes

Nanoporous membranes were fabricated by coating sols with various levels of silica and zirconia content onto α -Al₂O₃ cylindrical porous tubes (average pore size 2.1 μ m; outer diameter 1 cm; length 10 cm). First, α -alumina particles with average diameters of 2.0 and 0.2 μ m were coated onto the outer surface of the tubes with the sol-A as the binder to create a smooth and homogeneous

surface, followed by firing at 550 °C for 15 min. Then the largest colloidal sol (sol-A) was coated onto the tubes and fired at 550 °C. These procedures were repeated 4-5 times to reduce the pore sizes of membranes to approximately 1.2 nm. Finally, the smallest size of colloidal sol (sol-B) was coated onto the surface, which was repeated twice, followed by different firing temperatures at 200 and 550 °C.

The pore size distribution of nanoporous membranes was evaluated by nanoporimetry (NPP) [20] using hexane as a condensable vapor. The basic principle of NPP is based on the capillary condensation of a vapor (hexane) inside nanopores and on the blocking of the permeation of non-condensable N₂. Pore diameters were calculated using the Kelvin equation of capillary condensation and assuming complete wetting by the hexane. The membranes were pretreated in an oven at 200 °C for 20 min to remove the humid air in the membrane pores before measurement of the pore size distribution of porous membranes by NPP. The permeance of nitrogen through the porous membrane was measured as a function of the vapor pressure of hexane in a mixture of nitrogen and hexane at 40 °C. As reported previously [8], the pore sizes of nanoporous membranes estimated by nanoporimetry showed reasonable correlation with nanofiltration separation ability, although the Kelvin equation is theoretically applicable for pores larger than 2 nm. The average pore sizes and N₂ permeance of membranes by nanoporimetry are summarized in Table 2.

2.3 Nanofiltration membrane performance: hydrothermal and chemical stability

NF experiments were carried out under a continuous stirred cell at 800 rpm using a magnetic stirrer in order to avoid the effect of concentration polarization. The feed solution was pressurized with a plunger pump at 1.0 MPa and was recycled to the feed tank at a flow rate of approximately 20 ml/min, while the permeate flux was less than 1 ml/min so that it is reasonable to assume a constant feed concentration. Molecular weight cut-off curves for nanofiltration at 25 °C were determined using single components of neutral organic solutes with different molecular weights at 500 ppm: isopropyl alcohol (60), glucose (180), maltose (342), raffinose (504), and cyclodextrin

(973). The concentrations of the feed and permeate were measured using a total organic carbon analyzer (Shimadzu, TOC-VE, Japan). Different types of membranes were treated in water at 90 °C by immersion in a flask under atmospheric pressure for 4, 10, 25, 50, 75, and 100 h, and the water was refreshed in the flask every 12 h. Then, membrane performance was evaluated by the water permeability and the rejection of solutes at 25 °C. The water permeability (L_p) was obtained using Eq. (2) as the ratio of water flux (J) to effective transmembrane pressure (ΔP), and was analyzed using Eq. (3) based on Hagen-Poiseuille flow, as follows;

$$J = \frac{V}{A \times \Delta t} \quad (1)$$

$$J = L_p \Delta P \quad (2)$$

$$L_p = \frac{r_p^2 A_k}{8 \mu \Delta x} \quad (3)$$

where J is the water flux (volume-based) in $\text{m}^3/(\text{m}^2 \text{ s})$, A is the effective area of membrane permeation in m^2 , V is the volume of permeated water in m^3 over the time interval, Δt , in s, L_p is the water permeability in $\text{m}^3/(\text{m}^2 \text{ s Pa})$, ΔP is the applied pressure difference in Pa, r_p is the effective pore size, A_k is the porosity, μ is the viscosity of the solution flowing through pores, and Δx is the effective thickness for separation. It should be noted that the effective thickness was similar to the top layer, which is responsible for separation. Once structural parameters, including r_p , Δx and A_k are given, it is possible to predict L_p .

The observed rejection (R) in the % of each solute was calculated from the following equation:

$$R = \left(1 - \frac{C_p}{C_r} \right) \times 100\% \quad (4)$$

where C_p and C_r are the solute concentration in the permeate and the retentate, respectively. The molecular weight cut-off (MWCO) value of membranes was determined as the molecular weight of a solute at 90% rejection.

Chemical stability for membrane performance was evaluated in acid and alkaline solutions. $\text{SiO}_2\text{-ZrO}_2$ (5/5, 3/7) membranes fired at 550 °C after treatment in water at 90 °C for 100 h were

used for static corrosion tests. The solutions were prepared using demineralized water with hydrochloric acid (HCl) and sodium hydroxide (NaOH) at pH 2 and 12, respectively. The membranes were immersed in 500 ml of acid/alkaline solutions under continuous stirring at room temperature, and these were exchanged with fresh solutions weekly. After exposure times of 1 day, then for 3 and 7 days followed by 2-4 weeks, the membrane performance was evaluated according to the water permeability (L_p) and the molecular weight cut-off (MWCO) at 25 °C with pH 7.

3. Results and discussion

3.1 Characteristics of SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ powders

The microstructural properties of membrane materials were characterized using several analytical methods in order to study the stability of the membranes. XRD observations can be used to clarify whether SiO₂-ZrO₂ was a composite or just a simple mixture of SiO₂ and ZrO₂. Fig. 1 shows the XRD patterns of the SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ powders fired at 200 and 550 °C. Amorphous SiO₂ peaks fired at 200 and 550 °C were centered at $2\theta = 23^\circ$, which is consistent with a previous report that pure SiO₂ showed an amorphous peak with an equivalent Bragg angle at $2\theta = 21.8^\circ$ [21]. As the ZrO₂ content increased in mixed SiO₂-ZrO₂ oxides, the peak shifted gradually towards higher 2θ values, while simultaneously the intensity gradually decreased. The shift of the SiO₂ peak towards higher 2θ values has been reported by introduction of metallic oxides (ZrO₂) to SiO₂ matrix to form Si-O-M (M is the second metal atom) [22, 23]. This shift was ascribed to replacing Si atoms with Zr atoms, which induced phase-separation of ZrO₂ when SiO₂-ZrO₂ with a high Zr content was fired at high temperatures [24]. All the XRD patterns of powders fired at 200 °C showed mainly amorphous structures.

SiO₂-ZrO₂ (3/7) and ZrO₂ powders fired at 550 °C clearly showed sharp peaks corresponding to a crystalline tetragonal structure of zirconia along with some small peaks of monoclinic structures. The transformation from an amorphous to a tetragonal/monoclinic structure may have induced stress in the membrane pores and enhanced the risk of crack formation [11, 25]. Sol-gel-derived ZrO₂ powder prepared from a similar precursor system is known to crystallize at

approximately $2\theta = 31^\circ, 35^\circ, 50^\circ$, and 60° by firing at high temperatures, forming a tetragonal phase [14, 26]. A similar phenomenon has been observed for $\text{SiO}_2\text{-ZrO}_2$ (3/7) powder fired at 550°C , although it was a composite $\text{SiO}_2\text{-ZrO}_2$, while $\text{SiO}_2\text{-ZrO}_2$ (5/5) powder fired at 550°C showed tiny crystalline tetragonal structures at 31° and 50° . $\text{SiO}_2\text{-ZrO}_2$ powders with zirconia content lower than approximately 70 mol% gave an amorphous structure. This may be because composite structures of $\text{SiO}_2\text{-ZrO}_2$ sols with a high ZrO_2 content might have induced crystallization of the ZrO_2 phase during firing at high temperatures. Therefore, the zirconia content and firing temperatures influenced the texture, structure and morphology of the $\text{SiO}_2\text{-ZrO}_2$ composite oxides.

Fig. 1 XRD patterns of SiO_2 , $\text{SiO}_2\text{-ZrO}_2$ (9/1, 7/3, 5/5, 3/7) and ZrO_2 powders. (a) fired at 200°C and (b) fired at 550°C .

N_2 adsorption-desorption isotherm curves of the SiO_2 , ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ composite oxides with different zirconia contents are shown in Figs. 2 (a) and (b), and the enlarged portion (a-1 and b-1) shows the low adsorption. All samples fired at 200°C and 550°C showed type I adsorption isotherms, which indicated that the samples were microporous structures with pore diameters of less than 2 nm [27]. The SiO_2 powder showed the highest adsorption while the adsorption for $\text{SiO}_2\text{-ZrO}_2$ decreased with increases in zirconia content, as reported by several authors [28-30]. Lower adsorptions generally mean denser structures so the densification of $\text{SiO}_2\text{-ZrO}_2$ microstructures might have occurred as the ZrO_2 content increased. The addition of ZrO_2 to SiO_2 clearly affected the formation process of micropores.

Fig. 2 N₂ adsorption-desorption isotherms at -196 °C for SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ powders. (a, a-1) fired at 200 °C and (b, b-1) fired at 550 °C. Note: Fig (a-1 and b-1) is an enlarged portion that shows low adsorption.

Fig. 3 shows the specific surface area and pore volume of SiO₂-ZrO₂ powders with different zirconia content fired at 200 and 550 °C. At 200 °C, the values for specific surface area and pore volume were higher than those fired at 550 °C. This was consistent with a previous report [18, 31], showing that the specific surface area and pore volume was decreased with an increase in firing temperature. Furthermore, the specific surface areas of SiO₂-ZrO₂ powders with different molar ratios were decreased by increasing the ZrO₂ composition in SiO₂-ZrO₂ sols, as reported earlier [32, 33]. There was a drastic decrease in the specific surface area at 30 mol% of zirconia content, and then a gradual decrease was observed up to 50 mol% of zirconia content. The experimentally obtained specific surface areas were lower than those obtained by assuming a mixture of SiO₂ and ZrO₂ powders, which can be ascribed to the formation of a SiO₂-ZrO₂ composite structure. In addition, it was interesting that the adsorption, the specific surface area, and the pore volume for SiO₂-ZrO₂ (3/7) and ZrO₂ powders fired at 550 °C were larger than those fired at 200 °C probably because the composite SiO₂-ZrO₂ fired at 550 °C became heterogeneous, as suggested in the XRD results.

Fig. 3 (a) Specific surface area and (b) Pore volume for SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ powders fired at 200 and 550 °C. Dashed curves were calculated by assuming a mixture of SiO₂ and ZrO₂ powders.

The stability of SiO₂-ZrO₂ membranes with different molar ratios can be predicted by the solubility of silica and zirconia. Figs. 4 (a) and (b) show the solubility of Si and Zr in deionized water at 25 and 90 °C for SiO₂, SiO₂-ZrO₂ (9/1, 5/5, 3/7), and ZrO₂ powders. At 25 °C, the solubility of Si in water for SiO₂ powders fired at 200 and 550 °C were much higher than that for SiO₂-ZrO₂ (9/1, 5/5, 3/7) powders, and it increased dramatically in water at 90 °C in the initial 4 h, then decreased gradually after repeating the dissolution experiments for as long as 20 h. The dissolution of Si for powders fired at 200 °C was higher than those fired at 550 °C probably due to the high surface area during firing at low temperature [16]. Farinas et al. [34] reported that the dissolution of Si was influenced by the surface area and firing temperature. The lower the surface area and the higher the firing temperature, the lower was the amount of Si dissolution. In particular, SiO₂-ZrO₂ (5/5, 3/7) fired at 550 °C showed a solubility of zero in water at 90 °C after repeated dissolution experimentation for 16 h. Si dissolution of zero, irrespective of a sufficient amount of powders remaining in the dissolution experiment, can be explained by the fact that the composition on the surface of the powder became poor in Si and rich in Zr with repeated dissolution, resulting in a stabilization of the structure. This indicates that the SiO₂-ZrO₂ (ZrO₂ ≥ 50%) composition was quite stable in water at 25 and 90 °C. On the other hand, the dissolutions of Zr in water at 25 and 90 °C for SiO₂-ZrO₂ (9/1, 5/5, 3/7) and ZrO₂ powders fired at 200 and 550 °C were negligible at approximately 0.05-0.07 ppm, as shown in Fig. 4 (b). Therefore, the stability of SiO₂-ZrO₂

membranes in water at 90 °C is dependent on not only SiO₂-ZrO₂ composition but also on the firing temperature.

Fig. 4 Solubility of Si (a) and Zr (b) in water at 25 and 90 °C for SiO₂, SiO₂-ZrO₂ (9/1, 5/5, 3/7) powders fired at 200 °C (blue line) and 550 °C (red line) as a function of treated time. Treatment time of zero indicates solubility at 25 °C and that of 4-20 h indicates solubility at 90 °C.

3.2 Nanopermporometry characterization of SiO₂-ZrO₂ membranes of different Si/Zr molar ratios

The pore size distributions of the SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ membranes were evaluated by nanopermporometry using the Kelvin equation [20], as shown in Fig. 5. Moreover, the average pore sizes of membranes, which are defined as 50% of the dimensionless permeability of nitrogen, are listed in Table 2. The experimental uncertainties of average pore diameters were about ± 0.05 nm. SiO₂ and SiO₂-ZrO₂ (9/1, 7/3, 5/5) membranes fired at 200 and 550 °C showed similar pore size distributions and average pore sizes of approximately 0.65-0.80 nm, while SiO₂-ZrO₂ (3/7) and ZrO₂ membranes fired at 550 °C showed larger pore size distributions than those fired at 200 °C. This can be ascribed to the crystallization and the following grain growth of ZrO₂ by firing at 550 °C. On the other hand, a ZrO₂ membrane fired at 200 °C showed very low nitrogen permeation of 3×10^{-8} mol/ (m² s Pa), which made it difficult to evaluate pore size distribution and average pore size using nanopermporometry. The decreased nitrogen permeation of a ZrO₂ membrane fired at 200 °C can be explained by an amorphous ZrO₂ phase with low porosity, which leads to a denser structure, as indicated by the N₂ adsorption results. Therefore, the firing temperatures clearly affected the average pore size of SiO₂-ZrO₂ membranes with zirconia content larger than approximately 50 mol%.

Fig. 5 Dimensionless permeability of nitrogen as a function of Kelvin diameter (vapor: hexane) for (a) SiO₂, (b) SiO₂-ZrO₂ (9/1), (c) SiO₂-ZrO₂ (7/3), (d) SiO₂-ZrO₂ (5/5), (e) SiO₂-ZrO₂ (3/7), and (f) ZrO₂ membranes fired at 200 and 550 °C.

Table 2

Average pore size and N₂ permeance of membranes by nanopermoporometry

Membrane	Firing [°C]	Average pore diameter [nm]	N ₂ permeance [10 ⁻⁶ mol/ (m ² s Pa)]
SiO ₂	200	0.70	2.0
	550	0.75	3.2
SiO ₂ -ZrO ₂ (9/1)	200	0.80	4.2
	550	0.80	4.6
SiO ₂ -ZrO ₂ (7/3)	200	0.80	3.4
	550	0.75	3.0
SiO ₂ -ZrO ₂ (5/5) [18]	200	0.65	4.5
	550	0.70	5.4
SiO ₂ -ZrO ₂ (3/7)	200	0.85	5.4
	550	1.00	6.8
ZrO ₂	200	-*	0.03
	550	1.05	2.0

* Nanopermoporometry could not be applied to evaluate pore sizes due to low N₂ permeance.

3.3 Hydrothermal stability of SiO₂-ZrO₂ membranes with different Si/Zr molar ratios in hot water

Fig. 6 shows the water permeability (L_p) and the rejection at 25 °C for SiO₂, SiO₂-ZrO₂ (9/1),

7/3, 5/5, 3/7), and ZrO₂ membranes fired at 200 and 550 °C as a function of treatment time in water at 90 °C. Before treatment of membranes in hot water, the L_p of SiO₂ and SiO₂-ZrO₂ (9/1, 7/3, 5/5) membranes fired at 200 °C were slightly larger than those fired at 550 °C. The decreased water permeability with an increase in firing temperature was ascribed to hydrophilicity/hydrophobicity and porosity changes [18]. As discussed previously in relation to Fig. 3, the specific surface areas and pore volumes of SiO₂ and SiO₂-ZrO₂ (9/1, 7/3, 5/5) powders fired at 200 °C were larger than those fired at 550 °C, which suggested that the water permeability decreased with an increase in firing temperature for SiO₂-ZrO₂ membranes with zirconia content of less than 50 mol%. On the other hand, SiO₂-ZrO₂ (3/7) and ZrO₂ membranes fired at 550 °C showed a larger rate of water permeability than those fired at 200 °C due to the formation of the crystalline structures and the resultant larger pores at high firing temperatures, which was consistent with the results of XRD and nanopermporometry.

After treatment of membranes [by immersion](#) in water at 90 °C for SiO₂ and SiO₂-ZrO₂ (9/1, 7/3) membranes fired at 200 and 550 °C, the water permeability increased dramatically during treatment time, while the rejection of solutes decreased immediately, as shown in Figs. 7 (a-1,-2, b-1,-2, c-1,-2). In particular, the rejection of glucose for SiO₂ and SiO₂-ZrO₂ (9/1) membranes, even when fired at 550 °C, was decreased to almost zero. The increase in water permeability and the decrease in the rejection of solutes for SiO₂ and SiO₂-ZrO₂ (9/1, 7/3) membranes can be explained by the dissolution of Si into water at 90 °C (Fig. 4), which enlarged the membrane pore sizes, as schematically shown in Fig. 8 (a). Additionally, Fig. 9 (a) shows the pore size distributions of SiO₂-ZrO₂ (9/1) membrane fired at 550 °C, as evaluated by nanopermporometry before/after treatment in water at 90 °C. It was clear that SiO₂-ZrO₂ (9/1) membrane after treatment showed increases in the average pore size from 0.80 to 1.15 nm. Therefore, it can be concluded that SiO₂ and SiO₂-ZrO₂ (9/1, 7/3) membranes (rich silica) were unstable in water at 90 °C.

On the other hand, as shown in Fig. 6 (d), the water permeability for SiO₂-ZrO₂ (5/5) membranes fired at 200 and 550 °C increased dramatically after membrane treatment in water at 90

°C for 4 h, and were stable for as long as 100 h. This increase in water permeability was ascribed to increased hydrophilicity in nanoporous membranes and to the dissolution of silica into water at 90 °C. Interestingly, SiO₂-ZrO₂ (5/5) membrane fired at 200 °C, the rejection of glucose decreased rapidly from 80 to 60% after treated membrane for 4 h and showed stable values for as long as 100 h, while the rejection of glucose for SiO₂-ZrO₂ (5/5) membrane fired at 550 °C remained stable during treatment time for as long as 100 h, as shown in Figs. 7 (d-1,-2). The decrease in the rejection of glucose for SiO₂-ZrO₂ (5/5) membrane fired at 200 °C can be explained by the dissolution of silica in water, as previously discussed in Fig. 4. The SiO₂-ZrO₂ (5/5) powder fired at 200 °C showed a larger degree of the solubility of silica than that fired at 550 °C, which led to an increase in pore sizes and a decrease in rejection of glucose, as schematically shown in Fig. 8 (b). Therefore, the SiO₂-ZrO₂ (5/5) membrane fired at 550 °C was more hydrothermally stable in water at 90 °C than those fired at 200 °C. This was also confirmed by the nanoporimetry results, as shown in Fig. 9 (b). The SiO₂-ZrO₂ (5/5) membrane fired at 550 °C before/after treatment in water at 90 °C showed a similar pore size distribution and an average pore size. Moreover, as reported previously [19], we evaluated the hydrothermal stability of SiO₂-ZrO₂ (5/5) membranes in water at 90 °C first by immersion (static test) followed by filtration (dynamic test as long as for 12 h). The water permeability and the rejection of solutes at 25 °C showed similar values after hydrothermal treatment by static and dynamic tests. This indicated that SiO₂-ZrO₂ membranes achieved hydrothermal stability after the first immersion treatment.

On the contrary, after the treatment of SiO₂-ZrO₂ (3/7) and ZrO₂ membranes, water permeability was decreased dramatically, as shown in Figs. 6 (e, f), while the rejection of solutes was increased (Figs. 7 (e-1,-2 and f-1,-2)) during the initial 10 h treatment in water at 90 °C, the values remained stable for as long as 100 h. This can be explained by the formation of OH groups in the membrane pores [14, 35, 36], as schematically shown in Figs. 8 (c, d), which reduced the pore sizes and consequently led to a decreased water permeability and an increased rejection. Moreover, as shown in the nanoporimetry results in Fig. 9 (c), the average pore size of a SiO₂-ZrO₂ (3/7)

membrane fired at 550 °C was decreased from 1.05 to 0.90 nm after treatment membrane in water at 90 °C. Therefore, the decreased water permeability and increased rejection for SiO₂-ZrO₂ (3/7) membranes were mainly due to the decrease in membrane pore sizes and also to changes in hydrophilicity, as well as to interactions between the solute/solvent and the membrane surface.

Fig. 6 Water permeability (L_p) at 25 °C as a function of time after treatment in water at 90 °C for membranes fired at 200 and 550 °C. (a) SiO₂ membranes, (b) SiO₂-ZrO₂ (9/1) membranes, (c) SiO₂-ZrO₂ (7/3) membranes, (d) SiO₂-ZrO₂ (5/5) membranes, (e) SiO₂-ZrO₂ (3/7) membranes, and (f) ZrO₂ membranes.

Fig. 7 Rejection of solutes at 25 °C as a function of time after treatment in water at 90 °C for membranes fired at 200 and 550 °C. (a-1, -2) SiO₂ membranes, (b-1, -2) SiO₂-ZrO₂ (9/1) membranes, (c-1, -2) SiO₂-ZrO₂ (7/3) membranes, (d-1, -2) SiO₂-ZrO₂ (5/5) membranes, (e-1, -2) SiO₂-ZrO₂ (3/7) membranes, and (f-1, -2) ZrO₂ membranes.

Fig. 8 Schematic of SiO_2 , $\text{SiO}_2\text{-ZrO}_2$ (9/1, 7/3, 5/5, 3/7) and ZrO_2 membrane pores after treatment in water at 90 °C.

Fig. 9 Dimensionless permeability of nitrogen as a function of Kelvin diameter (vapor: hexane) before/after treatment in water at 90 °C for 10 h. Membranes were dried at 200 °C at least 15 min before measurement by nanoporometry; (a) $\text{SiO}_2\text{-ZrO}_2$ (9/1), (b) $\text{SiO}_2\text{-ZrO}_2$ (5/5), and (c) $\text{SiO}_2\text{-ZrO}_2$ (3/7) membranes fired at 550 °C.

The performances of SiO_2 , $\text{SiO}_2\text{-ZrO}_2$ (9/1, 7/3, 5/5, 3/7) and ZrO_2 membranes in water at 90 °C are summarized in Table 3. The SiO_2 and $\text{SiO}_2\text{-ZrO}_2$ (9/1, 7/3) membranes fired at 200 and 550 °C were unstable in water at 90 °C due to a dramatic increase in water permeability and decreased rejection ($\text{MWCO} > 1000$). On the other hand, $\text{SiO}_2\text{-ZrO}_2$ (5/5, 3/7) and ZrO_2 membranes were more stable in hot water than the SiO_2 and $\text{SiO}_2\text{-ZrO}_2$ (9/1, 7/3) membranes. The $\text{SiO}_2\text{-ZrO}_2$ (5/5) membrane fired at 550 °C gave a constant MWCO of 300 after treated membranes in water at 90 °C while the MWCO for $\text{SiO}_2\text{-ZrO}_2$ (5/5) membrane fired at 200 °C was slightly increased from 240 to 310. In addition, the MWCO of the $\text{SiO}_2\text{-ZrO}_2$ (3/7) membranes fired at 200 and 550 °C decreased dramatically from 420 to 220 and from 800 to 290, respectively, while the MWCO for

ZrO₂ membranes fired at 200 and 550 °C decreased slightly from 180 to 160 and from 1200 to 1000, respectively. The changes in L_p and MWCO after treatment in hot water were ascribed to decreases in the membrane pores, as discussed previously in Figs. 8 (c) and 9 (c).

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Table 3

Summary of the membrane performances in water at 90 °C

Membrane	Firing [°C]	Water permeability [10 ⁻¹² m ³ /(m ² s Pa)]	MWCO [g/mol]
SiO ₂	200	1.1, 21*	340, > 1000*
	550	0.8, 19*	280, > 1000*
SiO ₂ -ZrO ₂ (9/1)	200	4.0, 58*	340, > 1000*
	550	2.1, 17*	340, > 1000*
SiO ₂ -ZrO ₂ (7/3)	200	4.1, 25*	400, > 1000*
	550	1.9, 13*	320, 800*
SiO ₂ -ZrO ₂ (5/5) [19]	200	3.2, 8.8*	240, 310*
	550	2.0, 4.9*	300, 300*
SiO ₂ -ZrO ₂ (3/7)	200	11, 5.2*	420, 220*
	550	15, 6.5*	800, 290*
ZrO ₂	200	0.12, 0.07*	180, 160*
	550	1.7, 1.1*	1200, 1000*

*After treatment in water at 90 °C

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The Ferry-Renkin equation can be used to estimate the rejection using a membrane pore size and a solute radius. The membrane pores were assumed to consist of circular capillaries with a radius (r) that compares to a solute molecule radius (a). The rejection of a membrane can be calculated using the following equation [37].

$$R = \left[1 - 2 \left(1 - \frac{a}{r} \right)^2 + \left(1 - \frac{a}{r} \right)^4 \right] \times 100\% \quad (5)$$

The correlation between the solute radius (a , in Å) and the molecular weight (MW, in g/mol) of a solute is as follows [38]:

$$a = 0.33(MW)^{0.46} \quad (6)$$

Fig. 10 shows the molecular weight cut-offs of SiO₂-ZrO₂ membranes before/after treatment in water at 90 °C as a function of the water permeability. For comparison, the performances of SiO₂-ZrO₂ (9/1), Al₂O₃, ZrO₂, TiO₂ and polymeric nanofiltration membranes are also added. SiO₂-ZrO₂ (5/5, 3/7) membranes showed high performance after treatment in water at 90 °C; L_p ranged from 3×10^{-12} to 1.5×10^{-11} m³/ (m² s Pa) and MWCO ranged from 200 to 400. SiO₂-ZrO₂ (5/5, 3/7) membranes showed high permeability and low MWCO, compared with ceramic and polymeric nanofiltration membranes. The curve in the figure was calculated using Eqs. (3), (5) and (6) and assuming that the thickness of the separation layer (top layer) was 0.65 µm, as observed by SEM [18], and assuming a porosity of 0.1, showing a consistent trend with the experimental data.

Fig. 10 The trade-offs in molecular weight cut-off (MWCO) at 25 °C as a function of the water permeability (L_p) for SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ membranes (closed/open keys indicate before/after treatment in water at 90 °C; a curve inside the figure is calculated using Ferry's equation).

3.4 Chemical stability of SiO₂-ZrO₂ (5/5, 3/7) membranes in acid and alkaline solutions

The chemical stability tests of SiO₂-ZrO₂ (5/5, 3/7) nanofiltration membranes were conducted in corrosive liquids with strong acid (pH 2) and alkaline solutions (pH 12). Evaluation of membrane corrosion was based on the change in the water permeability and rejection of membranes, as shown in Fig. 11 and summarized in Table 4. After soaking at pH 2, SiO₂-ZrO₂ (5/5, 3/7) membranes showed stable water permeabilities and MWCOs for as long as 4 weeks, confirming a high level of corrosion resistance. On the other hand, during the first corrosion test at pH 12 for 1

day, the water permeability and the MWCO of SiO₂-ZrO₂ (5/5, 3/7) membranes increased dramatically and then showed stable values for as long as 4 weeks. Based on these data, it appears that the SiO₂-ZrO₂ (5/5, 3/7) membranes showed high chemical stability not only in acid (pH 2) for as long as 4 weeks, and but also in alkaline solutions (pH 12).

An increase in the water permeability and a decrease in rejection can be explained by an increase in the pore size due to the dissolution of Si, as shown in Fig. 12. The dissolution of Si for SiO₂ powders depended on pH. The dissolution of Si at pH 12 was larger than that at either pH 7 or 2, which was much higher than that for the dissolution of Si in SiO₂-ZrO₂ (5/5, 3/7) powders. Moreover, SiO₂-ZrO₂ (5/5, 3/7) powders at pH 2 and 7 showed the lowest levels for the dissolution of Si (0.40 ppm) and Zr (0.03 ppm). At pH 12, however, the dissolution of Si and Zr for SiO₂-ZrO₂ (5/5, 3/7) powders increased dramatically. The solubility of Si reportedly increased at high pH because of the formation of silicate ions from the addition to Si(OH)₄ in solution, while the solubility at low pH was much lower, which could be increased by the reaction of Si(OH)₄ with acids [47]. Bai et al. [48] reported that the cations (Na⁺) from inorganic salts increased the dissolution rate of Si, but the anions (Cl⁻) did not affect the dissolution rate of Si. These results are consistent with the literature [49, 50], suggesting that the water permeability of SiO₂-ZrO₂ (5/5, 3/7) membranes was increased after soaking in the NaOH solution at pH 12 due to the dissolution of Si. Moreover, the specific surface area of silica, as well as the conditions of temperature, pressure, and electrolyte concentration also affected the dissolution of Si [51, 52].

In addition, the dissolution experiment of SiO₂ and SiO₂-ZrO₂ (5/5, 3/7) powders was repeated by refilling with acid and alkaline solutions of pH 2 and 12, and is shown in Fig. 13. The dissolution of Si for powders at pH 2 was less than that at pH 12. Interestingly, the solubility of Si for SiO₂-ZrO₂ (5/5, 3/7) powders at pH 2 for 21 days (second times) decreased from 0.40 to 0.05 ppm. The same trend was also observed for pH 12. The decrease in the dissolution of Si with the repeating dissolution experiments can be explained as follows. Initially, the surface was covered with a SiO₂-ZrO₂ composite, and the SiO₂-rich portion on the surface might have dissolved into an aqueous phase, leaving a ZrO₂-rich phase. Repeated dissolution made the surface of the powders

rich in ZrO_2 , and these were even covered with ZrO_2 , leading to a stable surface.

Fig. 11 The water permeability (L_p) and the rejection of solutes at 25 °C as a function of treatment time after soaking membranes at pH 2 and 12; (a-1,-2, -3) $\text{SiO}_2\text{-ZrO}_2$ (5/5) membranes and (b-1,-2, -3) $\text{SiO}_2\text{-ZrO}_2$ (3/7) membranes.

Fig.12 (a, b) Solubility of Si and Zr for SiO_2 , $\text{SiO}_2\text{-ZrO}_2$ (5/5, 3/7) powders fired at 550 °C in acid (HCl, pH 2) and alkaline solutions (NaOH, 12) at 25 °C for 7 days.

Fig.13 (a, b) Solubility of Si for SiO_2 , $\text{SiO}_2\text{-ZrO}_2$ (9/1, 5/5) powders fired at 550 °C in acid (pH 2) and alkaline solutions (pH 12) at 25 °C as a function of time (7 days for first dissolution, 14-28 days for repeating dissolution); the solubility of Zr for $\text{SiO}_2\text{-ZrO}_2$ (5/5, 3/7) powders were 0.03-0.09 ppm.

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Table 4
 Summary of the water permeability and MWCO for SiO₂-ZrO₂ (5/5, 3/7) membrane performance in acid and alkaline solutions

Membranes	Corrosion test	Water permeability [10 ⁻¹² m ³ /(m ² s Pa)]	MWCO [g/mol]
SiO ₂ -ZrO ₂ (5/5)	pH 7	5.6	280
	pH 2 (1 day)	5.7	280
	pH 2 (4 weeks)	5.7	280
	pH 7	5.0	240
	pH 12 (1 day)	8.3	320
	pH 12 (4 weeks)	8.4	320
SiO ₂ -ZrO ₂ (3/7)	pH 7	6.0	270
	pH 2 (1 day)	6.2	270
	pH 2 (4 weeks)	6.2	270
	pH 7	5.2	220
	pH 12 (1 day)	12.6	380
	pH 12 (4 weeks)	12.6	380

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4. Conclusions

SiO₂-ZrO₂ nanofiltration membranes with different molar ratios (SiO₂, SiO₂-ZrO₂ (9/1, 7/3, 5/5, 3/7) and ZrO₂ sols), which were prepared by coating the sol onto cylindrical α -alumina porous tubes fired at 200 and 550 °C, showed an average pore size ranging from 0.65 to 1.05 nm. SiO₂ and SiO₂-ZrO₂ (9/1, 7/3) membranes fired at 200 and 550 °C showed the same average pore size at approximately 0.70-0.80 nm, while firing at 550 °C increased the average pore size of SiO₂-ZrO₂ (5/5, 3/7) and ZrO₂ membranes due to the resultant crystalline structure of ZrO₂.

The stability of membrane performance was evaluated by the water permeability and the rejection of solutes at 25 °C after treatment in water at 90 °C. SiO₂ and SiO₂-ZrO₂ (9/1, 7/3) membranes showed decreased rejection of solutes after treatment for 4 h. The decrease in the rejection was explained by the dissolution of silica, which led to an increase in the sizes of membrane pores. On the other hand, SiO₂-ZrO₂ (5/5, 3/7) and ZrO₂ membranes were stable after treatment in hot water for 10 h and showed stable values in terms of water permeability and rejection for treatment times as long as 100 h. Interestingly, after treatment during the initial 4 hr, the water permeability of SiO₂-ZrO₂ (5/5) membranes fired at 550 °C increased dramatically

(rejection was constant), while the water permeability of SiO₂-ZrO₂ (3/7) and ZrO₂ membranes was decreased (rejection increased). The increase/decrease in water permeability after hydrothermal treatment for SiO₂-ZrO₂ membranes can be ascribed to the balance of hydrophilicity/hydrophobicity, dissolution of Si, and the generation of OH groups.

For chemical stability of nanofiltration membranes in acid and alkaline solutions, the SiO₂-ZrO₂ (5/5, 3/7) membranes showed high stability in a corrosive test at pH 2 throughout an exposure time of 4 weeks. On the other hand, in a corrosive test at pH 12, the water permeability of the SiO₂-ZrO₂ (5/5, 3/7) membranes increased dramatically after 1 day of soaking, indicating membrane corrosion. However, after the corrosion test at pH 12 for 4 weeks, the water permeability and MWCO were as stable as in the initial corrosion (1 day), so that the membrane appeared completely stable. Therefore, SiO₂-ZrO₂ (5/5, 3/7) membranes were confirmed to show high corrosion resistance at pH 2 and 12.

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Graphical abstract

SiO₂-ZrO₂ nanofiltration membranes of different Si/Zr molar ratios

- ✓ Water permeability (L_p) ranged from 10^{-12} to 10^{-11} m³/(m² s Pa).
- ✓ MWCOs controlled from 200-1000.
- ✓ SiO₂-ZrO₂ (5/5, 3/7) membranes showed high hydrothermal and chemical stability.