Effect of firing temperature on the water permeability of SiO₂–ZrO₂ membranes for nanofiltration

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Abstract

SiO₂-ZrO₂ membranes were successfully prepared by coating SiO₂-ZrO₂ (molar ratio 5/5) sols on cylindrical α -alumina porous supports with average pore sizes of 2.1, 2.9 and 3.6 μm followed by firing at 550 °C. The pore sizes of the SiO₂-ZrO₂ membranes, which were evaluated by nanoporometry using hexane, were 1.20 and 0.65 nm after coating with SiO₂-ZrO₂ sols of 35 and 19 nm in diameter, respectively. The membrane pore sizes were not affected by the pores of the supports, but, instead, were controlled by the colloidal sizes of the SiO₂-ZrO₂ sols that made up the top layer. SiO₂-ZrO₂ membranes, which were fired at 200, 300, 400 and 550 °C, increased slightly from 0.60 to 0.70 nm with an increase in the firing temperature, while water permeability (L_p) tended to decrease with increases in the firing temperature that ranged from $(3.3\text{--}0.8)\times 10^{-12} \text{ m}^3/(\text{m}^2 \text{ s Pa})$. The decreased water permeability was ascribed to chemical and physical changes by firing temperature such as hydrophilicity/hydrophobicity, porosity, etc. The water permeabilities of SiO₂-ZrO₂ membranes showed stable flux due to the addition of zirconia into the silica sol, showing improved stability in water. Nanofiltration performance was evaluated using aqueous solutions and showed molecular weight cut-offs ranging from 200 to 350.

Keywords: SiO₂-ZrO₂ membranes, nanofiltration, firing temperature; water permeability

1. Introduction

Membranes for water treatment can be categorized into inorganic and polymeric membranes. Inorganic membranes, which include ceramic membranes such as alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), etc., have received much attention because of their excellent stability in acidic and basic pHs, their thermal stability at high temperatures, and their high mechanical strength by comparison with polymeric membranes [1]. Ceramic membranes with pores that average several micrometers in diameter are categorized as microfiltration (MF), and are prepared by powder sintering methods, but the pore sizes are not small enough for use in molecular separation. Therefore, ceramic membranes with pore sizes in the nanometer range are prepared using ceramic microfiltration membranes as a substrate, followed by sol-coating, drying, and a firing process. Nanoporous membranes, particularly nanofiltration (NF) membranes, which have pore sizes of 1-2 nm and molecular weight cut-off (MWCO) in the range from 200-1,000, have been prepared by the sol-gel process from a variety of metal oxides such as alumina, silica, zirconia, titania, etc. Van Gestel et al. [2] reported ceramic membranes with a $\gamma\text{-Al}_2\text{O}_3$ top layer that were prepared by a sol-gel procedure and were only chemically stable in non-aqueous or mild aqueous liquids (pH 3-11). For nanofiltration membranes in an aqueous solution that are intended for applications in strong acids or alkaline media, $\alpha\text{-Al}_2\text{O}_3$ has become the preferred support with a top layer of either zirconia or titania, which has proven to be more stable than γ -alumina membranes in aqueous solutions. Van Gestel et al. [3] developed disc-type membranes that were comprised of either a microporous ZrO_2 toplayer on $\gamma\text{-Al}_2\text{O}_3$ or a ZrO_2 interlayer using $\alpha\text{-Al}_2\text{O}_3$ supports, and they found ZrO_2 membranes fired at 400 °C showed MWCOs in the range of 200-300 in the nanofiltration of aqueous polyethylene glycol solutions and high stability at low and high pH values. Voigt et al. [4] reported that TiO_2 capillary membranes fired at 400 °C showed a MWCO of approximately 250. Recently, TiO_2 membranes with nominal MWCOs of 200 were commercialized and evaluated for the rejection of organic chemicals [5].

In addition, silica is one of the most attractive membrane materials because the pore sizes can be controlled in a wide range from ultramicropores to mesopores. However, the hydrothermal stability of silica is a serious problem because it dissolves in water at room temperature, and its solubility increases with temperature. Doping silica with various types of metal ions such as zirconia (ZrO_2), titania (TiO_2), aluminum (Al), nickel (Ni) can improve its stability against water and can also provide novel separation characteristics [6]. We reported the use of SiO_2 - ZrO_2 membranes for gas separation and pervaporation. Yoshida et al. [7] prepared silica-zirconia membranes with different zirconia content (Si/Zr: 9/1, 7/3 and 5/5) by coating the sol on cylindrical α -alumina porous tubes fired at 570 °C to test H_2 separation performance under hydrothermal conditions. SiO_2 - ZrO_2 membranes were hydrothermally treated at 500 °C in a gas mixture (H_2 , N_2 and H_2O). The permeance of H_2 and N_2 through Si/Zr (9/1) and Si/Zr (7/3) membranes was decreased drastically, which was likely due to the densification of the silica matrix by water vapor at high temperature during the first 60 minutes, then it decreased slightly from 60-600 minutes and approached a constant value. However, the H_2 and N_2 permeance of Si/Zr (5/5) membranes was unchanged. The addition of a zirconia content larger than 40 mol% is known to render silica-zirconia membranes quite stable for the pervaporation performance of aqueous solutions, while a zirconia content of less than 30 mol% is not stable in water/isopropyl alcohol (IPA) mixtures, because silica dissolves easily into water [8, 9].

A limited number of studies have investigated SiO_2 - ZrO_2 membranes for nanofiltration in aqueous solutions. Tsuru et al. [10] prepared three silica-zirconia (Si/Zr molar ratio 9/1) membranes for nanofiltration by coating a silica-zirconia sol (colloidal diameter: 42 nm) on cylindrical α -alumina porous microfiltration membranes, followed by the coating of a final colloidal solution (colloidal diameter: 11, 13 and 16 nm) with firing at 570 °C. The membrane showed MWCOs of 200, 500 and 1,000 Da, respectively, indicating the pore diameters of the silica-zirconia membranes were controlled by the colloidal diameters of the sol solutions in the final coating stage. The water permeabilities of silica-zirconia (9/1) membranes showed a steady flux after a gradual decrease

during the initial two days. The decrease in water permeability was explained as silanol functional groups being generated by hydration of the silica-zirconia surface in the water and reducing the effective pore diameters for the permeation of aqueous solutions. Yazawa et al. [11] prepared SiO₂-ZrO₂ membranes with molar ratios of 9/1, 7/3, 5/5, and 3/7 by applying coatings of porous ceramic substrates for the desalination of aqueous NaCl solutions, but that study did not discuss pore size tuning in the range of nanofiltration.

The development of separation membranes with high flux, selectivity and stability is a highly anticipated industry goal. High flux can be achieved by using a thin and porous structure and appropriate interaction between the permeating molecules and the pore surface [8]. In the present study, the SiO₂-ZrO₂ (5/5) sols of controlled sizes were prepared by the concentration of alkoxides. The effect of the pore size of the supports on the pore size and water permeability of the SiO₂-ZrO₂ membranes was discussed. A particular focus of the present study was put on different firing temperatures of SiO₂-ZrO₂ membranes and the effect on water permeability and separation of aqueous solutions for nanofiltration.

2. Experimental

2.1. Preparation of SiO₂-ZrO₂ (5/5) colloidal sols

SiO₂-ZrO₂ composite colloidal sols with a molar ratio of 5/5 and with total alkoxide concentrations of 1 and 2 wt% were prepared by hydrolysis and condensation reactions of tetraethoxysilane (TEOS) and zirconium-tetra-butoxide solutions (80% ZrBT in 1-butanol), as shown in Table 1. TEOS which is less reactive than ZrBT, was partially hydrolyzed in ethanol for 3 h, and then ZrBT was added by dropping into the solution with stirring for co-condensation reactions. After 12 hr, a large amount of water and hydrochloric acid were added in order to control the pH of the solutions (<2), and the solution was boiled for 8 h to control the colloidal size. The total amount of solution was kept constant by adding water during the boiling period.

Table 1 Compositions and average colloidal diameters of SiO₂–ZrO₂ (5/5) sols

SiO ₂ -ZrO ₂ (5/5) sol	TEOS [g]	ZrBT [g]	H ₂ O [g]	HCl (35%) [g]	Colloidal diameter [nm]
1 wt%	1.76	3.24	0.61	3.15	19
2 wt%	3.52	6.48	1.22	3.15	35

The sizes of colloidal sols (particle size distribution) were measured using a dynamic laser light scattering technique (Malvern, Zen3600) at 25 °C. X-ray diffraction (XRD, Rigaku, RINT2000, Japan) and scanning electron microscopy (FESEM, Hitachi S-4800, Japan) were used to characterize SiO₂-ZrO₂ powders fired at 200-900 °C and morphologies of SiO₂-ZrO₂ membranes, respectively. SiO₂-ZrO₂ powders were evaluated for N₂ adsorption-desorption (BEL JAPAN INC., Japan) at a liquid nitrogen temperature of 77 K, and for H₂O adsorption at 25 °C. The samples were pretreated at 180 °C for 12 hr under vacuum prior to the adsorption measurements. Fourier transform infrared spectra (FT-IR, JASCO, Japan) were recorded in the range of 4,000-600 cm⁻¹ with a resolution of 4 cm⁻¹ and SiO₂-ZrO₂ powders were diluted (1:10 by weight) with potassium bromide (KBr) powder.

2.2. Fabrication of SiO₂-ZrO₂ membranes

Three types of α -Al₂O₃ cylindrical porous supports (HU-A01, HU-A02 and HU-A03; average pore size: 2.1, 2.9, 3.6 μ m; outer diameter: 1 cm; length: 10 cm) were prepared to investigate the effect of the pore sizes on the permeation properties of SiO₂-ZrO₂ membranes. α -Al₂O₃ powders in the range of 5-10 μ m were used as the starting raw materials. Each powder was added with clays as Si-sources in order to control the Al/Si ratio to 9/1 (weight based). After mixing with crystalline cellulose (as organic binder) with additional vigorous mixing, α -Al₂O₃ cylindrical supports were extruded in the shape of 10 mm of outer diameter and 8 mm in inner diameter, followed by drying and sintering under air at 1,000-1,600 °C.

SiO₂-ZrO₂ membranes were prepared by coating the SiO₂-ZrO₂ sols with a cloth on cylindrical alumina porous supports, as follows. First, α -alumina particles (average diameters 2 μ m and 0.2 μ m), using the largest size of colloidal sol (2 wt% SiO₂-ZrO₂ sol) as the binder, were coated on the surface of the cylindrical supports in order to make the surface smooth and homogeneous, followed by firing at 550 °C for 15 min. Then, 2 wt% SiO₂-ZrO₂ sol diluted to 0.5 wt% was coated on the tubes and fired at 550 °C for 15 min [7]. These procedures were repeated several times for each sol coating. Finally, 1 wt% SiO₂-ZrO₂ sol diluted to 0.5 wt% was coated on the surface, followed by calcinations under air at different firing temperatures (200, 300, 400, and 550 °C).

The pore size distribution of porous membranes was estimated using hexane or water as a condensable vapor, based on the nanoporimetry method [12]. The principle of nanoporimetry is based on the capillary condensation of a vapor in porous membranes and its ability to block the permeation of a non-condensable gas (N₂). This technique allows the measurement of pores that are less than 50 nm in size. In the case of a capillary with a small pore size, vapor condenses at a vapor pressure (P) that is lower than the saturated vapor pressure (P_s). The Kelvin diameter (d_k), which increases with an increase in the vapor pressure of condensable gas in the feed, was used to calculate pore sizes.

$$d_k = -\frac{4\sigma\nu\cos\theta}{RT\ln(P/P_s)} \quad (1)$$

where σ , ν , θ , R and T are the surface tension, the molar volume, the contact angle, the universal gas constant, and the temperature, respectively.

2.3. Nanofiltration (NF) experiments

NF experiments were carried out using the apparatus (Fig. 1) with a stirred cell under vigorous agitation at 800 rpm in order to avoid any possibility of concentration polarization. The feed solution was fed under a continuous feed-flow rate of 20 ml/min at a constant temperature of 25 ± 1 °C and an applied pressure ranging from 0.2 to 1.0 MPa. The permeate solution was collected using

a microtube pump, while the retentate was recycled back to the feed tank. The solutes used for nanofiltration were neutral-organic with different molecular weights; glucose (180), maltose (342), raffinose (504), and cyclodextrin (973), in aqueous solutions at concentrations of 500 ppm. The concentrations of the feed and permeate were measured using a total organic carbon analyzer (Shimadzu, TOC-VE). The permeate flow rate was measured by the weight of the water collected per time and returned to the feed tank during filtration. The following permeation model was used, which describes volume flux (J_v) proportional to effective transmembrane pressure ($\Delta P - \Delta \pi$), and is similar to the Hagen-Poiseuille and Darcy's equation [13]:

$$J_v = L_p(\Delta P - \Delta \pi) \quad (2)$$

where J_v is the permeate volume flux in $\text{m}^3/(\text{m}^2 \text{ s})$, L_p is the water permeability in $\text{m}^3/(\text{m}^2 \text{ s Pa})$, and ΔP and $\Delta \pi$ are the applied pressure difference and osmotic pressure difference in Pa, respectively. It should be noted that a glucose solution of 500 ppm was 0.0068 MPa, the osmotic pressure of which was negligible compared with an applied pressure of 1 MPa.

The rejection (R) of solutes, was defined as follows:

$$R = \left(1 - \frac{C_p}{C_r}\right) \times 100\% \quad (3)$$

where C_p (mg/L) and C_r (mg/L) are the concentration in the permeate and the retentate, respectively.

Fig. 1 Schematic diagram of the experimental apparatus for NF experiments.

3. Results and discussion

3.1. Characteristics of SiO₂-ZrO₂ sols and powders

SiO₂-ZrO₂ (5/5) colloidal sols with different colloidal sizes were prepared by hydrolysis and condensation. The sizes of SiO₂-ZrO₂ colloidal sols were measured using a dynamic laser light scattering technique, and are summarized in Table 1. It can be clearly seen that the 2 wt% SiO₂-ZrO₂ sol (35 nm) was larger size than the 1 wt% SiO₂-ZrO₂ sol (19 nm). The particle size was increased with an increase in the concentration of the SiO₂-ZrO₂ sol, which is consistent with our previous reports [6, 7, 14]. This can be explained as a higher concentration enhancing the growth of colloidal sol sizes [15]. Therefore, 2 wt% SiO₂-ZrO₂ sol was first coated on the α -alumina supports, followed by coating with 1 wt% SiO₂-ZrO₂ sol, in order to accomplish a coating of large to small sol sizes to form a graded structure as a selective layer.

XRD observations of SiO₂-ZrO₂ powders can show whether or not SiO₂-ZrO₂ powders are composite or simple mixtures of SiO₂ and ZrO₂. In the present study, SiO₂-ZrO₂ powders were prepared by a quick-drying method where SiO₂-ZrO₂ sols were dropped on a platinum plate that was maintained at 180 °C for instant drying, followed by firing at 200, 400, 550, 600, 700, 800, and 900 °C for 15 min. As shown in Fig. 2, it was found that SiO₂-ZrO₂ fired from 200 to 550 °C showed no crystalline structure, which suggests that the SiO₂-ZrO₂ oxides were amorphous in structure, and the added SiO₂ hindered the crystallization of ZrO₂. However, SiO₂-ZrO₂ fired at 600 °C showed a tiny crystal of approximately 2 θ to 31 degrees with a pattern that corresponded to the tetragonal structure of zirconia crystals (or the heterogeneity of composite SiO₂-ZrO₂) [6], and the peak intensities of zirconia became stronger and sharper with increases in firing temperature from 700 to 900 °C, which led to the growth of crystals and the formation of larger pores. Pure ZrO₂ is reported to the crystalline to the tetragonal phase at approximately 500 °C and to the monoclinic phase with further increases in temperature above 600 °C [16]. Andrianainarivelo et al. [17] also

reported that the crystallization of zirconia took place between 600 and 1,300 °C. Therefore, we chose a firing temperature of SiO₂-ZrO₂ membranes that was less than 600 °C in order to achieve an amorphous structure.

Fig. 2 XRD patterns of SiO₂-ZrO₂ powders fired at different temperatures.

N₂ adsorption-desorption isotherms for the SiO₂-ZrO₂ powders are given in Fig. 3 (a). SiO₂-ZrO₂ powders fired at 200 and 550 °C showed adsorption isotherms of type I (microporous) combined with type IV (mesoporous), according to IUPAC classification [18]. Especially, the SiO₂-ZrO₂ powder fired at 200 °C showed a higher adsorption than that fired at 550 °C. Values for the BET surface area of the SiO₂-ZrO₂ mixed oxides are listed in Table 2, which summarizes the effect of firing temperature of SiO₂-ZrO₂ powders on structural properties. Initially, SiO₂-ZrO₂ powder fired at a low temperature (200 °C) was amorphous, as indicated in the XRD results, and showed a high surface area. The micropores grew gradually with the firing temperatures and phase transformations happened at higher temperatures. Therefore, it can be concluded that increasing the firing temperature of SiO₂-ZrO₂ powders involves a gradual decrease in the surface area [2, 19, 20]. The surface area was approximately 10 m²/g, which was quite small, compared with pure SiO₂. This is consistent with previous work [8], and was because SiO₂ did not exist as a SiO₂ phase separated from ZrO₂, but instead formed SiO₂-ZrO₂ composite oxides. Fig. 3 (b) shows the water adsorption per unit of surface area at a P/P_s of less than 0.1 for SiO₂-ZrO₂ powders fired at 200 and 550 °C. At

200 °C, there was a drastic increase in the adsorption amount of water at a low P/P_s , suggesting that SiO₂-ZrO₂ fired at 200 °C consisted of a larger number of hydrophilic micropores than that fired at 550 °C. This is consistent with a previous report showing that water adsorption was decreased with increasing in the firing temperatures [20], and that SiO₂-ZrO₂ powder fired at 200 °C was more hydrophilic than that fired at 550 °C.

Fig. 3 (a) N₂ adsorption-desorption isotherms of SiO₂-ZrO₂ powders at 77 K.

Fig. 3 (b) H₂O adsorption per unit surface area of SiO₂-ZrO₂ powders at 298 K.

Table 2 N₂ adsorption results of SiO₂-ZrO₂ powders fired at 200 and 550 °C

Firing (°C)	S _{BET} (m ² /g)
200	13.45
550	6.86

Fig. 4 shows the IR spectra of SiO₂-ZrO₂ powders after firing at 200, 300, 400, and 550 °C. The broad peaks of hydroxyl groups centered at 3,200 cm⁻¹ were decreased with an increase in firing temperatures. In addition, other peaks at 1,640 and 3,550 cm⁻¹ were assigned to OH groups, specifically to the H-O-H bending vibration of water and -SiOH groups, respectively, and were clearly decreased with increases in the firing temperature. Other peaks at 1,090, 800 and 980 cm⁻¹ were ascribed to Si, Si-O-Si and Si-OH, respectively [16, 21-24]. A shift to a higher wave number for the Si-O-Si band due to the formation of ZrO₂, which became clearer with increases in firing temperature, indicated that the silicate network had broken down to involve Si-O-Zr linkages

(heterogeneity of zirconia and silica). The high firing temperature might have led to the phase segregation of ZrO_2 . If the number of Si-O-Zr linkage increases, the number of Si in Si-O-Si linkages in the silanol groups on the surface will decrease [23]. Araki et al. [21] reported that the number of hydroxyl and silanol groups decreased with an increase in the firing temperatures (100-400 °C) of $\text{SiO}_2\text{-ZrO}_2$ membranes. Therefore, firing $\text{SiO}_2\text{-ZrO}_2$ membranes from 200 to 550 °C produced a gradual decrease in the surface OH concentrations and silanol groups, which led to the development of hydrophobic surface chemistry.

Fig. 4 FT-IR spectra of $\text{SiO}_2\text{-ZrO}_2$ powders of firing at 200, 300, 400 and 550 °C.

3.2. Effect of the pore sizes of supports on the N_2 permeance and water permeability of $\text{SiO}_2\text{-ZrO}_2$ membranes

Pore size distributions (PSD) of the three supports, measured by permoporometry with a bubble point and Hg-intrusion porosimetry, are shown in ESI-1 and the characteristic of the three supports is summarized in Table 3. Permoporometry with bubble-point method measures the pore size distribution of a membrane and provides information on the smallest pore sizes that can be effective for permeation, and showed sharp pore size distributions at 0.67, 1.03 and 1.33 μm of HU-A01, -A02 and -A03, respectively. On the other hand, Hg-intrusion uses crashed samples to provide information on pore sizes based on pore volume. The average pore sizes of HU-A01, -A02 and -A03, measured by Hg-intrusion porosimetry, were successfully controlled from 2.1 to 3.6 μm by the

size of the α -Al₂O₃ particles. It should be noted that the order of pore sizes, as determined by Hg-intrusion porosimetry, was consistent with those determined by the permoporometry method using a bubble point.

As summarized in Table 3, with an increase in pore size, the bending strength which confirms high mechanical strength in the range of 25-50 MPa, showed a decrease tendency. Air and water permeance was increased with increases in pore size, and both were sufficient for nanofiltration due to a high porosity of 47 to 55% and to a large pore size.

Table 3 Characteristics of three types of α -Al₂O₃ supports used in this study

Supports	HU-A01	HU-A02	HU-A03
Pore size distribution (PSD)			
Bubble point [μm]	0.67	1.03	1.33
Hg-intrusion [μm]	2.14	2.90	3.61
Bending strength [MPa]	53	33	25
Air permeance* [$\text{mol}/(\text{m}^2 \text{ s Pa})$]	1.1×10^{-4}	2.4×10^{-4}	3.3×10^{-4}
Water permeance* [$\text{m}^3/(\text{m}^2 \text{ s Pa})$]	1.1×10^{-5}	2.4×10^{-5}	3.8×10^{-5}
Porosity [%]	47	51	55

* Measurement at pressure of 0.1 MPa

Fig. 5 (a) shows SEM photographs of the cross-section of a SiO₂-ZrO₂ membrane, which consisted of an α -Al₂O₃ support layer, an α -Al₂O₃ particle layer with a thickness of several micrometers, and a top SiO₂-ZrO₂ layer coated with 2 and 1 wt% SiO₂-ZrO₂ sols. The top SiO₂-ZrO₂ layer of the membrane was evidently thin (approximately 0.5 μm) as the selective layer. The pore sizes of the top layer were too small to be observed by SEM and no visible cracks/defects were observed at either higher (Fig.5 (a)) or lower magnifications (Fig.5 (b)).

Fig. 5 SEM photograph of SiO₂-ZrO₂ membranes prepared using HU-A01 support by coating with 2 and 1 wt% SiO₂-ZrO₂ sol. (a) cross-section, $\times 5000$; (b) the membrane surface, $\times 200$.

The pore size distributions of the SiO₂-ZrO₂ membranes were evaluated by nanoporimetry using hexane as a condensable vapor under the assumption of complete wetting ($\cos\theta = 1$) for the calculation of Kelvin diameters. Fig. 6 (a) shows the dimensionless permeability of nitrogen as a function of Kelvin diameters. SiO₂-ZrO₂ membranes after coating 2 and 1 wt% SiO₂-ZrO₂ sols on the 3 types of supports and firing at 550 °C showed similar pore size distributions irrespective of the pore size of the supports including HU-A01, HU-A02, and HU-A03. The average pore size, defined at 50% of dimensionless permeability, was approximately 1.3 nm after coating with 2 wt% SiO₂-ZrO₂ sol with a colloidal size of 35 nm, as shown in Table 1. Further coating with a 19 nm 1 wt% SiO₂-ZrO₂ sol on a SiO₂-ZrO₂ membrane, which had already been coated with 2 wt% SiO₂-ZrO₂ sol, reduced the pore sizes to approximately 0.65 nm. It was clear that the pore sizes of SiO₂-ZrO₂ membranes were controlled by the colloidal sol size of the SiO₂-ZrO₂ sols on top layer. Moreover, after coating with 2 and 1 wt% SiO₂-ZrO₂ sols, the three supports demonstrated a similar N₂ permeance: 10.0×10^{-6} and 4.7×10^{-6} mol/ (m² s Pa), respectively, as shown in Fig. 6 (b). Rather than the support, it was the type of SiO₂-ZrO₂ sol that was used to coat the top layer that was the determining factor in controlling the pore size. In addition, the water permeability (L_p) of the SiO₂-ZrO₂ membrane was similar for three types of supports, as shown in Fig. 7.

Fig. 6 (a) Dimensionless permeability of nitrogen as a function of Kelvin diameter (vapor: hexane).
 (b) N_2 permeances and average pore sizes of SiO_2 - ZrO_2 membranes coated with 2 and 1 wt% SiO_2 - ZrO_2 sol and fired at 550 °C.

Fig. 7 Water permeability of SiO_2 - ZrO_2 membranes after coating 1 wt% SiO_2 - ZrO_2 sol on different supports (pure water, $\Delta P = 1$ MPa at 25 °C).

Fig. 8 shows the N_2 permeation resistance, which is the reciprocal of the permeance of the α -alumina support, the particle layer, and the 2 and 1 wt% SiO_2 - ZrO_2 layer. After coating with 1 wt% SiO_2 - ZrO_2 sol as a selective layer, the N_2 permeation resistance increased dramatically (1.2×10^5 m² s Pa/mol), while N_2 permeation after coating with the particle layer and 2 wt% SiO_2 - ZrO_2 sol showed a low resistance of 0.3×10^5 and 0.5×10^5 m² s Pa/mol, respectively. The water permeability (L_p) after coating with 2 and 1 wt% SiO_2 - ZrO_2 sols is shown in Fig. 9 (a). The L_p decreased from 25.7×10^{-12} to 1.3×10^{-12} m³/(m² s Pa) after the coating with 1 wt% SiO_2 - ZrO_2 sol (smaller colloidal size), because the pore size of SiO_2 - ZrO_2 membranes was decreased from 1.3 nm to 0.65 nm. Therefore, it is reasonable that the SiO_2 - ZrO_2 layer, which showed the largest N_2 permeance

resistance, controlled the performance of the SiO₂-ZrO₂ membranes. However, as shown in Fig. 9 (b), the rejection of solutes, including glucose (180), maltose (342), raffinose (504), and cyclodextrin (973), was increased from 10 to 80-98%, which was consistent with the pore sizes, as determined by Nanopermporometry. Therefore, it can be concluded that the pore sizes of SiO₂-ZrO₂ membranes were successfully controlled by the colloidal sizes of the SiO₂-ZrO₂ sols used for coating the top layer.

Fig. 8 N₂ permeance resistance of α -alumina support, coating with particle layer, 2 wt% and 1 wt% SiO₂-ZrO₂ sol firing 550°C by using HU-A01 as support.

Fig. 9 (a) Water permeability (L_p) and (b) rejection of coating with 2 and 1wt% SiO₂-ZrO₂ sol fired at 550 °C.

3.3. The effect of firing temperature on the nanofiltration performance of SiO₂-ZrO₂ membranes

Fig. 10 shows the dimensionless permeability of nitrogen (using hexane as condensable vapor) as a function of Kelvin diameters. Four SiO₂-ZrO₂ membranes, which were prepared by coating with 2 wt% SiO₂-ZrO₂ sol fired at 550 °C, showed the same pore size distribution and an average pore size

of approximately 1.2 nm, which confirmed reproducibility. The SiO₂-ZrO₂ membranes were further coated with 1 wt% SiO₂-ZrO₂ sol and fired at different temperatures: 200, 300, 400, and 550 °C. The average pore size of SiO₂-ZrO₂ membranes were similar ranging from 0.60-0.70 nm, and the detailed analysis reveals a tendency toward a slight increase with an increase in the firing temperature from 200 to 550°C, as shown in Fig. 11. Wu et al. [25] reported that the membrane pore sizes were increased with increases in firing temperature, and a drastic increase was observed at the temperatures of phase transformation. This is the reason why the SiO₂-ZrO₂ membranes fired at 200-550 °C showed a slight increase in the average pore size due to the amorphous phase of SiO₂-ZrO₂ for firing temperatures below 600 °C. Moreover, after coating with 1 wt% SiO₂-ZrO₂ sols, the N₂ permeance of SiO₂-ZrO₂ membranes increased slightly from 0.45×10^{-5} to 0.54×10^{-5} mol/ (m² s Pa) with an increase in the firing temperature. This indicates that the pore sizes of the SiO₂-ZrO₂ membranes were primarily determined by the colloidal sol sizes.

Fig. 10 Dimensionless permeability of nitrogen as a function of Kelvin diameter; 2 wt% SiO₂-ZrO₂ sol were fired at 550 °C; 1 wt% SiO₂-ZrO₂ sol were fired at 200, 300, 400 and 550 °C.

Fig.11 Average pore size and N₂ permeance of SiO₂-ZrO₂ membranes after coating with 1 wt% SiO₂-ZrO₂ sol as a function of firing temperature.

Fig. 12 (a) shows the time course for the water permeability (L_p) of SiO₂-ZrO₂ membranes coated with 1 wt% SiO₂-ZrO₂ sol fired at 200 and 550 °C. SiO₂-ZrO₂ (5/5) membranes fired at 200 and 550 °C showed a slight decrease in water permeability (L_p) in the initial 30 hr, then reached stable values for as long as 100 hr. The L_p of a SiO₂-ZrO₂ membrane fired at 200 °C showed higher than one fired at 550 °C, which will be discussed later. For the case of SiO₂-ZrO₂ (9/1), the water permeability of SiO₂-ZrO₂ (9/1) membranes decreased gradually during the first 2 days before reaching a stable flux. The decrease in water permeability was explained by the hydration of the silica-zirconia surface in water to form SiOH and ZrOH groups [6, 10, 11, 26]. That result suggested that the increase in zirconia in the SiO₂-ZrO₂ sol improved the stability of the SiO₂-ZrO₂ membranes in water. Fig. 12 (b) shows the permeate flux (J_v) of the SiO₂-ZrO₂ membranes as a function of applied pressure. The permeate flux of both SiO₂-ZrO₂ membranes fired at 200 and 550 °C increased linearly to applied pressure.

Fig. 12 (a) Water permeability (L_p) of SiO₂-ZrO₂ membranes fired at 200 and 550 °C as a function of time course ($\Delta P=1.0$ MPa, 25 °C).

Fig. 12 (b) The permeate flux (J_v) of SiO₂-ZrO₂ membranes fired at 200 and 550 °C as a function of applied pressure.

Fig. 13 shows the rejection and water permeability of SiO₂-ZrO₂ membranes (1 wt% sol-coating) fired at 200-550 °C. Rejections of maltose, raffinose and cyclodextrin for SiO₂-ZrO₂ membranes fired at 200 and 300 °C were higher than 95%, while those for SiO₂-ZrO₂ membranes fired at 400

and 550 °C showed a decreased tendency. The decrease in rejection of SiO₂-ZrO₂ membranes with increases in the firing temperature was explained due to a slight increase in the size of membrane pores. SiO₂-ZrO₂ membranes fired at 200, 300, 400, and 550 °C showed a MWCO at 90% rejection of approximately 200, 250, 275 and 350 g/mol, respectively. Nanofiltration (NF) membranes were successfully prepared with MWCOs ranging from 200 to 1,000 [27, 28].

The water permeability (L_p) showed a tendency to decrease with increases in firing temperature that ranged from 200 to 550 °C. Based on N₂ adsorption data (Table 2), the decreased water permeability can be explained by the decreased surface area, which was caused by the densification and low porosity of SiO₂-ZrO₂ membranes fired at high temperature. However, this cannot explain why the values for pore sizes and N₂ permeance were slightly increased with increases in firing temperature, as shown in Fig. 11. Therefore, it was suggested that the effects of surface chemistry such as hydrophilicity/hydrophobicity partially contributed to the decrease in water permeability. As discussed previously, the FT-IR results suggested that a low firing temperature resulted in an increase in hydrophilicity. In addition, Araki et al. [21] studied the effect of firing temperatures of silica-zirconia (5/5) membranes on the dehydration of isopropyl alcohol/water mixtures in pervaporation. The water flux of IPA/water mixtures was reportedly reduced with increasing firing temperatures due to a decrease in the number of silanol groups by the sintering. It was clear that firing temperatures affected the water permeability of SiO₂-ZrO₂ membranes not only in pervaporation but also in nanofiltration.

Fig. 13 Water permeability (L_p) and rejection at $\Delta P = 1 \text{ MPa}$ as a function of firing temperatures.

Fig. 14 (a) and (b) shows the dimensionless permeability of nitrogen based on nanoporimetry measurement using the condensable vapor of hexane and water as a function of the Kelvin diameter for $\text{SiO}_2\text{-ZrO}_2$ membranes fired at 200 and 550 °C, respectively. Nanoporimetry characterization using hexane and water enables the determination of pore sizes as well as hydrophilicity/hydrophobicity of the nano-sized pores (ESI-2). Our previous study [29, 30] revealed that in hydrophilic pores, similar pore-size distributions were obtained under the assumption of a contact angle of zero for water and hexane as condensable vapors, indicating capillary condensation occurred at the same Kelvin diameters. On the other hand, in hydrophobic pores, the pore size distribution measured with water vapor shifted to larger sizes because a higher vapor pressure of water was required for capillary condensation.

The nitrogen permeability of $\text{SiO}_2\text{-ZrO}_2$ membranes fired at 200 and 550 °C was decreased drastically at a low relative pressure of vapor (P/P_s), that is, vapor pressure of condensable vapors in a small pore, due to the capillary condensation of a vapor or to the adsorption of a vapor and a

subsequent the blocking of nitrogen permeation. It was interesting, that when the pore size distributions of SiO₂-ZrO₂ membranes fired at 550 °C were measured using water as a condensable vapor, they showed a larger pore size distribution than when measured using hexane as a condensable vapor. On the other hand, SiO₂-ZrO₂ membranes fired at 200 °C showed only a slightly larger pore size distribution when using water than when using hexane. It should be noted that the pore size distribution of SiO₂-ZrO₂ membranes fired at 200 and 550 °C were approximately the same, when measured using hexane, as shown in Fig.10. Hexane, which has a low degree of surface tension, can wet both hydrophilic and hydrophobic pores, which makes it reasonable to assume that hexane vapors would have a contact angle of zero [12, 29, 30] in the Kelvin equation (Eq. (1)). However, water vapor cannot condense in hydrophobic pores. It was suggested that the contact angle of SiO₂-ZrO₂ membranes fired at 200 and 550 °C were 21° and 36°, respectively (ESI-3). Therefore, the water was condensed in the pores of a SiO₂-ZrO₂ membrane fired at 200 °C at a lower P/P_s than that fired at 550 °C due to hydrophilic surface chemistry. In conclusion, the firing temperature affected the hydrophilicity/hydrophobicity of the SiO₂-ZrO₂ membranes, which is consistent with the water adsorption and FTIR results.

Fig. 14 (a) and (b) Dimensionless permeability of nitrogen as a function of Kelvin diameter by using hexane and water as condensable vapour (assumption: $\theta_{\text{hexane}} = \theta_{\text{water}} = 0$); SiO₂-ZrO₂ membrane fired at 200 and 550 °C, respectively (upper x-axis indicates relative pressure of water and hexane).

For comparison, the performances of the ceramic nanofiltration membranes with ceramic supports are summarized in Table 4. γ - Al_2O_3 , ZrO_2 and TiO_2 are major materials that are used for nanofiltration in aqueous solutions. In addition, SiO_2 - ZrO_2 composite oxide is another class of materials for nanofiltration. We were successful in increasing the ZrO_2 composition in SiO_2 - ZrO_2 (5/5) membranes. The prepared SiO_2 - ZrO_2 membrane fired at 200 °C showed a relatively high degree of water permeability and a small molecular weight cut-off (MWCO). Therefore, we concluded that a firing temperature of 200 °C improves the water permeability of SiO_2 - ZrO_2 membranes.

Table 4 Comparison of the performance of the ceramic nanofiltration membranes

Membrane	Water permeability [$10^{-12} \text{ m}^3/(\text{m}^2 \text{ s Pa})$]	Firing [°C]	MWCO [g/ mol]	Reference
γ - Al_2O_3	3.0	450	380	[24]
	3.8	450	450	[24]
	6.3	400	900	[31]
ZrO_2	0.5	350	354	[32]
	0.8	400	1195	[32]
TiO_2	1.8	350	890	[33]
	2.0	450	500	[34]
	3.0	450	250	[34]
	36	300	3000	[35]
	27	250	450	[4]
Si/Zr (9/1)	0.8	570	1200	[36]
	1.5	570	200	[10]
	6.6	570	500	[10]
Si/Zr (5/5)	3.3	200	200	This work
	2.0	300	250	This work
	1.1	400	275	This work
	0.8	550	350	This work

4. Conclusions

SiO₂-ZrO₂ nanoporous membranes, which were prepared by the coating of SiO₂-ZrO₂ sols on different types of porous α -alumina supports (HU-A01; 2.1 μ m, HU-A02; 2.9 μ m and HU-A01-3; 3.6 μ m), showed approximately the same average pore size, N₂ permeance and water permeability irrespective of the pore sizes of the supports. Therefore, the use SiO₂-ZrO₂ sols with appropriate colloidal sol sizes as a selective layer can play an important role in determining the average pore size and water permeability of a membrane.

SiO₂-ZrO₂ (molar ratio 5/5) membranes fired at 200, 300, 400 and 550 °C were evaluated for nanofiltration of aqueous solutions (glucose, maltose, raffinose and cyclodextrin). Firing temperature affected both the surface chemistry and the pore structure of the SiO₂-ZrO₂ membranes. The water permeability (L_p) of membranes was decreased with increasing firing temperatures from 3.3×10^{-12} to 0.8×10^{-12} m³/ (m² s Pa). The SiO₂-ZrO₂ membranes with average pore sizes of approximately 0.60-0.70 nm showed a molecular weight cut-off (MWCO) that ranged from 200-350 g/mol.

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