



# SiO<sub>2</sub>-ZrO<sub>2</sub> nanofiltration membranes of different Si/Zr molar ratios: Stability in hot water and acid/alkaline solutions



Waravut Puthai, Masakoto Kanazashi, Hiroki Nagasawa, Toshinori Tsuru\*

Department of Chemical Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan

## ARTICLE INFO

### Keywords:

SiO<sub>2</sub>-ZrO<sub>2</sub> membrane  
Si/Zr molar ratios  
Nanofiltration  
Hydrothermal stability  
pH stability

## ABSTRACT

SiO<sub>2</sub>-ZrO<sub>2</sub> nanofiltration membranes were fabricated by coating different molar ratios of SiO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub> (9/1, 7/3, 5/5, 3/7), and ZrO<sub>2</sub> sols onto  $\alpha$ -alumina porous tubes and firing at 200 and 550 °C. The SiO<sub>2</sub> and SiO<sub>2</sub>-ZrO<sub>2</sub> (9/1, 7/3, 5/5) membranes fired at 200 and 550 °C showed pore diameters ranging from 0.65 to 0.80 nm, while SiO<sub>2</sub>-ZrO<sub>2</sub> (3/7) and ZrO<sub>2</sub> membranes fired at 550 °C showed larger pores than those fired at 200 °C due to the formation of crystalline structures in the ZrO<sub>2</sub>.

SiO<sub>2</sub>-ZrO<sub>2</sub> membranes with a zirconia content larger than 50 mol% showed high hydrothermal stability in hot water (90 °C). After treating SiO<sub>2</sub>-ZrO<sub>2</sub> (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 SiO<sub>2</sub>-ZrO<sub>2</sub> (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, SiO<sub>2</sub>-ZrO<sub>2</sub> (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.

## 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 (ZrO<sub>2</sub>), titania (TiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), and silica (SiO<sub>2</sub>) 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 TiO<sub>2</sub> nanofiltration membranes onto  $\alpha$ -alumina capillary supports and studied nanofiltration performance at temperatures ranging from 30 to 80 °C. Voigt et al. [9] developed TiO<sub>2</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> NF membranes in acid and alkaline solutions. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membranes showed limited stability in aqueous media (pH 3–11), while the TiO<sub>2</sub> and ZrO<sub>2</sub> membranes demonstrated high stability at pH values ranging from 1 to 13. Schaep et al. [12] reported that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanofiltration membranes were unstable at pH 2 or lower after an exposure time of 26 h. Moreover, SiO<sub>2</sub> 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 SiO<sub>2</sub>-ZrO<sub>2</sub> membranes for gas separation and pervaporation. Yoshida et al. [15] prepared SiO<sub>2</sub>-ZrO<sub>2</sub>

\* Corresponding author.

E-mail address: [tsuru@hiroshima-u.ac.jp](mailto:tsuru@hiroshima-u.ac.jp) (T. Tsuru).

membranes with different ZrO<sub>2</sub> contents (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<sub>2</sub> and H<sub>2</sub> under water vapor. They found that the pores for N<sub>2</sub> permeation were decreased with increases in ZrO<sub>2</sub> content, suggesting the SiO<sub>2</sub>-ZrO<sub>2</sub> matrix was densified by the increase in zirconia content. For hydrothermal stability, the N<sub>2</sub> and H<sub>2</sub> permeance of SiO<sub>2</sub>-ZrO<sub>2</sub> (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<sub>2</sub> and H<sub>2</sub> permeance of SiO<sub>2</sub>-ZrO<sub>2</sub> (5/5) membranes was unchanged. Asaeda et al. [14,16] reported that SiO<sub>2</sub>-ZrO<sub>2</sub> 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 SiO<sub>2</sub>-ZrO<sub>2</sub> membrane performance for nanofiltration in an aqueous solution, although SiO<sub>2</sub> composites have a great advantage in pore-size controllability. Tsuru et al. [17] prepared SiO<sub>2</sub>-ZrO<sub>2</sub> (9/1) membranes for nanofiltration in order to study their stability in an aqueous solution at 25 °C. The water permeability of SiO<sub>2</sub>-ZrO<sub>2</sub> (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 SiO<sub>2</sub>-ZrO<sub>2</sub> surface in the water, which reduced the effective pore diameters for the permeation of water. We reported [18] the nanofiltration of SiO<sub>2</sub>-ZrO<sub>2</sub> (5/5) membranes fired at 200, 300, 400, and 550 °C. The water permeability of SiO<sub>2</sub>-ZrO<sub>2</sub> (5/5) membranes decreased with an increase in the firing temperature due to chemical and physical changes. The water permeability of SiO<sub>2</sub>-ZrO<sub>2</sub> (5/5) membranes decreased slightly during the initial 30 h, and then reached stable values. Moreover, SiO<sub>2</sub>-ZrO<sub>2</sub> (5/5) membranes showed high hydrothermal stability in hot water [19], suggesting that doping zirconia into silica sols improved the stability of SiO<sub>2</sub>-ZrO<sub>2</sub> membranes in water. In order to develop SiO<sub>2</sub>-ZrO<sub>2</sub> 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, SiO<sub>2</sub>-ZrO<sub>2</sub> nanofiltration membranes with different molar ratios were prepared by coating SiO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub> (9/1, 7/3, 5/5, 3/7), and ZrO<sub>2</sub> sols onto cylindrical supports in order to clarify the hydrothermal and chemical stability of SiO<sub>2</sub>-ZrO<sub>2</sub> 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 SiO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub> (9/1, 7/3, 5/5, 3/7), and ZrO<sub>2</sub> sols and powders

SiO<sub>2</sub>, ZrO<sub>2</sub> and SiO<sub>2</sub>-ZrO<sub>2</sub> 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-but-oxide 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.

SiO<sub>2</sub>, ZrO<sub>2</sub> and four types of SiO<sub>2</sub>-ZrO<sub>2</sub> 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

**Table 1**

Composition and average colloidal diameters of SiO<sub>2</sub>-ZrO<sub>2</sub> sols.

Composition		TEOS	ZrBT	H <sub>2</sub> O	HCl (35%)	C <sub>2</sub> H <sub>5</sub> OH	Colloidal diameter <sup>a</sup>
[mol%]		[g]	[g]	[g]	[g]	[g]	[nm]
SiO <sub>2</sub>	sol-A	10.1	–	3.5	3.0	110	21
	sol-B	5.1	–	1.7	3.0	110	10
SiO <sub>2</sub> -ZrO <sub>2</sub> (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 <sub>2</sub> -ZrO <sub>2</sub> (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 <sub>2</sub> -ZrO <sub>2</sub> (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 <sub>2</sub> -ZrO <sub>2</sub> (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 <sub>2</sub>	sol-A	–	12.5	0.02	3.0	110	48
	sol-B	–	6.3	0.01	3.0	110	35

<sup>a</sup> Z-average size (mean size) by dynamic light scattering (DLS).

ZrO<sub>2</sub> in the mixed oxides SiO<sub>2</sub>-ZrO<sub>2</sub> and by N<sub>2</sub> 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 ± 5%. Corrosion tests of powders in aqueous solutions at pH 2 and 12 were performed at 25 °C for 7 days using SiO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub> (5/5, 3/7) and ZrO<sub>2</sub> 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).

### 2.2. Fabrication of SiO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub> (9/1, 7/3, 5/5, 3/7) and ZrO<sub>2</sub> membranes

Nanoporous membranes were fabricated by coating sols with various levels of silica and zirconia content onto α-Al<sub>2</sub>O<sub>3</sub> cylindrical porous tubes (average pore size 2.1 μm; outer diameter 1 cm; length 10 cm). First, α-alumina particles with average diameters of 2.0 and 0.2 μm 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 nanoporometry (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 N<sub>2</sub>. 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

Download English Version:

<https://daneshyari.com/en/article/4989257>

Download Persian Version:

<https://daneshyari.com/article/4989257>

[Daneshyari.com](https://daneshyari.com)