論文の要旨

題目 SiO_2-ZrO_2 NANOFILTRATION MEMBRANES WITH CONTROLLED PORE SIZES: PREPARATION, STABILITY AND PERFORMANCE

（制御された細孔径を有する SiO_2-ZrO_2 ナノ濾過膜：製膜、安定性および性能）

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The overall objective of this dissertation research is to study the preparation of SiO_2-ZrO_2 nanofiltration membranes with controlled pore sizes, and to evaluate hydrothermal and chemical stability. The brief descriptions of each chapter in this dissertation are shown below:

Chapter 1 is **"General introduction"** which provides the background and motivation of the current research. Preparation and characterization of nanoporous membranes by the sol-gel processing are summarized, and then the mechanism of nanofiltration mass transport is proposed. The purpose of this study is explained in detail.

Chapter 2 is **"Effect of firing temperature on the water permeability of SiO_2–ZrO_2 membranes for nanofiltration)"** which describes SiO_2-ZrO_2 membranes were successfully prepared by coating SiO_2-ZrO_2 (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 SiO_2-ZrO_2 membranes, which were evaluated by nanopermporometry using hexane, were 1.20 and 0.65 nm after coating with SiO_2-ZrO_2 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 SiO_2-ZrO_2 sols that made up the top layer. The average pore sizes of SiO_2-ZrO_2 membranes 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 (3.3-0.8)×10^{-12} $m^3/(m^2\ s\ Pa)$. The decreased water permeability was ascribed to chemical and physical changes by firing temperature such as hydrophilicity/hydrophobicity, porosity, etc. The water permeabilities of SiO_2-ZrO_2 membrane showed stable flux due to adding zirconia into 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.

Chapter 3 is "**Nanofiltration performance of SiO_2-ZrO_2 membranes in aqueous solutions at high temperatures**" In this research; nanofiltration performance at high temperatures was examined using SiO_2-ZrO_2 membranes fired at 200 and 550 °C. After SiO_2-ZrO_2 membranes were treated in water at 90 °C for 4 h, the water permeability (L_p) at 25 °C for both membranes increased approximately 3-fold and remained constant as long as 100 h treatment, indicating stability in aqueous solutions as high as 90°C. The increase in water permeability of SiO_2-ZrO_2 membranes was ascribed to increased hydrophilicity and dissolution of silica into water at 90 °C. Molecular weight cut-offs (MWCOs) for SiO_2-ZrO_2 membrane fired at 550 °C did not change with treatment time (MWCOs = 300) while the MWCOs for SiO_2-ZrO_2 membranes fired at 200 °C increased from 240 to 300. SiO_2-ZrO_2 membranes fired at 550 °C showed higher hydrothermal stability than those fired at 200 °C.

The effect of temperature on SiO_2-ZrO_2 membrane performance was evaluated for nanofiltration at temperatures range of 25 to 90 °C. The rejection of glucose and maltose decreased with an increase in temperature for SiO_2-ZrO_2 membranes both fired at 200 and 550 °C, while the permeate flux increased. On the other hand, the temperature has no influence on rejection of raffinose, which was always larger than 95%.

Chapter 4 is "**<u>SiO_2-ZrO_2 nanofiltration membranes of different Si/Zr molar ratios: Stability in hot water and acid/alkaline solutions</u>**" In this study, SiO_2-ZrO_2 nanofiltration membranes were fabricated by coating different molar ratios of SiO_2, SiO_2-ZrO_2 (9/1, 7/3, 5/5, 3/7), and ZrO_2 sols onto α-alumina porous tubes and firing at 200 and 550 °C. The SiO_2 and SiO_2-ZrO_2 (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_2-ZrO_2 (3/7) and ZrO_2 membranes fired at 550 °C showed larger pores than those fired at 200 °C due to the formation of crystalline structures in the ZrO_2. SiO_2-ZrO_2 membranes with a zirconia content larger than 50 mol% showed high hydrothermal stability in hot water (90 °C). After treating SiO_2-ZrO_2 (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_2-ZrO_2 (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 changes pore sizes and hydrophilicity. Moreover, SiO_2-ZrO_2 (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.

Chapter 5 is "**<u>Development and permeation properties of SiO_2-ZrO_2 nanofiltration membranes with a MWCO of < 200</u>**" SiO_2-ZrO_2 (5/5, 3/7) nanofiltration membranes with a low molecular weight cut-off (MWCO) were fabricated by coating different Si/Zr molar ratios of 5/5 and 3/7 sols from large to small colloidal sol sizes on cylindrical α-alumina porous supports with firing at 550 °C. The pore sizes of the membranes were controlled by the SiO_2-ZrO_2 colloidal sol sizes used for the top layer. SiO_2-ZrO_2 membranes with a MWCO of less than 60, and 160-180 for neutral solutes showed water permeabilities of $(0.2\text{-}0.4)\times10^{-12}$ and $(1.9\text{-}2.7)\times10^{-12}$ $m^3/(m^2\ s\ Pa)$, respectively. The solute rejections were strongly dependent on the type of solutes; the rejection of alcohols was much higher than those of glycols and sugars. SiO_2-ZrO_2 membranes with a low MWCO showed hydrothermal stability and high nanofiltration performance in water at 90 °C. The water permeabilities of membranes increased from 2.5×10^{-12} to 11.9×10^{-12} $m^3/(m^2\ s\ Pa)$ in operating temperatures from 25 to 90 °C, while the MWCO increased slightly from 150 to 210. This indicates that SiO_2-ZrO_2 membranes with a low MWCO showed excellent nanofiltration performance at high temperatures.

Chapter 6 is "**<u>Conclusions and Recommendations</u>**" Main conclusions and recommendations were presented here.