学　位　論　文　概　要

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 membranes and application to nanofiltration (NF) applications. At first we focused on fabrication of SiO_2-ZrO_2 membranes with Si/Zr molar ratio of 5/5 by varying the firing temperature effect and evaluated nanofiltration performance. 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 temperatures while the water permeability of membrane decreased with increasing firing temperatures from 3.3×10^{-12} to 0.8×10^{-12} $m^3/(m^2$ s Pa) with molecular weight cut-off (MWCO) range from 200-350 g/mol. The decreased water permeability can be explained by the chemical and physical changes by firing temperatures. SiO_2-ZrO_2 (5/5) membranes showed stability in water for as long as 100 h. We also studied NF performance of SiO_2-ZrO_2 (5/5) membranes at high temperatures. After treatment of the membranes by immersion in water up to 90 °C for 4 h, the water permeability at 25 °C of SiO_2-ZrO_2 (5/5) fired at 200 and 550 °C increased approximately 3-fold and remained stable values for as long as 100 h for treatment in water at 90 °C. The increased water permeability was due to an increase in the hydrophilicity and to the dissolution of silica into water at 90 °C. SiO_2-ZrO_2 (5/5) membranes fired at 550 °C were excellent in hydrothermal stability in hot water (rejection of solutes did not change after treatment for 100 h). On the other hand, the MWCOs of SiO_2-ZrO_2 (5/5) membranes increased from 300 to 380 by operating temperature from 25 to 90 °C. In addition, we studied the stability of membrane performance with SiO_2-ZrO_2 membranes of different Si/Zr molar ratios. SiO_2 and SiO_2-ZrO_2 (9/1, 7/3) membranes were unstable in water at 90 °C (the permeate flux increased, rejection of glucose decreased almost zero). On the contrary, after treatment of SiO_2-ZrO_2 (3/7) and ZrO_2 membranes, the water permeability decreased, while the rejection increased. This can be explained by the formation of OH groups in the membrane pores, which led to smaller pore sizes. For chemical stability of membranes in acid and alkaline solutions, the SiO_2-ZrO_2 (5/5, 3/7) membranes showed stability in a corrosive test at pH 2 and 12. Finally, we fabricated SiO_2-ZrO_2 nanofiltration membranes with low MWCO. The pore sizes of membranes were controlled by the SiO_2-ZrO_2 colloidal sol sizes (12-17 nm) used for the top layers. SiO_2-ZrO_2 (5/5, 3/7) membranes with a MWCO of less than 60 and 160-180 for neutral solutes showed water permeability of 0.4×10^{-12} and 2.7×10^{-12} $m^3/(m^2$ s Pa), respectively. SiO_2-ZrO_2 membranes with 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.