論文の要旨

題 目　Preparation, characterization, and performance evaluation of TiO_2-ZrO_2 membranes for nanofiltration

（ナノ濾過 TiO_2-ZrO_2膜の作製，特性評価および透過特性の評価）

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TiO_2 and ZrO_2 are known as superior inorganic materials in terms of chemical and physical stability. Therefore, these types of membranes are more suitable and preferable for filtration applications under harsh environments. However, it is difficult to control and achieve pure TiO_2 and ZrO_2 membranes with small pore size in the nanofiltration (NF) range (0.5-2 nm) due to their low phase-transformation temperature. To overcome this problems, composite mixed oxide membranes have been investigated. A limited number of studies have reported the development of TiO_2-ZrO_2 membranes for NF applications. However, as far as could be ascertained, no paper has ever reported in detail regarding the effect of the type of sols, firing temperature, and Ti/Zr ratio on the structure and performance of the membranes. In addition, no paper has ever reported hydrothermal stability and NF performance at high temperature of TiO_2-ZrO_2 membranes. Therefore, in order to optimize the membrane performance, TiO_2-ZrO_2 membranes with different type of sols, firing temperatures, and Ti/Zr ratios were prepared. Moreover, hydrothermal stability and NF performance at high temperature were evaluated. The main contributions of this research can be withdrawn from the following:

Chapter 1 is "**General introduction**", which provides an overview of ceramic nanofiltration membranes, research background and purpose of this study.

Chapter 2 is "**Preparation, characterization, and evaluation of TiO_2-ZrO_2 nanofiltration membranes fired at different temperatures**". TiO_2-ZrO_2 nanofiltration membranes were successfully prepared using a sol-gel method. Two types of TiO_2-ZrO_2 sols (polymeric and colloidal sols) with molar ratios of 5/5 were coated onto α-Al_2O_3 cylindrical porous supports followed by firing at different temperatures. The structures of the membranes were amorphous up to a firing temperature of 500 °C. Measurements of the N_2 permeance and water permeability revealed that values for average pore size, N_2 permeance, and water permeability (L_p) of the prepared membranes were increased with increases in the firing temperature, and a drastic increase was observed at the temperature of transformation from an amorphous to a crystalline phase. For the membranes fired at 200 - 600 °C, the average pore size and N_2 permeance was 0.5 - 0.8 nm and 0.14-0.54x 10^{-5} mol/(m^2 s Pa), respectively; nanofiltration performance showed molecular weight cut-offs (MWCOs) of 200 - 810 g/mol, and L_p of 2-12x10^{-12} m^3/(m^2 s Pa), respectively. In the present study, values for the structure and separation performance of the membranes were successfully controlled by the use of different sizes of sols and by manipulating the firing temperature.

Chapter 3 is "**Hydrothermal stability and permeation properties of TiO2-ZrO2 (5/5) nanofiltration membranes at high temperatures**". The hydrothermal stability of TiO_2-ZrO_2 nanofiltration (NF) membranes fired at 200, 400, and 550 °C was examined at 90 °C for 4-100 h, followed by an evaluation of the NF performance at 25 °C. After hot-water treatment, the water permeability (L_p) of a membrane fired at 200 °C had slightly increased, while that of membranes fired at 400 and 550 °C had drastically decreased. Meanwhile, the values for molecular weight cut-off (MWCO) were decreased for all membranes. The L_p and MWCO changed during the initial 20

h and remained constant for as long as 100 h, confirming the stability in an aqueous solution at 90 °C. The permeation properties of water and neutral solutes were evaluated for temperatures that ranged from 25 to 85 °C. The water permeability increased with an increase in temperature, while the rejection of solutes decreased. Based on analysis using the Spiegler-Kedem equations, the reflection coefficient was constant irrespective of permeation temperature, while both water and solute permeability was increased with an increase in the permeation temperature, which revealed that the permeation mechanism of water and neutral solutes are an activated process. In addition, the activation energies of solute permeability were found to be higher than those of water permeability.

Chapter 4 is "**TiO_2-ZrO_2 membranes of controlled pore sizes with different Ti/Zr ratios for nanofiltration**". TiO_2-ZrO_2 colloidal and polymeric sols were successfully prepared using the sol-gel method. The effects of aging and Ti/Zr molar ratios on TiO_2-ZrO_2 sols and powders were investigated. The particle size of colloidal sols was decreased with an increase in aging time, while the particle size of the polymeric sols increased. TiO_2-ZrO_2 polymeric sols with Ti/Zr molar ratios that varied from 10/0 to 0/10 showed an increase in particle size with an increase in the Zr-content. In addition, TiO_2-ZrO_2 powders derived from colloidal sols had a crystalline structure without firing. With firing at temperatures that approach 500 °C, however, TiO_2-ZrO_2 powders derived from polymeric sols had a structure that was more amorphous than that of pure TiO_2 and ZrO_2 powders, but the most amorphous structure was achieved at a Ti/Zr molar ratio of 5/5.

TiO_2-ZrO_2 nanofiltration (NF) membranes, which were prepared by coating colloidal and polymeric sols onto α-Al_2O_3 porous supports, showed an average pore size and molecular weight cut-offs (MWCOs) in the NF range. Average pore size, N_2 permeance, water permeability (L_p), and MWCOs of the membranes were generally decreased with an increase in ZrO_2 content with an optimum addition of ZrO_2 that approached an equimolar composition. TiO_2-ZrO_2 (9/1, 7/3, 5/5) membranes showed a relatively low MWCO and a moderate L_p, which suggested that those membranes would be good for nanofiltration.

Chapter 5 is "**Conclusions and recommendation**". Main conclusions presented in this thesis are summarized and recommendations are provided for further study.