論 文 の 要 旨

題 目　Development of bis(triethoxysilyl)ethane (BTESE)-derived organosilica membranes: thermal and oxidation stability, gas permeation properties, and application to membrane reactor

(有機無機オルガノ BTESE 膜の作製：耐熱性，耐酸性，ガス透過特性，および膜反応への応用)

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The overall objective of this research in doctor course is to study the preparation of bis(triethoxysilyl)ethane (BTESE)-derived membranes with high gas permeance, and selectivity, and to evaluate the thermal, oxidation, and chemical stability. The brief descriptions of each chapter in this dissertation are shown below.

Chapter 1 is "**General introduction**" which summarizes the research background of separation processes and membrane processes, and gas permeation model of organosilica membrane. Also, the purpose of this study is presented in detail.

Chapter 2 is "**Network engineering of a BTESE membrane for improved gas performance via a novel pH-swing method**". Organosilica microporous membranes were fabricated from 1, 2-bis (triethoxysilyl) ethane (BTESE)-derived sols prepared in acidic pH via the pH-swing method. This method includes two steps whereby a specific amount of NH_3 was added into the acid sols and switched to acid after a reaction of several minutes. It was found that the size of the BTESE-derived sols by pH-swing could be controlled via the H_2O/BTESE molar ratio and the reaction time in alkali. Under the same H_2O/BTESE ratio of 60, the BTESE-derived sols prepared in the pH-swing method showed an increase in sol size in contrast with the acid method, and the sol size was easily controlled by the dominating reaction in alkali pH — the condensation reaction. Gas permeation results showed that some gases (He, H_2, N_2, C_3H_8, SF_6) permeated the membrane that was prepared using the pH-swing sols (pH-swing membrane) at approximately twice the rate shown by the membrane prepared using acid sols (acid membrane); H_2 permeance levels of the pH-swing membrane and the acid membrane were 3.4×10^{-6} and 1.6×10^{-6} mol/(m^2 s Pa) at 200 °C, respectively. The pH-swing membrane also maintained similar H_2/C_3H_8 permeance ratios ranging from 2,600~5,800, confirming that pH-swing processing is an innovative method for improvement in the gas permeance of BTESE-derived organosilica membranes. One possible reason for these results could be that the membranes prepared using the pH-swing sols increased the size of the sols, which reduced the sol penetration into the intermediate layer. Moreover, the high cross-linking that was caused by pH-swing increased the thermostability of the BTESE-derived organosilica networks. The CO_2/CH_4 and CO_2/N_2 permeance ratios for the pH-swing membrane were as high as 90 and 28, respectively, at 50 °C.

Chapter 3 is "**Improved thermal and oxidation stability of bis(triethoxysilyl)ethane (BTESE)-derived membranes, and their gas-permeation properties**". The conventional method to fabricate bis(triethoxysilyl)ethane (BTESE)-derived organosilica membranes begins with a coating of BTESE-derived sols that is then fired at temperatures that do not exceed 300 °C, because the organic linking ethane groups start to thermally decompose at temperatures higher than 300 °C. In the present study, however, thermal stability of BTESE membranes was further enhanced by firing at much higher temperatures (550−700 °C), which promises to enable future applications such as H_2 purification at high temperatures and gas separation under an oxidizing atmosphere. The selectivity of 700 °C-fired membranes for H_2/CH_4 was as high as 100 with H_2 permeance of approximately 10^{-6} mol/(m^2 s Pa). Moreover, even after heat treatment at 550 °C under N_2 and then under air, BTESE-derived membranes prepared at 550 °C showed high selectivity values of approximately 100 and 2000 for H_2/CH_4 and H_2/CF_4, respectively. By comparison, the selectivities for H_2/CH_4 and H_2/CF_4 of membranes prepared at 300 °C were approximately 30 and 200, respectively. The BTESE powders were characterized by FT-IR, N_2 adsorption, Electro-Probe Microanalyzer (EPMA), and TGA. The large carbon/silicon ratio and residual weight for powders with multiple heat treatments under N_2 and then under air, suggested that high-temperature treatment under N_2 increased the thermal stability and oxidizing resistance. These results showed that calcination temperatures, atmosphere, and heat treatment are the key factors influencing the thermal and oxidation stability of these BTESE membranes.

Chapter 4 is "**Chemical stability of SiO_2–based separation membrane and application to O_2/SO_3 separation**". SO_3 decomposition using a catalytic membrane reactor (CMR) is a promising technology to improve the economic viability of thermochemical water-splitting Iodine-Sulfur (IS) process for large-scale CO_2-free hydrogen production. However, this strategy faces two major challenge: the chemical stability of membrane materials under SO_3, and the control of pore size distribution for effective molecular sieving. In the present study, microporous membranes were proposed for SO_3/O_2 separation, that is, the membrane support was calcined by using α-Al_2O_3, the intermediate layer was prepared from silica-zirconia, and the top layer was prepared from bis(triethoxysilyl)ethane (BTESE). SiO_2–ZrO_2 membranes with a pore size larger than 1 nm and a high Si/Zr molar ratio and α-Al_2O_3 were found to have excellent resistance to SO_3, which was confirmed by the negligible change in gas permeance. Subsequently, in binary-component gas separation at 550 °C, microporous BTESE-derived membrane achieved an O_2/SO_3 selectivity of 10 (Knudsen selectivity: 1.6) while maintaining high O_2 permeance of 2.5×10^{-8} mol/(m^2 s Pa).

Chapter 5 is "**Conclusions and recommendations**". Main conclusions are summarized in this the chapter and recommendations are provided for further study.