

論 文 の 要 旨

題 目 Preparation of organosilica membranes and the application to gas separation
in the presence of water
(オルガノシリカ膜の作製と水蒸気共存下でのガス分離への応用)

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Organosilica membranes based gas separations have been considered to clean and low energy system, such as in natural gas purification, or CO₂ capture from coal-fired power plant. Most of membranes were prepared with great hydrophilicity from top to bottom to enhance membrane performance. However, water vapor has a great effect on these hydrophilic membranes. The development of hydrophobic top and intermediate layers for organosilica membranes, and improvement of separation performance become very important. The key objective of this thesis is to study the effect of water vapor on organosilica membranes, and prepare hydrophobic organosilica membranes which are expected to keep separation performance under wet conditions as well as under dry conditions. The main work of this research is as follow.

Chapter 1 is “**General introduction**”. The research background of membranes for gas separation under dry and wet conditions was overviewed and the purpose of this study was proposed.

Chapter 2 is “**CO₂ permeation through hybrid organosilica membranes in the presence of water vapor**”. Two types of organoalkoxysilanes, bis(triethoxysilyl)ethane (BTESE) and bis(triethoxysilyl)octane (BTESO) were used as precursors to prepare membranes via sol-gel method. The two membranes showed distinct properties on porous structures and water affinity because of differences in the bridging methylene numbers between the two Si atoms. Under dry conditions, the BTESE and BTESO membranes showed CO₂ permeances as high as 7.66×10^{-7} and 6.63×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ with CO₂/N₂ selectivities of 36.1 and 12.6 at 40 °C, respectively. In the presence of water vapor, the CO₂ permeances were decreased for both membranes, but the effect of water vapor on CO₂ permeation is slighter for BTESO membranes than that for BTESE membranes due to more hydrophobicity and denser structures with a longer linking-bridge group. Both of hybrid organosilica membranes showed good reproducibility and stability in water vapor.

Chapter 3 is “**Preparation of organosilica membranes on hydrophobic intermediate layers and evaluation of gas permeation in the presence of water vapor**”. Hydrophobic Me-SiO₂ sols were prepared by using tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) as co-precursors, coated on macroporous α -Al₂O₃ supports through multi-layered coatings. By characterization of nanoporometry using hexane and water as condensable vapors, Me-SiO₂ layers showed pore diameter of approximately 2 nm and exhibited hydrophobic properties and that SiO₂-ZrO₂ layers were hydrophilic. Under dry conditions, BTESO/Me-SiO₂ showed a gas permeation trend that was similar to that of BTESO/SiO₂-ZrO₂. The selectivity of H₂/SF₆ for BTESE/Me-SiO₂ (334) was much lower than that of BTESE/SiO₂-ZrO₂ (>20,000) due to the inhomogeneous coatings of BTESE on the Me-SiO₂ layers. Under humidified conditions, BTESE/Me-SiO₂ and BTESO/Me-SiO₂ with hydrophobic intermediate layers, exhibited less

decrease in CO₂ permeance compared with either BTESE/SiO₂-ZrO₂ or BTESO/SiO₂-ZrO₂, both of which were prepared with hydrophilic intermediate layers. The water vapor resulted in a negligible effect on gas permeance for totally hydrophobic BTESO/Me-SiO₂, while a little larger decrease was observed for hydrophilic top layers of BTESE/Me-SiO₂, showing that membranes with hydrophobic surface chemistry can effectively resist water vapor condensation or adsorption during gas permeation.

Chapter 4 is “**Plasma-assisted multi-layered coating towards improved gas permeation properties for organosilica membranes**”. H₂O vapor plasma was used for the modification of hydrophobic Me-SiO₂ intermediate layer by generating hydrophilic groups on the surface without changing either the bulk hydrophobicity or the pore size. After plasma treatment of the Me-SiO₂ layers, BTESE or BTESO-derived sols were coated as separation layers. The gas selectivity for BTESE membrane was improved after water plasma treatment, which allowed better adhesion between each layer via the enhanced hydrophilic modification by water plasma. Under wet conditions, the CO₂ permeance for both membranes were decreased, slightly larger decrease than for membranes without plasma treatment, but much less than the BTESE and BTESO membranes prepared on hydrophilic SiO₂-ZrO₂ intermediate layers. High gas permeation properties were obtained in the presence of water for organosilica membranes prepared from hydrophobic top layers to hydrophobic intermediate layers via plasma-assisted multi-layered coatings.

Chapter 5 is “**Conclusions**”. Several important conclusions of this study are given in detail and suggestions are provided for further study.