論 文 の 要 旨

題 目 Tailoring the microporous structure of a ceramic composite for development of molecular sieving membranes

(セラミック複合物のマイクロポーラス制御による分子ふるい膜の開発)

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In this thesis, organic coordination/complexation ligands have been applied for the modification of a SiO_2-ZrO_2 ceramic composite. The various sections seek to deepen the understanding and access further opportunities offered by organic coordination/complexation ligands modification of ceramic composite membranes.

First, the chemical modification of SiO_2-ZrO_2 via the sol-gel method was successfully accomplished by chelating acetylacetonate ($acac^-$) with zirconium tetrabutoxide (ZrTB) prior to co-hydrolysis and condensation with tetraethoxysilane (TEOS), which was then used to fabricate a gas separation layer. The $acac^-$-modified SiO_2-ZrO_2-derived membrane showed a high H_2 permeance of 9.9 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} with a H_2/SF_6 permeance ratio of 7,600, which was better than the results when using a pure SiO_2-ZrO_2-derived membrane (H_2 permeance: 1.4 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1}, H_2/SF_6 permeance ratio: 11).

In the next phase, the microstructural control of ligand-modified SiO_2-ZrO_2 composite membranes was attempted. Hybrid materials with crosslinking between the organic moieties were made by utilizing network forming Si precursor and chelating ligands. The effects of using a network-forming and network-modifying ligand were studied. Gas permeation experiments showed that the organic crosslink-derived membranes possess molecular sieving properties (H_2 permeance: ≈10^{-7} mol m^{-2} s^{-1} Pa^{-1}; H_2/N_2 selectivity: ≈20-30) that are superior to those of non-crosslink-derived membranes (H_2 permeance: ≈10^{-7} mol m^{-2} s^{-1} Pa^{-1}; H_2/N_2 selectivity: ≈7-11).

Furthermore, the preparation of a carbonized SiO_2-ZrO_2 composite membrane was studied. The sol synthesis of the precursor SiO_2-ZrO_2-acetylacetonate composite was optimized by studying the effect of water/alkoxide molar ratio and relative Si/Zr atomic ratio on the final carbon-SiO_2-ZrO_2 properties. A combination of SiO_2 and ZrO_2 in a ratio of 9/1 in a carbon-SiO_2-ZrO_2 membrane showed an H_2 permeance of 16 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} over a similarly pore-distributed unmodified SiO_2-ZrO_2 membrane with an H_2 permeance of 3 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1}. More interestingly, a combination of SiO_2 and ZrO_2 in a ratio of 5/5 displayed a unique pressure-induced CO_2 flow switching behaviour.

The various modification techniques offered more insights for molecular separations.