

論文の要旨

題目: **Development of high-performance SiC-based membranes derived from preceramic precursors and application to gas separation and pervaporation**

(プレセラミック前駆体を用いた高性能 SiC 膜の開発とガス分離および浸透気化分離への応用)

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Membrane separation process has become one of the emerging technologies that undergo a rapid growth for the past few decades. The development of advanced membranes for molecular separation with excellent separation performances, a simple fabrication process, and low-cost is always being pursued by membrane developers. The overall of this dissertation research is focused on the development and microstructure tuning of SiC-based membranes for gas separation and PV application. Two types of preceramic precursors, PCS and TiPCS were chosen for the fabrication of SiC-based membranes and Ti-containing SiC-based membranes, respectively. Conventional SiC-based membranes derived from PCS are mainly used for H₂/N₂ separation due to their narrow and small pore sizes. However, few studies have investigated the microporosity of ceramic products pyrolyzed at moderate temperatures (350-800 °C), and the relationship between the microporous structure and curing process for molecular separation remains unclear. Furthermore, Ti-containing SiC-based ceramics have many superior properties, however, the research on them is limited to fibers and bulk ceramics at high temperatures ($\geq 1,000$ °C). Here, we are the first to propose the fabrication of SiC-based membranes to obtain sub-nanopores by doping with Ti for molecular separation of small/mid-sized molecules from large molecules.

The high separation performance which could be obtained by adjusting the pore size of the SiC-based membranes, is expected to make SiC-based membranes suitable for separation not limited to H₂/N₂ separation but also in a wide range of applications for molecular separation. From these requirements, the main work of this research is as follows:

- (i) Tuning the microstructure of PCS-derived SiC-based separation membranes via thermal-oxidative cross-linking;
- (ii) Investigation of physicochemical properties and microstructural variations of TiPCS under different curing and pyrolysis conditions;
- (iii) Development of high-performance sub-nanoporous SiC-based membranes derived from TiPCS for gas separation and PV applications.

This thesis consists of 5 chapters, the brief descriptions are shown below:

Chapter 1 is “**General introduction**” which involves the background and motivation of the current research.

Chapter 2 is “**Development and microstructure tuning of conventional SiC-based membranes derived from polycarbosilane**”. The main interest was focused on tuning the microstructure of the PCS-derived membranes via air-curing temperature. The elemental composition and microstructure of the final ceramic material could be precisely tailored via the air curing process. The most promising PCS-derived membranes, which were cured at 250 °C and then pyrolyzed at 750 °C, had high thermal stability and oxidation resistance at 500 °C in addition to excellent permeation properties: H₂ permeance of $1-2 \times 10^{-6}$ mol/(m² s Pa) at 500 °C with H₂/N₂ selectivity of 31 and H₂/C₃H₈ selectivity of 1,740; and, CO₂ permeance of 1.8×10^{-6} mol/(m² s Pa) at 27 °C with CO₂/CH₄ selectivity of 40. This is the first study to propose the concept of tailoring the microstructure of SiC-based membranes by controlling the curing process.

Chapter 3 is “**Development of high-performance sub-nanoporous SiC-based membranes derived from polytitanocarbosilane**”. Many studies have characterized TiPCS-derived ceramics by firing at high temperatures (> 1,000 °C), however, few studies have investigated the microporosity of ceramic products pyrolyzed at moderate temperatures. This work marks the first fabrication of TiPCS-derived SiC-based membranes with sub-nanopores via the pyrolysis of a commercial polytitanocarbosilane polymer, Tyranno Coat, at temperature ranges of 350-850 °C. The dependence of the polymer-to-ceramic transformation process of TiPCS on pyrolysis temperature was systematically investigated. The pore characteristics and the surface areas of TiPCS-derived ceramic powders were strongly dependent on the pyrolysis temperatures. The evolution of the network structure of TiPCS during the pyrolysis process began with a dense polymer structure (≤ 350 °C) that was then passed through a loose transitional structure (350-650 °C), and then transformed into a relatively denser ceramic structure (> 650 °C). Additionally, the titanium components in TiPCS effectively inhibited and/or reduced the densification of the network structures at elevated temperatures. The network structure of TiPCS-derived SiC-based membranes showed trends similar to those of TiPCS-derived ceramic powders. The membrane prepared at 750 °C featured sub-nanopores, reproducibility, and attractive selectivities (H₂/SF₆, 16,600; and N₂/SF₆, 2,100) with a high H₂ permeance at a magnitude of 10^{-6} mol/(m² s Pa). These SiC-based membranes demonstrated great potential for the separation of small and mid-sized molecules from large molecules such as N₂/SF₆ separation and PV removal of water or methanol from liquid mixtures. The TiPCS membranes exhibited separation performance for methanol/methyl acetate mixtures with a total flux of 0.38 kg/(m² h) and a methanol/methyl acetate separation factor of 35 for 10 wt% MeOH in a MeOH/MeOAc binary mixture at 60 °C.

Chapter 4 is “**Study on the effect of oxidative cross-linking on the structure and performance of polytitanocarbosilane-derived SiC-based membranes**”. In this section, special attention was focused on a process of thermal-oxidative curing that was used to induce cross-linking and the effect of this process on the ceramic yield, thermal stability, oxidation resistance, and microstructure of TiPCS. The cross-linked TiPCS powders showed a ceramic yield and thermal stability that were higher than that from the non-cross-linked version. In addition, the cross-linked TiPCS with uniform micropores showed higher levels of N₂ and CO₂ adsorption capacity, BET surface area, and micropore volume than the non-cross-linked versions, and the cross-linking process enhanced the stability of the pore structure at high temperature. The pore formation behavior induced by the cross-linking process of TiPCS chains was closely related to the gas permeation properties in SiC-based membranes. The cross-linked TiPCS membranes showed higher oxidation resistance than their non-cross-linked counterparts at 300 °C under air. Furthermore, the influence of the concentration of the TiPCS precursor coating solution was optimized. The cross-linked, optimized membranes demonstrated great performance for the pervaporation removal of methanol in binary azeotropic systems of either MeOH/butyl acetate or MeOH/toluene. Moreover, the membranes showed high hydrothermal stability together with an H₂O permeance of 1.64×10^{-6} mol/(m² s Pa) and a high H₂O/N₂ selectivity of 40 in an equimolar H₂O/N₂ mixture (50 kPa: 50 kPa) at 300 °C. The TiPCS membrane is a promising candidate for gas dehumidification in membrane contactor systems that must operate at high temperatures.

Chapter 5 is “**Conclusions**”. The main conclusions of this study are summarized and recommendations for further study are presented here.