審 査 の 結 果 の 要 旨

(Summary of results)

Title of Thesis DEVELOPMENT OF ORGANIC - INORGANIC HYBRID MEMBRANES FOR CARBON DIOXIDE / METHANE SEPARATION

（CO_2 / CH_4 分離のための有機-無機ハイブリッド膜の開発）

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This thesis deals with the development of hybrid membranes for the separation of carbon dioxide from natural gas. Hybrid membranes are promising materials since they combine the advantages of both organic and inorganic materials.

Chapter 1 introduces different types of membrane materials for the separation of CO_2/CH_4 mixtures, followed by a detailed explanation of fundamentals of transport mechanisms and synthesis methods in order to highlight the importance of the investigated hybrid membrane materials for this research.

Chapter 2 describes studies to optimize the synthesis conditions of alkylamine silica membrane for CO_2/CH_4 separation. The hybrid membrane was prepared by depositing an alkylamine silica selective layer on top of a multilayered alumina support using chemical vapor deposition (CVD). First, CVD parameters were optimized using (3-aminopropyl)trimethoxysilane. It was found that the best combination used a N/Si ratio of 20% and a reaction temperature of 673 K. The membrane had a CO_2 permeance of $2.3x10^{-7}$ mol $m^{-2}s^{-1}Pa^{-1}$ and an ideal CO_2/CH_4 selectivity of 40 measured at a temperature of 393 K and a partial pressure difference of 0.10 MPa. The membrane pore size was determined by Tsuru's method and was 0.40 nm. The surface morphology and composition were also determined using SEM and XPS analyses, respectively.

Chapter 3 presents a study of the effect of primary and secondary amine groups on the performance of CO_2/CH_4 separation membranes. The compounds 3-aminopropyltrimethoxysilane and (3-methylaminopropyl)trimethoxysilane were selected as primary and secondary alkylamine-silica precursors, respectively. An amine free membrane prepared using propyltrimethoxysilane as precusor was used as reference membrane. The selective layer was also deposited by CVD using the optimum conditions determined beforehand. The performance of the membranes increased in the order: amine-free < primary amine < secondary amine. The secondary amine had a pore size of 0.43 nm and achieved a CO_2 permeance of $1.3x10^{-7}$ mol $m^{-2}s^{-1}Pa^{-1}$, an ideal CO_2/CH_4 selectivity of 140, which are in the commercial range. The transport mechanism of CO_2 through the amino-silica hybrid membranes was surface diffusion which was confirmed by mixed gas permeance tests. The secondary amino-silica hybrid membrane was stable for 60 h under a relative humidity of 20 %.

Chapter 4 describes mixed matrix membranes (MMMs), which consist of inorganic particles dispersed in a polymeric matrix. The zeolite SAPO-34 and polyetherimide were selected as the inorganic filler and the polymeric matrix for the synthesis of the supported MMMs. Two polymer solvents, dichloroethane and N-methyl-2-pyrrolidone, were investigated for the preparation, and the dichloroethane solvent resulted in a membrane with better CO_2/CH_4 selectivity. Various SAPO-34 amounts from 0 to 10 wt% were dispersed in the polymer precursor which was dissolved in dichloroethane. The membrane with 5 wt% SAPO-34 content presented the highest performance with a CO_2 permeance of $4x10^{-10}$ mol $m^{-2}s^{-1}Pa^{-1}$ and an ideal CO_2/CH_4 selectivity of 60. Based on mixed gas permeances and time-lag measurements, the separation of CO_2 and CH_4 was found to be dominated by the difference in the gas solubilities. Particle agglomeration was observed at 10 wt% zeolite content.

Chapter 5 determines optimum points within the Robeson upper boundary which is an empirical line linking the highest permeabilities and selectivities in polymer membranes. Four gas pairs: CO_2/N_2, O_2/N_2, CO_2/CH_4, and N_2/CH_4 were considered for the study. The constraints for the optimal points were the cost of the membrane, the number of units required for a separation, and the compression requirements. The total costs included the fees for utilities and capital costs, and interest payments. The optimum points obtained were for CO_2/N_2 a permeability of 3,200 barrers and a selectivity of 24, for O_2/N_2 a permeability of 550 barrers and a selectivity of 4, for CO_2/CH_4 a permeability of 2,000 barrers and a selectivity of 20, and for N_2/CH_4 a permeability of 110 barrers and a selectivity of 2. Secondary alkylamine silica membrane and mixed matrix membrane with 5 wt% SAPO-34 content were evaluated using the proposed simulation. The alkylamine membrane resulted in the lowest operating costs for the separation of CO_2 and CH_4 mixtures.

Chapter 6 describes the conclusions of the thesis and summarizes the findings of the investigated hybrid membranes. It also presents suggestions for future work which would lead to the improvement of the obtained membrane performance such as the investigation of the effect of the number of secondary amine functionality in the alkylamine-silica membranes or the reaction between SAPO-34 and polytherimide using alkylamine silane to enhance the dispersion in the matrix.

This thesis passes the requirements for the doctoral degree thesis in engineering and it can be judged to contribute to the development of chemical systems engineering.