

論文の内容の要旨
Thesis Summary

論文題目 DEVELOPMENT OF ORGANIC - INORGANIC HYBRID MEMBRANES FOR CARBON DIOXIDE / METHANE SEPARATION

(CO₂/CH₄分離のための有機-無機ハイブリッド膜の開発)

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Purification of natural gas using membrane technology has been attracting great attention recently [1]. Currently, membrane processes have 5 % of the natural gas treatment market and are mainly used for carbon dioxide (CO₂) removal. Carbon dioxide reduces the heating value of natural gas, corrodes process equipment, and freezes at a relatively high temperature. Therefore, CO₂ needs to be removed. Various membranes for CO₂/CH₄ separation are available and are classified into three main categories; organic, inorganic and hybrid (mixed organic and inorganic) membranes [2]. Organic membranes are generally composed of polymers. Polymeric membranes have low selectivity and stability at high temperatures and plasticize easily in contact with highly pressurized CO₂. As a result, processes for CO₂ separation using organic membranes are usually performed at relatively low temperatures. Inorganic membranes for CO₂ separation are mainly zeolite membranes, and silica membranes. Inorganic membranes are more stable but suffer generally from difficulty in scale up without creating defects within the membrane.

This thesis deals with the development of hybrid membranes for CO₂/CH₄ separation. Hybrid membranes are promising materials since they combine the advantages of organic and inorganic materials. Two types of hybrid materials were investigated; alkylamine silica membranes and mixed matrix (inorganic particles mixed in polymeric matrix) membranes. First, silica membranes were modified with amine groups because there is affinity between amine functionalities and CO₂. Amine group functionalized silica membrane materials are particularly effective for CO₂ separation and are believed to work by forming carbamates in a reversible manner [3]. This gives rise to a facilitated transport mechanism [4]. Second, a silicoaluminophosphate zeolite (SAPO-34) was dispersed in a thermally resistant polymer (a polyetherimide) because SAPO-34 is selective to CO₂ permeance and it is expected to enhance the polymer membrane performance. Third, a theoretical analysis was carried out to find the optimal point for a separation within the Robeson upper boundary. The Robeson boundary is an empirically derived line which gives the best combinations of permeability and selectivity for different polymers in a given separation [5]. The optimum points of four gas pairs (CO₂/N₂, O₂/N₂, CO₂/CH₄, and N₂/CH₄) on this line were determined on the basis of the cost of the membrane, the number of units required to achieve a specific separation, and the compression requirements.

Chapter 1 introduces different types of membrane materials for the CO₂/CH₄ separation, followed by a detailed explanation of basic knowledge such as transport mechanism, synthesis method in order to highlight the importance of the investigated hybrid membrane materials for this research.

Chapter 2 involves the functionalization of a microporous silica layer with alkylamine groups and optimizes the experimental conditions for the CO₂/CH₄ separation. The originality of the work consisted of the use of the chemical vapor deposition CVD method to prepare the membranes

Intermediate alumina layers were deposited on the inner side of an alumina support using a sol-gel method in order to have a defect-free amine-silica layer. Then, the top-most layer was deposited by CVD. The CVD conditions were optimized using silica (tetraethylorthosilane: TEOS) and amine silica (3-aminopropyltrimethoxysilane: APTES) precursors. The membrane support was attached to gas delivery lines and heated in a furnace to 673 K. It was found that the best results were obtained with a N/Si ratio of 20% (APTES-20) resulting in a CO₂ permeance of 2×10^{-7} mol m⁻²s⁻¹Pa⁻¹ and an ideal CO₂/CH₄ selectivity of 40 measured at a

temperature of 393 K and a partial pressure difference of 0.10 MPa. Smaller N/Si ratios led to the formation of a dense silica network and small pores. Higher ratios resulted in the formation of a loose structure that allowed both CO₂ and CH₄ to permeate easily. The pore size of APTES-20 membrane was determined by Tsuru's method to be 0.40 nm. This method is derived from the gas translation model [6] is applied by fitting experimental and simulated permeances of various gases. Field emission scanning electron microscope (FE-SEM) images of the membrane surface showed a defect free topmost layer with globular structure indicating that the CVD laid down a fine layer on the support. The thickness of the selective layer of the APTES-20 membrane was 23 nm. The N_{1s} spectra measured by XPS analysis of the APTES-20 membrane was divided into two features which were assigned to -NH₂ and -NH₃⁺ [7]. The detection of -NH₃⁺ indicated that carbamates may have been formed, which resulted from the interaction of CO₂ with amine groups. It was deduced from the temperature dependency that the transport mechanism for CO₂ permeation was facilitated transport and for CH₄ passage was gas-translation.

Chapter 3 investigates the effect of primary and secondary amine functionalities on the performance of synthesized membranes. The originality of the work consisted of the choice of structurally homologous reagents to probe the effect of amine structure on performance.

Alkylamine silica hybrid membranes were synthesized using TEOS as silica precursor, and 3-aminopropyltrimethoxysilane and (3-methylaminopropyl)trimethoxysilane as primary and secondary alkylamine-silica precursors, respectively. An amine free membrane prepared using propyltrimethoxysilane (PTMS) as precursor was used as a reference membrane. The selective layer was also deposited by CVD using the optimum conditions determined previously. The permeance and the CO₂/CH₄ selectivity showed a significant improvement in the presence of amine functionalities. The membranes with secondary amine functionality (M-II) seemed to carry out facilitated transport of CO₂ through the membrane better than those with primary amine (M-I) or no amine (M-0). The latter had the lowest separation factor). The M-II membrane achieved a CO₂ permeance of 1.3×10^{-7} mol m⁻²s⁻¹Pa⁻¹, a CO₂/CH₄ selectivity of 140 with a pore size of 0.43 nm. The primary amine membrane displayed a CO₂ permeance of 2.1×10^{-8} mol m⁻²s⁻¹Pa⁻¹, a CO₂/CH₄ selectivity of 70 with a pore size of 0.36 nm. The amine-free membrane had a CO₂ permeance of 2.1×10^{-8} mol m⁻²s⁻¹Pa⁻¹, a CO₂/CH₄ selectivity of 4 and a pore size of 0.37 nm. The pore sizes were also estimated by Tsuru's method. The membranes with no amine and with primary amine groups had approximate similar pore sizes; however, the presence of amine groups improved the CO₂/CH₄ separation. Even though the membrane with secondary amine had pores larger than the CH₄ diameter (0.38 nm), the CO₂/CH₄ ratio was increased indicating that amine addition augmented the CO₂ transport through the membrane. The transport mechanism of CO₂ through the amine silica hybrid membranes was the facilitated transport mechanism. The M-II hybrid membrane was stable for 60 h under a relative humidity of 20%, suggesting that water can stabilize the amine surface groups upon CO₂ adsorption/desorption cycles [8] and that water helped to form stable reactive intermediates [9]. The obtained permeances of alkylamine silica membranes were beyond the 10⁻⁷ mol m⁻²s⁻¹Pa⁻¹ level which is considered necessary for commercial application.

Chapter 4 deals with mixed matrix membranes (MMMs). The MMMs are prepared by dispersing inorganic particles in a polymeric matrix. The originality of the work consisted of using two different materials with different physical properties to achieve enhanced performance.

The SAPO-34 crystals were selected for the separation because of their selective pore size (0.38 nm) to CO₂ (diameter 0.33 nm). The polyetherimide was selected since it is thermally and chemically stable. First, SAPO-34 zeolite was synthesized using hydrothermal synthesis. Ludox AS-40 colloidal silica, aluminum isopropoxide, and phosphoric acid were used as silica, alumina, and phosphoric oxide sources, respectively, for the crystal synthesis. Tetraethylammonium hydroxide was used as a structure directing agent in the crystal synthesis. The

obtained SAPO-34 presented high crystallinity confirmed by X-ray diffraction (XRD) analysis, and sheet like morphology observed by SEM images. Second, experimental analysis of two polymer solvents showed that dichloromethane evaporated faster and had better CO₂/CH₄ selectivity than N-methyl-2-pyrrolidone, a conventional solvent used for the polyetherimide membranes. Third, 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 CO₂ permeance of 4×10^{-10} mol m⁻²s⁻¹Pa⁻¹ and a CO₂/CH₄ selectivity of 60. The gas diffusivity and solubility in the MMMs were calculated from time-lag measurement technique [10]. The separation occurred based on the difference of the gas solubility. The SAPO-34 decreased CH₄ permeance by increasing its diffusion pathway. Particle agglomeration was observed at 10 wt% zeolite loadings in the polymeric matrix which may be due to the incompatibility between SAPO-34 surface and PEI [11].

Chapter 5 determines optimum points within Robeson upper boundary which is an empirical line linking the most permeable polymer membranes at a particular selectivity. The originality of the work consisted of demonstrating, for the first time, the existence of maxima in the boundary where costs are reduced.

The constraints used to limit the optimal points consisted of the cost of the membrane, the number of units required to achieve a specific separation, and the compression requirements. The total costs included the fees for utilities and capital costs, and interest payments. Assumptions made in the development of the mathematical model were negligible pressure drop and composition change within a membrane unit (perfect mixing), a constant unit recovery, an invariant permeability and selectivity of the gases, a constant pressure difference between the feed and permeate, and an unaltered operating temperature of 298 K in each stage. The simulation was performed with MATLAB 7.0.4. Several parameters including product purity, recovery, operating pressure, membrane selectivity and membrane thickness were investigated to find an optimum cost required for the separation of CO₂/N₂, O₂/N₂, CO₂/CH₄ and N₂/CH₄ gas streams. The model results were verified against other economic studies reported previously. First, the relationship between pair gas selectivity, permeability and number of units was investigated. It was found that at high selectivities and low permeabilities, the number of units was minimal. In the case of CO₂/CH₄ separation, the calculation showed that only one unit was required to achieve a purity of 90% with reasonable selectivities. Second, the effect of the operating pressures on the membrane costs were studied since the driving force (pressures) was related to membrane area. It was found that the costs of compressing gas mixtures increased as the pressures increased allowing the use of lower permeabilities and higher selectivities. Third, the tradeoff relationship between compression costs and membrane performance was investigated. The results had exponential behavior and showed that membranes with small permeabilities operating at high pressures had lower costs than at low pressures. As a result, the membrane costs were the main contributor to the separation expenditure and operating pressures had small effect. Forth, it was observed that the total costs of the separation were in tradeoff between the membrane and the compression costs. This resulted in a minimized cost of operation. Finally, the optimum points for specific operating pressures and purity were determined. The optimum points did not necessarily correspond to the minimal number of units. For example in the case of CO₂/CH₄ separation, the optimum point at an operating pressure of 1 MPa and 90% purity required two units while it was demonstrated before that only one stage was enough to achieve same purity. In fact, the maxima in the Robeson boundary depended simultaneously on the targets of production (production rate, purity and recovery), the composition of the feed and the properties of the membranes.

Chapter 6 contains 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.

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