Development of Innovative Gas Separation Membranes Through Sub-Nanoscale Materials Control

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Introduction

Separating CO_2 from other gases present in flue or synthesis gas, in conjunction with a suitable means of storing the CO_2, could allow the utilization of abundant fossil fuel reserves with significantly decreased emissions of CO_2 to the atmosphere. This project intends to develop a variety of efficient, low-cost polymeric and inorganic membranes that separate CO_2. Material structure engineering at the scale of gas molecules will be used to increase permeability and selectivity. As the polymeric based materials, cardo polymer based carbon membrane is being prepared. Effect of symmetric/asymmetric structure on the resulting subnano structure and separation performance will be investigated. As the inorganic materials, zeolite / functionalized mesoporous membranes is being prepared. Ultra thin, defect free membrane preparation will be investigated.

Background

Membrane separation of CO_2 from other gases is an active field, but the best membranes today are likely too energy intensive and expensive to be implemented on a large scale. Gas separation in membranes is driven by a pressure difference across the membrane. In order to obtain a sufficiently pure stream of CO_2, selectivity for CO_2 must be high. In addition, to obtain high permeate flow rate, high permeability is required, too. Many current systems require large membrane area and cascading the permeate through multiple membrane stages to achieve the desired flow rate and purity. New type membranes are required to have high permeability and selectivity, as well as long-term durability. Two areas of gas separation membrane research are polymer and inorganic membranes. Polymer membranes are relatively easy to manufacture and are suited for low temperature applications. The polymer morphology and mobility determine the gas permeability and selectivity. In addition, molecular sieve ability can be obtained by carbonizing polymeric materials. Inorganic membranes have much greater thermal and chemical stability. Appropriately sized pores in materials including zeolites and silicas can act as molecular sieves that separate gas molecules by effective size. Surface adsorption and diffusion inside the pores can also play a role in separating gas molecules. Since the effective sizes of CO_2, N_2, H_2, and other gases present in fossil fuel conversion systems are very similar, membrane pore spaces must be controlled on a scale

comparable to the size differences among these gas molecules. This will be achieved for a variety of membrane types using several different techniques. In this project, we are going to develop new type membranes with well-controlled subnano-structure from both organic and inorganic materials: carbon-based membrane, functionalized mesoporous oxide membrane and molecular sieving zeolite membrane.

Results

(1) Planning and preparatory work

The research work based on chemical and physical sub-nano structure control consists of the following areas (a)～(f):

(a) Selection of optimum membrane materials

(b) Establishment of techniques for controlling sub-nano scale structure and morphology

(c) Development of the technology for the preparation of ultra thin active layers for separation

(d) Fabrication of membrane modules for laboratory testing

(e) Evaluation of membrane modules

(f) Design and evaluation of the systems optimized for the newly developed membranes

We have been conducting our research based on this research schedule.

As the preparatory work, we have set up a new laboratory for the project. In addition, we have prepared apparatus for the production, characterization of the new membranes of subnano-scale materials, such as vacuum purge furnace, plasma apparatus, vacuum ultraviolet rays apparatus, hydrothermal synthesis and gas permeation test apparatus.

(2) Experimental results

(2.1) Carbon membrane

(2.1.1) Selection of the precursors for the carbon membranes

We have selected several cardo polyimide polymers with various side chains as the precursors for carbon membranes[1)]. Various cardo polyimides with different side chains will be used to control the microporous structure of the resulting carbon membrane. In addition, we have conducted TG-MS analyses of these candidate precursors to investigate the relationship between the molecular structure of the precursors and the resulting carbon subnano structure.

(2.1.2) Selection of porous ceramic supports for the carbon composite membranes

In addition to use the asymmetric hollow-fiber polyimide membranes, we are planning to form carbon membranes on the thermally-stable porous ceramic supports. So far, we

have investigated several ceramic supports having different pore diameter, and found that pore diameter of 100 nm is suitable to coat the precursor (i.e., cardo polyimide) on it and to form carbon membrane without peeling off.

(2.2) Inorganic membrane

(2.2.1) Synthesis of zeolite membranes for CO_2 separation

We have been undertaking a simulation forecast of the optimum pore structure for CO_2 separation in cooperation with a university, and investigating the synthesis method of a new type of porous materials effective for CO_2 separation. Before starting this project (not in GCEP), we have already studied that CO_2 adsorption and separation properties of various zeolites by both the adsorption experiment and grand canonical ensemble molecular dynamics simulation (GCMD) technique. Based on the simulation results, we have selected some candidate zeolite structure for CO_2 separation and have started synthesis new zeolite membrane. In order to control the morphology of zeolite seed crystal for membrane preparation, synthetic condition of zeolite seed crystals have been studied.

(2.2.2) Development of synthetic method of mesoporous thin film without defect.

We have studied surface modification and functionalization method of the pore wall of various mesoporous silicas that are specialized for CO_2 capture and separation; already reporting that the CO_2 adsorption capacities of aminosilane modified SBA-15 mesoporous silicas [2)]. Mesoporous silica MCM-48 membrane was synthesized on a porous alumina support. Then the obtained MCM-48 membrane was modified by chemical grafting of aminosilanes. CO_2 separation properties of amine-grafted MCM-48 membranes were evaluated by the measurement of gas permeability using a mixture of CO_2 and N_2. Extremely high CO_2/N_2 separation selectivity ($\alpha_{(CO2/N2)} = 800$) was obtained at 373K. This result showed a possibility of CO_2 separation at high temperature.

Based on this study, we have started fabrication of organic-inorganic hybrid type membranes using mesoporous solids. Various mesoporous silica membranes with different pore size/structure on porous alumina substrate and glass substrate were prepared by hydrothermal, sol-gel spin-coating and sol-gel dip-coating technique. From the TEM and SEM observation, it was revealed that these membranes had uniform pore structure with no defect.

Progress

After half a year since this project started, we are ready to start detailed investigation on the preparation of subnano structure that we proposed.

(1) Carbon membrane

(1.1) Precursors for the carbon membrane have been selected based on the size and quantity of ablated moieties determined by TG-MS analyses. Hollow-fiber asymmetric structure and ceramic-supported structure were chosen as the morphology of the ultrathin carbon membrane membranes. Porous ceramic membranes with appropriate pore diameter were selected as the porous support.

(1.2) Sets of preparation apparatus such as vacuum purge furnace, plasma apparatus, vacuum ultraviolet rays apparatus are ready.

(1.3) Preliminary study on coating polyimide on the ceramic porous support has been conducted. Carbonization of cardo polyimide membranes have just started.

(2) Inorganic membrane

(2.1)Based on the simulation results, we have selected some candidate zeolite structure for CO_2 separation and have started synthesis new zeolite membrane.

(2.2) Preliminary study on preparation of mesoporous silica thin layer on the porous alumina support and surface functionalization has been conducted.

(2.3) Apparatus for the screening test is ready.

Future Plans

(1) Carbon membrane

Hollow fiber and/or ceramic-supported cardo polymer membranes will be carbonized by vacuum purge furnace, vacuum ultraviolet rays, plasma etc. To prepare the optimum structure, detailed investigations on each preparation step will be conducted.

(1.1) Coating of cardo polyimide onto the porous ceramic porous support and/or preparation of hollow-fiber asymmetric polyimide membranes.

(1.2) Carbonization of polyimide membranes using vacuum purge furnace.

(1.3) Partial carbonization of polyimide membranes using plasma apparatus, vacuum ultraviolet ray apparatus etc.

(1.4) Affinity control of carbon membrane to optimize the CO_2 separation performance.

Subsequently, detailed characterization and separation performance measurement will be conducted on the prepared carbon membranes.

(2) Inorganic membrane

(2.1) Design and preparation of inorganic hoop structure:
Preparation of various zeolite/mesoporous oxide membrane with different pore size/structure.

(2.2) Surface fictionalization of mesoporous oxide membrane by chemical grafting of guest-material.

(2.3) Screening test:
Various kinds of ultra thin zeolite membranes with different pore diameter and pore

structures, and various functionalized mesoporous membranes would be examined as screening test.

Publications

1. Y. Sakamoto, K. Nagata, K. Yogo, K. Yamada, "Preparation and CO2 separation properties of amine modified mesoporous silica membrane", 71th meeting of The Society of Chemical Engineers, Japan, Mar. 30, 2006.

References

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2. Hiyoshi, N., Yogo, K. and Yashima T. Adsorption Characteristics of Carbon Dioxide on Organically Functionalized SBA-15. *Microporous Mesoporous Mater.* **84** 357-365 (2005)

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