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Annual Scientific Progress Report

Advanced CO_2/H_2 separation materials incorporating active functional agents

Investigators

Yuichi Fujioka	Group Leader, Chief Researcher (Dr. Eng.), Chemical Research Group
Shingo Kazama	Senior Researcher (Dr. Eng.), Chemical Research Group
Katsunori Yogo	Senior Researcher (Ph.D.), Chemical Research Group
Teruhiko Kai	Researcher (Ph.D.), Chemical Research Group
Ryousuke Shimizu	Researcher (Ph.D.), Chemical Research Group
Kazuya Goto	Researcher (Ph.D.), Chemical Research Group
Ryo Nagumo	Researcher (Ph.D.), Chemical Research Group

Research Institute of Innovative Technology for the Earth (RITE)
9-2 Kizugawadai, Kizugawa-shi Kyoto 619-0292, JAPAN
[1] fujioka@rite.or.jp

1. Research Subject

Advanced CO_2/H_2 separation materials incorporating active functional agents

2. Objectives

We are developing advanced composite materials having molecular interaction forces using a nanocomposite controlling technology based on concepts we have already developed as part of our previous research project, especially concepts related to nanoscale controlling technologies in polymeric and inorganic materials. The forces can selectively extract CO_2 from CO_2 and H_2 mixed gas. The materials consist of active functional agents in the nanopores of a porous substrate. We control the figures, surface atoms/molecules and the compositions of the pore and functional compounds to create the desired molecular interaction forces. Our research seems to provide microscopic insight into molecular dynamics in nanopore structures and result in the future production of excellent separation materials.

One objective of this research is to realize the development of an excellent CO_2 separation membrane for CCS. Such an innovative material will greatly reduce the energy consumption and costs in the separation process. To obtain innovative composite materials effectively, the development of both polymeric and inorganic functional agents should be essential and useful.

3. Research ideas

Core Concept

Fig. 1 shows the basic outline of the CO_2 molecular gate membrane. In Fig.1 (b), the pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of H_2 permeating to the other side of the membrane is greatly limited and high concentrations of CO_2 can be obtained. The molecular gate membrane can achieve reverse size separation of CO_2 and H_2. Fig. 1 (c) shows further detail of the amine compounds, such as polyamidoamine (PAMAM) dendrimers. In the figure, one CO_2 molecule makes a carbamate ion pair with two amine moieties of the membrane material. The carbamate ion pair works as a quasi cross linkage that restricts H_2 permeation through the membrane. Since carbamate ion pairs are in equilibrium with free CO_2 and amine moieties, CO_2 can release from the original carbamate ion pair and jump down to the next amine moieties with CO_2 concentration gradient in the membrane. As a result, only CO_2 molecules permeate the membrane.

The CO_2 molecular gate needs strict morphological arrangement. In Fig. 1 (c), a strict morphological control of the distance between two amine moieties is required for the perfect CO_2 molecular gate. If the distance is too small and allows strong hydrogen bonding of the amine moieties, the membrane will not have sufficient CO_2 permeability (Fig. 2 (a)). On the other hand, if the distance is too large, there will not be enough carbamate ion pairs for the gate. It is critical this is avoided for better CO_2 selectivity (Fig. 2(b)). Excess water absorbed in an existing PAMAM dendrimer membrane has been observed to lead to a sharp decrease in CO_2 selectivity. A large excess of water absorbed into the membrane seems to enlarge the molecule distance of the dendrimer membrane, resulting in insufficient formation of

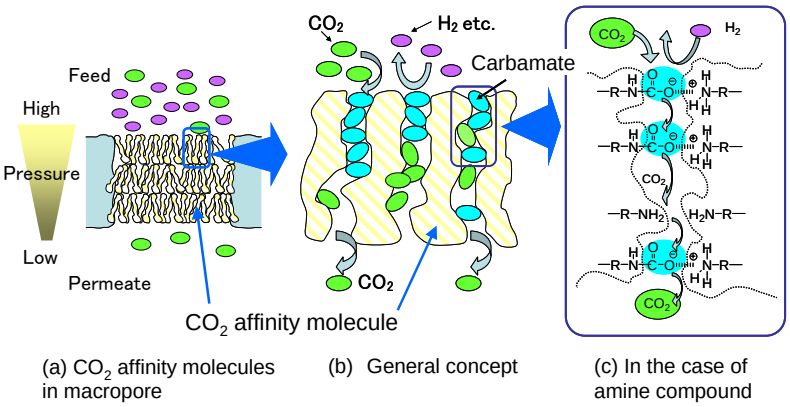

Fig. 1 Concept of CO_2 molecular gate membrane

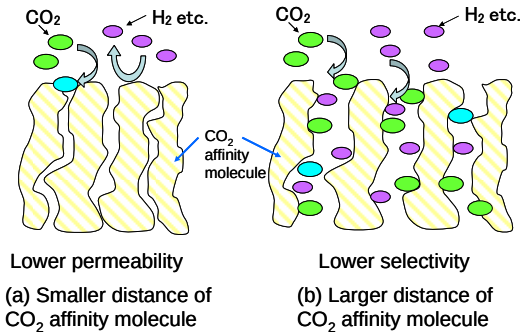

Fig. 2 Morphological deformation and the molecular gate function

carbamate ion pairs. Excess CO_2 molecules absorbed physically in the membrane at an elevated pressure will also enlarge the molecule distance.

A promising way of maintaining the best morphology for the gate is the incorporation of a CO_2 affinity agent into a rigid nanoporous substrate. The rigid pore works as a barrier to restrict the expansion of the CO_2 affinity agent induced by physically absorbed H_2O and CO_2 (Fig. 3). As a result, the rigid pore is best for maintaining materials in the best morphology for the CO_2 molecular gate function.

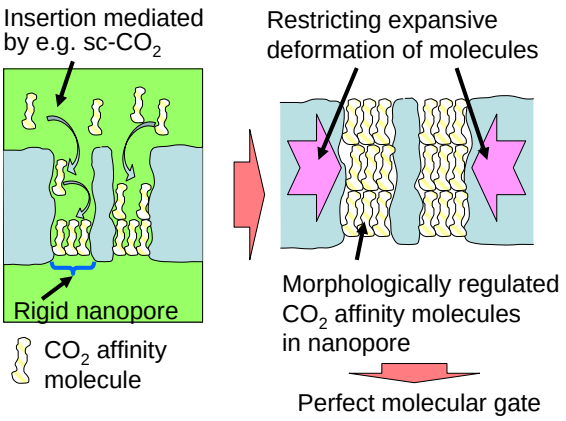

Fig. 3 Insertion of CO_2 affinity molecule into rigid nanopore and resulting restricted deformation of the molecules

Our methodology

To include a CO_2 affinity molecule in a nanopore, selection of the medium carrying the CO_2 affinity agent into the nanopores is critically important. The medium should be able to penetrate the nanopores freely and have sufficient solubility of the CO_2 affinity molecules. From this view point, supercritical CO_2 (Sc-CO_2) and subcritical CO_2 are selected as the medium. Additionally, Sub- and Sc-CO_2 would help to form a quasi cross linkage for the better morphology of the CO_2 molecular gate in nanopores during membrane preparation. In this case, the CO_2 molecule works as a structure directing agent.

To obtain the optimum morphology for a CO_2 molecular gate, Sc-CO_2 will be applied to a mediator that transfers the CO_2 affinity agent to the nanopores as in Fig. 3. Sc-CO_2 will assist in the preparation of the optimum morphology by carbamate formation during membrane fabrication.

Impact

The success of our research will provide an excellent CO_2/H_2 separation membrane for which the CO_2/H_2 selectivity and CO_2 permeance are 300 and 5×10^{-9} m^3 m^{-2} s^{-1} Pa^{-1} or more, respectively. The membrane will be preferably used for CO_2 capture in IGCC + CCS processes such as FutureGen. The membrane is estimated to reduce CO_2 capture cost to 10 USD/t-CO_2 or less in the processing and distribution of CCS.

5. Results

Our new research in GCEP has been launched at September 1, ’08. Some major apparatuses for supercritical-CO_2 experiment have been installed in this 6-month and actual study has been started. The status of the achievement is as followed;

(1) Sc-CO_2 displacement method for optimal morphology of CO_2 affinity molecules:

The CO_2 molecular gate needs strict morphological arrangement of CO_2 affinity molecules as shown in Fig. 3. Sc-CO_2 displacement method is selected to form optimal structure in the nanopores. In this method, CO_2 affinity molecules and monomers (or polymers) that are soluble in other organic solvent are sent to support layers of membrane. Only the organic solvent is extracted by Sc-CO_2 and the phase change from Sc-CO_2 to gaseous CO_2 make the polymerization in the monomers or the cure of polymer. In this procedure CO_2 affinity molecules are distributed all of the nanopores rigidly in the state of a nascent polymeric membrane. The preferable molecular gate structure can be obtained with the interaction of CO_2, the CO_2 affinity materials and the polymer.

(2) Preparation densely-packed active functional agent (CO_2 affinity molecule) in a nanoporous substrate

The major approaches for this procedure are depicted in Fig. 4 (a) and (b). We try to develop two types of novel methods for membrane preparation. One is an insertion of CO_2 affinity molecules by pressure control deposition in Sc-CO_2, and another is an interfacial reaction in nanopores by counter flow diffusion of reactants. The detail concepts of the methods are described as follows:

(a) Insertion of CO_2 affinity molecule mediated by sc-CO_2

Sc-CO_2 has been extensively studied for chemical reactions, material synthesis and extraction because of its environmentally-friendly nature. It possesses low viscosity, high diffusivity and zero surface tension. So it can easily penetrate into narrow space of inorganic materials and molecular-size gap of organic materials. Furthermore, Sc-CO_2 solvation force can be controlled by changing temperature and pressure. That is, CO_2 affinity molecules dissolved in Sc-CO_2 are precipitated in membrane substrate by pressure control as shown in Fig. 4 (a). Here, solubility data of the CO_2 affinity molecules in Sc-CO_2 are necessary to determine the operation conditions, and hence accumulated. Figure 5 shows experimental setup for solubility measurement. We measured the phase transition pressure from the two phases (immiscible) to a single phase (miscible) of the fluid in a high-pressure view cell. The CO_2 fluid contains CO_2 affinity molecules and solubility enhancer. Figure 6 shows the phase diagram of the system containing the CO_2 affinity reagent, solubility enhancer and Sc-CO_2. The ordinate and abscissa represent the transition pressure and the mole fraction of the CO_2 affinity regent in the system, respectively. As shown in the figure, solubility of

CO_2 affinity molecules was regulated by the system pressure. The information would be usefully applied to insert the CO_2 affinity molecules in the substrate.

(b) Interfacial reaction in nanopores

Thin active layer is indispensable for achieving high CO_2 permeance. To obtain the stable thin layer of CO_2 affinity molecules, we try to apply the counter flow diffusion for the membrane preparation. Our concept shows in Fig. 4 (b). In Sc-CO_2, reactant (A) and (B) dissolved in the opposite side of the membrane can diffuse into the porous substrate and react to make the product (C) as the thin active layer. Here, it is important for the reactants to have sufficient solubility in Sc-CO_2.

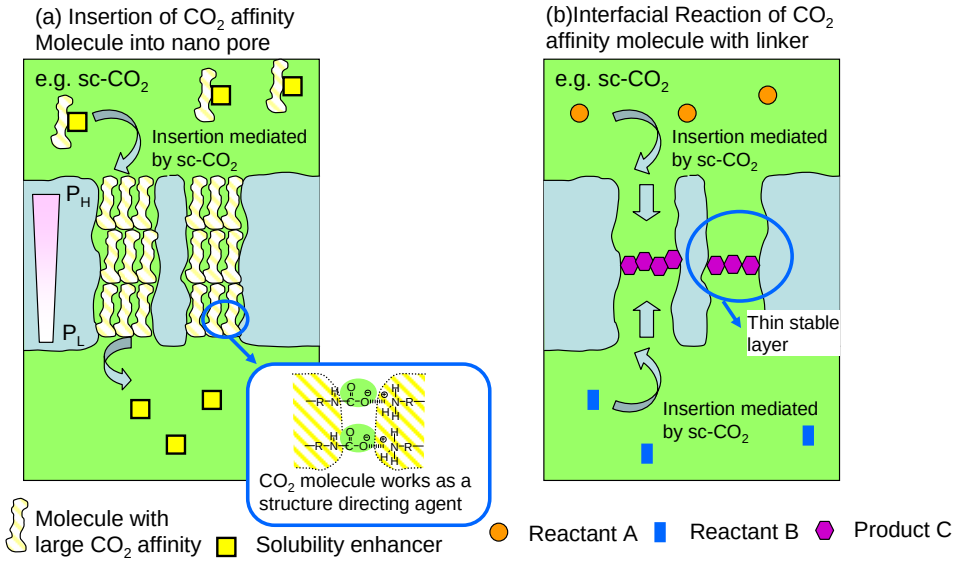

Fig. 4 Methodology for incorporation of CO_2 affinity molecule

Fig. 5 Experimental setup for solubility measurement

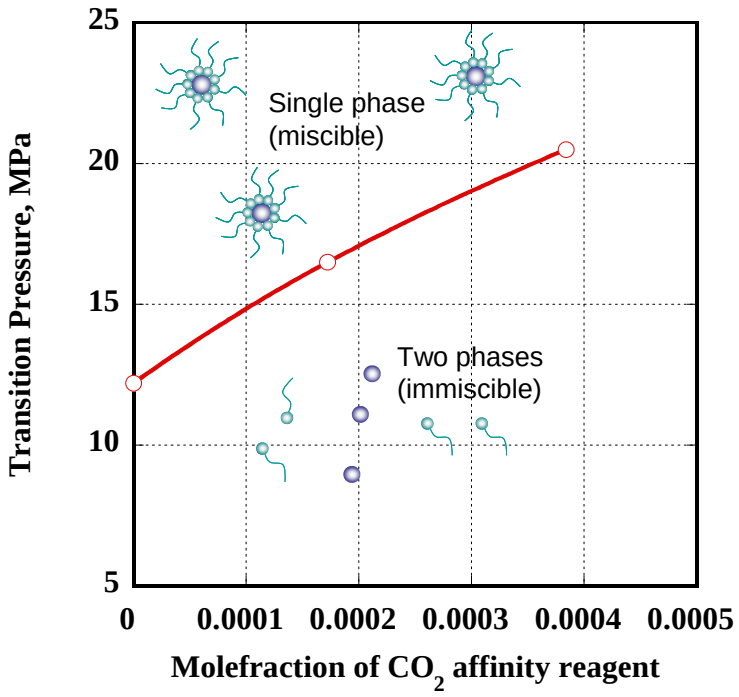

Fig. 6 Solubility of CO_2 affinity reactant with enhancer in Sc-CO_2 at 313 K

6. Progress in the period of September 1 – March 31

- Survey of Sc-CO_2 technologies and creation of a few novel methods for membrane preparation.
- Three kinds of apparatuses for high-pressure experiments were designed, installed and made a trial run.
- Solubility of CO_2 affinity molecules in Sc-CO_2 was measured.

7. Future plan

- Membrane preparation by Supercritical CO_2 displacement method
- Membrane preparation by pressure control deposition method.
- Membrane preparation by counter flow diffusion method.
- Solubility data accumulation of various CO_2 affinity molecules in Sc-CO_2