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## **Annual Scientific Progress Report**

# **Advanced CO<sub>2</sub>/H<sub>2</sub> separation materials incorporating active functional agents**

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## **1. Research Subject**

Advanced CO<sub>2</sub>/H<sub>2</sub> 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<sub>2</sub> from CO<sub>2</sub> and H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> molecular gate membrane. In Fig.1 (b), the pathway for gas molecules is occupied solely by CO<sub>2</sub>, which acts as a gate to block the passage of other gases. Consequently, the amount of H<sub>2</sub> permeating to the other side of the membrane is greatly limited and high concentrations of CO<sub>2</sub> can be obtained. The molecular gate membrane can achieve reverse size separation of CO<sub>2</sub> and H<sub>2</sub>. Fig. 1 (c) shows further detail of the amine compounds, such as polyamidoamine (PAMAM) dendrimers. In the figure, one CO<sub>2</sub> 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<sub>2</sub> permeation through the membrane. Since carbamate ion pairs are in equilibrium with free CO<sub>2</sub> and amine moieties, CO<sub>2</sub> can release from the original carbamate ion pair and jump down to the next amine moieties with CO<sub>2</sub> concentration gradient in the membrane. As a result, only CO<sub>2</sub> molecules permeate the membrane.

The CO<sub>2</sub> 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<sub>2</sub> molecular gate. If the distance is too small and allows strong hydrogen bonding of the amine moieties, the membrane will not have sufficient CO<sub>2</sub>

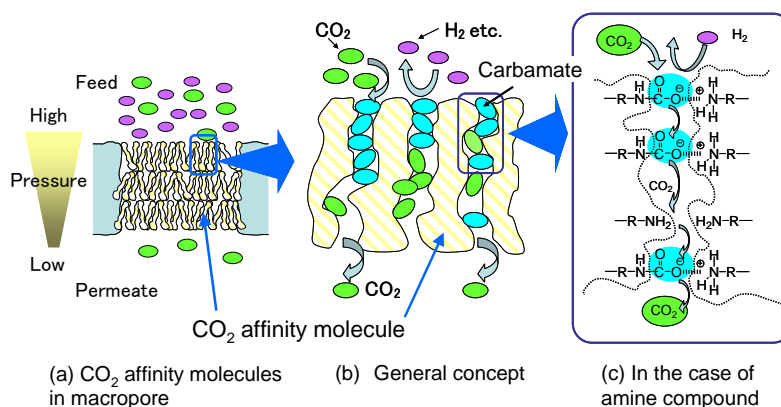


Fig. 1 Concept of CO<sub>2</sub> molecular gate membrane

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<sub>2</sub> selectivity (Fig. 2(b)). Excess water absorbed in an existing PAMAM dendrimer membrane has been observed to lead to a sharp decrease in CO<sub>2</sub> 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

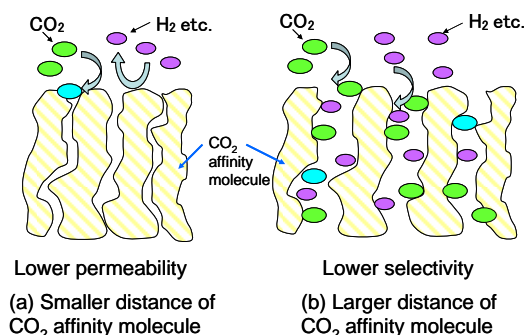


Fig. 2 Morphological deformation and the molecular gate function

carbamate ion pairs. Excess CO<sub>2</sub> 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<sub>2</sub> affinity agent into a rigid nanoporous substrate. The rigid pore works as a barrier to restrict the expansion of the CO<sub>2</sub> affinity agent induced by physically absorbed H<sub>2</sub>O and CO<sub>2</sub>

(Fig. 3). As a result, the rigid pore is best for maintaining materials in the best morphology for the CO<sub>2</sub> molecular gate function.

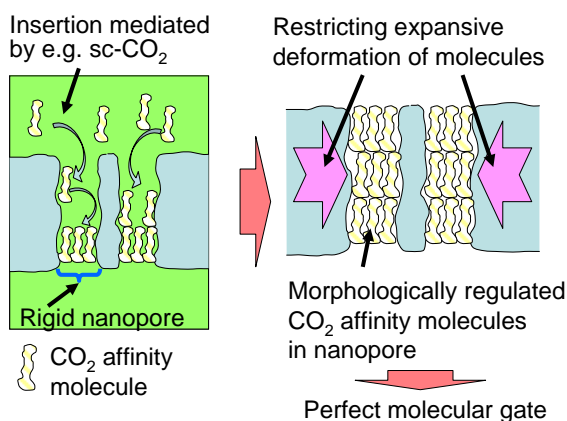


Fig. 3 Insertion of CO<sub>2</sub> affinity molecule into rigid nanopore and resulting restricted deformation of the molecules

#### Our methodology

To include a CO<sub>2</sub> affinity molecule in a nanopore, selection of the medium carrying the CO<sub>2</sub> 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<sub>2</sub> affinity molecules. From this view point, supercritical CO<sub>2</sub> (Sc-CO<sub>2</sub>) and subcritical CO<sub>2</sub> are selected as the medium. Additionally, Sub- and Sc-CO<sub>2</sub> would help to form a quasi cross linkage for the better morphology of the CO<sub>2</sub> molecular gate in nanopores during membrane preparation. In this case, the CO<sub>2</sub> molecule works as a structure directing agent.

To obtain the optimum morphology for a CO<sub>2</sub> molecular gate, Sc-CO<sub>2</sub> will be applied to a mediator that transfers the CO<sub>2</sub> affinity agent to the nanopores as in Fig. 3. Sc-CO<sub>2</sub> 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<sub>2</sub>/H<sub>2</sub> separation membrane for which the CO<sub>2</sub>/H<sub>2</sub> selectivity and CO<sub>2</sub> permeance are 300 and  $5 \times 10^{-9} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  or more, respectively. The membrane will be preferably used for CO<sub>2</sub> capture in IGCC + CCS processes such as FutureGen. The membrane is estimated to reduce CO<sub>2</sub> capture cost to 10 USD/t-CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> displacement method for optimal morphology of CO<sub>2</sub> affinity molecules:

The CO<sub>2</sub> molecular gate needs strict morphological arrangement of CO<sub>2</sub> affinity molecules as shown in Fig. 3. Sc-CO<sub>2</sub> displacement method is selected to form optimal structure in the nanopores. In this method, CO<sub>2</sub> 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<sub>2</sub> and the phase change from Sc-CO<sub>2</sub> to gaseous CO<sub>2</sub> make the polymerization in the monomers or the cure of polymer. In this procedure CO<sub>2</sub> 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<sub>2</sub>, the CO<sub>2</sub> affinity materials and the polymer.

(2) Preparation densely-packed active functional agent (CO<sub>2</sub> 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<sub>2</sub> affinity molecules by pressure control deposition in Sc-CO<sub>2</sub>, 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<sub>2</sub> affinity molecule mediated by sc-CO<sub>2</sub>

Sc-CO<sub>2</sub> 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<sub>2</sub> solvation force can be controlled by changing temperature and pressure. That is, CO<sub>2</sub> affinity molecules dissolved in Sc-CO<sub>2</sub> are precipitated in membrane substrate by pressure control as shown in Fig. 4 (a). Here, solubility data of the CO<sub>2</sub> affinity molecules in Sc-CO<sub>2</sub> 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<sub>2</sub> fluid contains CO<sub>2</sub> affinity molecules and solubility enhancer. Figure 6 shows the phase diagram of the system containing the CO<sub>2</sub> affinity reagent, solubility enhancer and Sc-CO<sub>2</sub>. The ordinate and abscissa represent the transition pressure and the mole fraction of the CO<sub>2</sub> affinity reagent in the system, respectively. As shown in the figure, solubility of

CO<sub>2</sub> affinity molecules was regulated by the system pressure. The information would be usefully applied to insert the CO<sub>2</sub> affinity molecules in the substrate.

(b) Interfacial reaction in nanopores

Thin active layer is indispensable for achieving high CO<sub>2</sub> permeance. To obtain the stable thin layer of CO<sub>2</sub> affinity molecules, we try to apply the counter flow diffusion for the membrane preparation. Our concept shows in Fig. 4 (b). In Sc-CO<sub>2</sub>, 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<sub>2</sub>.

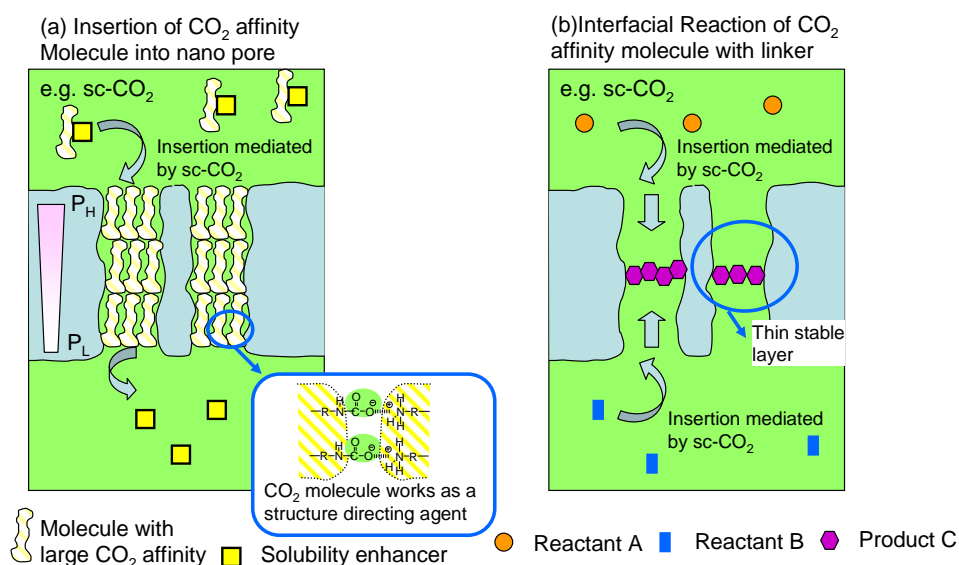


Fig. 4 Methodology for incorporation of CO<sub>2</sub> affinity molecule



Fig. 5 Experimental setup for solubility measurement

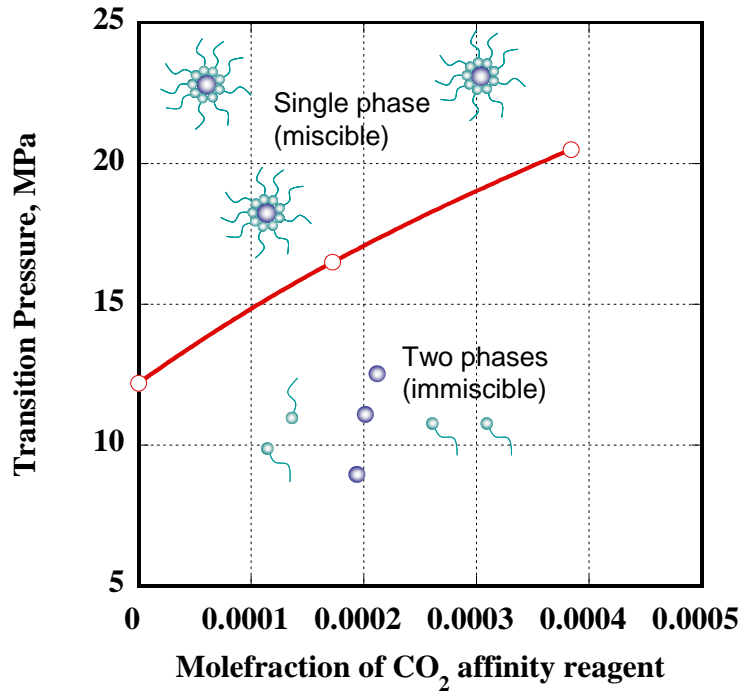


Fig. 6 Solubility of CO<sub>2</sub> affinity reactant with enhancer in Sc-CO<sub>2</sub> at 313 K

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

- Survey of Sc-CO<sub>2</sub> 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<sub>2</sub> affinity molecules in Sc-CO<sub>2</sub> was measured.

## **7. Future plan**

- Membrane preparation by Supercritical CO<sub>2</sub> displacement method
- Membrane preparation by pressure control deposition method.
- Membrane preparation by counter flow diffusion method.
- Solubility data accumulation of various CO<sub>2</sub> affinity molecules in Sc-CO<sub>2</sub>