

# Preparation and CO<sub>2</sub> separation properties of amine-modified mesoporous silica membranes

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## Abstract

Mesoporous silica membranes were prepared on porous alumina supports by both hydrothermal and sol–gel spin-coating methods. SEM images showed that these techniques deposited dense mesoporous silica layers of 200 and 500 nm, respectively, on the alumina supports. TEM and XRD observations showed that these membranes have a highly ordered cubic structure with a pore diameter of 2 nm. Gas permeation properties of these mesoporous silica membranes were governed by the Knudsen diffusion mechanism. Surface modification of the pore walls of mesoporous silica membranes by grafting amino-silane greatly improved the CO<sub>2</sub> permselectivities. The amine-modified mesoporous silica membranes showed high CO<sub>2</sub>/N<sub>2</sub> separation properties for a mixture of 20% CO<sub>2</sub> and 80% N<sub>2</sub> at 373 K. The CO<sub>2</sub>/N<sub>2</sub> selectivities of the membranes prepared using hydrothermal and sol–gel spin-coating methods were 50 and 800, respectively.

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## 1. Introduction

The increasing atmospheric concentration of carbon dioxide (CO<sub>2</sub>) due to fossil fuel combustion is a serious environmental problem. Recently, CO<sub>2</sub> capture and sequestration has attracted considerable attention as one of the options to reduce CO<sub>2</sub> emission [1]. Various processes, such as liquid solvent absorption [2], membrane separation [3] and pressure (and/or temperature) swing adsorption (P(T)SA) [4] have been proposed for separation and recovery of CO<sub>2</sub> emitted by power plants, steel works, etc. However, the costs of CO<sub>2</sub> separation from flue gases account for approximately 70–80% of the total cost of

CO<sub>2</sub> sequestration [1]. Therefore, it is important to develop a new efficient and energy-saving technique for CO<sub>2</sub> separation.

Membrane separation processes are generally more energy efficient and easier to operate than other separation processes. In particular, inorganic membranes such as zeolite and porous oxide would be suitable materials for the separation of carbon dioxide at high temperature and high pressure, because they are more resistant to severe conditions than organic membranes. Polymer membranes show good affinity for CO<sub>2</sub> and high CO<sub>2</sub>/N<sub>2</sub> separation properties, however, thermal expansion/mobility of polymers at high temperatures causes degradation of CO<sub>2</sub> selectivity.

Since zeolites and mesoporous silica possess well defined micro/meso pores, considerable attention has been focused on the production of membranes that are capable of highly selective separation of gases [5,3,6]. Mesoporous silica thin membranes on porous substrates have been prepared by templating silicates with various surfactant micelles and

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using dip-coating/spin-coating techniques and hydrothermal treatment [7–15].

However, as regards the application of mesoporous membranes for CO<sub>2</sub> separation, since CO<sub>2</sub> is a heavier molecule than other coexistent gas components such as H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CO and CH<sub>4</sub>, porous CO<sub>2</sub> selective membranes cannot operate by simple Knudsen diffusion. Therefore, CO<sub>2</sub> permselectivity of porous membranes would be attained by enhancing the affinity of pore walls for CO<sub>2</sub> adsorption over that of the other gases.

Organically functionalized mesoporous silica has recently attracted considerable attention because of the wide range of applications as adsorbents and catalysts [16,17]. Since mesoporous silica has uniform, large pores as well as a high surface area, a large number of active sites or adsorption sites can be introduced uniformly on its pore walls by surface modification with organosilane molecules.

We have already studied surface modification and functionalization of the pore walls of various mesoporous silicas that are specialized for CO<sub>2</sub> capture and separation; and have reported that the CO<sub>2</sub> adsorption capacities of aminosilane-modified SBA-15 mesoporous silicas in the presence of water vapor were comparable to those in the absence of water vapor [18].

If such a material is prepared as a thin film, the molecular movement of functional groups connected to the rigid inorganic pore wall is restricted, and it seems that a decrease in CO<sub>2</sub> selectivity due to an increase in the free volume by thermal expansion/movement of the polymeric material in the high temperature region can be restricted.

However, it is hard to utilize SBA-15 or MCM-41, which have 2D tube-like structures, as membranes for gas separation because the pore channels of these mesoporous silica membranes are not oriented perpendicular to the surface of the substrate. On the other hand, pore channels of mesoporous silica with cubic or 3D structures, such as MCM-48 or SBA-16, do not depend on the direction, and so are expected to work as effective gas separation layers.

In this work, mesoporous silica membranes with a cubic structure on porous Al<sub>2</sub>O<sub>3</sub> substrate were synthesized by two kinds of methods, hydrothermal treatment and spin coating. Amine modification of the internal surface of mesoporous silica membrane was performed by chemical grafting of amino-silane in order to increase the CO<sub>2</sub> affinity of the membranes. Moreover, the CO<sub>2</sub> separation performance of the membranes was evaluated by the permeability of CO<sub>2</sub> and N<sub>2</sub> using a CO<sub>2</sub>/N<sub>2</sub> mixed gas.

## 2. Experimental

Mesoporous silica membranes were prepared by hydrothermal treatment and spin-coating of silica sol, abbreviated as MS/Al<sub>2</sub>O<sub>3</sub>(H) and MS/Al<sub>2</sub>O<sub>3</sub>(S), respectively. These membranes were modified by chemical grafting of 3-aminopropyltriethoxysilane (APS), leading to the formation of APS/MS/Al<sub>2</sub>O<sub>3</sub>(H) and APS/MS/Al<sub>2</sub>O<sub>3</sub>(S). A prep-

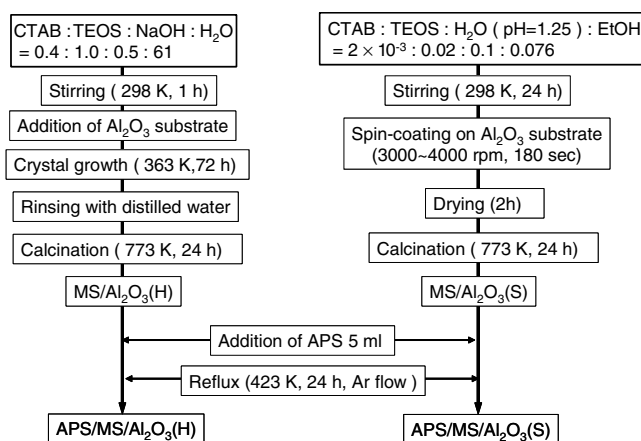


Fig. 1. Scheme of membrane preparation procedure.

aration scheme for these mesoporous silica membranes is given in Fig. 1.

### 2.1. Preparation of mesoporous silica membrane by hydrothermal treatment

MCM-48 membrane was prepared as follows: The substrate used for membrane deposition was an asymmetric porous Al<sub>2</sub>O<sub>3</sub> disk (∅ 18.5 mm, thickness 3 mm) consisting of a dense layer with an average pore diameter of 70 nm and a substrate layer with a pore diameter of 700 nm (Noritake Co., Ltd.). The alumina substrate was soaked in 1 M HNO<sub>3</sub> for 24 h. It was then washed with distilled water three times, followed by acetone, and then dried at 383 K for 24 h. A mixture of 55 ml of water, 1.0 g of NaOH and 7.3 g of cetyltrimethylammoniumbromide (CTAB) was stirred at 323 K until the CTAB was completely dissolved. The solution of CTAB and NaOH was cooled to room temperature and 10.4 g of tetraethoxysilane (TEOS) was added to the solution and it was stirred for 30 min., leading to formation of the silica sol. The molar ratio of the silica sol was TEOS:CTAB:H<sub>2</sub>O:NaOH = 0.4:1.0:61:0.5. The porous alumina substrate was then immersed in the silica sol for 90 min. The silica sol and the alumina disk were transferred to a teflon vessel, and the support was placed horizontally in this for 72 h at a temperature of 363 K. Excess precipitate on the alumina disk was carefully removed from the surface with a teflon spatula. The product was thoroughly washed with distilled water and then dried in an oven at 333 K. Finally, mesoporous silica membrane (MS/Al<sub>2</sub>O<sub>3</sub>(H)) was obtained by calcination at 773 K with a heating and cooling ratio of 0.5 K/min. An MCM-48 powder was also prepared by the same method, without porous Al<sub>2</sub>O<sub>3</sub> substrate as a reference.

### 2.2. Preparation of mesoporous silica membrane using spin-coating of silica sol

Al<sub>2</sub>O<sub>3</sub> substrate was immersed in liquid paraffin for 12 h at room temperature, in order to prevent silica sol from

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