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## Alkylamine–silica hybrid membranes for carbon dioxide/methane separation

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## ABSTRACT

Hybrid membranes are promising materials for the purification of natural gas from carbon dioxide. The present paper investigates the effect of the incorporation of primary and secondary amine functional groups on the performance of an organic–inorganic hybrid silica membrane for CO<sub>2</sub>/CH<sub>4</sub> separation. Hybrid membranes were synthesized by chemical vapor deposition using 3-aminopropyltrimethoxysilane and (3-methylaminopropyl)trimethoxysilane as primary and secondary alkylamine–silica precursors, respectively. The amino functionalized membranes were compared to an amine-free membrane prepared using propyltrimethoxysilane as precursor. The amine-free membrane had a pore size of 0.37 nm, and at 393 K a CO<sub>2</sub> permeance of  $2.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 4. The primary amine membrane had a pore size of 0.36 nm, and at 393 K displayed a CO<sub>2</sub> permeance of  $2.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 70. The secondary amine membrane had a pore size of 0.43 nm and achieved a CO<sub>2</sub> permeance of  $1.3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 140. The pore sizes were estimated by Tsuru's method. The transport mechanism of CO<sub>2</sub> throughout the amino-silica hybrid membranes was surface diffusion. The secondary amino-silica hybrid membrane was stable for 60 h under a relative humidity of 20%.

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## 1. Introduction

Purification of natural gas using membrane technology has been attracting great attention recently [1,2]. Currently, membrane processes have less than 5% of the natural gas treatment market and are mainly used for carbon dioxide (CO<sub>2</sub>) removal [3]. The number of patents [4] and processes [5,6] utilizing membranes for CO<sub>2</sub> elimination have been increasing. Carbon dioxide reduces the heating value of natural gas, corrodes process equipment, and freezes at a relatively high temperature and therefore, needs to be removed.

Various membranes for CO<sub>2</sub>/CH<sub>4</sub> separation are available and are classified into three main categories; organic, inorganic and hybrid membranes [7]. 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 CO<sub>2</sub> [8]. As a result, processes for CO<sub>2</sub> separation using organic membranes are usually performed at relatively low temperatures [9]. Inorganic membranes for CO<sub>2</sub> separation are mainly

zeolite membranes [10–15], silicate based membranes [16,17], and silica membranes [18–20]. Inorganic membranes are more stable but suffer generally from difficulty in scale up without creating defects within the membrane [2]. Hybrid membranes are combinations of organic and inorganic materials. Amino group functionalized membrane materials are particularly effective for CO<sub>2</sub> separation and are believed to work by forming carbamates in a reversible manner [21]. This gives rise to a facilitated transport mechanism [21–23]. Consequently, the selectivity of CO<sub>2</sub> can be increased along with its permeance, in contrast to other gases such as N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>, which do not form complexes with the amine groups. Amino-modified silica can be deposited either by sol–gel or chemical vapor deposition (CVD) methods. Paradis et al. [24] used a sol–gel procedure to prepare amino-silica hybrid membranes. Primary, mixed primary and secondary alkylamino-silicate, and imidazole precursors were investigated. They reported a CO<sub>2</sub>/N<sub>2</sub> selectivity of 4.9 at 423 K using 3-aminopropyltriethoxysilane as primary alkylamine precursor. Xomeritakis et al. [25] synthesized membranes using 3-aminopropyltriethoxysilane as sol–gel precursor and obtained a CO<sub>2</sub> permeance of  $2.6 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 70 at 295 K. Gopalakrishnan et al. [26] stated that gas selectivity of membranes produced by the CVD method were much higher than those of membranes prepared by

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the sol–gel method. Li [27] reported that CVD is a reproducible method giving a defect free thin layer compared to the sol–gel method. Ohta et al. [28] were able to control pore sizes in silica membranes prepared by CVD. The CVD method has been successfully applied for the deposition of metal oxide or silica layers on the surface of porous and non-porous substrates [29–33]. In CVD, reactants in the gas phase are simultaneously introduced into a pre-heated reaction chamber on the same or opposite side of a membrane support and then reacted to form a selective solid layer [34–37]. Only few works report the deposition of amino-silica selective layers using the CVD method for CO<sub>2</sub>/CH<sub>4</sub> separation. Han et al. [38] deposited 3-aminopropylmethyldiethoxysilane by CVD on a ceramic support and obtained a CO<sub>2</sub> permeance of  $3.7 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 20 at 923 K. Suzuki et al. [39] prepared an alkyl amino-silica membrane using a mixture of 3-aminopropyltrimethoxysilane and tetraethylorthosilicate and reported an optimum membrane performance using a 20% alkylamine/silica ratio with a CO<sub>2</sub> permeance of  $2.3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and an ideal CO<sub>2</sub>/CH<sub>4</sub> selectivity of 40 measured at a temperature of 393 K and a partial pressure difference of 0.10 MPa.

In actual applications, the natural gas stream often contains water vapor [40]. However, the performance of inorganic membranes in the literature has been mainly measured under dry conditions. Pure silica membranes degrade under humid conditions. In contact with water and at high temperatures, Si–O–Si linkages are reversibly hydrolyzed to silanol groups which rearrange the structure leading to densification of the silica network [41]. Several efforts have been made in order to overcome this problem. They can be summarized into three main approaches; (1) doping the silica matrix with metal ions [42], (2) incorporating hydrophobic groups within the silica matrix such as fluorocarbons [43] or methyl groups [44], (3) substituting alkyl silicate reactants either by transition metal alkoxides [45,46] or by bridged silica [46–49] precursors.

This work investigates the relationship between the performance and the microstructure of alkyl amino-silica hybrid membranes for the separation of CO<sub>2</sub> from CH<sub>4</sub>. Primary and secondary amine functionalities were introduced into the silane backbone and the obtained hybrid membranes were compared to an amine-free silica membrane. The hybrid selective layer was deposited using chemical vapor deposition at atmospheric pressure and 673 K. It was found that the secondary amine enhanced the permeance of CO<sub>2</sub> and increased the CO<sub>2</sub>/CH<sub>4</sub> selectivity compared to primary or amine-free membranes. The secondary amine hybrid membrane was also stable after 60 h exposure in 20% relative humidity.

## 2. Experimental

### 2.1. Materials

Porous alumina tubes (length: 3 cm, outside diameter: 10 mm, thickness: 1 mm, pore size: 5 nm) obtained from the Pall Corporation were used as membrane supports, and were connected to dense alumina tubes using glass joints in order to facilitate the manipulation of the membranes. The joints were made from glass powder bought from the Nippon Electric Glass Co., Ltd, and were fabricated by heating the pieces to 1273 K for 10 min using heating and cooling rates of 5 K min<sup>-1</sup>.

Aluminum isopropoxide (AIP, Sigma-Aldrich, ≥ 98.0%), acetic acid (CH<sub>3</sub>COOH, Wako, 60.0–61.0%) and nitric acid (HNO<sub>3</sub>, Wako, 95.0%) were purchased from Tokyo Chemical Industry. Polyvinyl alcohol (PVA, Wako, 99.7 mol% hydrolyzed, M. W. ~78,000) was procured from Polysciences Inc. They were used for the preparation of boehmite sols, precursors of the alumina intermediate layers.

The silica precursor was tetraethylorthosilicate (TEOS, TCI, ≥ 96.0%, CAS number 78-10-4). The alkylamine compound, propyltrimethoxysilane (PTMS, Sigma-Aldrich, 97%, CAS number 1067-25-0) was used as an amine-free silica precursor. The primary alkylamine compound, (3-aminopropyltrimethoxysilane (APTMS, Sigma-Aldrich, ≥ 98.0%, CAS number 13822-56-5) and the secondary amine compound, (3-methylaminopropyl) trimethoxysilane (MAPTMS, Sigma-Aldrich, 97%, CAS number 3069-25-8) were selected as amino-silica precursors. All silanes were supplied from Tokyo Chemical Industry. Pure Ar, He, H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and SF<sub>6</sub> gases with a purity of 99.9% were acquired from Tokyo Koatsu Yamazaki Co., Ltd.

### 2.2. Membrane synthesis

The synthesis consisted of first depositing two intermediate γ-alumina layers in order to produce a uniform surface, then the topmost selective layer. The intermediate layers were coated on the inner side of the porous tubular alumina support through a sol–gel process. Large and small particle size boehmite sols with 80 and 40 nm diameters, respectively, were synthesized following previously reported procedures [50,51]. The fresh support was dip-coated for 10 s in a suspension of the large sols followed by 3 h calcination at 923 K, and then this was repeated for the smaller sols. The topmost selective layer was deposited by chemical vapor deposition [52] using a flow apparatus (Fig. 1). The previously prepared membrane support was attached to gas delivery lines

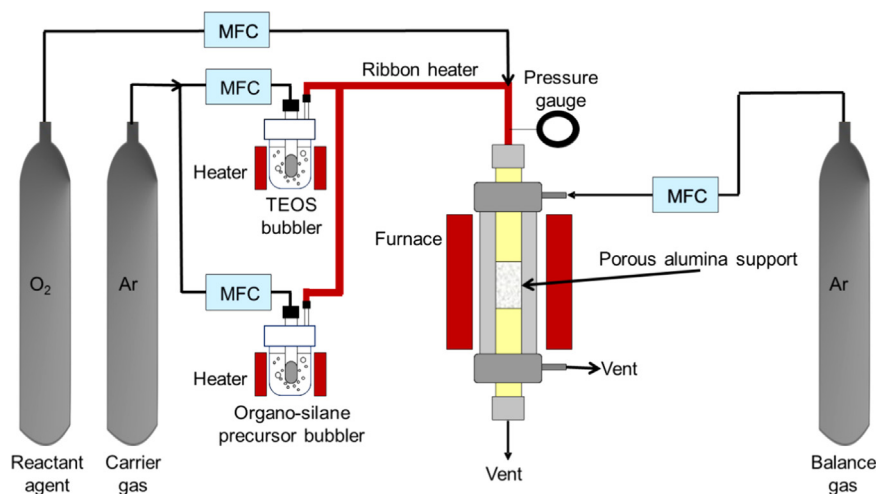


Fig. 1. Topmost layer deposition experimental set up.

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