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# Gas permeation properties of amine loaded mesoporous silica membranes for $CO_2$ separation

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## ABSTRACT

Gas permeation properties of amine loaded mesoporous silica membranes for $CO_2$ separation were evaluated using a mixture of $CO_2/N_2$ under dry and wet conditions. Although the 3-aminopropyl loaded mesoporous silica membrane was highly $CO_2$ selective under dry conditions, its selectivity declined in the presence of water. By contrast, 3-trimethoxysilylpropyldiethylenetriamine (TA) loaded mesoporous silica membranes showed high $CO_2$ selectivity even under wet conditions. Water condensed within the mesopores inhibited $CO_2$ permeation of the 3-aminopropyl loaded membrane. However, the subnanometer effective pore size of the TA loaded membrane (because of the long molecular length of TA), meant that $CO_2$ molecules still preferentially permeated in the presence of water. The size of mesopores and modifying reagents significantly influences $CO_2$ selectivity. In addition, the affinity between organoamines and polar molecules may also be exploited to increase selectivity.

*Keywords:* Mesoporous silica; Membrane; $CO_2$ separation; Amine; Wet condition; Gas adsorption

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## 1. Introduction

Since the discovery of ordered mesoporous silicas such as M41S [1,2] and FSM-16 [3], various applications for these materials with uniform and large pore sizes, extremely high surface areas and large pore volumes have been investigated, e.g., catalyst supports [4,5], adsorbents [6–14], drug delivery systems [15] and electronic devices such as a low-k film [16]. In particular, their relatively large pore sizes compared to microporous materials such as zeolites mean that various large organic molecules can enter the pores, and these organic molecules can be immobilized on the pore surface through reaction with surface silanol groups. Amongst the considerable investigations into various modified mesoporous silicas [17–19], amine-modified mesoporous silicas with their surface basicity are of great interest for practical applications such as basic catalysts [5], removal of hazardous metals [6] and $CO_2$ separation [7–14]. In particular, amine modified mesoporous silicas as adsorbents for $CO_2$ separation have been extensively investigated for a decade. Various amines could be used as modification reagents to create materials for $CO_2$ separation, e.g., organosilanes including amines [7–10], ethylenediamine [11], polyethyleneimine [12] and polyamidoamine dendrimers [13]. A variety of mesoporous silicas have also been studied, including M41S [12,14], SBA-12 [10], SBA-15 [11,13], and MSU-H [9].

Membrane separation techniques are among the most promising alternatives for $CO_2$ recovery processes with lower energy consumption, and have also been investigated using these amine loaded mesoporous

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silicas [20,21]. We have previously reported [20] that a 3-aminopropyl modified mesoporous silica membrane showed high $CO_2$ selectivity and its selectivity was enhanced with temperature under dry conditions. However, for practical applications, the effect of water within the emitted $CO_2$ on the membrane performance is extremely important since a huge amount of energy is required for dewatering processes. Here, two types of amine loaded mesoporous silica membranes were synthesized and their gas permeation properties in the presence of water were evaluated.

## 2. Experimental

### 2.1. Preparation of mesoporous silica membranes

Porous α-alumina substrates with a diameter of 18.5 mm (mean pore diameter 0.07 μm) were purchased from Noritake Co., Limited. Mesoporous silica membranes were prepared on the porous α-alumina substrates by both the hydrothermal synthesis method and the spin-coating method previously reported in the literature [20,22]. Mesoporous silica membranes synthesized by the hydrothermal synthesis method and the spin-coating method are denoted as MS(H)/$Al_2O_3$ and MS(S)/$Al_2O_3$, respectively.

### 2.2. Surface modification of mesoporous silica membranes

3-aminopropyltriethoxysilane (APS) and 3-trimethoxysilylpropyl-diethylenetriamine (TA) were used as amine modification reagents. APS and TA loaded mesoporous silica membranes were prepared by chemical grafting of APS and TA. 5 mL of aminosilane was dropped onto the surface of each mesoporous silica membranes placed in a vessel. The membranes were heated at 423 K for 24 h under Ar flow (to prevent hydrolysis and condensation of aminosilanes). Amine-grafted mesoporous silica membranes were then rinsed several times with anhydrous toluene to remove unreacted aminosilanes.

### 2.3. Synthesis of amine loaded mesoporous silica

To investigate the relationship between the membrane performance and the structural properties of the amine loaded mesoporous silica, APS and TA loaded MCM-41 (denoted as APS/MCM-41 and TA/MCM-41) were synthesized. Mesoporous silica MCM-41 was synthesized according to the literature [23]. Cetyltrimethylammonium bromide (CTAB) was dissolved in deionized water. After complete dissolution of CTAB, sodium silicate was added to the mixture. The silicate sol was stirred at room temperature for 30 min. and then 10 wt.% sulfuric acid was added drop wise into the mixture. After further stirring for 30 min, the pH was adjusted to 10 by drops of 50 wt.% sulfuric acid. The mixture obtained was placed into a Teflon-lined stainless-steel vessel and heated at 363 K for 48 h. The solid product was filtered, rinsed several times with water and dried at 373 K overnight, followed by calcination at 823 K for 12 h. Amine loading was carried out by immersing 2 g of calcined MCM-41 in 100 ml of toluene and adding 2 ml of the appropriate aminosilane coupling reagent (APS or TA) followed by heating at 383 K in nitrogen flow for 48 h. Products were rinsed with toluene several times and dried at 333 K overnight.

### 2.4. Characterization

The amine loaded mesoporous silica membranes were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Gas permeation tests were carried out using differential pressure gas permeation equipment. Pure $N_2$ or $CO_2$ gas was used at 293 K to evaluate the permeation of the mesoporous silica membrane. For the amine loaded mesoporous silica membranes, a mixture of $CO_2$ and $N_2$ was used as the feed gas and the water vapor pressure was controlled by supplying the feed gas through a water tank with controlled temperature. The permeation side was in vacuum and the gas permeance was determined by TCD gas chromatography. To confirm the pore structure of the amine loaded mesoporous silicas, $N_2$ adsorption/desorption isotherms were measured at 77 K and water vapor adsorption isotherms were also evaluated at 313 K.

## 3. Results and discussion

### 3.1. Characterization of the mesoporous silica membranes

MS(H)/$Al_2O_3$ and MS(S)/$Al_2O_3$ were characterized by XRD and the ordered mesoporous structure was confirmed by the sharp peak in the XRD patterns at 2–3 ° 2θ on both samples. The thicknesses of the mesoporous silica layers on MS(H)/$Al_2O_3$ and MS(S)/$Al_2O_3$ were approximately 2 and 0.3 μm, as shown in Fig. 1. The thinner layer of MS(S)/$Al_2O_3$ was achieved by preventing penetration of the silica solution into the alumina substrate by using a pretreatment described in the literature [20], resulting in no formation of a composite layer containing both mesoporous silica and the alumina substrate. As expected, the mesoporous silica membrane synthesized by hydrothermal synthesis was thicker, since formation of a composite layer is inevitable with this synthesis [24]. To confirm the membrane quality of MS(H)/$Al_2O_3$ and MS(S)/$Al_2O_3$, single gas permeation tests using nitrogen and carbon dioxide were carried out at 293 K. The gas permeance values and ideal separation factors are shown in Table 1. The nitrogen permeance

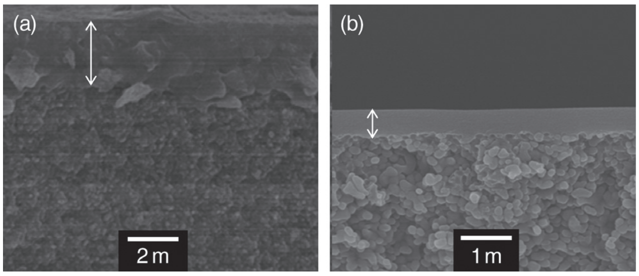

Fig. 1. SEM images of the cross section of MS(H)$Al_2O_3$, (a) and MS(S)$Al_2O_3$, (b).

values for MS(H)/$Al_2O_3$ and MS(S)/$Al_2O_3$ at a 150 kPa pressure drop were $9.6 \times 10^{-8}$ and $6.1 \times 10^{-7}$ mol $s^{-1}$ $m^{-2}$ $Pa^{-1}$, respectively. These permeance values are consistent with the inversely proportional relationship between permeance and membrane thickness. No dependence of nitrogen permeance on pressure drop was observed for either MS(H)/$Al_2O_3$ or MS(S)/$Al_2O_3$ and the ideal separation factor obtained was close to the reciprocal square root of the molecular weight ratio, indicating that the gas permeation was governed by Knudsen diffusion. Under the conditions used in this study, Knudsen diffusion is only expected to dominate the permeance of inorganic gas through pores less than 5 nm [25]. Therefore, both our mesoporous silica membranes must not have any cracks or pinholes larger than 5 nm. These results suggest that both mesoporous silicas have similar membrane quality, except for the membrane thickness.

### *3.2. Gas permeation of amine loaded mesoporous silica membranes*

Table 2 shows the $CO_2/N_2$ permeation performance of the APS and TA loaded mesoporous silica membranes. APS/MS(H)/$Al_2O_3$ showed $CO_2$ selectivity at all temperatures studied with selectivity increasing with temperature. The $CO_2$ permeance increased

Table 1
Gas permeation properties of mesoporous silica membranes

| | Permeance [mol $s^{-1}$ $m^{-2}$ $Pa^{-1}$]$^a$ | | Ideal separation factor $CO_2/N_2$ [-] | Membrane thickness [μm] |
|---|---|---|---|---|
| | $CO_2$ | $N_2$ | | |
| α-$Al_2O_3$ | $1.1 \times 10^{-6}$ | $1.1 \times 10^{-6}$ | 1.0 | – |
| MS(H)/$Al_2O_3$ | $8.5 \times 10^{-8}$ | $9.6 \times 10^{-8}$ | 0.9 | 2.5 |
| MS(S)/$Al_2O_3$ | $5.1 \times 10^{-7}$ | $6.1 \times 10^{-7}$ | 0.8 | 0.3 |

$^a$Single gas permeation at 293 K, 150 kPa feed pressure.

Table 2
$CO_2/N_2$ permeation properties of aminosilane loaded mesoporous silica membranes

| | Temp. [K] | $H_2O$ [%] | Permeance [mol $s^{-1}$ $m^{-2}$ $Pa^{-1}$]$^a$ | | Separation factor $\alpha_{CO_2/N_2}$ [-] | Reference |
|---|---|---|---|---|---|---|
| | | | $CO_2$ | $N_2$ | | |
| APS/MS(H)/$Al_2O_3$ | 313 | 0 | $1.5 \times 10^{-11}$ | $3.0 \times 10^{-13}$ | 50 | This study |
| | 333 | 0 | $6.1 \times 10^{-10}$ | $8.5 \times 10^{-12}$ | 72 | This study |
| | 353 | 0 | $5.2 \times 10^{-10}$ | $1.8 \times 10^{-12}$ | 289 | This study |
| | 373 | 0 | $6.1 \times 10^{-10}$ | $1.8 \times 10^{-12}$ | 339 | This study |
| | 313 | 3 | $2.3 \times 10^{-12}$ | $2.5 \times 10^{-13}$ | 9 | This study |
| TA/MS(H)/$Al_2O_3$ | 333 | 0 | $6.9 \times 10^{-10}$ | $2.3 \times 10^{-12}$ | 300 | This study |
| | 333 | 3 | $1.1 \times 10^{-11}$ | $4.3 \times 10^{-14}$ | 256 | This study |
| TA/MS(S)/$Al_2O_3$ | 333 | 0 | $2.8 \times 10^{-10}$ | $1.4 \times 10^{-11}$ | 20 | This study |
| APS/MS(S)/$Al_2O_3$ | 313 | 0 | $5.0 \times 10^{-12}$ | $3.4 \times 10^{-13}$ | 15 | 20 |
| | 333 | 0 | $1.2 \times 10^{-10}$ | $5.4 \times 10^{-13}$ | 222 | 20 |
| | 373 | 0 | $1.0 \times 10^{-9}$ | $1.2 \times 10^{-12}$ | 833 | 20 |

$^a$$CO_2/N_2$ = 20/80, 150 kPa feed pressure.

significantly above 333 K under dry conditions. $CO_2$ permeance is governed by the adsorption-desorption process through the formation of ammonium carbamate as shown in Eq. 1 [7,11,12]:

$$2R - NH_2 + CO_2 \leftrightarrow R - NHCOO^- + {}^+H_3N - R \qquad (1)$$

This reaction is exothermic so that the interaction between $CO_2$ and amines is weakened at higher temperature. In our previous work [20], the $CO_2$ permeance through the APS/MS(S)/$Al_2O_3$ increased with temperature up to 373 K. The APS/MS(H)/$Al_2O_3$ in this study showed similar behavior. The TA/MS(H)/$Al_2O_3$ membrane showed higher $CO_2$ selectivity than that of the APS/MS(H)/$Al_2O_3$ membrane because of lower $N_2$ permeance for the TA/MS(H)/$Al_2O_3$ at 333 K under dry conditions. To evaluate the relationship between the membrane performance and the pore structure of the amine loaded mesoporous silica, the structural properties of the APS/MCM-41 and TA/MCM-41 are summarized in Table 3 and their BJH pore size distributions are shown in Fig. 2. As can be expected, the BET surface area and total pore volume of the TA/MCM-41 were greatly reduced, as a result of the much longer molecular length of TA (approximately 1.8 nm) and no mesopores were observed in the BJH pore size distribution. On the other hand, the decrease in pore size, surface area and pore volume for the APS/MCM-41 was relatively small because of the smaller molecular length of APS. From these results, the higher $CO_2$ selectivity of the TA/MS(H)/$Al_2O_3$ could be explained by the much denser packing of TA within the pores of the mesoporous silica layer because $N_2$ molecules are likely to permeate the interstitial space between aminosilanes immobilized in the mesopores.

Table 3
Structural properties of unloaded and amine loaded MCM-41 powders

| | $N_2$-BET [$m^2$/g] | $H_2O$-BET [$m^2$/g] | Pore volume [$cm^3$/g] |
|---|---|---|---|
| MCM-41 | 990 | 160 | 0.90 |
| APS/MCM-41 | 505 | 210 | 0.34 |
| TA/MCM-41 | 12 | 257 | 0.03 |

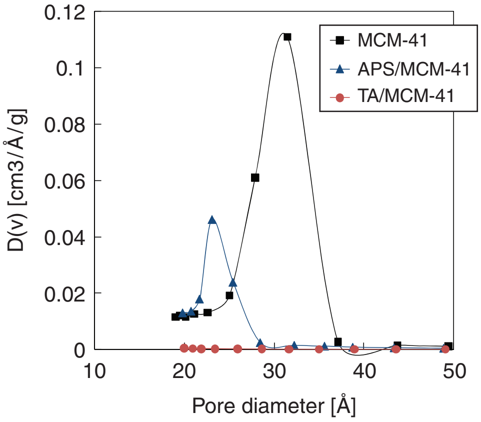

Fig. 2. BJH pore size distribution of unloaded, APS loaded and TA loaded MCM-41 powders.

The TA/MS(S)/$Al_2O_3$, however, showed much lower $CO_2$ selectivity. Considering that the $N_2$ permeance of the TA/MS(S)/$Al_2O_3$ was one order of magnitude higher than that of the TA/MS(H)/$Al_2O_3$, the aminosilane density within the mesopores of TA/MS(S)/$Al_2O_3$ might be insufficient to achieve high $CO_2$ selectivity. In addition, its $CO_2$ permeance was slightly lower than that of APS/MS(H)/$Al_2O_3$ and TA/MS(H)/$Al_2O_3$ even though the membrane of TA/MS(S)/$Al_2O_3$ was much thinner. $CO_2$ molecules could diffuse within the mesoporous layer through the repeated chemical adsorption/desorption steps shown in Eq. (1). It is likely that the reactivity of an amino pair with $CO_2$ is determined by the distance of the amino groups from each other in the pores. In other words, $CO_2$ permeability should be influenced by the surface density of amino groups within the pores since this affects the reactivity of the amine pair with $CO_2$. Therefore, these results imply that the density of the aminosilanes is lower on the TA/MS(S)/$Al_2O_3$ than on the other membranes.

To evaluate the effect of water on membrane performance, gas permeation tests were also carried out on APS/MS(H)/$Al_2O_3$ and TA/MS(H)/$Al_2O_3$ using a binary gas mixture of $CO_2$/$N_2$ with water vapor. As shown in Table 2, the $CO_2$ selectivity of APS/MS(H)/$Al_2O_3$ was decreased in the presence of water vapor. Generally, as a result of their large and uniform pore size, a steep capillary condensation occurs during water adsorption on mesoporous silicas, as is clearly shown in the water vapor adsorption isotherm for MCM-41 in Fig. 3. The adsorption isotherm for APS/MCM-41, also shown in Fig. 3, exhibited a similar steep capillary condensation step at $P/P_0$ = 0.5–0.6 at 313 K. This means its pore size was sufficiently large for capillary condensation of water, despite the reduction in pore size as a result of the APS modification. The relative humidity used for our gas permeation measurements was approximately 60%, which is sufficient for capillary condensation to occur. This condensed water in the mesopores must interfere with the $CO_2$ permeation, resulting in low $CO_2$ selectivity. Fig. 4 shows the temperature dependence of gas permeances and $CO_2$ selectivity for APS/MS(H)/$Al_2O_3$.

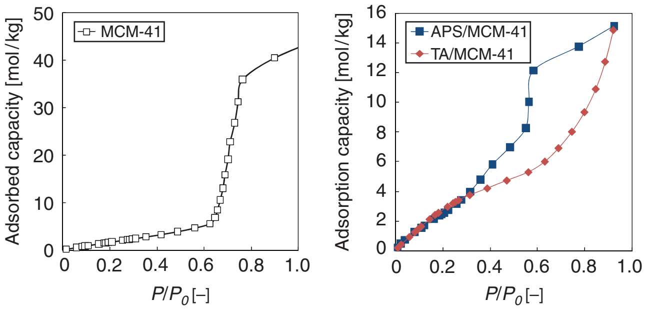

Fig. 3. Water vapor adsorption isotherms of MCM-41 and amine loaded MCM-41 at 313 K.

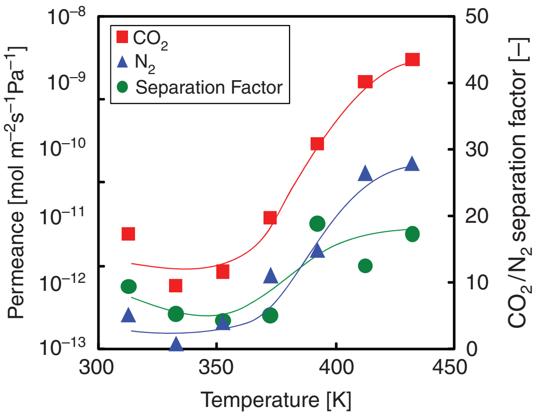

Fig. 4. Gas permeation of the APS/MS(H)/$Al_2O_3$ membrane with a binary mixture. $CO_2/N_2$ = 20/80 at 150 kPa total feed pressure in the presence of water vapor.

At less than 353 K, the membrane performance was relatively independent of temperature because of pore blocking by the condensed water. Both the $CO_2$ and $N_2$ gas permeances, as well as the $CO_2$ selectivity, increased with temperature above 373 K as the condensed water within the pores was desorbed. The $CO_2$ selectivity was, however, still lower than that under dry conditions. This lower selectivity was caused by the smaller increase of the $CO_2$ permeances with temperature than that under the dry condition although the $N_2$ permeance was similar. This indicates that the adsorbed water even above 373 K would prevent the diffusion of $CO_2$ as well as $N_2$. In addition, Luechinger and co-workers reported that pure APS modified M41S was found to have a certain amount of $Q^3$ species by $^{29}$Si MAS NMR spectra, leading to poor hydrothermal stability [26]. Hence, the low $CO_2$ selectivity at high temperature might be caused by the structure collapse of the modified aminosilane layer in the pores above 373 K. However, further investigation should be required to know the reason for the low $CO_2$ selectivity in the presence of water.

In the case of TA/MS(H)/$Al_2O_3$, the decrease of $CO_2$ selectivity in the presence of the water was insignificant. A comparison of the water vapor adsorption isotherms of TA/MCM-41 with APS/MCM-41 shows that the water adsorption behavior of TA/MCM-41 was completely different with no steep capillary condensation observed. As mentioned above, the grafted TA molecules might fill the mesopores. However, the water adsorption isotherm cleary showed the existence of micropores in which water molecules can adsorb. The interspace formed by the complicated entanglement of TA could become micropores in which only gas molecules can diffuse, preventing the steep capillary condensation of water. It is expected that the condensed water could inhibit the diffusion of inorganic gases as can be seen in the case of APS/MS(H)/$Al_2O_3$. In other words, the TA/MS(H)/$Al_2O_3$ membrane, with no capillary condensation of water, could permit the permeation of inorganic gases. In addition, the BET surface area measurements of the TA/MCM-41 using $N_2$ and $H_2O$ imply that polar molecules such as $CO_2$ and $H_2O$ can adsorb preferentially (compared to nonpolar ones, such as $N_2$) on TA loaded mesoporous silica. Therefore, the high $CO_2$ selectivity in the presence of water could be associated with the greatly enhanced surface interaction between TA and polar molecules and smaller effective pore size of the TA/MS(H)/$Al_2O_3$ from the long molecular length of TA.

## 4. Conclusions

Two types of amines were loaded into mesoporous silica membranes and the gas permeation properties of the membranes were evaluated. Densely packed amines provided $CO_2$ selectivity on the APS and TA loaded mesoporous silica membranes under dry conditions, and Both the APS/MS(H)/$Al_2O_3$ and TA/MS(H)/$Al_2O_3$ sample was highly $CO_2$ selective. However, the $CO_2$ selectivity of APS/MS(H)/$Al_2O_3$ was decreased by the presence of water. Under wet conditions, the pore filling of condensed water in APS/MS(H)/$Al_2O_3$ occurred, since this material had sufficiently large pores for the capillary condensation of water. By contrast, the TA/MS(H)/$Al_2O_3$ membrane was $CO_2$ selective in the presence of water. The molecular size of TA was sufficiently large to fill the mesopores, resulting in a small, subnanometer, effective pore size. In addition, compared to APS/MCM-41, TA/MCM-41 exhibited a significantly higher $H_2O$ BET surface area and a very low $N_2$ BET surface area. This indicates that the interaction of polar molecules such as $H_2O$ and $CO_2$ with these materials was stronger than that of nonpolar molecules like $N_2$. Therefore, the combination of the smaller effective pore size after modification and the amines with high affinity for polar molecules leads to very effective $CO_2$ selectivity for this amine loaded mesoporous silica membrane in the presence of water.

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