Enhanced CO₂ Separation Performance for Tertiary Amine-Silica Membranes via Thermally Induced Local Liberation of CH₃Cl

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A facile method for the fabrication of amine-silica membranes with enhanced CO₂ separation performance was proposed via the thermally induced liberation of small molecules from quaternary ammonium salt. Quaternary ammonium-silica (QA-SiO₁.₅) xerogel powders/films were fabricated via sol-gel processing and their thermal stability was systematically studied using thermogravimetric mass spectrometer, Fourier transform infrared, energy dispersive spectroscopy, and positron annihilation lifetime spectroscopy analysis. CO₂ sorption performances of QA-SiO₁.₅ derived xerogel powders were quantitatively compared after assigning their relevant parameters to a dual-mode sorption model. The gas permeation performances of membranes derived from QA-SiO₁.₅ were evaluated in terms of kinetic diameter and temperature dependence of gas permeance, and activation energy (Eₚ) required for gas permeation. The results indicate that liberation of the CH₃Cl molecules from these membranes significantly improved both CO₂ permeation and CO₂/N₂ separation capabilities. Therefore, the present study provides insight that should be useful in the development of high-performance CO₂ separation membranes via the effect of the thermally induced liberation of small molecules.

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Keywords: organosilica, quaternary ammonium salt, thermally induced liberation, CO₂ separation membrane, dual-mode sorption model

Introduction

Excessive CO₂ emissions into the atmosphere contribute to global warming and concern for the state of the climate. It is apparent there is significant need for technologies that can accomplish efficient CO₂ capture and separation. The inherent advantages of energy-efficiency, cost-effectiveness, and the promotion of a smaller footprint make membrane technology an economically and environmentally promising method to mitigate these global challenges.¹⁻³ Hence, many versions of membranes for CO₂ separation from gas mixtures (e.g., CO₂/H₂, CO₂/N₂, CO₂/CH₄, etc.) have been designed and manufactured on a small-to-medium scale over the past few decades.²⁻⁴⁻⁵ Amorphous silica-based membranes have attracted considerable attention for the chemical, thermal, and mechanical stability that allows their practical application under harsh conditions such as high temperature and/or high pressure. These membranes feature ultramicropores (<7 Å) and are generally processed via a facile sol-gel approach for the generation of ultrathin active separation layers that combine superior productivity and permselectivity, and show great potential to exceed the Robeson upper boundaries seen in conventional polymeric membranes.⁶⁻⁷

Generally, amorphous silica membranes have a microporous structure that allows them to separate penetrating gas molecules via molecular sieving and surface diffusion mechanisms with extremely high levels of H₂/gas (gas = N₂, C₃H₆, SF₆, etc.) selectivity.⁸ However, due to the similar kinetic diameters of CO₂ (3.3 Å) and N₂ (3.64 Å), tuning of the membrane pore size for high-performance separation remains a challenge. To overcome this limitation, various CO₂-philic moieties and/or molecules have been introduced to the amorphous silica microporous structure to significantly improve CO₂ sorption performance via the conjugation effect of solubility and diffusivity of the penetrating molecules that defines gas-separation performance.⁹ Amine or carboxyl groups have been widely employed in modifications of silica matrix for enhanced CO₂ sorption via impregnation, cocondensation, and postsynthesis grafting approaches.⁹⁻¹⁶ These membranes have the advantage of suppressing the effect of membrane swelling as well as enhancing CO₂ sorption (or solubility) performance in a membrane matrix. Indeed, with the introduction of
flexible CO$_2$-philic moieties, the rigid pore volume of a microporous silica matrix tends to significantly diminish, and the “free-volume pores” induced by the flexible chains are restrained due to the rigidity of the Si-O-Si skeleton. Consequently, the formation of a dual, flexible-rigid, membrane matrix has resulted in an appealing level of CO$_2$/N$_2$ permselectivity at the expense of small decreases in gas permeance, as gas transport across these membranes switches from molecular sieving to a primarily solution-diffusion (or adsorption-diffusion) mechanism. To prevent significant reductions in gas permeance, particularly that of CO$_2$, and simultaneously maintain a consistent level of CO$_2$/gas (gas = H$_2$, N$_2$, CH$_4$, etc.) permselectivity for dual, flexible-rigid, and structured membranes, sufficient accessible porosity for CO$_2$ is important. Furthermore, for practical process designs of membrane separation applications from an economic perspective, increases in membrane permeance are more important than increases in selectivity to enhance the competitiveness for flue gas CO$_2$ capture.$^{17}$ Polaris$^{TM}$ is a successful commercially available membrane developed by Membrane Technology and Research (MTR) Inc. that provides only moderate selectivity but a level of CO$_2$ permeance ($>1000$ GPU) that is 10–50 fold that of conventional cellulose membranes.$^{17}$

The typical “template method” is one of the most popular approaches to create porosity for macroscale porous materials, but it is less effective in the processing of high-performance CO$_2$/N$_2$ separation membranes. Recently, some important attempts for processing ultramicroporous membranes that demonstrate high levels of gas permeance have included the use of polymers with intrinsic microporosity (PIM)$^{18–21}$ and thermally rearranged polymers (TR polymers)$^{22}$ high-temperature pyrolysis of polymeric membranes (the so-called carbon molecular sieving membranes), and low-temperature thermal liberation of small molecules in block or graft copolymers.$^{23–25}$ Okamoto et al. (2005) reported a low-temperature pyrolysis method to produce a flexible pyrolytic membrane using sulfonated polyimides.$^{24}$ During relatively lower-temperature (450°C, under a nitrogen atmosphere) pyrolysis, the -SO$_3$H groups decompose and create microvoids, which results in higher permeability for C$_3$H$_6$ and higher permselectivity for C$_3$H$_6$/C$_2$H$_6$. Chung et al. (2011) prepared flexible and highly permeable polyimide membranes by grafting thermally liable molecules on a cross-linkable polyimide. The resultant membranes showed ultra-fine micropores and consequently improved CO$_2$ permeability with an appealing level of CO$_2$/CH$_4$ selectivity. In addition, we previously studied a series of amine-functionalized silica membranes wherein membranes with sterically hindered amines (including tertiary amines) demonstrated a mild affinity to CO$_2$, which led to greater potential for CO$_2$ permeation based on both activation energy and CO$_2$/N$_2$ selectivity.$^{26–28}$ Therefore, we proposed the concept of a mild-affinity membrane that could provide superior CO$_2$ separation performance under mild conditions (room temperature) due to the optimized balance between CO$_2$ sorption and diffusion performance.

In the present study, we proposed a novel tertiary amine-silica membrane fabricated from a polycondensed quaternary ammonium-silica (Trimethyl[3-(trimethoxysilyl)propyl]ammonium chloride, QA-Si) intermediate membrane via a thermally induced local liberation of chloromethane (CH$_3$Cl). At a relatively lower curing temperature of 250°C, the quaternary ammonium salts decompose into equivalent CH$_3$Cl molecules that result in ultrafine microvoids that promote the transport of CO$_2$ molecules across the resultant membrane, as illustrated in Figure 1. The effect of liberating CH$_3$Cl from QA-Si can be obtained via either direct calcination at 250°C or two-step calcination (first step, 180°C and second step, 250°C). The proposed method has at least two advantages compared with conventional modification approaches such as sol-gel-derived cocondensation: (i) avoidance of the embedding of amine groups (high amine accessibility) enabled by the local liberation of CH$_3$Cl molecules from each quaternary ammonium unit, which could create accessible porosity for gas transport; and, (ii) avoidance of the deactivation of amine groups during the preparation of sols that use acids such as HCl as a catalyst, which results in a partial deactivation of amine groups due to the strong acid-base interactions that are difficult to reactivate by the removal of bound acid groups under mild conditions. To the best of our knowledge, this is the first demonstration of the effect of the thermally induced liberation of quaternary

![Figure 1. Illustration of the preparation process for QA-Si-derived membranes with and without the local liberation of CH$_3$Cl.](wileyonlinelibrary.com)
ammonium-based organosilica membranes with improved CO₂ separation performance, which could provide important technological insights applicable to the development of high-performance CO₂ separation membranes.

**Experimental**

### Preparation of amine-silica sols/xerogels/membranes

Trimethyl[3-(trimethoxysilyl)propyl]ammonium chloride (QA-Si) precursor was prehydrolyzed under a QA-Si/H₂O/HCl/EtOH system using HCl and EtOH as catalyst and solvent, respectively. The initial molar ratio of QA-Si/H₂O/HCl in the ethanol solutions was maintained at 1/120/0.3, and the weight % of the precursors was adjusted to 3% via the use of fresh ethanol. The hydrolysis and polycondensation reactions were conducted at ambient temperature for 12 h, and the resultant sols were stored in a refrigerator at 4°C for future use. A tertiary amine-silica precursor-derived sol of 3-(trimethoxysilyl)-N, N-dimethylpropan-1-amine (TA-Si) was also fabricated analogously as the control. All the analogous xerogel powders, denoted as QA-SiO₁.₅ and TA-SiO₁.₅, were derived from QA-Si and TA-Si sols, respectively, and fabricated via fast solvent evaporation at ~100°C under an air atmosphere, which then was followed by calcination under a N₂ atmosphere. TA-SiO₁.₅ and QA-SiO₁.₅ xerogel powders/films were further denoted simply as TA-x and QA-x, respectively, wherein “x” refers to the calcination temperature. In the case of QA-x-y, “y” refers to the temperature of the postheat treatment of QA-x.

Porous 3-alumina tubes (porosity: 50%, average pore size: 1 µm, length: 100 mm, outside diameter: 10 mm), kindly supplied by the Nikkato Corporation (Japan), were used as supports for the TA-SiO₁.₅ and QA-SiO₁.₅ membranes. The supports were bonded with nonpermeable Al₂O₃ tubes (half-open and open-ended) via sintering prior to the membrane-coating processes. A well-developed SiO₂-ZrO₂ composite colloidal sol with a concentration of 2 wt % is described elsewhere, and was prepared in advance to be used as the binder for the coating of x-alumina particle layers and for the formation of a SiO₂-ZrO₂ sublayer. x-alumina particles with average diameters of 2 and 0.2 µm were evenly dispersed with a 10 wt % concentration into the as-prepared SiO₂-ZrO₂ colloidal sol via ultrasonic processing. These two types of x-alumina particle dispersions were sequentially coated onto the outer surface of a porous support that was calcinated at 550°C for 15 min following each coating process to form two intermediate x-alumina particle layers. The procedures for each type of the x-alumina particles were repeated three times to cover large pores, which could have resulted in pinholes in the final membrane. The SiO₂-ZrO₂ sol was diluted to 0.5 wt % using pure water and then coated onto the x-alumina particle layer to form a sublayer to control the average pore size to approximately 1 nm, followed by calcination at 550°C for 15 min. The topmost selective layer was finished with a coating of TA-Si- or QA-Si-derived sols, followed by calcination under nitrogen for 1 h, as described elsewhere. Prior to the coating, as-prepared TA-Si- or QA-Si-derived sols were diluted to a concentration of 0.25 wt % using fresh ethanol. The resultant membranes were identified as having similar TA-SiO₁.₅ and QA-SiO₁.₅ xerogel powders according to the calcination temperature.

### Characterization of amine-silica sols and xerogels

The thermal stabilities and decomposition behaviors of the initial amine-silica xerogels were observed using a thermogravimetric mass spectrometer (TG-MS, TGA-DTA-PIMS 410/S, Rigaku, Japan) and Fourier transform infrared (FTIR) spectroscopy (FTIR-JASCO, Japan). The element composition, particularly C₁, of amine-silica xerogels fired at different temperatures under N₂ was determined using a JCM 5700 scanning electron microscope (SEM, JEOL, Japan) equipped with an EX-37001 energy dispersive spectroscopy (EDS) accessory (JEOL, Japan) and using X-Ray Photoelectron Spectroscopy (XPS) analysis (JEOL RE series JES-RE1X ESR spectrometer).

Positron annihilation lifetime spectroscopy (PALS) measurements for the amine-silica films fabricated on silicon wafers were conducted with a positron incident energy of 1.2 keV and at room temperature under vacuum using a ²²Na-based pulsed positron beam at the National Institute of Advanced Industrial Science and Technology (AIST, Japan). For each measurement 5 million annihilation event counts were accumulated. A multiexponential analysis was applied to the recorded lifetime data to deduce the average lifetimes of positron and positronium (Ps), the positron-electron bound state. In the analysis, three annihilation components, ascribed to a free positron and Ps existing either as spin-antiparallel para-positronium p-Ps or spin-parallel ortho-positronium o-Ps, were assumed to obtain optimum fitting. The average lifetimes longer than 1 ns due to the annihilation of o-Ps were determined as τ₃ with relative intensities of I₃ along with the shorter average lifetime components of τ₁ and τ₂ due to the annihilations of p-Ps and free positrons. The pore radius, r, for the films was estimated from τ₃ based on a semiempirical quantum mechanical model developed by Tao and Eldrup, as follows

\[
\tau_3 = 0.5 \left[ 1 - \frac{r}{r_0 + 0.166} + \frac{1}{2\pi} \sin \left( \frac{2\pi r}{r_0 + 0.166} \right) \right]^{-1}
\]

### Gas adsorption evaluation of amine-silica xerogel powders

N₂ and CO₂ adsorption/desorption isotherms were performed using BELMAX equipment (BEL JAPAN INC., Japan). Prior to the measurement, xerogel samples that had been fired at different temperatures under N₂, were evacuated at 180°C for 12 h. A typical dual-mode sorption model that has been widely employed to describe and analyze sorption properties of gas molecules in glassy polymers was used for modeling CO₂ adsorption isotherms for QA-SiO₁.₅ and TA-SiO₁.₅ xerogel powders. Generally, this model involves two modes of sorption sites that obey Henry’s law of dissolution and a Langmuir-type sorption. The dual-mode sorption model is expressed as follows

\[
C = C_D + C_H = k_Dp + \frac{C_Hbp}{1 + bp}
\]

where C is the total gas concentration in the xerogel powders, C_D and C_H are the CO₂ concentrations contributed from Henry’s law and Langmuir-type sorption, respectively, k_D is the sorption coefficient based on Henry’s law, and C_H and b are the Langmuir parameters in terms of maximum capacity and affinity constant, respectively.
Membrane performance evaluation

Single-gas (He, 2.6 Å; H2, 2.89 Å; CO2, 3.3 Å; N2, 3.64 Å) permeation tests were conducted based on the conventional constant pressure/variable volume technique for temperatures ranging from 35 to 200°C with an experimental setup as schematically shown elsewhere.26 The flow rate of the feed gas was controlled with a mass flow controller (HORIBASTEC, Japan), and the pressure was adjusted using a back-pressure regulator. The flow rates of both the retention side and the permeate side were measured using film flow meters (HORIBASTEC, Japan). In a typical measurement, the permeate stream (inner side) was maintained at atmospheric pressure, and the pressure drop across the membrane was maintained at ~1 bar. Prior to measurement, the membrane was allowed to outgas in a He flow of 50 cm³/min at 200°C for at least 6 h to remove any possible water adsorbed in/on the membrane. The permeation measurement was conducted after the membrane reached a steady state with respect to the furnace temperature and the pressure difference between the shell and the inner side of the membrane. Values for gas permeance and ideal selectivity were calculated using Eqs. 3 and 4, respectively

\[ P_i = \frac{F_i}{A \Delta \rho} \]  
\[ \alpha_{ij} = \frac{P_i}{P_j} \]

where \( P_i \) and \( P_j \) are the permeance values for components \( i \) and \( j \), respectively, \( F_i \) is the molar flow rate of component \( i \), \( A \) is the membrane effective area, \( \Delta \rho \) is the partial pressure drop of component \( i \) between the shell and inner side of the tubular membrane, and \( \alpha_{ij} \) is the ideal selectivity (permeance ratio) of component \( i \) over \( j \).

Binary gas (CO2/N2, 15 vol % CO2) permeation tests were also conducted at 35°C. The flow rate of the feed gas was controlled by a mass flow controller (HORIBASTEC, Japan) and the pressure was adjusted by a back-pressure regulator. The flow rates of both the retentate and the permeate streams were measured using film flow meters (HORIBASTEC, Japan). The gas compositions of the retentate and the permeate for the binary gas separation were measured using a mass spectrometer gas analyzer (AMTEK, US), for which Ar with a flow rate of 60 cm³/min was used as a standard gas for calibration.

Results and Discussion

Characterizations of TA-SiO1.5 and QA-SiO1.5 xerogel powders/films

The initial xerogel powders without thermal treatment were applied to TG-MS measurement to probe their thermal properties. Figure 2 shows the TG curves and the simultaneous mass spectra of the evolved gases of QA-SiO1.5 and TA-SiO1.5 xerogels during pyrolysis. Clear two-stage TG curves were observed for both QA-SiO1.5 and TA-SiO1.5 xerogel samples (Figure 2a). In the first stage, weight losses of 40 and 20% were detected at temperatures that ranged from 200 to 350°C for QA-SiO1.5 and TA-SiO1.5, respectively. These losses were due mainly to the evolution of the unhydrolyzed ethoxy groups and to further condensation-induced water/alcohol evaporation, which was further confirmed by the FTIR analysis described below. Furthermore, an additional important contribution to the weight loss of QA-SiO1.5 was from the thermal-induced liberation of CH3Cl molecules based on mass signals of m/z = 50 and 52, as shown in Figure 2b, and on the impressive endothermic peak of the heat flow shown in Figure 2a. The possible dealkylation reaction of polycondensed QA-SiO1.5 is illustrated in Figure 3, and in this reaction a quaternary ammonium salt group preferentially decomposed into a ternary amine group and a CH3Cl molecule (m/z = 50, 52) at a decomposition-starting temperature of approximately 230°C. The additional 20% weight loss of QA-SiO1.5 (40%) could be ascribed to this dealkylation reaction with respect to TA-SiO1.5 (20%). In the second stage, further (30%) weight losses were observed for both QA-SiO1.5 and TA-SiO1.5 under heating that ranged from 400 to 550°C, which was accompanied by a significant evolution of H2O (m/z = 18) and C2H4 (m/z = 28), as shown in Figures 2b, c. Weight losses in this stage were mainly attributed to the further condensation of Si-OH groups and decomposition of organic moieties.

Figure 2. (a) TG and Heat-flow curves of QA-SiO1.5 and TA-SiO1.5 xerogel powders, and m/z signals of (b) QA-SiO1.5 and (c) TA-SiO1.5 xerogel powders (He atmosphere, 300 cm³/min; heating rate, 5°C/min).

Figure 3. Possible dealkylation reaction of polycondensed QA-SiO1.5 with liberation of CH3Cl molecules.
FTIR analysis of TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ was performed using thin films coated on KBr plates, as shown in Figure 4. All the samples fired at different temperatures demonstrated the characteristic absorption peaks of Si-O-Si stretching vibration at 1000–1300 cm$^{-1}$, which showed a red (low wavenumber) shift for TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ samples as the calcination temperature increased. Simultaneously, the spectra for both TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ showed reductions in -CH$_3$/-CH$_2$ stretching and deformation at 2700–3000 cm$^{-1}$ and 1300–1500 cm$^{-1}$, respectively, which almost disappeared after calcination at 200$^\circ$C, but it was almost completely removed as the calcination temperature increased to 250$^\circ$C. This indicates that the amine groups in TA-SiO$_{1.5}$ xerogel powders were activated (freed from counterions) at a temperature comparable to, or higher than, 250$^\circ$C. Conversely, QA-SiO$_{1.5}$ xerogel powders demonstrated a much higher Cl concentration compared with TA-SiO$_{1.5}$, which was derived from the quaternary ammonium compound ([N(CH$_3$)$_3$]Cl$^-$) and also was rapidly decreased to a negligible level (0.13%) following calcination at 250$^\circ$C probably due to the liberation of CH$_3$Cl molecules, as confirmed by TG-MS analysis. Overall, the amine groups in TA-SiO$_{1.5}$ xerogel powders could be transformed to activated tertiary amines at a temperature of 250$^\circ$C. Therefore, the amine type in QA-SiO$_{1.5}$ xerogel powders could be identified as quaternary in QA-180 while that in QA-250 and QA-180–250 were identified as tertiary.

Figure 6 shows the PALS data for the QA-180 and QA-180–250 films fabricated on silicon wafers. The data for both samples clearly displayed long-lived components longer than 1 ns due to the annihilation of o-Ps in either rigid or free-volume pores of the present amine-silica films. The o-Ps component for the QA-180–250 film that was obtained from the postheat treatment of the QA-180 film indicated a considerably longer

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**Table 1. Atomic Composition of TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ Xerogel Powders Estimated by XPS Measurement**

<table>
<thead>
<tr>
<th>Material</th>
<th>C1s [%]</th>
<th>O1s [%]</th>
<th>Si2s [%]</th>
<th>N1s [%]</th>
<th>Amine (N) Density [mmol-N/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-250</td>
<td>75.8</td>
<td>11.0</td>
<td>7.00</td>
<td>6.10</td>
<td>4.40</td>
</tr>
<tr>
<td>QA-180</td>
<td>61.1</td>
<td>21.4</td>
<td>11.0</td>
<td>6.50</td>
<td>4.40</td>
</tr>
<tr>
<td>QA-250</td>
<td>75.1</td>
<td>11.5</td>
<td>6.80</td>
<td>6.50</td>
<td>4.70</td>
</tr>
</tbody>
</table>

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FTIR analysis of TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ was performed using thin films coated on KBr plates, as shown in Figure 4. All the samples fired at different temperatures demonstrated the characteristic absorption peaks of Si-O-Si stretching vibration at 1000–1300 cm$^{-1}$, which showed a red (low wavenumber) shift for TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ samples as the calcination temperature increased. Simultaneously, the spectra for both TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ showed reductions in -CH$_3$/-CH$_2$ stretching and deformation at 2700–3000 cm$^{-1}$ and 1300–1500 cm$^{-1}$, respectively, which almost disappeared after calcination at 400$^\circ$C. These quantitatively indicated an increase in amorphous SiO$_{1.5}$ (100–400$^\circ$C) or SiO$_2$ (>400$^\circ$C) and a reduction in -CH$_3$/-CH$_2$- groups due to further hydrolysis or alcohol condensation (100–300$^\circ$C) and thermolysis (>400$^\circ$C). Overall these observations are consistent with the TG-MS spectra of TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ xerogel powders and indicate that organic moieties containing amine groups could remain in the resultant xerogel powders/films at calcination temperatures as high as 300$^\circ$C. The quantitative evaluation of amine groups of TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ xerogel powders fired at temperatures of 180 or 250$^\circ$C to be utilized for membrane formation was performed using XPS, and the results are listed in Table 1. As expected, all the samples fired at either 180 or 250$^\circ$C demonstrated considerable N1s atom fractions (6–7%), indicating the rich presence of amine groups. In addition, the amine densities detected for the samples tested were comparable with values that ranged from 4 to 5 mmol-N/g.

To further confirm the liberation of CH$_3$Cl molecules from QA-SiO$_{1.5}$ xerogel powders as well as the activation of amine groups for both TA-SiO$_{1.5}$ and QA-SiO$_{1.5}$ samples, EDS analysis was performed and the results are shown in Figure 5 and Table 2. The Cl element in TA-SiO$_{1.5}$ xerogel powders was from the HCl used during the preparation of sols as a catalyst. This was the remaining portion that could stably exist in the xerogel powders at 200$^\circ$C, but it was almost completely removed as the calcination temperature increased to 250$^\circ$C. This indicates that the amine groups in TA-SiO$_{1.5}$ xerogel powders were activated (freed from counterions) at a temperature comparable to, or higher than, 250$^\circ$C. Conversely, QA-SiO$_{1.5}$ xerogel powders demonstrated a much higher Cl concentration compared with TA-SiO$_{1.5}$, which was derived from the quaternary ammonium compound ([N(CH$_3$)$_3$]Cl$^-$) and also was rapidly decreased to a negligible level (0.13%) following calcination at 250$^\circ$C probably due to the liberation of CH$_3$Cl molecules, as confirmed by TG-MS analysis. Overall, the amine groups in TA-SiO$_{1.5}$ xerogel powders could be transformed to activated tertiary amines at a temperature of 250$^\circ$C. Therefore, the amine type in QA-SiO$_{1.5}$ xerogel powders could be identified as quaternary in QA-180 while that in QA-250 and QA-180–250 were identified as tertiary.

Figure 6 shows the PALS data for the QA-180 and QA-180–250 films fabricated on silicon wafers. The data for both samples clearly displayed long-lived components longer than 1 ns due to the annihilation of o-Ps in either rigid or free-volume pores of the present amine-silica films. The o-Ps component for the QA-180–250 film that was obtained from the postheat treatment of the QA-180 film indicated a considerably longer
average lifetime, which suggested that the liberation of CH3Cl due to the postheat treatment could have induced an increase in the pore size. Table 3 lists the average lifetimes analyzed from the observed PALS data along with their intensities for the QA-180 and QA-180–250 films and their pore sizes estimated from the long-lived o-Ps lifetimes. Film QA-180–250 demonstrated a higher value in τ3 than that of the film QA-180, and the estimated pore sizes for the films QA-180 and QA-180–250 were 0.441 nm and 0.706 nm, respectively. These results signify that the liberation of CH3Cl from the matrix of QA-SiO1.5 materials may create additional voids or may alter the sizes of either rigid or free-volume pores. It is important to note, however, that the liberation effect did not create cracks or defects following the postheat treatment, as shown in Supporting Information Figure S2.

**Gas sorption performance of TA-SiO1.5 and QA-SiO1.5 xerogel powders**

Figure 7 shows the N2 (−196°C) and CO2 (35°C) adsorption isotherms of TA-SiO1.5 and QA-SiO1.5 xerogel powders. As confirmed by TG-MS (Figure 2), FTIR (Figure 3), and XPS analysis (Table 2), the main organic chains containing amine (tertiary type) groups could stably exist in these xerogel products when fired at temperatures lower than 300°C. Hence, the abundant flexible organic moieties led to a significant reduction in the rigid pore volumes of silica-based networks, as reported elsewhere.26,27,33 The negligible N2 adsorption amount (<0.2 cm3(STP)/g) on the xerogel powders shown in Figure 7a indicates the formation of a dual flexible-rigid network, in which “free-volume pores” were created instead of rigid pores. Therefore, without special interactions the adsorption of N2 by the organic chains on the rigid surfaces/pores or voids was significantly prohibited, particularly at extremely low temperatures (e.g., −196°C) that could freeze the flexible organic chains. CO2, however, could dissolve in the flexible organic phase and react with the amine groups at mild temperatures (35°C), which resulted in a much higher adsorption amount (almost reversible based on adsorption/desorption isotherms) on these xerogel powders compared with that of N2. In addition, the calculated values for amine efficiency (mmol CO2/mmol N) were 0.006 for QA-180, 0.03 for TA-250, and 0.06 for QA-250. Specifically, in the case of TA-SiO1.5 xerogel powders prepared as the control, TA-250 fired at 250°C exhibited more impressive CO2 adsorption than TA-180 fired at 180°C. This can be attributed to (i) the enhanced porosity and the sizes of “free-volume pores” induced by a higher calcination temperature that can result in further alcohol condensation (as well as hydrolysis in a small amount, if possible) of the silica-based network and (ii) the reaction of amine groups induced by the removal of bound HCl (as shown in Figure 2). The same holds true in the case of QA-SiO1.5 xerogel powders. Most important and interesting, however, is that the adsorption capacity of QA-250 xerogel powders that is greater than either the QA-180 or TA-250 versions can be additionally attributed to the local liberation of CH3Cl molecules, which may create voids around newly generated tertiary amine groups (as confirmed by PALS measurements), which equates to accessible porosity for CO2 molecules and increases the practicality and efficiency of amines.

**Table 2. Residual Cl Content in TA-SiO1.5 and QA-SiO1.5 Xerogel Powders Fired at 150, 200, and 250°C Under N2**

<table>
<thead>
<tr>
<th>Material</th>
<th>TA-SiO1.5 Cl [at %]</th>
<th>TA-SiO1.5 Cl/Si [molar ratio]</th>
<th>QA-SiO1.5 Cl [at %]</th>
<th>QA-SiO1.5 Cl/Si [molar ratio]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.8</td>
<td>0.49</td>
<td>8.0</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>0.42</td>
<td>8.4</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>0.017</td>
<td>0.706</td>
<td>0.017</td>
</tr>
</tbody>
</table>

*The theoretical value in the fresh sol of TA-Si was 0.3 ± 0.1.

**Table 3. PALS Data for the QA-180 and QA-180–250 Films Fabricated on Silicon Wafers, as Recorded at a Positron Incident Energy of 1.2 keV**

<table>
<thead>
<tr>
<th>Sample</th>
<th>τ1 [ns]</th>
<th>I1 [%]</th>
<th>τ2 [ns]</th>
<th>I2 [%]</th>
<th>τ3 [ns]</th>
<th>I3 [%]</th>
<th>τ4 [ns]</th>
<th>I4 [%]</th>
<th>Pore Size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA-180</td>
<td>0.125</td>
<td>6.10</td>
<td>0.359</td>
<td>69.5</td>
<td>1.43</td>
<td>24.4</td>
<td>0.441</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QA-180–250</td>
<td>0.125</td>
<td>13.7</td>
<td>0.343</td>
<td>40.8</td>
<td>2.92</td>
<td>49.5</td>
<td>0.706</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[Color figure can be viewed at wileyonlinelibrary.com]
CO₂ sorption performances were quantitatively compared via a dual-mode sorption model, and the fitting parameters are summarized in Table 4. Using the dual-mode model mathematically shown in Eq. 2, the contributions of Henry’s law and the Langmuir mode to the apparent sorption performance could be separated. Generally, the amount of CO₂ adsorbed/dissolved, as predicted by Henry’s law, equates to superior mobility that contributes to the diffusion process. However, the amount of CO₂ adsorbed according to the Langmuir mode tends to show restrained mobility due to relatively higher levels of affinity or binding energy. Generally, the sorption coefficient \( S \) of CO₂ in these xerogel powders derived from Eq. 2 can be expressed by the dual-mode sorption parameters

\[
S \equiv \frac{C}{p} = S_D + S_H = k_D + \frac{C_D p}{1 + b p}
\]

(5)

where \( S_D \) and \( S_H \) are sorption coefficient values contributed from Henry’s law and Langmuir’s type sorption, respectively. Therefore, \( S_D \) always exhibits a positive correlation with pressure while \( S_H \) demonstrates a decreasing trend as pressure increases. Therefore, the sorption coefficient under infinite-dilution conditions (\( S_0 \)), as expressed in Eq. 6, could provide important information that could determine whether CO₂ will adsorb or dissolve in these xerogel powders

\[
S_0 = \lim_{p \to 0} S = S_D + S_H \approx k_D + C_D b
\]

(6)

where \( S_D \) and \( S_H \) are the sorption coefficients contributed from Henry’s law and Langmuir’s type sorption under infinite-dilution conditions, respectively.

The sorption parameters of TA-SiO\(_{1.5}\) and QA-SiO\(_{1.5}\) xerogel powders fitted using the dual-mode model demonstrated high correlation coefficients, which suggests that CO₂ adsorption behaviors could be well described by this model. Specifically, QA-250 exhibited much higher values in sorption parameters in terms of \( k_D \) and \( C_D b \) compared with all the other samples fired either at 180 or 250°C. This again indicates that the local liberation of CH₃Cl could significantly promote CO₂ sorption for QA-SiO\(_{1.5}\) materials.

**Gas permeation performance of TA-SiO\(_{1.5}\) and QA-SiO\(_{1.5}\) membranes**

Three types of membranes including QA-180 (subsequently denoted as QA-180–250 after in situ post-heat treatment at 250°C under N\(_2\)), QA-250, and TA-250 were fabricated by the coating of relevant sols and subsequent calcination under the same conditions as with their homonymic xerogel powders.

**Table 4. Fitting Parameters of TA-SiO\(_{1.5}\) and QA-SiO\(_{1.5}\) Xerogel Powders Using a Dual-Mode Sorption Model**

<table>
<thead>
<tr>
<th>Material</th>
<th>( k_D ) [mol/(m(^3) kPa)]</th>
<th>( b ) [kPa(^{-1})]</th>
<th>( C_H ) [mol/m(^3)]</th>
<th>( C_H b ) [mol/(m(^3) kPa)]</th>
<th>Correlation coefficient [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-180</td>
<td>0.0008</td>
<td>0.1333</td>
<td>0.0030</td>
<td>0.0004</td>
<td>0.9154</td>
</tr>
<tr>
<td>TA-250</td>
<td>0.0016</td>
<td>0.0880</td>
<td>0.1613</td>
<td>0.0142</td>
<td>0.9976</td>
</tr>
<tr>
<td>QA-180(^a)</td>
<td>0.0006</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>QA-250</td>
<td>0.0042</td>
<td>0.1038</td>
<td>0.1212</td>
<td>0.022</td>
<td>0.9951</td>
</tr>
</tbody>
</table>

\(^a\)The density of TA-SiO\(_{1.5}\) and QA-SiO\(_{1.5}\) xerogel powders was assumed to be constant and approximate to the value of amorphous silica at 2.2 g/cm\(^3\).

\(^b\)QA-180 tended to show a single sorption type in Henry’s law and showed difficulty in fitting using a dual-mode sorption model with an acceptable correlation coefficient.

**Figure 8. Kinetic diameter dependence of gas permeance for TA-SiO\(_{1.5}\) and QA-SiO\(_{1.5}\) membranes at (a) high and (b) low temperatures.**

Figure 8 shows the kinetic diameter dependence of gas permeance for these as-prepared membranes at both high and low temperatures. The kinetic diameter dependence on gas permeance at high temperatures (200 or 180°C), for which gas sorption could be ultra-low and the organic chains could be sufficiently mobile, tended to reflect the sizes of the “free-volume pores” of these xerogel membranes (Figure 8a). Membrane QA-180, which was fired at the lower temperature and thus was minus the liberation of CH₃Cl molecules, exhibited the steepest trend in kinetic diameter dependence. In addition, TA-250 fired at a higher temperature, but also without the liberation of CH₃Cl molecules, simply showed slightly higher gas permeance compared with membrane QA-180. This indicates that the effect of calcination temperature at this level was insufficient to play a significant role in gas separation performance. However, membrane QA-180 after in situ postheat treatment at 250°C under N\(_2\) (QA-180–250), as well as membrane QA-250 (directly prepared at 250°C) demonstrated significantly improved gas permeance (details can be found in Table 5). It would be reasonable to assign this result to the liberation effect of CH₃Cl molecules. It was interesting that the kinetic diameter dependence of gas permeance at low temperature for membranes fired at 250°C (TA-250, QA-180–250, and QA-250) exhibited similar values from He to CO₂ (Figure 8b), which indicated an improved relative-permeability for CO₂ due to the increases in CO₂ sorption performance as the operation temperature decreased. Conversely, membrane QA-180
continued to show a “steep decrease” in kinetic diameter dependence because of the dense structure that reduced amine accessibility and thus restrained CO₂ sorption and transport performance. As clearly shown in Table 5, membranes QA-180–250 and QA-250 demonstrated impressive improvements in gas permeance for He and CO₂, and a simultaneous slightly elevated gas permeance for N₂ compared with those membranes without the effect of local liberation (QA-180 and TA-250). The gas permeability for He/N₂ and CO₂/N₂ of membranes QA-180–250 and QA-250 was thus increased evidently due to the improvement in smaller-sized microporosity that can contribute to greater permeance for smaller (He, H₂) and sorptive (CO₂) gases than for a larger and less-sorptive gas such as N₂.

Figure 9 shows the effect of the feed pressure on the CO₂ and N₂ permeance and on CO₂/N₂ selectivity in the binary CO₂-N₂ separation system of QA-180 and QA-250 membranes. As expected, both CO₂ permeance and CO₂/N₂ selectivity increased dramatically and demonstrated an impressive decrease in the function of feed pressure after the liberation of CH₃Cl molecules (membrane QA-250). This phenomenon is usually observed in CO₂ separation membranes via surface diffusion or facilitated transport mechanisms. However, in the case of the QA-180 membrane, both CO₂ and N₂ permeances were almost independent of feed pressure in the entire ranges applied, which indicated weak interactions (mainly physical sorption/solubility) between the ammonium-silica matrix and CO₂ molecules.

Table 6 compares the CO₂ separation performance of QA-SiO₁.₅ membranes with reported amine-silica membranes under dry conditions. QA-180–250 and QA-250 membranes with a liberation effect of CH₃Cl demonstrated an appealing level of CO₂ separation performance, particularly in CO₂ permeance, compared with most reported amine-silica membranes. Most importantly, given that the thermally induced local liberation effect of CH₃Cl is easily applied to numerous versions of ammonium salt-incorporated membranes, the present study provides new insight applicable to the development of high-performance CO₂ separation membranes.

### Analysis of the membrane microstructure by gas permeation behaviors

To compare the activation energies of TA-SiO₁.₅ and QA-SiO₁.₅ membranes during gas permeation, gas permeance dependence on temperature was systematically studied. The gas permeance (P) that is generally a product of the diffusivity (D) and solubility (S) coefficients (P = DS, where l is the membrane thickness), as well as the diffusivity coefficient (D), could be represented using Arrhenius-type equations. Meanwhile, the solubility coefficient (S) is usually described via a Van’t Hoff expression

\[
P = P_0 \exp \left( \frac{-E_p}{RT} \right) \tag{7}
\]
\[
D = D_0 \exp \left( \frac{-E_d}{RT} \right) \tag{8}
\]
\[
S = S_0 \exp \left( \frac{-\Delta H_s}{RT} \right) \tag{9}
\]

where \( P_0, D_0, \) and \( S_0 \) are the pre-exponential factors, \( E_p \) and \( E_d \) are the apparent activation energies for permeation and diffusion, respectively, \( \Delta H_s \) is the effective sorption enthalpy,
is often observed (matrix. Thus, a decreasing trend in the function of temperature (i) the condensability (critical temperature), (ii) the enthalpy of the condensation of the penetrant (gas molecules) is mainly decided by (i) the relative difference between its kinetic diameter and the size of the membrane pores (“free-volume pores” or rigid pores), and (ii) the segment mobility of the membrane matrix. Therefore, the ever-increasing nature of the function of temperature ($E_p > 0$) is always demonstrated. The solubility, however, is greatly influenced by (i) the condensability (critical temperature), (ii) the enthalpy of the condensation of the penetrant, and (iii) the affinity/interactions with the membrane matrix. Thus, a decreasing trend in the function of temperature is often observed ($\Delta H_s < 0$).\textsuperscript{7,38,39} For gases He, H\textsubscript{2}, and N\textsubscript{2}, which demonstrate rather lower critical temperatures and enthalpies of condensation and no special interactions with the membrane matrix, the values of $\Delta H_s$ are always negligible; thus, $E_p$ could reflect the energy barriers for diffusivity of gas penetrates across a membrane ($E_p \approx E_d$).

Figure 10 shows the wide range (35–200°C) of gas permeance dependence on temperature for TA-SiO\textsubscript{1.5} and QA-SiO\textsubscript{1.5} membranes, and the corresponding values of $E_p$ in Eq. 7 are tabulated in Table 7. The membranes fired at 250°C (TA-250, QA-180–250, and QA-250) underwent very similar trends (slopes) in permeance dependence on temperature in the cases of He and N\textsubscript{2}, and even for that of CO\textsubscript{2}. The values of $E_p$ derived from the slopes shown in Figure 10 were thus comparable (Table 7). In the cases of He and N\textsubscript{2}, the comparable values of $E_p$ (He, 11–13 kJ/mol; N\textsubscript{2}, 12–15 kJ/mol) reflected the comparable sizes of “free-volume pores” and the mobility of the organic chains of these membranes. Thus, it is plausible that these membranes demonstrated equal values for $E_p$(CO\textsubscript{2}), and, in turn, comparable values for $E_p$(CO\textsubscript{2}) (4–5 kJ/mol), which led to a reflection of comparable values for $\Delta H_s$(CO\textsubscript{2}) ($E_p = E_d + \Delta H_s$). Indeed, membranes fired at 250°C possessed the same amine type (tertiary amines) and thus demonstrated comparable apparent enthalpies of sorption ($\Delta H_s$). Despite the comparable values of $E_p$, membranes QA-180–250 and QA-250 displayed higher levels of gas permeance for all the gases considered when compared with the TA-250 membrane due to the elevated microporosity and/or free-volume (or rigid) pore size induced by the liberation effect of CH\textsubscript{3}Cl. It is noteworthy that, without a decomposition of ammonium salts, the QA-180 membrane demonstrated higher values in $E_p$ for both He and CO\textsubscript{2} suggesting both a dense microstructure and weak interactions between the membrane matrix and CO\textsubscript{2} molecules. Overall, these results reveal that the thermally induced liberation effect of CH\textsubscript{3}Cl in QA-SiO\textsubscript{1.5} membranes created an ultrathin microporosity for the permeation of smaller gases, and particularly for CO\textsubscript{2}.

In addition, the relationships between $E_p$(CO\textsubscript{2}) and $E_p$(CO\textsubscript{2})-$E_p$(N\textsubscript{2}), which can be used to roughly predict CO\textsubscript{2}/N\textsubscript{2} separation performance,\textsuperscript{26–28} are compared in Figure 11. As described elsewhere,\textsuperscript{28} the potentials for CO\textsubscript{2} permeation and CO\textsubscript{2}/N\textsubscript{2} separation could be reflected via the values of $E_p$(CO\textsubscript{2}) and $E_p$(CO\textsubscript{2})-$E_p$(N\textsubscript{2}). Lower values for both can predict high performance for CO\textsubscript{2}/N\textsubscript{2} separation. Therefore, in our previous work,\textsuperscript{28} we used the relationship of $E_p$(CO\textsubscript{2}) versus $E_p$(CO\textsubscript{2})-$E_p$(N\textsubscript{2}) to compare the CO\textsubscript{2}/N\textsubscript{2} separation capability among hindered (PA-Si and SA-Si as shown in Figure 11) and unhindered (TA-Si) amine-functionalized silica membranes, in which membrane TA-Si showed greater potential in applications for CO\textsubscript{2}/N\textsubscript{2} separation due to lower values for both $E_p$(CO\textsubscript{2}) and $E_p$(CO\textsubscript{2})-$E_p$(N\textsubscript{2}). In the present study, after the liberation of CH\textsubscript{3}Cl molecules, tertiary amine types of QA-SiO\textsubscript{1.5} membranes (QA-180–250 and QA-250) demonstrated comparable, or even lower, values for $E_p$(CO\textsubscript{2}) and $E_p$(CO\textsubscript{2})-$E_p$(N\textsubscript{2}), which indicated an enhanced CO\textsubscript{2} separation performance.

Despite a nonporous structure, the free-volume pore sizes of TA-SiO\textsubscript{1.5} and QA-SiO\textsubscript{1.5} membranes were estimated using a modified gas translation (GT) model that was previously

![Figure 10. Temperature dependence of (a) He, (b) CO\textsubscript{2}, and (c) N\textsubscript{2} permeance of TA-SiO\textsubscript{1.5} and QA-SiO\textsubscript{1.5} membranes.](image-url)
developed by our group.\textsuperscript{40,41} The GT or activated-Knudsen diffusion model used to describe the gas permeation performance of microporous membranes was originally proposed by Xiao and Wei\textsuperscript{42} and Shelekhin,\textsuperscript{43} as expressed by Eq. 10

\[ P_i = \varepsilon d_p \rho_i \sqrt{\frac{8RT}{\pi M_i RT t}} \]  

(10)

where \( P_i \) and \( M_i \) are the gas permeance and the molecular weight of the \( i \)th component, respectively, \( \varepsilon \), \( d_p \), and \( t \) are the porosity, pore size, and tortuosity of the membrane, respectively, \( R \) is the universal gas constant, \( T \) is the absolute temperature; \( \rho_i \) indicates the probability of the diffusion of the \( i \)th component through the pore, which can be expressed as shown in Eq. 11

\[ \rho_i = \rho_{e,i} \exp \left( -\frac{E_{p,i}}{RT} \right) \]  

(11)

where \( E_{p,i} \) is the kinetic energy to overcome the diffusion barrier, \( \rho_{e,i} \) is the pre-exponential factor that indicates the probability of the \( i \)th component for an infinite level of kinetic energy; \( \rho_{e,i} \) also corresponds to the geometrical probability that is the effective area for permeation, as defined by Eq. 12

\[ \rho_{e,i} = \frac{1}{3} \frac{A_i}{A_0} = \frac{1}{3} \left( \frac{d_p}{d_i} \right)^2 \] 

(12)

where \( A_i \) is the area of the pore opening for effective permeation of the \( i \)th component, \( A_0 \) is the cross-sectional area of the pore, \( d_i \) is molecular size of \( i \)th component, and the fraction 1/3 indicates the one-dimensional direction through the membrane pore. It should be noted that the GT model assumes no molecular size for permeating molecules. This is unrealistic, however, particularly in the cases of gases permeating through ultramicro pores, in which the pore size and the gas molecular sizes are comparable. Therefore, in the modified GT model, an effective diffusion distance \((d_p-d_i)\) of the \( i \)th component with a molecular size of \( d_i \) was used instead of \( d_p \), as expressed in Eq. 10. By combining Eqs. 10–12, the modified GT model can be expressed in Eq. 13

\[ P_i = \varepsilon (d_p - d_i) \sqrt{\frac{8RT}{\pi M_i RT t}} \exp \left( -\frac{E_{p,i}}{RT} \right) \]  

(13)

\[ k_{0,i} = \sqrt{\frac{8\varepsilon}{\pi 3\pi d_i}} (d_p - d_i)^3 = k_0 (d_p - d_i)^3 \]  

(14)

where \( k_0 \) is a constant that depends only on the membrane porous structures, as given by Eq. 15

\[ k_0 = \sqrt{\frac{8\varepsilon}{\pi 3\pi d_i}} \]  

(15)

According to Eq. 14, the following would be true

\[ k_{0,i}^{1/3} = k_0^{1/3} d_p - k_0^{1/3} d_i \]  

(16)

Therefore, a linear relationship between \( d_i \) and \( k_{0,i}^{1/3} \) with a slope of \( k_0^{1/3} \) and an intercept of \( k_0^{1/3} d_0 \) can be expected. The mean effective pore size of the membrane can be easily estimated from the plot of \( k_{0,i}^{1/3} \) and \( d_i \). In this study, we assumed this model would be applicable to membranes with free-volume pores. Figure 12 shows the relationships between \( k_{0,i}^{1/3} \) and \( d_i \) for the membranes prepared in this study (Details can be found in Supporting Information Tables S1 and S2). Good linear relationships were observed in the obtained \( k_{0,i}^{1/3} \) expressed in Eq. 16. Membrane QA-180 demonstrated the smallest estimated mean effective pore size of 0.39 nm, whereas membranes QA-180-250 and QA-250 exhibited similar pore sizes (0.49–0.51 nm), which are comparable to, or slightly larger than, the TA-250 membrane (0.47 nm). These estimated mean effective pore sizes are consistent with the He/N\textsubscript{2} selectivity trend of these membranes at high temperatures, as shown in Table 5, where QA-180 (53) membranes showed much higher values in He/N\textsubscript{2} selectivity than the other membranes, the values of which were similar (23–25). This suggests that the liberation effect of CH\textsubscript{3}Cl molecules as well as a higher calcination temperature resulted in an impressive

![Figure 11. Relationships of \( E_p(CO_2) \) versus \( E_p(NO_2) \) for as-prepared membranes (Data of membranes PA-Si, SA-Si and TA-Si are adapted from Ref. 28).](Color figure can be viewed at wileyonlinelibrary.com)

![Figure 12. The values for \( k_{0,i}^{1/3} \) and the relationship to the kinetic diameters of gas molecule \( d_i \).](Color figure can be viewed at wileyonlinelibrary.com)
increase in the mean effective pore size from QA-180 to QA-250 (or QA-250). According to Fick’s first law and the dual-mode sorption model, the concentration-averaged effective diffusivity coefficient \( D \) for CO\(_2\) could be estimated using the dual-mode sorption parameters and gas flux, as expressed in Eq. 17

\[
J = -D \frac{\partial C}{\partial x} = -D \frac{\partial \left( k_{DP} + \frac{C_P^b h}{(1 + b h_p)^2} \right)}{\partial x} = -D k_D + C_P^b h \left( \frac{1}{(1 + b h_p)^2} \right) \frac{\partial p}{\partial x}
\]

(17)

where \( J \) is the flux through the membrane, and \( x \) is the distance across the gas transport direction in the membrane from the feed side (\( x = 0, p = p_1 \)) to the permeate side (\( x = l, p = p_2 \)). After integration of Eq. 17 from \( x = 0 \) to \( x = l \), the following can be obtained

\[
D = \frac{J l}{(p_1 - p_2) k_D + \frac{C_P^b h}{(1 + b h_p)^2}} = \frac{P l}{k_D + \frac{C_P^b h}{(1 + b h_p)^2}}
\]

(18)

Figure 13 compares CO\(_2\) solubility (based on Eq. 5) of these xerogel materials and CO\(_2\) permeation performance in terms of CO\(_2\) permeance and diffusivity at 35°C (The membrane thickness was assumed to be approximately 270 nm based on FE-SEM observations). [Color figure can be viewed at wileyonlinelibrary.com]

Conclusions

Quaternary ammonium-silica xerogel materials (QA-SiO\(_{1.5}\)) were fabricated via sol-gel processing and their thermal stabilities were systematically compared with tertiary amine-silica xerogel materials (TA-SiO\(_{1.5}\)) as a control using TG-MS, FTIR, EDS, and PALS analysis. The thermally induced decomposition reaction of quaternary ammonium salts [-N(CH\(_3\))\(_3\)+Cl] in QA-SiO\(_{1.5}\) xerogels occurred at ~230°C with local liberation of CH\(_3\)Cl molecules. CO\(_2\) sorption performances of QA-SiO\(_{1.5}\) and TA-SiO\(_{1.5}\) xerogel powders fired at temperatures before and after the liberation of CH\(_3\)Cl molecules were quantitatively studied via the dual-mode sorption model. The thermally induced local liberation effect of CH\(_3\)Cl demonstrated great potential for improvement in the CO\(_2\) sorption performance of QA-SiO\(_{1.5}\) membranes due to the generation of ultrafine microporosity that could increase amine accessibility for CO\(_2\). Gas permeation performance of the membranes indicated that the liberation of CH\(_3\)Cl did not greatly change the CO\(_2\) diffusivity (35°C) within the membranes. The significantly improved gas permeation performance, particularly CO\(_2\)/N\(_2\) separation properties, were mainly the result of impressive increases in CO\(_2\) sorption performance induced by the local liberation of quaternary ammonium salts. The present study may provide insight applicable to the development of high-performance CO\(_2\) separation membranes with ultramicroporosity.

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Literature Cited


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