Amorphous silica-based alkylamine-functionalized hybrid membrane materials were synthesized through polymer-derived ceramics (PDCs) route, in order to selectively transport CO₂. Commercially available perhydropolysilazane (PHPS) was chemically modified with primary and secondary amino silane derivatives, and subsequently oxidized in air at room temperature to afford alkylamine-functionalized amorphous silica materials. CO₂ uptake by the powdered samples was investigated by the thermogravimetric analysis under CO₂ atmosphere, in-situ diffuse reflectance infrared fourier transform spectroscopic analysis and measurement of CO₂ sorption isotherm. In the case of alkylamine-functionalized silica samples, CO₂ uptake mechanism involved chemisorption at very low partial pressures and physisorption at higher partial pressures, demonstrated by the temperature dependence of CO₂ isotherms. The reaction paths and sorption mechanisms related to the nature of the functionalized amino groups were discussed from a viewpoint to develop CO₂-selective facilitated transport ceramic-based membranes.

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Key-words : Organoamine-functionalized silica, Perhydropolysilazane, Polymer-derived ceramics (PDCs), Carbon dioxide, Membrane, Facilitated transport

1. Introduction

CO₂ capture from large emitting sources is considered as one of the most challenging issues of the 21st century, since it's associated with the expansion of human activities along with the cost of separation and recovery.¹ The Paris Agreement which has been adopted at the 21st session of the Conference of the Parties (COP21) to the United Nations Framework Convention on Climate Change (UNFCCC) emphasizes the need for urgency in addressing climate change, as it represents a potentially irreversible threat to human societies and the planet. An appropriate and effective international response requires the widest possible cooperation by all countries, with a view to accelerating the reduction of global greenhouse gas emissions and holding the increase in the global average temperature to well below 2°C above pre-industrial levels, and pursuing efforts to limit the temperature increase to 1.5°C.² Therefore the development of energy efficient techniques that focus on carbon separation and sequestration as a central strategy, has been suggested in order to reduce atmospheric CO₂ in a meaningful and coherent manner.

Membranes for CO₂ separation, either amine-modified inorganic oxide or polymer membranes, are based on the high permeability of CO₂ compared to those of other gases. By impregnating or tethering active groups such as alkylamines onto their internal surfaces, porous solid sorbents represent a promising alternative that combines the favorable properties of liquid-amine absorption and gas-solid adsorption, with the purpose of membrane application.

The generally accepted CO₂ adsorption mechanism using amines, originally proposed by Caplow,³ and reintroduced by Danckwerts,⁴ has been widely established using variety of hydrophilic mesoporous materials loaded with basic organic amine functionality such as MCM-41,⁵ MCM-48,⁶ SBA-12,⁷ SBA-15,⁷ SBA-16⁸ and γ-alumina.⁹

The chemistry between CO₂ and amines is a reversible equilibrium.⁹ As shown in Fig. 1, in anhydrous environment, amines can react reversibly with CO₂ to give ammonium carbamates through zwitterionic intermediates [Eq. (1)].

![Fig. 1. Synthetic route for alkyl-amine-functionalized PHPS-derived amorphous silica-based organic-inorganic hybrids.](http://dx.doi.org/10.2109/jcersj2.124.P10-1)
2R₁R₂NH + CO₂ = (R₁R₂NH⁺COO⁻ + R₁R₂NH₂)
Zwitterion intermediate

\[ \Delta \text{ R₁R₂NHCOO}^- + \text{R₁R₂NH}_2^+ \] (1)

R₁R₂NH + CO₂ \xrightarrow{H₂O} HOCOOR + R₁R₂NH₂⁺ (2)

Because primary amines provide more stable carbamates, even a weak base, such as water, might be enough to drive the reaction forward. For secondary amines, a stronger base might be required, which gives an overall third-order reaction. In anhydrous environment, the zwitterion readily reacts with a second neighboring amine to give the carbamate and ammonium ion pair [Eq. (1)]. In this dynamic process, the limiting stoichiometry is CO₂:N = 1:2, as two equivalents of amines are required for the capture of one equivalent of CO₂. Studies have shown that for humid CO₂ capture with solid-tethered amines, carbamate form initially and then are converted to carbones and bicarbonates. Thus, one equivalent of amine and one H₂O molecule are required to capture one CO₂ molecule through carbonate or hydrogen carbonate formation [Eq. (2)]. While this mechanism is suitable for the reaction of primary and secondary amines with CO₂, the resultant reaction pathway is mainly dictated by the stability of the zwitterion intermediate and the subsequent carbamate.

Typical literature methods of alkylamine-functionalized silica-based materials have been reported, namely the acid- and or base-catalyzed sol–gel method, as well as the surface modification of mesoporous silica materials. These techniques however are not suitable for the fabrication of CO₂ separation membranes, because of the acidic catalysis that leads to the undesired ammonium salt formation, thus preventing the amine function from capturing CO₂, while the basic-catalysis is not suitable for fabrication of thin surface coatings but particles.

As one of promising synthetic routes in order to overcome these limitations, we have recently reported synthesis of amorphous silica-based hybrid membranes through the polymer-derived ceramics (PDCs) route. Alkylamine-functionalized amorphous silica hybrid materials were successfully synthesized by chemical modification of a commercially available perhydropolysilazane (PHPS) with (3-trimethoxysilyl propyl) diethylene triamine followed by room temperature oxidation. CO₂-perm-selectivities to other gas molecules such as nitrogen and helium were also achieved for the PHPS-derived alkylamine-functionalized silica membrane fabricated on a mesoporous γ-alumina-modified macroporous α-alumina, which showing this PDCs route has the potential to open a new field of study for the development of CO₂-selective ceramic-based facilitated transport membranes.

To enhance the CO₂-selective membrane performance, it is essential to recognize the relationships between the nature of functionalized amino group, CO₂ uptake properties, permeation condition such as temperature and humidity, and the resulting facilitated transport CO₂ perm-selectivity. However, the alkylamine functionalized in our previous study was complicated, consisting of one primary amino group and two secondary amino groups \[-(\text{CH}_2)_n\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2-\text{NH}_2\]. In this study, primary amine- and secondary amine silica hybrids were designed and synthesized through the PDCs route, and their CO₂ adsorption-desorption properties were discussed from a viewpoint to develop highly efficient CO₂-selective facilitated transport ceramic-based membranes.

2. Experimental procedures

2.1 Precursor synthesis

In this study, commercially available perhydropolysilazane (PHPS, Type NN110, 20% xylene solution, AZ Electronic Materials, Japan) was used as a starting polymer precursor. An oxygen-saturated solution of PHPS in xylene (20 wt%, 0.35 mL) was diluted in dry toluene (7 mL) then charged in a Schlenk equipped with a stirrer and dry argon (Ar) inlet. The chemical modification step was conducted by adding dropwise under stirring the amino silane modifier (3-aminopropyl triethoxysilane (APTS)) or 3-methyl aminopropyl trimethoxysilane (MAPTS), Reagent Grade, KISHIDA CHEMICAL Co. Ltd., Osaka, Japan) to the solution of PHPS at a N(PHPS)/OR(amino silane modifier) molar ratio of 2/1, in the presence of a catalytic amount of pyridine (0.1 mL). After the addition was completed, the mixture was heated at 70°C for 2 h under flowing Ar.

2.2 Oxidative crosslinking

The room temperature oxidation of the chemically modified PHPSs were performed according to our published procedure. After cooling down to room temperature, the mixture was poured into a Teflon plate to evaporate the reaction solvents. After subsequent room temperature oxidation in air for 5 h, the amorphous silica-based white powder was ground using a mortar and a pestle, then dried at 120°C in air.

2.3 Characterization

Fourier transform infrared (FT-IR) spectra of the samples were recorded on KBr pellets in the wavenumber range of 4000–400 cm⁻¹ (Model FT/IR-4200 FT-IR, Jasco, Japan). The thermal behavior up to 900°C in air of polymer-derived amorphous silica-based materials was studied by thermogravimetric-differential thermal analysis (TG-DTA, Model TG6100, Rigaku, Tokyo, Japan). Nitrogen (N₂) adsorption isotherms were measured at 77 K and in the relative pressure range of 0 to 1 (Model Belsorp Max, BEL Japan Inc., Osaka, Japan). Prior to the measurement, polymer-derived amorphous silica-based powder samples were degassed at 120°C under vacuum for 1 h. Specific surface area was calculated from the isotherm data using the Brunauer–Emmett–Teller (BET) method.

To evaluate CO₂ affinity, thermogravimetric (TG) analysis under CO₂ atmosphere was conducted using the same TG-analyzer. Dry CO₂ was used for the runs and high purity Ar was used as the purging gas for sorbent regeneration. According to the published procedure, CO₂ adsorption-desorption measurements were conducted under continuous run at 40°C Ar (40 min), CO₂ (40 min) then Ar (40 min), respectively. In a typical experimental procedure, a sample weight of ca. 8 mg was loaded in a TG unit using an aluminum sample pan, after being dried 1 h at 120°C under vacuum to remove any moisture and CO₂ adsorbed from air, then the sample was kept for 40 min under Ar at 40°C. The gas was then switched to dry CO₂ for 40 min at the same temperature, with an input flow rate of 0.5 L/min and output flow rate of 0.2 L/min. After desorption step, the sorbents were regenerated in Ar at the same temperature. The corresponding CO₂ capture capacities were normalized by the SSA of the samples.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analyses were carried out using a diffuse reflectance sample holder coupled with an environmental temperature chamber (Model HC900, S. T. Japan Inc., Tokyo, Japan) mounted on a FT-IR spectrometer (Model Spectrum TM100, Perkin Elmer Japan Co., Ltd., Tokyo, Japan). Within the chamber, the sample was
kept under Ar atmosphere at 40°C for 40 min, and FT-IR spectrum was recorded to characterize the initial state of the sample surface. Then, in order to identify the formed species, FT-IR spectrum was recorded after maintaining CO₂ atmosphere for 40 min. Subsequently, the inlet stream was switched back to the inert Ar stream and FT-IR spectrum was recorded after 40 min. Dry CO₂ was used for the runs and high purity Ar as the purging gas for sorbent regeneration.

3. Results and discussion

3.1 Chemical structure

FT-IR spectrum of as-received PHPS [Fig. 2(A)(a)] exhibits absorption bands at 3400 (vN–H), 2160 and 890 (vSi–H), 1180 (δN–H) and 840–1020 cm⁻¹ (δSi–N–Si). After exposure to vapour from aqueous NH₃, the absorption bands corresponding to the as-received PHPS completely disappears and new absorption bands appear at 3400 (Si–OH) and 1090 cm⁻¹ (Si–O–Si) [Fig. 2(B)(a)]. In addition to these bands, after functionalization with APS [Fig. 2A(b)] and conversion into amorphous silica-based hybrid, the sample exhibits C–H absorption bands in the vicinity of 2950 to 2850 cm⁻¹ [Fig. 2(B)(b)]. The region of N–H bands [antisymmetric and symmetric stretching NH₂ bands at 3355 and 3284 cm⁻¹] detected for APS and shown in Fig. 2(A)(b) is however overlapped by a broad O–H band, attributed to physically adsorbed water and the vibrating hydroxyl groups attached to the silicon atom at the surface. As shown in Fig. 2(B)(c), similar FT-IR spectroscopic features are observed for another sample after functionalization with MAPS [Fig. 2(A)(c)] and conversion into amorphous silica-based hybrid. These results are well consistent with our previous study on the amorphous hybrid silica using (3-trimethoxysilyl propyl) diethylenetriamine (RTMS), and the chemically modified PHPSs synthesized in this study were successfully converted to alkylamine-functionalized amorphous silica hybrids.

3.2 Results of TG–DTA in air

To determine the amount of alkyl-amino in the polymer-derived amorphous silica, TG–DTA was performed on the samples after room temperature oxidation in air. The results are summarized and shown in Fig. 3. The PHPS-derived amorphous silica (SiO₂) shows a weight gain of approximately 2% at 250 to 400°C, then a slight weight loss of about 2% at 400 to 600°C. Finally, the sample keeps almost the initial weight above 600°C. The observed weight gain may be caused by oxidation reactions occurring at the structural defects within the Si–O–Si amorphous network as a result of the ambient temperature synthesis applied in this study, while the weight loss is thought to be due to the partial dehydrocondensation among the Si–OH groups. The alkylamine-functionalized amorphous silica hybrid derived from PHPS modified with APS (AP-SiO₂) shows an endothermic weight loss of 10% up to 300°C and another weight loss of 10% at 300 to 600°C with a broad exothermic peak centered at around 300°C. In addition to the similar first weight loss of 10% up to 200°C, the silica hybrid derived from PHPS modified with MAPS (MAP-SiO₂) also shows an exothermic weight loss of 15% at 200 to 600°C.

The first weight loss detected for the SiO₂ hybrids is due to the evaporation of residual organic solvents such as xylene. On the other hand, the second weight loss is assigned to the combustion of alkylamino groups, and the amounts of –CH₂CH₂CH₂NH₂ in AP-SiO₂ and –CH₂CH₂CH₂NHCH₃ in MAP-SiO₂ are calculated to be 1.9 and 2.3 mmol·g⁻¹, respectively. These values are compatible with that reported for APS-modified SBA-15.

3.3 N₂ adsorption/desorption isotherm and BET specific surface area

N₂ adsorption/desorption isotherms of PHPS-derived samples are shown in Fig. 4. PHPS-derived amorphous SiO₂ exhibits a typical type IV isotherm according to the IUPAC classification method, as recognized by the appearance of a hysteresis loop, the defining feature associated with the occurrence of
mesopore condensation [Fig. 4(a)]. Although the maximum volume of adsorbed N2 varied from approximately 320 to 600 cm³ (STP) g⁻¹, AP-SiO2 and MAP-SiO2 also show similar type IV isotherms with hysteresis loops [Figs. 4(b) and 4(c)]. The Brunauer-Emmet-Teller (BET) specific surface area (SSA) for the PHPS-derived amorphous SiO2 was calculated to be 567 m²·g⁻¹.

As previously reported for the hybrid SiO2 (RTM-SiO2) synthesized by using RTMS,8) upon alkylamine functionalization, the SSAs dropped to 390 and 231 m²·g⁻¹ for the AP-SiO2 and the MAP-SiO2, respectively (Table 1). However, these values are much larger than that for the RTM-SiO2 (16 m²·g⁻¹),8) and it is found that such a drastic decrease in the SSA can be efficiently suppressed by using APS or MAPS as a chemical modifier for alkylamine functionalization.

### 3.4 TG-monitoring of CO2 adsorption–desorption

The CO2 adsorption capacities at 40°C of AP-SiO2 and MAP-SiO2 were evaluated as 0.47 and 0.29 mmol·g⁻¹, respectively, by the TG-analysis (Table 1). These capacity values are compatible with those previously reported for amine-grafted SBA-15 sorbents (0.2 to 0.4 mmol·g⁻¹ at 25–60°C).23,24) Then, the corresponding capture capacities were normalized by the specific surface areas of the samples, and compared with that of non-functionalized amorphous SiO2.8) As shown in Fig. 5, alkylamine-functionalized samples exhibit apparent CO2 affinity under CO2 flow. After the exposure for 40 min (total running time at 80 min), weight gains of AP-SiO2 and MAP-SiO2 reach 0.063 and 0.056 mg·m⁻², respectively, whereas the non-functionalized amorphous SiO2 shows a much lower uptake of about 0.029 mg·m⁻². The CO2 capture enhancement is therefore attributed to the introduction of alkylamino groups to the polymer-derived amorphous SiO2.

In an attempt to regenerate the samples at the same temperature (40°C) under Ar flow, non-functionalized amorphous SiO2 desorbed instantly all its captured CO2 due to the absence of chemical affinity towards CO2. The CO2 desorption of the alkylamine-functionalized amorphous SiO2, however, underline two different behaviors depending on the nature of the amine group. In the case of the secondary amine-functionalized sample MAP-SiO2, most of the captured CO2 immediately desorbs under Ar flow, and the sample is completely regenerated after 10 min. This observation is consistent with the weaker interaction between sterically hindered secondary amine and CO2. Oppositely, the desorption behavior of the primary amine-functionalized sample AP-SiO2 shows a different pattern, even after 30 min, the CO2 desorption was uncompleted leaving approximately 12.3% of the captured CO2 in the material. This result is thought to reflect stronger interactions between the primary amine and CO2 molecule.

### 3.5 DRIFTS-monitoring of CO2 adsorption

Figure 6 shows the IR spectra of PHPS-derived non-functionalized amorphous SiO2, AP-SiO2 and MAP-SiO2, normalized by BET specific surface area (SSA).

![Fig. 4. Nitrogen adsorption–desorption isotherms of (a) PHPS-derived amorphous SiO2, (b) APS-modified PHPS-derived amorphous silica (AP-SiO2), and (c) MAPS-modified PHPS-derived amorphous silica (MAP-SiO2).](image)

![Fig. 5. CO2 adsorption behavior under continuous Ar-CO2-Ar run at 40°C of PHPS-derived amorphous SiO2, AP-SiO2 and MAP-SiO2, normalized by BET specific surface area (SSA).](image)

### Table 1. Properties of PHPS-derived alkylamine-functionalized amorphous SiO2

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Alkylamine</th>
<th>SSA /m²·g⁻¹</th>
<th>Amine content /N-mmol·g⁻¹</th>
<th>CO2 adsorption capacity /mg·m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHPS-derived SiO2</td>
<td>None</td>
<td>567</td>
<td>None</td>
<td>0.029</td>
</tr>
<tr>
<td>AP-SiO2</td>
<td>–X-NH₂</td>
<td>390</td>
<td>1.9</td>
<td>0.063</td>
</tr>
<tr>
<td>MAP-SiO2</td>
<td>–X-N(CH₃)H</td>
<td>231</td>
<td>2.3</td>
<td>0.056</td>
</tr>
</tbody>
</table>
sorption, sample exhibits a new absorption band at 1520 cm

bending vibration of protonated amine

As shown in Fig. 6(b), before CO2 adsorption, AP-SiO2 exhibits its characteristic absorption bands at 1593 and 1413 cm

AP-SiO2 exhibits new absorption bands due to the formation of ammonium carbamate [Fig. 7(b)], and monodentate bicarbonate [Fig. 7(c), X = H], respectively, while those at 1552 and 1389 cm

Before CO2 adsorption, MAP-SiO2 also exhibits an absorption band assigned to bending vibration of protonated amine 

However, compared with AP-SiO2 having primary amine, ammonium carbamate formation was apparently suppressed, and the sample shows dominant absorption bands at 1498 and 1390 cm

3.6 CO2 adsorption–desorption isotherms

CO2 sorption can be explained by physical and/or chemical adsorption on solid sorbents. Generally, physical adsorption involves weak van der Waals forces and decreases with increasing temperature, whereas chemisorption implies the formation of chemical bonding, thus being more stable to temperature. The identified species formed by the reactions between the alkylamine-functionalized ammonium SiO2 and CO2 (Fig. 7) could be involved in the chemical adsorption. Thus in order to study the nature of the interactions occurring at the surface of alkylamine-functionalized SiO2 samples as a potential for CO2-selective facilitated transport membranes, CO2 adsorption/desorption isotherms were carried out at 0, 20, 50 and 80°C, and the volumes of adsorbed CO2 were normalized by the SSAs. Figure 8 shows the CO2 adsorption isotherm at 50°C of PHPS-derived ammonium SiO2, AP-SiO2 and MAP-SiO2. PHPS-derived non-functionalized SiO2 exhibits a typical linear isotherm according to the physisorption mechanism [Fig. 8(a)]. On the other hand, AP-SiO2 shows sharp CO2 uptakes at very low partial pressures (~0.001) due to the great affinity toward CO2 – a Lewis acid – for the basic amine sites [Fig. 8(b)] compared to PHPS-derived ammonium SiO2 which shows virtually no adsorption in this pressure range [Fig. 8(a)]. The adsorbed amount is however apparently higher at very low partial pressures for the primary amine AP-SiO2 sample compared to that of MAP-SiO2 [Fig. 8(c)].

As the zwitterion intermediate (R,R-NH(CH3)COO−) that forms prior to the carbamate is relatively stable for primary amine, such preference can be reasonably assigned to stronger chemisorption of the monomolecular CO2 layer at the internal surface of the AP-SiO2 in the form of ammonium carbamate [Fig. 7(a)]. For the secondary amine MAP-SiO2, the zwitterion intermediate is much less stable than for primary amines, plausibly due to steric effects of the alkyl group, recovered CO2 from the is decomposition can be triggered in the presence of water to form carbonate species [Eq. (3)], [24] [Figs. 7(c) and 7(d)]. Whilst the non-functionalized SiO2 and MAP-SiO2 samples show almost equivalent physisorption slopes, the higher CO2 adsorption ramp rate is observed for

As the zwitterion intermediate (R,R-NH(CH3)COO−) that forms prior to the carbamate is relatively stable for primary amine, such preference can be reasonably assigned to stronger chemisorption of the monomolecular CO2 layer at the internal surface of the AP-SiO2 in the form of ammonium carbamate [Fig. 7(a)]. For the secondary amine MAP-SiO2, the zwitterion intermediate is much less stable than for primary amines, plausibly due to steric effects of the alkyl group, recovered CO2 from the is decomposition can be triggered in the presence of water to form carbonate species [Eq. (3)], [24] [Figs. 7(c) and 7(d)]. Whilst the non-functionalized SiO2 and MAP-SiO2 samples show almost equivalent physisorption slopes, the higher CO2 adsorption ramp rate is observed for
the primary amine functionalized sample AP-SiO₂, which highlights a stronger physisorption behavior toward CO₂.

The temperature dependence of the CO₂ isotherm of the AP-SiO₂ [Fig. 9(a)] and MAP-SiO₂ [Fig. 9(b)] shows a drastic decrease in the adsorption slopes as the temperature increases. As a result, the adsorption capacities at 1 atm of the alkyl-amine functionalized SiO₂ samples are strongly dependent on the temperature, and drop by 77% for the AP-SiO₂ and MAP-SiO₂ samples as the temperature increases from 0 to 80°C.

These CO₂ isotherms also provide quantitative thermodynamic values such as the activation energy, which can be extracted from the Arrhenius plot of the volumes of adsorbed CO₂ as a function of temperature at a constant partial pressure [Eq. (3)].

\[
\ln V_{\text{CO}_2} = \ln A - \frac{E_a}{R} T
\]  
(3)

where \(E_a\) is the activation energy, \(R\) the gas constant, \(T\) absolute temperature, and \(A\) the pre-exponential factor. To clarify the dominant adsorption mechanism at lower partial pressures, \(p/p_o = 0.01\) was selected and plotted (Fig. 10). A plot of \(ln V_{\text{CO}_2}\) versus \(1/T\) provides a straight line in the temperature interval from 0°C (273 K) to 80°C (353 K), and the obtained values of \(E_a\) for AP-SiO₂ and MAP-SiO₂ are \(-2.3\) and \(-1.7\) kJ·mol⁻¹, respectively. The absolute values of the observed activation energies are much lower than that reported for CO₂ chemisorption to primary amine-modified SiO₂ at 298 K (11.5 ± 0.4 kJ·mol⁻¹). Moreover, the observed values are negative, i.e. negative temperature depen-
dency. These experimental results reveal that, even at \( p/p_0 = 0.01 \), the CO\(_2\) adsorptions to AP-SiO\(_2\) and MAP-SiO\(_2\) have been already governed by the physisorption mechanism based on an exothermic process which occurs more readily at lower temperatures and decreases with a rise in the temperature (principle of le Chatelier).

The experimental data showed a good agreement with the thermodynamic predictions of a chemisorption behavior for alkylamine-functionalized SiO\(_2\) samples at very low partial pressures (\( p/p_0 \ll 0.01 \)) followed by a physisorption behavior demonstrated by the temperature dependence illustrated in Fig. 9. However, it should be noted that, at 0 to 50°C, the CO\(_2\) physisorption rates of PHPS-derived amorphous-SiO\(_2\) was remarkably enhanced by the primary amine functionalization, and in the case of secondary amine-functionalization, critical temperature for the physisorption enhancement was found around 20°C. Moreover, the secondary amine-functionalization showed better efficiency in CO\(_2\) chemisorption (CO\(_2\):N = 1:1) and facile regeneration, which are considered as potential advantages in maintaining CO\(_2\) facilitated transport through ceramic-based porous membranes.

4. Summary

In this study, commercially available perhydropolysilazane (PHPS) was chemically modified with primary and secondary alkylamino silane derivatives, and subsequently oxidized in air at room temperature to afford alkylamine-functionalized amorphous SiO\(_2\) hybrids, and the results can be summarized as follows:

1. The amounts of primary amino group (CH\(_3\)CH\(_2\)CH\(_2\)-NH\(_2\)) in AP-SiO\(_2\) and secondary amino group (CH\(_2\)CH\(_2\)CH\(_2\)-NHCH\(_3\)) in MAP-SiO\(_2\) were calculated to be 1.9 and 2.3 mmol g\(^{-1}\), respectively by the TG-analysis up to 900°C in air.

2. The CO\(_2\) adsorption capacity of the PHPS-derived amorphous SiO\(_2\) was successfully improved by the alkylamine functionalization, and those at 40°C of AP-SiO\(_2\) and MAP-SiO\(_2\) were evaluated as 0.063 and 0.056 mg m\(^{-2}\), respectively.

3. DRIFTS analyses revealed that the species formed during the CO\(_2\) chemisorption depended on the nature of the functionalized amino group. The dominant species formed in-situ were identified as ammonium carbamates and carbonates for AP-SiO\(_2\) and MAP-SiO\(_2\), respectively.

4. CO\(_2\) sorption isotherm measurements at 0 to 80°C of the alkylamine-functionalized SiO\(_2\) samples revealed that the CO\(_2\) uptake mechanism involved chemisorption at very low partial pressures and physisorption at higher partial pressures.

5. Compared to the primary amine-functionalized AP-SiO\(_2\), the secondary amine-functionalized MAP-SiO\(_2\) showed potential advantages such as better efficiency in the CO\(_2\) chemisorption (CO\(_2\):N = 1:1) and facile regeneration for developing CO\(_2\)-selective facilitated transport membranes.

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