

Development of Amino-Functionalized Silica by Co-condensation and Alkylation for Direct Air Capture

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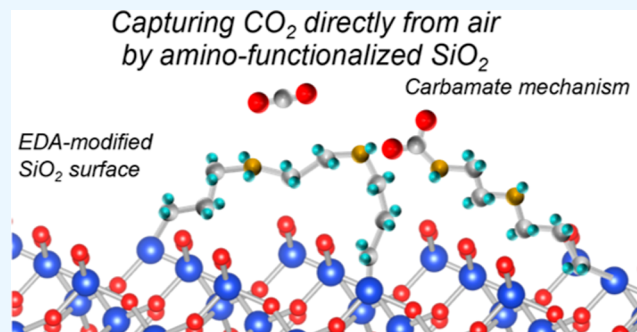


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ABSTRACT: CO₂ chemisorption using amine-based sorbents is one of the most effective techniques for carbon capture and storage. Solid CO₂ sorbents with amines immobilized on their surface have been attracting attention due to the easy collection of sorbents and reusability. In this study, we developed a solid CO₂ adsorbent by co-condensation of a silanizing reagent having a chloroalkyl group and tetraethyl ethoxysilane, followed by alkylation of the chloroalkyl group with diamine. The fabricated amine-immobilized silica with a high density of amino groups on its surface achieved the chemical adsorption of 400 ppm of CO₂ with 4.3 wtCO₂ % loading, CO₂ release upon heating at 80 °C, and reusability for adsorption and desorption cycles with high amine utilization efficiency (0.20 mol_{CO₂}/mol_N). This surface modification method is applicable to various amines bearing more than two amino functional groups, enabling the development of solid CO₂ sorbents for the selective capture of low-concentration CO₂ directly from the air.



1. INTRODUCTION

Carbon dioxide (CO₂) is a greenhouse gas that is among the key factors behind global climate change.^{1,2} Significant efforts have thus been made to suppress the rapid increase in the concentration of atmospheric CO₂. To limit the global temperature increase to 1.5 °C by 2100, there is a need to achieve net negative carbon emissions.³ In the net-zero emissions scenario in which net CO₂ emissions are reduced to zero by 2050, most CO₂ emissions can be reduced by decarbonization of energy sources by using H₂ and biofuels and capturing and storing industrially emitted CO₂; however, to realize net-zero CO₂ emission, capturing the already-emitted atmospheric CO₂, which is known as direct air capture (DAC), must also play a role.⁴ It is thus essential to develop DAC techniques for realizing net-zero or negative CO₂ emission.

Solvent systems using alkaline bases or amines such as 2-aminoethanol are widely used as sorbents for exhausted gases containing a high concentration of CO₂.^{5–7} Given the limitation of equilibrium of the reaction of sorbent and CO₂ at a low CO₂ partial pressure, the CO₂ absorption reaction is prohibited in the solvent systems, especially for low concentrations of CO₂.⁸ The most well-studied approaches utilize alkaline hydroxides or oxides, such as NaOH and CaO, and their conversion into metal carbonates. However, the regeneration of carbonates into hydroxides or oxides requires a high temperature, so the regeneration cost of the sorbent is also problematic. Carbon Engineering established cost-efficient plant-scale operation of DAC and regeneration system by using

KOH/Ca(OH) sorbent (1,000,000 t_{CO₂}/year).⁹ Clime Works and Global Thermostat developed DAC systems with an amine-based solid sorbent.^{9–11} Solid sorbents have attracted attention due to the easy collection of sorbents and their reusability. Physisorbent materials such as zeolites, activated carbons, or metal–organic frameworks are typically not effective for low CO₂ partial pressures and are poorly tolerant of humidity, while they are widely used for CO₂ at high pressure.¹² Amine-based solid sorbents have potential for capturing CO₂ at a low pressure, being tolerant of water vapor and being reusable after regeneration at a mild temperature.^{12–14}

Amine-based solid sorbents developed to date can be classified into three main types as described below.¹² (i) The first type is supported amine-based polymers on support materials such as carbon and silica (SiO₂). Such materials can be simply synthesized via the impregnation of amine-based polymer dispersion, such as poly(ethylenimine), poly(allylamine), and tetraethylenepentamine, into the pores of porous carbon and SiO₂ supports with a large surface

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Table 1. Contained Amount of Chloropropyl Groups in SiO₂-0.5Cl and Amino Groups in SiO₂-100EDA(0.5Cl)

sample	elemental analysis (%)			modified amount (mmol _{-Cl} or _{-N} /g)	S _{BET} (m ² /g)	-Cl density (μmol _{-Cl} /m ²)
	C	H	N			
SiO ₂ -0.5Cl	13.36	3.43	n.d.	3.7 ^a	573	6.5
SiO ₂ -100EDA(0.5Cl)	18.87	5.16	6.69	4.8 ^b		

^aCalculated from the C content as chloropropyl groups. ^bCalculated from the N content as amines (not as EDA).

area.^{15–21} However, in these materials, the physically adsorbed polyamines are easily desorbed. Besides, the CO₂ loading is relatively low compared with that of the contained amino groups. In other words, amino groups are ineffectively used at a low rate for CO₂ adsorption. (ii) To solve the above problems, porous sorbents with amino groups chemically bonded to the surface have been developed. In this so-called grafting method, amine-containing organosilanes, such as aminopropyl organosilane, react with the surface hydroxyl group of SiO₂ (silanol group) to form amino-functionalized SiO₂.^{13,22–31} These sorbents exhibit a relatively high amine utilization efficiency and thermal stability. However, the loading of amines is relatively low because of the low density of surface silanol groups to react with organosilanes, and the types of organosilanes are limited. (iii) To further develop amine-based solid sorbents, surface amino-functionalization methods have been investigated as a kind of grafting method. Jones et al. developed hyperbranched aminosilica, which is synthesized by in situ ring-opening polymerization of aziridine attached on the surface silanol group.^{32–34} Another approach is the combination of grafting of aminopropyl organosilane and ring-opening polymerization of L-lysine *N*-carboxyanhydride.³⁵ In addition, Yaghi et al. reported a covalent organic framework modified with tris(3-aminopropyl)amine by a combination of cycloaddition of chloroethyl vinyl ether and alkylation of a chloro group with amine.³⁶ These methods achieve high amine loadings and dispersion, in addition to thermal stability, leading to relatively high CO₂ loading at low CO₂ pressures. However, the amine utilization efficiency, represented by the ratio of adsorbed CO₂ to contained amino groups, could be theoretically improved up to 50% since the carbamate mechanism that is dominant at low CO₂ pressure forms the ion pairs of an alkylammonium carbamate anion with an ammonium cation.³⁷ The surface design of an amine-based sorbent can reach larger CO₂ loadings with high amine utilization efficiency. In addition to the high loadings of amines per mass and volume of sorbents, the improvement in the amine utilization efficiency is also one aspect to achieve and further develop cost-efficient DAC systems using amine-based sorbents.

The structures of CO₂ adsorbed on amino-functionalized SiO₂ have been well investigated, and it is known that the CO₂ adsorption mechanism is sensitive to the partial pressure of CO₂ and contained moisture.^{37,38} Low amine utilization efficiency of existing sorbents is known to be due to the different amine–CO₂ interacted products at low CO₂ pressure compared with those at high pressure.^{37,39–42} Under high CO₂ pressure, carbamic acid is formed by the reaction of the terminal primary amino groups with CO₂ at a 1:1 ratio. Besides, secondary amines form alkylammonium carbamate anions associated with ammonium cations derived from primary or secondary amines.⁴⁰ Thus, a high amine utilization efficiency can be achieved at a high CO₂ pressure. Meanwhile, the ion pairs of an alkylammonium carbamate anion with an ammonium cation or surface silanol group are mainly formed

from terminal and secondary amines at low CO₂ pressure.^{37,41} Another possibility for CO₂ adsorption is bicarbonate species on the surface silanol group, although proportionally they are insignificant compared with the carbamate ion pairs. To efficiently utilize amino groups, caution should be taken regarding the effect of the surface silanol group.³⁹ Surface silanol can be bound to terminal or secondary amino groups, leading to the deactivation of the amino groups for CO₂ capture. There is thus a need for precise control and rational design of the SiO₂ surface compared to the case of simple polyamine impregnation. In particular, the density of alkylammonium and silanol groups should be designed to maximize the utilization efficiency of amino groups.

Here, to achieve high-density amino-group-modified SiO₂, we developed a combination method of co-condensation of a silanizing reagent having a chloroalkyl group and tetraethyl ethoxysilane (TEOS) and subsequent alkylation of a chloroalkyl group with diamine. While the typical grafting of organosilanes limited the modified amount on SiO₂ surface, the condensation method enables us to achieve high organosilane density. Various kinds of organosilanes are applicable to this method, and the density of organic functional groups could be controlled by the ratio of organosilanes to TEOS.^{43–46} Besides, there are reported ways for further surface modification of organic functional groups of SiO₂. Alkyl halide group of SiO₂ could be substituted by NH₃ or N-containing molecules such as diamines.^{29,47–49} Considering the formation of ion pairs of an alkylammonium carbamate anion with an ammonium cation at low CO₂ pressure, amino groups with long alkyl chains are needed to interact with the neighboring amino group. The deactivation of amino groups by surface silanol groups should be simultaneously suppressed.³⁹ Moreover, the alkyl halide group of SiO₂ could be modified by various N-containing molecules such as diamines and triamines, enabling us to design the surface with amino groups. Thus, in this study, we fabricated amino-group-modified SiO₂ by a combination of co-condensation of chloroalkyl silanes with TEOS and amine modification via alkylation of the chloroalkyl group with diamines, which is a class of a chemical immobilization method, and studied the suitable surface for capturing low-concentration CO₂. This method can control the density of alkylammonium groups and the types of alkylammonium species. We achieved high CO₂ loading (4.3 wt_{CO₂} %) and amine utilization efficiency of high-density diamine-modified SiO₂ under a low concentration of CO₂. This work provides a simple method of optimizing the surface of solid sorbents for DAC.

2. RESULTS AND DISCUSSION

In this study, we attempted to synthesize an amino-functionalized SiO₂ by co-condensation of a silanizing reagent having a chloroalkyl group and tetraethyl ethoxysilane, followed by alkylation of the chloroalkyl group with amines bearing more than two amino functional groups. Table 1

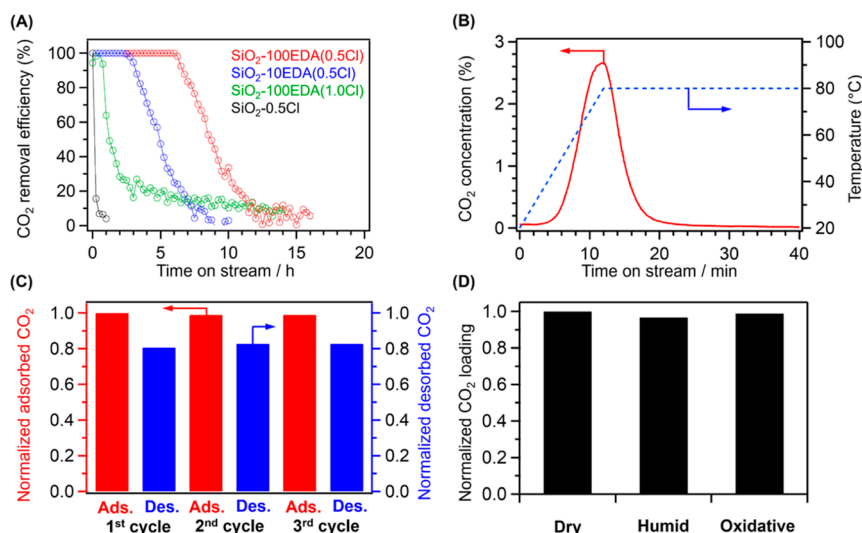


Figure 1. (A) CO₂ removal efficiency over SiO₂-YEDA(XCl) under 400 ppm of CO₂-N₂ flow. Red: SiO₂-100EDA(0.5Cl), blue: SiO₂-10EDA(0.5Cl), green: SiO₂-100EDA(1.0Cl), black: SiO₂-0.5Cl. Sample: 100 mg, gas: 400 ppm of CO₂-N₂, flow rate: 10 sccm, pretreatment: heating at 80 °C for 30 min under a N₂ flow of 10 sccm. (B) CO₂ desorption property of SiO₂-100EDA(0.5Cl) after CO₂ adsorption. The fed gas was switched to N₂ at a flow rate of 10 sccm with elevation of the temperature at 5 °C/min up to 80 °C. (C) Normalized CO₂ adsorption capacity during adsorption and desorption cycles over SiO₂-100EDA(0.5Cl). Desorption was performed at 80 °C. (D) Normalized CO₂ adsorption capacity under 400 ppm of CO₂-N₂ after humid treatment and O₂ treatment at 80 °C compared with that upon pretreatment in dry conditions.

summarizes the properties of SiO₂-0.5Cl fabricated by the co-condensation of alkoxy silanes with a CPTES/TEOS molar ratio of 0.5 and SiO₂-100EDA in which SiO₂-0.5Cl was refluxed in toluene solution of EDA with an EDA/chloropropyl group ratio of 100. From the C content of SiO₂-0.5Cl evaluated by CHN elemental analysis, the amount of chloropropyl groups contained was estimated to be 3.7 mmol_{-Cl}/g. SEM imaging and EDS mapping of SiO₂-0.5Cl suggested that the chloropropyl groups were entirely located on the particles (Figure S1). The functional group density of SiO₂-0.5Cl was 6.5 μmol_{-Cl}/m², corresponding to one-fifth of the surface Si atoms having chloropropyl groups, as shown in Figure S2. The N content suggested that SiO₂-100EDA had 4.8 mmol_{-N}/g of terminal or secondary amines in modified EDA. Assuming that all EDA was attached to the surface of SiO₂-100EDA with monodentate coordination, only 65% of the chloropropyl groups were alkylated. The absorption band assignable to the stretching vibration mode of C-Cl in FT-IR spectra of SiO₂-0.5Cl disappeared in that of SiO₂-100EDA (Figure S3). However, EDS mapping of SiO₂-100EDA revealed that the detected Cl/Si ratio was surely reduced (from 6.6% to 0.7%), but Cl species in the chloropropyl groups remained after the alkylation reaction. Those indicated that the chloropropyl group on the surface was easily alkylated, while some of them were prevented from alkylation due to inaccessibility. N₂ adsorption and desorption measurements performed at 77 K revealed the specific surface area (*S*_{BET}) of SiO₂-0.5Cl to be 573 m²/g, having a type IV isotherm with a mesoporous structure (Figure S4). The fundamental properties of the other SiO₂-YEDA(XCl) are summarized in Table S1.

The adsorption behavior of the fabricated sorbents was tested in a fixed bed flow reactor under the gas flow of 400 ppm of CO₂-N₂ as a model gas of air. Figure 1A shows the time course of the efficiency of the removal of CO₂ over SiO₂-YEDA(XCl). The CO₂ removal efficiency of SiO₂-100EDA(0.5Cl) was maintained at >99% over 6 h, after which it gradually decreased and leached to zero. The total amount of

adsorbed CO₂ was 0.98 mmol_{CO₂}/g (4.3 wt %). Since SiO₂-0.5Cl hardly showed the CO₂ adsorption capacity under the same conditions, the adsorption ability of SiO₂-100EDA(0.5Cl) was derived from the immobilized EDA. The amine utilization efficiency, which was calculated as the molar ratio of adsorbed CO₂ to amino groups, was 20%. Among the SiO₂-YEDA(XCl) fabricated in this study, SiO₂-100EDA(0.5Cl) showed the highest CO₂ adsorption capacity and amine utilization efficiency, as shown in Table S1.

Figure 1B shows the desorption property of captured CO₂. The desorption started at 50 °C, and concentrated CO₂-N₂ was obtained. The desorbed amount was comparable to the adsorbed amount (0.86 mmol_{CO₂}/g), with the results indicating that SiO₂-100EDA could release captured CO₂ even at 80 °C. The adsorption and desorption cycles indicated that the adsorption ability was maintained after regeneration and repeated reuse (Figure 1C). The effects of moisture and pure O₂ exposure in the pretreatment on the CO₂ adsorption capacity were also tested, as shown in Figure 1D. The CO₂ adsorption capacity was maintained after humid treatment. Some reports describe that the adsorption ability of amine-based sorbents improved under humid conditions due to improved accessibility to amine sites;^{22,24,34} however, our SiO₂-100EDA(0.5Cl) simply retained its CO₂ adsorption capacity. SiO₂-100EDA(0.5Cl) also showed resistance to oxidation in that the CO₂ adsorption capacity was maintained even after pure O₂ treatment at 80 °C. Further elongation of oxidative treatments resulted in the relative maintenance of the CO₂ adsorption capacity (Figure S5). FT-IR spectrum of the spent sorbent suggested the maintenance of the amino group with suppression of the oxidation or combustion of alkylamino groups, indicating the tolerance of our system to air contamination during the desorption. Indeed, the EDA chemically immobilized on the silica surface by alkylation showed thermal stability up to 240 °C, as revealed by the weight loss profile in Figure S6. Thus, SiO₂-100EDA(0.5Cl) acted as a sorbent for a low concentration of CO₂ regardless of

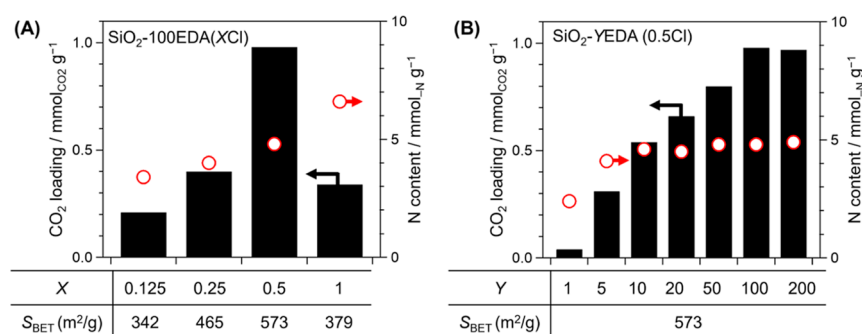


Figure 2. (A) CO₂ adsorption capacity for 400 ppm of CO₂-N₂ over SiO₂-100EDA(XCl) and (B) SiO₂-XEDA(0.5Cl). Amount of contained amino groups determined by CHN elemental analysis is presented on the right axis.

the humidity while maintaining the durability for regeneration at 80 °C and reuse.

In addition, the toluene solution of diamine could be repeatedly used for reflux. Figure S7 shows the CO₂ adsorption capacity of SiO₂-100EDA(0.5Cl) and SiO₂-0.5Cl refluxed in the toluene solution of EDA recycled for reuse the first or second time. Usage of the recycled toluene solution of EDA hardly affected the CO₂ adsorption capacity, providing a cost-effective and environment-friendly approach.

The effects of the conditions for fabricating SiO₂-YEDA(XCl) were confirmed. Figure 2 summarizes the CO₂ adsorption capacity as a function of the CPTES/TEOS ratio as X and the EDA/chloropropyl group molar ratio as Y. With regard to SiO₂-100EDA(XCl), the CO₂ adsorption capacity increased with increasing CPTES content up to X = 0.5 but declined at X = 1. When using an excess volume of CPTES (X > 1), SiO₂-XCl was dissolved in toluene solution during the reflux step. The immobilized chloropropyl and amino groups increased with an increasing CPTES content (Table S1). The trends in the CO₂ adsorption capacity of SiO₂-100EDA(XCl) matched those in the specific surface area of SiO₂-XCl, roughly suggesting that a high surface area of SiO₂-XCl was one essential factor for an efficient adsorbent.

Humid 400 ppm of CO₂-N₂ was supplied over SiO₂-100EDA(0.5Cl) and SiO₂-100EDA(0.25Cl) (Figure S8). SiO₂-100EDA(0.5Cl) showed a slight decrease in the level of CO₂ loading in the presence of H₂O vapor. On the other hand, SiO₂-100EDA(0.25Cl) showed an increase in CO₂ loadings under a humid CO₂ flow, although the CO₂ loading under dry 400 ppm of CO₂-N₂ was lower than that for SiO₂-100EDA(0.5Cl). We consider that the different trend in these two sorbents was owing to the arrangement of surface functional groups. Some amino groups over SiO₂-100EDA(0.25Cl) would be deactivated by interaction with surface silanol groups.³⁹ This would be due to the lower density of functional groups of SiO₂-100EDA(0.25Cl) (2.5 mmol_{-Cl} per 465 m²) than SiO₂-100EDA(0.5Cl) (3.7 mmol_{-Cl} per 573 m²). Low density of functional groups on the surface resulted in deactivation of amino groups by interaction with surface silanol groups. On the other hand, deactivation of amino groups was suppressed over SiO₂-100EDA(0.5Cl) with high density of functional groups due to steric hindrance. Under humid conditions, this interaction with surface silanol groups would be suppressed and thus the CO₂ adsorption capacity of SiO₂-100EDA(0.25Cl) increased. From the trends in the CO₂ adsorption capacity of SiO₂-100EDA(XCl) with different CPTES/TEOS ratios, the suppression of deactivation by silanol and modification of EDA in a monodentate

coordination are important in this system. Both the specific surface area and Cl content increased up to X = 0.5, and SiO₂-0.5Cl had the highest chloropropyl-groups density per surface. On the other hand, there is not much difference in apparent amino-group densities in SiO₂-100EDA(XCl) (X < 0.5). Nevertheless, the utilization efficiency of contained amines increased with CPTES content up to X = 0.5, resulting in the highest CO₂ loadings of SiO₂-100EDA(0.5Cl). The fact that SiO₂-100EDA(0.5Cl) contained the available amine groups for CO₂ adsorption compared to SiO₂-100EDA(0.125Cl) indicates the deactivation of amino groups by the interaction with surface silanol. At a low CPTES content (X = 0.125), EDA was mainly modified in a monodentate coordination; however, some of them bonded with the surface silanol groups, thus leading to a low utilization efficiency of amines. On the other hand, a high CPTES content (X = 0.5) resulted in monodentate and bidentate coordination of EDA with high density. This high-density modification of monodentate/bidentate coordinated EDA suppressed the deactivation by surface silanol groups. Indeed, the CO₂ capacity of SiO₂-100EDA(0.25Cl) increased under a humid CO₂ flow (Figure S8).

Figure 2B shows the CO₂ adsorption capacity as a function of EDA concentration during reflux for SiO₂-0.5Cl. The CO₂ adsorption capacity increased upon increasing the EDA concentration up to 100 times the molar concentration of surface chloropropyl groups of SiO₂-0.5Cl. A further increase of EDA concentration (Y > 200) did not affect the CO₂ adsorption capacity or the amount of immobilized amino groups. As mentioned above, the toluene solution of EDA could be reused, and the alkylated SiO₂-0.5Cl showed a CO₂ adsorption capacity comparable to that upon the use of fresh reflux solvent (Figure S7). The amount of immobilized amino groups almost plateaued for SiO₂-YEDA(0.5Cl) at Y > 5. Thus, the difference in the CO₂ adsorption capacity of SiO₂-100EDA(0.5Cl) and SiO₂-SEDA(0.5Cl) would derive from the difference in the immobilization forms of EDA between monodentate and bidentate coordination due to the EDA concentration during the reflux. At a low EDA concentration such as SiO₂-SEDA(0.5Cl), CO₂ loading was relatively low despite high amine loadings. If the EDA mainly bound in a bidentate coordination, terminal amino groups to form carbamate ion pairs was insufficient. At a high EDA concentration, the fraction of monodentate coordinated EDA increased, and thus low-concentration CO₂ was efficiently captured by terminal amines in a carbamate mechanism. These indicated that the coordination of diamines could be controlled by the EDA concentration during the reflux, and a high

concentration is favorable to monodentate coordination while keeping terminal amino groups.

The high CO₂ absorption capacity of SiO₂-100EDA(0.5Cl) at a low CO₂ pressure indicates efficient formation of the carbamate ion pairs.³⁹ The structure of CO₂ adsorbed over SiO₂-100EDA(0.5Cl) was confirmed by using infrared spectroscopy in transmittance mode. Figure 3A shows the

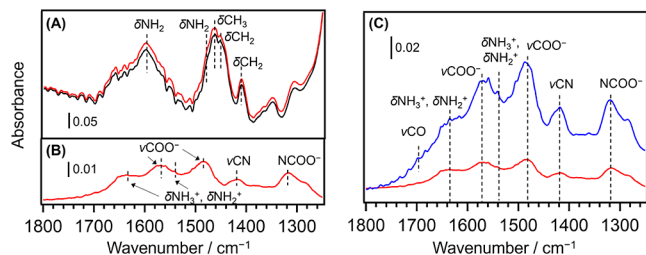


Figure 3. (A) FT-IR spectra of SiO₂-100EDA(0.5Cl) after pretreatment (black line) and under 400 ppm of CO₂-N₂ flow (red line). (B) FT-IR difference spectrum of SiO₂-100EDA(0.5Cl) before and after exposure to 400 ppm of CO₂-N₂ flow. (C) FT-IR difference spectra of SiO₂-100EDA(0.5Cl) under 400 ppm of CO₂-N₂ flow (red line) and 100% CO₂ flow (blue line). Spectra were measured in transmittance mode. The sample pellet was pretreated at 80 °C for 30 min under N₂ flow.

absorption spectra of SiO₂-100EDA(0.5Cl) after thermal pretreatment and after exposure to 400 ppm of CO₂. The stretching vibration of surface alkyl and amino groups on the SiO₂ surface was observed.^{50–52} The difference spectra in Figure 3B show the absorption bands assignable to the skeletal vibration of NCOO⁻ of carbamate (1320 cm⁻¹), C–N stretching vibration of carbamate (1410 cm⁻¹), NH₃⁺/NH₂⁺ deformation of ammonium ions (1635 and 1525 cm⁻¹), and (O=C=O)⁻ stretching vibration of carbamate (1570 and 1490 cm⁻¹). Thus, CO₂ was stored via the carbamate mechanism with the formation of an ion pair consisting of a carbamate anion from a terminal amine and an ammonium cation from a terminal/secondary amine.^{37,40} SiO₂-100EDA(0.5Cl) has terminal amino groups of monodentate immobilized EDA and secondary amino groups from monodentate/bidentate immobilized EDA, and thus the terminal/secondary amino groups and CO₂ associatively form carbamate species, as shown in Figure 4.

In contrast, the carbamic acid mechanism was observed at a high CO₂ partial pressure. Figure 3C shows difference spectra of SiO₂-100EDA(0.5Cl) under 100% and 400 ppm of CO₂. The absorption band of the C=O stretching vibration of carbamic acid (1700 cm⁻¹) clearly appeared under a flow of

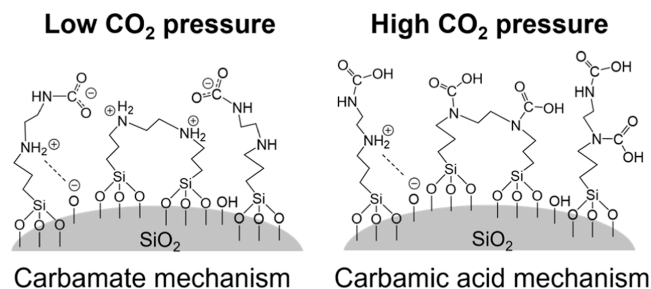


Figure 4. Mechanism of adsorption over SiO₂-100EDA(0.5Cl) at 400 ppm and a high CO₂ concentration.

100% CO₂. Thus, carbamic acid formed from terminal/secondary amino groups (Figure 4). This carbamic acid species disappeared under a low CO₂ pressure (Figure S9), suggesting the low adsorption energy as reported.^{53–55} Indeed, the amount of CO₂ adsorbed over SiO₂-100EDA(0.5Cl) increased under 20% CO₂ and utilization efficiency of the contained amines reached 84% (Table S1). Some amino groups would be deactivated by surface silanol. However, the CO₂ adsorption capacity for 400 ppm of CO₂ was hardly affected by humid pretreatment. Thus, the surface of SiO₂-100EDA(0.5Cl) was well designed for capturing CO₂ at low CO₂ pressure due to the high density of terminal amino groups surrounded by terminals of secondary amino groups, in addition to suppression of the undesirable interaction of amino groups with silanol.

This amine immobilization technique by the alkylation of chloroalkyl groups was applied to other diamines. Figure 5 and

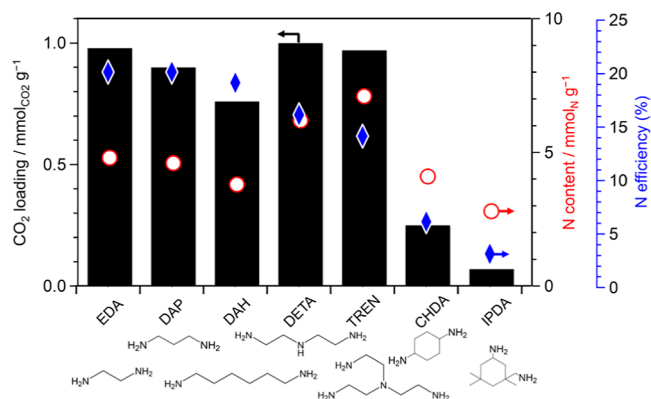


Figure 5. CO₂ adsorption capacity for 400 ppm of CO₂-N₂ over SiO₂-100amine(0.5Cl) using various amines. Amount of contained amino groups determined by CHN elemental analysis and amine utilization efficiency are presented on the right axis in red and blue, respectively.

Table S2 summarize the CO₂ adsorption capacity of SiO₂-100amine(0.5Cl) using various diamines in 400 ppm of CO₂ conditions. Diethylene triamine (DETA) and triethylamine (TREN) exhibited CO₂ adsorption capacity comparable to that of EDA. Diaminopropane (DAP) and diaminohexane (DAH) showed lower CO₂ adsorption capacity and amine loadings than EDA, suggesting that longer alkyl chains are not favorable for high-density modification. Cyclohexyl diamine (CHDA) and isophoronediamine (IPDA) having a cyclohexyl group showed low CO₂ adsorption capacity, while the efficiency of alkylation was dependent on the types of diamines. Among SiO₂-100amine(0.5Cl), SiO₂-100EDA(0.5Cl) exhibited the highest amine utilization efficiency. DETA and TREN resulted in high amine density, but the modified amino groups were ineffectively used for the CO₂ capture. The results on the effect of alkyl-chain length indicated that the immobilization form of diamine is important, in addition to the amine density. SiO₂-100DAP(0.5Cl) showed an amine content comparable to that of SiO₂-100EDA(0.5Cl) but a low CO₂ adsorption capacity. In this work, the surface of SiO₂ was designed with a high density of chloropropyl groups (6.5 μmol_{-Cl}/m²), corresponding to one-fifth of surface Si (Figure S2). Since the amine utilization efficiency was comparable among linear alkyl amines, the high CO₂ loading in SiO₂-100EDA(0.5Cl) was owing to the high

loadings of diamines. Diamines with the small alkyl group were suitable for highly dense modification via alkylation reaction on this chloropropyl group functionalized SiO₂. We concluded that the longer alkyl chain results in bidentate coordination, which would not favor high CO₂ adsorption capacity.

This immobilization method utilizing chloro-group alkylation is widely applicable to diamines, and the amine utilization efficiency reached 20% in 400 ppm of CO₂ conditions. Figure 6 and Table S3 summarize the CO₂ adsorption capacity against

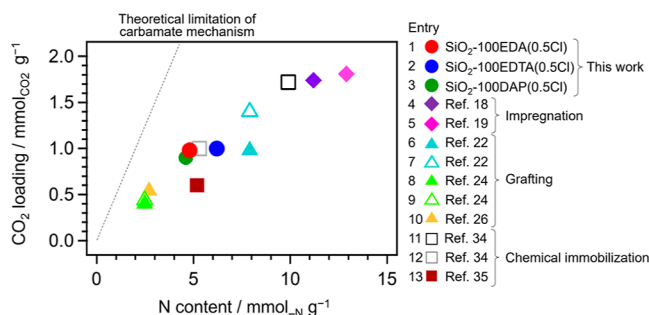


Figure 6. Comparison of CO₂ loading for 400 ppm of CO₂-N₂ over SiO₂-100EDA(0.5Cl) (red circle), SiO₂-100EDTA(0.5Cl) (blue circle), SiO₂-100DAP(0.5Cl) (green circle), and reported sorbents (details are summarized in Table S3). The figure plots CO₂ loading against N content. Rhombuses represent reported sorbents fabricated by impregnation of polyamine (entry 4, purple; entry 5, pink). Triangles represent reported sorbents fabricated by grafting of amino silanes (entries 6 and 7; filled and blank light blue, entries 8 and 9, filled and blank light green, entry 10, orange). Squares represent reported sorbents fabricated by chemical immobilization of amines (entry 11, black; entry 12, gray; entry 13, brown). Filled markers represent the results measured in dry CO₂, while blank markers represent the results measured in humid conditions.

the contained amines under ambient CO₂ pressure, namely, the amine utilization efficiency, over the reported solid CO₂ sorbents. In our study, SiO₂-100EDA(0.5Cl) achieved 20% utilization efficiency of amino groups [contained amino groups, 4.8 mmol_N/g; CO₂ adsorption capacity, 0.98 mmol_{CO₂}/g for SiO₂-100EDA(0.5Cl); and contained amino groups, 4.6 mmol_N/g; CO₂ adsorption capacity, 0.90 mmol_{CO₂}/g for SiO₂-100DAP(0.5Cl)], which to the best of our knowledge is comparable to the reported values for solid CO₂ sorbents in 400 ppm of CO₂ conditions. The impregnation of polyamine into mesoporous supports (entries 4 and 5) results in high amine content, while the loaded amino groups are insufficiently utilized.^{18,19} This trend is more clear in the summary graph of the amine utilization efficiency against the contained amines (Figure S10). Grafting of amino silanes onto the mesoporous support surface (entries 6–10)^{22,24,26} showed relatively high amine utilization efficiency (20%, entry 10) at low amine loading; however, the efficiency did not increase linearly at high amine loading. Humid conditions improved the CO₂ adsorption capacity, suggesting that some amino groups were deactivated by the interaction with surface silanol (entries 6 and 7).²² Meanwhile, the CO₂ adsorption capacity of SiO₂-100EDA(0.5Cl) was not affected by humid pretreatment; therefore, its surface was well designed to suppress deactivation by the surface silanol. Among the other methods using the chemical immobilization of amines, hyperbranched aminosilica, which is synthesized by in situ ring-opening polymerization of aziridine attached on the

surface hydroxyl group of SiO₂, has a high potential for high CO₂ loading comparable to the impregnation of polyamine (entry 11).³⁴ The highest amine efficiency of hyperbranched aminosilica was 19% (entry 12). Poly(L-lysine) brush-mesoporous SiO₂, fabricated by the ring-opening polymerization of L-lysine *N*-carboxyanhydride on an aminopropyl organosilane-grafted SiO₂ surface, contained an amount of amino groups comparable to that of SiO₂-100EDA(0.5Cl), but the amine utilization efficiency was relatively low (entry 13).³⁵ Among the listed sorbents, SiO₂-100EDA(0.5Cl) had a relatively high amine utilization efficiency (20%) comparable to the existing report. Besides, the co-condensation of silanes achieved high density of chloroalkyl groups. High amino group density with a combination of monodentate and bidentate coordinations of EDA resulted in the efficient utilization of amino groups to capture a low concentration of CO₂ while suppressing the inhibition by surface silanol.

3. CONCLUSIONS

In this study, we developed a solid CO₂ sorbent for capturing low-concentration CO₂ (400 ppm of CO₂-N₂ synthetic mixture) by a combination of co-condensation of chloroalkyl silane with tetraethyl ethoxysilane and the subsequent alkylation of a chloroalkyl group with diamine. This surface modification method using chloro-group alkylation showed applicability to various amines bearing more than two amino functional groups, with EDA and DAP showing the highest utilization efficiency of contained amines (20%). Among SiO₂-YEDA(XCl), SiO₂-100EDA(0.5Cl), which has a large surface area (573 m²/g) and high amine content (4.8 mmol_N/g), exhibited the highest CO₂ adsorption capacity of 0.98 mmol_{CO₂}/g (4.3 wt_{CO₂} %) for 400 ppm of CO₂. FT-IR spectroscopy revealed that the high terminal amino group density of SiO₂-100EDA(0.5Cl) allows the formation of ion pairs of a carbamate anion and an ammonium cation by association with surrounding secondary amino groups. SiO₂-100EDA(0.5Cl) could release CO₂ at 80 °C and maintained its adsorption property after desorption, in addition to being resistant to humid and oxidative pretreatment. The optimization of EDA concentration in reflux revealed that a high EDA concentration resulted in a high fraction of EDA with a monodentate coordination that is favorable to form carbamate species by using terminal amino groups. The effect of silanes ratios (CPTES/TEOS) revealed that the low chloropropyl density resulted in deactivation of terminal amino groups of monodentate-modified EDA by surface silanol of SiO₂. The optimized condition with high EDA concentration in reflux and high CPTES/TEOS ratio resulted in the copresence of monodentate and bidentate coordination of EDA with high density, thus leading to high CO₂ loadings with suppressed deactivation by silanol groups. Further development of this surface-tailored SiO₂ in terms of the amino-group density and surface area should lead to improved amine utilization efficiency and CO₂ adsorption capacity for DAC.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Tetraethoxysilane [Si(OC₂H₅)₄, TEOS, 99%], hydrogen chloride (2.5 M, HCl aq, 37%), ammonia (14.8 M, NH₃ aq, 28%), ethylenediamine [H₂N(CH₂)₂NH₂, EDA, 99.0%+], and isophorone diamine [(CH₃)₂C₆H₁₀(NH₂)-(CH₃)(CH₂NH₂), IPDA, >98.0%, cis and trans mixture] were purchased from FUJIFILM Wako Pure Chemical Co. Ltd. 3-

Chloropropyltriethoxysilane [Cl(CH₂)₃Si(OCH₂CH₃)₃, CPTES, >97.0%], diethylenetriamine [HN(CH₂CH₂NH₂)₂, DETA, >98.0%], 1,3-diaminopropane [H₂N(CH₂)₃NH₂, DAP, >98.0%], 1,6-diaminohexane [H₂N(CH₂)₆NH₂, DAH, >99.0%], *trans*-1,4-cyclohexanediamine [C₆H₁₀(NH₂)₂, CHDA, >98.0%], and tris(2-aminoethyl)amine [N-(CH₂CH₂NH₂)₃, TREN, >98.0%] were purchased from Tokyo Chemical Industry Co., Ltd. Ethanol (>99.5%), methanol (>99.8%), and toluene (>99.5%) were purchased from Kanto Chemical Co., Inc. The reagents were used without any purification.

4.2. Synthesis of Chloropropyl-Group-Immobilized Silica (SiO₂-XCl). Silica on which chloropropyl groups were immobilized was prepared by a sol–gel method using a chloroalkyl-group-containing silanizing agent as a precursor (Figure S11), with reference to a previous report.⁴⁷ CPTES and TEOS with a CPTES/TEOS molar ratio of *X* were added to a solution of 20 mL of ethanol and 10 mL of Milli-Q water in a Teflon beaker. Then, 1 mL of 2.5 M HCl (aq) was added, after which the solution was stirred for 2 h at pH 1.6. Then, 5 mL of 14.8 M NH₃ aq was added, after which the solution was stirred for ca. 20 h at pH 10.6. The obtained jelly like gel was centrifuged with 50% aqueous solution of methanol until the filtrate became neutral and dried in an oven at 60 °C for 3 days. The obtained sample is termed SiO₂-XCl (where *X*, the molar ratio of CPTES/TEOS, is 0.125–1.0).

4.3. Alkylation of Surface Chloropropyl Groups with Amines [SiO₂-Yamine(XCl)]. EDA-modified silica was obtained by refluxing SiO₂-XCl with an excess amount of EDA in toluene under a N₂ atmosphere.⁴⁷ The amount of EDA was determined based on the modified amount of chloropropyl groups, with the EDA/chloropropyl group molar ratio represented by *Y*. The fabricated SiO₂-XCl (0.5 g) was dispersed in 20 mL of a toluene solution of EDA and refluxed at 95 °C for 20 h under N₂ flow. The obtained sample was centrifuged with methanol twice and dried in an oven at 60 °C overnight. The obtained sample is termed SiO₂-YEDA(XCl) (where *Y*, the molar ratio of EDA/chloropropyl groups, is 1–200). The reusability of toluene solution was also confirmed. SiO₂-XCl was refluxed in the spent solution. The applicability of this approach was also tested for various diamines, namely, DETA, TREN, DAP, DAH, CHDA, and IPDA, referred to as SiO₂-Yamine(XCl).

4.4. Characterization of Fabricated SiO₂-XCl and SiO₂-Yamine(XCl). The weights of the C, H, and N atoms contained in the fabricated samples were determined by CHN elemental analysis (UNICUBE; Elementar Japan Co. Ltd.). The surface area of functionalized silica was estimated from the N₂ adsorption isotherm at –197 °C by the Brunauer–Emmett–Teller (BET) method using an adsorption analyzer (BELSORP MINI X; Microtrac Bel Co. Ltd.). The samples were pretreated at 200 °C for 3 h under evacuation. The thermal stability was evaluated by thermogravimetric analysis coupled with differential thermal analysis (TG-DTA2020SA; Bruker). The sample temperature was elevated at 10 °C/min under pure O₂ flow. The structure and elemental mappings of fabricated silica were observed by using a scanning electron microscope equipped with energy-dispersive X-rays at an acceleration voltage of 15.0 kV (SEM–EDS, JCM-7000 Neoscope; JEOL).

4.5. Evaluation of CO₂ Adsorption Capacity and Desorption Property. The CO₂ adsorption capacity was evaluated by using a gas flow system with a fixed bed reactor.

SiO₂-EDA (0.1 g) was pretreated at 80 °C under a N₂ flow. After the mixture was cooled to room temperature (25 °C), the fed gas was switched to diluted CO₂–N₂ (400 ppm or 20%) at a flow rate of 10 sccm. The CO₂ concentration downstream of the reactor was monitored by using an infrared spectrometer (GMP252; Vaisala GmbH). The amount of CO₂ adsorbed (*S*_{ads}) was calculated as follows

$$S_{\text{ads}} \text{ (mmol)} = S_{\text{app}} - S_{\text{blank}}$$

where *S*_{app} and *S*_{blank} are the apparent amounts of CO₂ adsorbed with and without the amine-based sorbent, respectively. The value of *S*_{app} was calculated as follows

$$S_{\text{app}} \text{ (mmol)} = \int_0^t C_{\text{CO}_2}(t) dt \times F$$

where *F* is the flow rate of the diluted CO₂ gas.

The CO₂ desorption property was evaluated after CO₂ adsorption. The fed gas was switched to N₂ at a flow rate of 10 sccm, and the sample temperature was elevated at 5 °C/min. Typically, the temperature was kept at 80 °C for 30 min.

The resistance to humid and oxidative conditions was also evaluated. With regard to the tolerance of humidity, the CO₂ adsorption property was tested by placing a water bubbler upstream of the sample tube. The relative humidity was 47% (monitored by a Testo 440 probe equipped with a humidity probe; Testo SE & Co. KGaA) at 25 °C. As for the tolerance of oxidative conditions, the samples were pretreated at 80 °C for 30 min under 100% O₂.

4.6. In Situ FT-IR Measurement during CO₂ Adsorption. Skeletal vibration and adsorbed species under a CO₂ flow were evaluated using a Fourier-transform infrared spectrometer equipped with a triglycine sulfate detector (FT-IR 4X; JASCO). The spectra were collected through the integration of 32 scans with a resolution of 4 cm^{–1}. Samples of 3 g were pressed into a pellet with a diameter of 10 mm. The pellet was placed on a flow-type in situ cell, and the spectra were measured in transmittance mode. Pretreatment was performed at 80 °C for 30 min under N₂ flow. The spectra after CO₂ adsorption were obtained under a flow of 400 ppm of CO₂–N₂ or pure CO₂.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c07256>.

SEM image, EDX mapping, N₂ adsorption desorption isotherm, TG profile, FT-IR spectra, and durability testing for humid and oxidative conditions (PDF)

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Author Contributions

S.K. and S.Y. designed this study. M.K. contributed to all experimental work and data analysis. S.K. conducted the experimental setup and data analysis. S.K. and S.Y. supervised this study. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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