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Low-Temperature Desorption of CO_2 from Carbamic Acid for CO_2 Condensation by Direct Air Capture

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Cite This: ACS Omega 2024, 9, 40075−40081

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ABSTRACT: The high temperature requirement for the desorption of absorbed CO_2 is one of the issues for the widespread use of direct air capture (DAC), which is a promising technology to reduce atmospheric CO_2 concentration. This work realized a liquid diamine absorbent−solid carbamic acid (CA) phase-change DAC system with CO_2 desorption at a low temperature by using a MeOH solvent. The CA of isophoronediamine [3-(aminomethyl)-3,5,5-trimethylcyclohexylamine, CA-IPDA] readily desorbed CO_2 in MeOH at 50 °C, while IPDA showed the capacity to absorb low-concentration CO_2 from air with an IPDA/CO_2 ratio of 1:1. The CA-IPDA desorbed more than half of the absorbed CO_2 at 60 °C without any gas flow, proving that this system can condense low-concentration CO_2 in air to pure CO_2 with low energy requirements. The low-temperature desorption of CO_2 from CA-IPDA was owing to the high solubility of CA-IPDA in MeOH and the easy CO_2 transfer between carbamic acid and MeOH to form methyl carbonate ions. This solubility control in the liquid−solid phase-change system opens up the low-energy DAC systems.
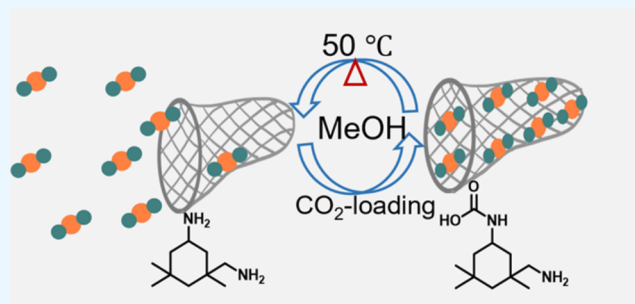
1. INTRODUCTION

The earth's natural systems are unable to mitigate the increased emissions of carbon dioxide (CO_2) resulting from industrialization. As a result, the concentration of CO_2 in the atmosphere has continued to rise and now exceeds 400 ppm, which has caused increasing instability of the global climate, although debates are still ongoing about the relationship between CO_2 concentration and the climate.[1,2] To counter this background, it is increasingly important to develop means of removing CO_2 from the atmosphere. Direct air capture (DAC) technologies have been considered as potential approaches to achieve this.[3−5] In particular, CO_2 capture by amine-based absorbents is one of the most economical and significant means to eliminate low concentrations of CO_2 in the atmosphere, because the amine-based absorbents react with low concentrations of CO_2 and release the absorbed CO_2 at relatively low temperatures in comparison with other CO_2 absorbents like zeolite and NaOH.[6−8] However, the high energy consumption involved in heating the absorbent to condense absorbed CO_2 has limited the commercial implementation of DAC technologies. Thus, CO_2 desorption at low temperatures is crucial for the development of cost-efficient DAC systems.

Typical amine-based absorbents require high-temperature heating to desorb absorbed CO_2. It was reported that a mixed absorbent involving a mixture monoethanolamine (MEA) and 2-(ethylamino)ethanol could release almost 80% of the absorbed CO_2 at 120 °C.[9] Glezakou et al. reported that a polarity swing achieved 80% from 2-[(methylamino)methyl]-

pyridine at 60 °C.[10] The addition of solid acid catalysts was also reported to increase the efficiency of CO_2 desorption from N-ethylethanolamine.[11] Solid-phase separation absorbents have also attracted attention as a way to reduce heat energy required for CO_2 desorption. Koech et al. reported that aminopyridines formed solid precipitate after CO_2 absorption and a temperature in excess of 120 °C was required to release the absorbed CO_2.[12] In addition, Custelcean et al. reported that guanidine formed a crystalline containing H_2O and CO_2 that desorbed CO_2 at 130 °C.[13,14] The required temperature in these systems was high due to the crystallization heat, but the absorbent volume for heating could be reduced compared to liquid absorbents, resulting in lower energy consumption.

Our group recently reported that diamines with a cyclohexyl group in DMSO or H_2O solvents efficiently absorb a low concentration of CO_2 by the spontaneous formation of solid carbamic acid (CA).[15] In particular, 3-(aminomethyl)-3,5,5-trimethylcyclohexylamine (isophoronediamine, IPDA) efficiently absorbed CO_2 at a 1:1 ratio of amine to CO_2 and desorbed all of the absorbed CO_2 at 60 °C in DMSO. This precipitation of CA was due to its low solubility in the liquid
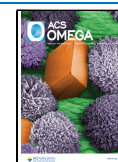
phase. Moreover, the low desorption temperature was due to the redissolution of CA in DMSO at 60 °C. These findings provided us with the concept of using solubility control to reduce the amount of heat required for CO_2 desorption. In this study, we found that the solid CA spontaneously disappeared upon the addition of methanol (MeOH) with heating the reactor in hot water (60 °C) (Figure 1 and Movie S1). In this
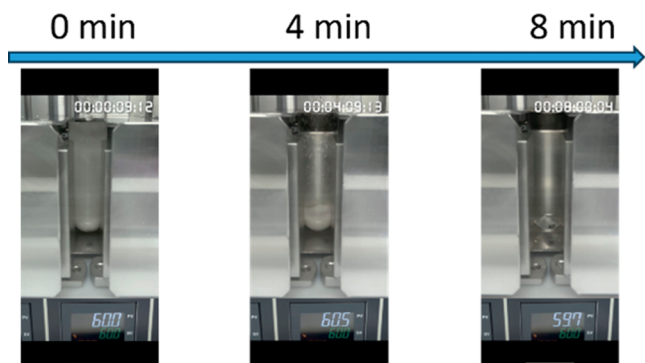

Figure 1. Rapid dissolution of CA-IPDA with CO_2 desorption in MeOH (see Movie S1). Condition: CA-IPDA, 1.0 mmol; MeOH, 5 mL; temperature, 60 °C.

way, condensed CO_2 could be obtained since the system can desorb CO_2 even under a moderate CO_2 concentration. Among the various solvents, MeOH showed efficient desorption capacity of CO_2 from CA of IPDA (CA-IPDA) under N_2 flow with this desorption starting at a temperature as low as 50 °C. MeOH solution of IPDA absorbed 400 ppm of CO_2 at a 1:1 ratio of amine to CO_2 accompanied by the formation of solid CA (CA-IPDA). Moreover, the MeOH solution in which CA-IPDA was dispersed desorbed CO_2 even without any gas flow, indicating that pure CO_2 could be obtained from this system. Thus, in this study, we proposed a system for efficient CO_2 condensation via DAC using solvent in the liquid−solid phase-change process.

2. RESULTS AND DISCUSSION

2.1. Synthesis of CA of IPDA. The CA of diamines (IPDA, PXDA, and MXDA) were fabricated by the bubbling of pure CO_2 in a MeOH solution of diamines. Elemental analysis, NMR, and FT-IR spectroscopy were performed to confirm their compositions. Elemental analysis of CA-IPDA revealed that pure monocarbamic acid of IPDA was obtained (Table S1). ^{13}C NMR spectra of CA-IPDA dissolved in D_2O showed the signals of carbamic acid at 164.9 ppm (−NH**C**OOH) (Figure S1), revealing the formation of the reported (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamic acid, $(CH_3)_3C_6H_4(NH_2)CH_2NHCOOH$.[15] PXDA and MXDA have similar ethylamine side groups, and the elemental analysis confirmed the monocarbamic acids formed from PXDA and MXDA (CA-PXDA and CA-MXDA, respectively). Absorption bands assignable to a carboxyl group (−COOH, 1620−1660 cm^{-1}), acetamide group (−NH−CO−, 1570−1600 cm^{-1}), and amino group (−NH$_2$, 1540−1560 cm^{-1}) were observed in the FT-IR spectra of CAs (Figure S2).[16] These results robustly indicated that the CA of diamines had been successfully obtained.

2.2. Desorption of CO_2 in MeOH with N_2 Bubbling. The effect of solvents for CO_2 desorption from CA suspension was tested to determine a potential solvent (Figure 2). A
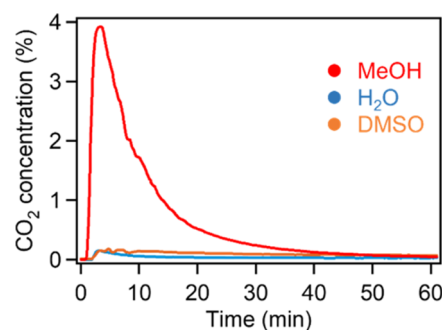
Figure 2. CO_2 desorption behavior of CA-IPDA. CA-IPDA, 1.0 mmol; solvent, MeOH, 2 mL; F_{gas} of N_2, 50 mL/min; temperature, 50 °C; heating time: 60 min. The amounts of desorbed CO_2 were as follows; MeOH, S_{dsp} = 0.99 mmol (red); H_2O, S_{dsp} = 0.06 mmol (blue); DMSO, S_{dsp} = 0.13 mmol (orange).

suspension of CA-IPDA was bubbled with a N_2 flow and heated at 50 °C for 60 min. From the elemental analysis, 0.214 g of CA-IPDA contained 1.0 mmol of CO_2 (20.5 wt %). In the case of MeOH, almost all CO_2 was desorbed at 50 °C under N_2 flow condition, and the suspension became transparent, while CA-IPDA in DMSO and H_2O resulted in insufficient desorption capacity. In our previous study, 15 mL of DMSO was required for the efficient CO_2 desorption from CA-IPDA at 60 °C.[15] The use of MeOH as a solvent could reduce the volume of solvent for desorption, which has a great advantage for reducing the amount of heating energy. One reason for the easy desorption of CO_2 from CA-IPDA was the high solubility of CA-IPDA in MeOH. Since the solid CA-IPDA required a temperature of at least 80 °C for CO_2 desorption as revealed by thermogravimetry (Figure S3), the dissolution of CA in the solvent played an important role in the efficient desorption of CO_2. Figure S4 clearly shows that the solubility of CA-IPDA in MeOH was twice that in H_2O. A high concentration of CA in the liquid phase due to high solubility resulted in efficient CO_2 desorption under N_2 bubbling. Another plausible reason for the efficient desorption of CO_2 in MeOH is the acceleration of the CO_2 desorption by the alcohol solvent. Recently, it has been reported that the addition of alcohol reduced the energy needed for CO_2 desorption, although this was not from studies of solid−liquid phase separation systems. Specifically, the desorption capacity of MEA aq. at 75 °C was dramatically increased by adding 40% EtOH, due to the formation of $C_2H_5OCO_2^-$ intermediates instead of HCO_3^-.[17] The addition of MeOH reduced the regeneration temperature of MEA aq. to below 100 °C, although MEA aq. typically requiring temperature above 120 °C to achieve CO_2 desorption.[18] The heat required for desorbing CO_2 using piperazine/diethylenetriamine aq. solution was also lowered by adding MeOH.[19] Thus, MeOH plays a role in enhancing the desorption of CO_2 besides just acting as a solvent.
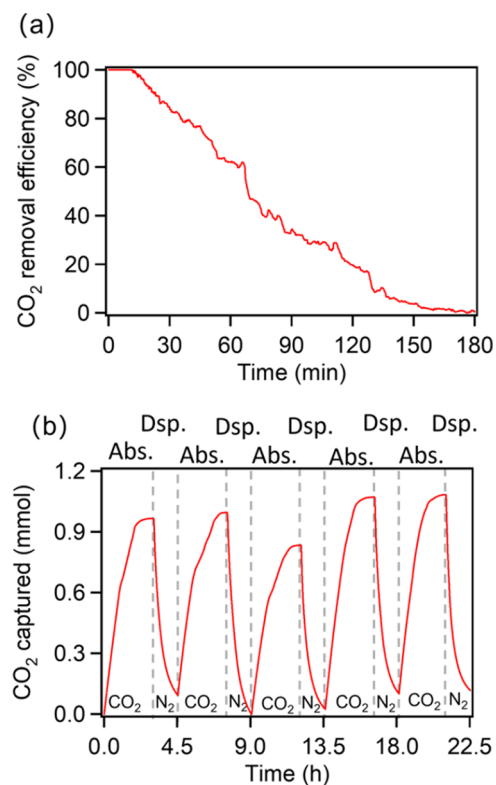
Next, we optimized the conditions for the desorption of CO_2 from CA-IPDA in MeOH. Figure 3a shows the temperature dependence of the amount of desorbed CO_2 (S_{dsp}). These results clearly show that 50 °C was enough to desorb CO_2 from CA-IPDA in MeOH. The desorption temperature in MeOH was much lower than those in DMSO and H_2O (Figure S5). As shown in Figure 3b, the effect of CA-IPDA concentration was examined in the range of 0.2−4.0 mmol (molar of CA-IPDA per volume of MeOH, $C_{CA-IPDA}$, 0.1−2 mol/L). S_{dsp} increased with increasing molar
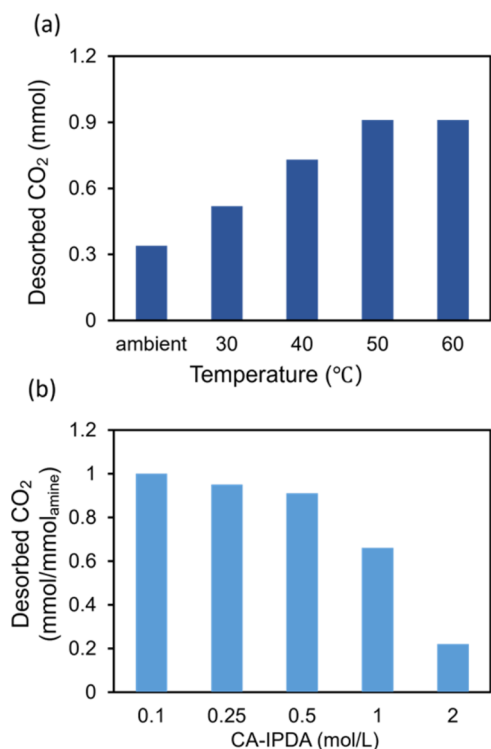
Figure 3. (a) CO_2 desorption capacity of CA-IPDA in MeOH at various temperatures. Conditions: CA-IPDA, 1.0 mmol; solvent, 2 mL; F_{gas} of N_2, 50 mL/min; and temperature, ambient. to 60 °C; heating time: 60 min. (b) CO_2 desorption capacity of CA-IPDA at various concentrations. Conditions: CA-IPDA, 0.2−4.0 mmol; solvent, 2 mL; F_{gas} of N_2, 50 mL/min; temperature, 40 °C; heating time: 60 min.


Figure 4. (a) Efficiency of removing CO_2 from air with IPDA in MeOH. Conditions: IPDA, 1.0 mmol; MeOH, 2 mL; F_{gas} of compressed air, 500 mL/min; temperature, ambient. Total amount of absorbed CO_2 (S_{abs} = 0.92 mmol). (b) Absorption−desorption cycles with IPDA in MeOH. For absorption: IPDA, 1 mmol; MeOH, 2 mL; F_{gas} of air, 500 mL/min; temperature, ambient. For desorption: F_{gas} of N_2, 100 mL/min; MeOH, 2 mL; temperature, 50 °C; time, 90 min.

of CA-IPDA and reached S_{dsp} > 0.90 at 0.50 mol/L. This indicates that the relatively low CA concentration in MeOH was required for the efficient desorption of CO_2 from CA-IPDA.

To address the possibility of applying this technique for absorbing the atmospheric concentration of CO_2,[20] the absorption capacity of IPDA in MeOH from air by IPDA in MeOH was also tested (Figure 4a). The efficiency of CO_2 removal, defined as the CO_2 concentration at the downstream of the sorbent relative to that of the inlet gas, was maintained at >99% for 10 min and then decreased monotonically. The total amount of absorbed CO_2 (S_{abs}) was 0.92 mmol. The solid precipitate appeared after 70 min. Although the DMSO and H_2O solution of IPDA maintained high CO_2 removal efficiency for a longer time (Figure S6), the MeOH sorbent system can be applied for the absorption of CO_2 present at a low concentration. Note that all of the MeOH solvent dried up during the absorption, although MeOH vapor was supplied into the flowed air. Recyclability of the sorbent is also a key for achieving low-cost and long-term industrial use. Figure 4b shows the recyclability of IPDA in MeOH under the absorption and desorption cycles. After the sufficient absorption of CO_2 from air, 2 mL of MeOH solvent was added to the precipitate and heated at 40 °C under a N_2 flow, leading to ca. 0.9 mmol of CO_2 desorption. The cycle capacity was more than 90% even after repeated use, although the CO_2-loading capacity fluctuated from 0.8 to 1.0 due to the change in the atmospheric CO_2 concentration.

The effect of MeOH solvent was tested for various diamines that readily form solid carbamic acids in MeOH. The CO_2 desorption capacity of CA-PXDA and CA-MXDA under N_2 bubbling was evaluated in 2 mL of MeOH at 50 °C (Figure 5a). CA-IPDA desorbed almost all CO_2 in 2 mL of MeOH. However, CA-PXDA and CA-MXDA did not achieve the complete desorption of CO_2 under these conditions. These results are also explained by the solubility of carbamic acids in MeOH. As shown in Figure 5b, the amount of CA-IPDA dissolved into 2 mL of MeOH was much higher than that for CA-PXDA and CA-MXDA bearing a benzyl group. We consider that the solid carbamic acid of IPDA first dissolved into the solvent, and then carbamic acid in the liquid phase desorbed CO_2. We also confirmed that some carbamic acid shown in Figure S7 could desorb CO_2 at 50 °C in MeOH because of its high solubility. Thus, the high CA solubility in the liquid phase resulted in a high desorption rate of CO_2.

We also estimated the electricity requirement of this system. Note that the experimental scale is far smaller than the industrial scale and that the internal heat loss by the gas or reactor is significant. Thus, we referred to an approach of estimating the energy requirement at the laboratory scale and performed the comparison with the energy requirement reported in a conventional solvent, namely, 5 M MEA aq.[21,22] 100 mL of MeOH in which 100 mmol of CA-IPDA was dispersed was heated at 65 °C under N_2 flow at 500 mL/min, and the internal temperature of the solution in the flask
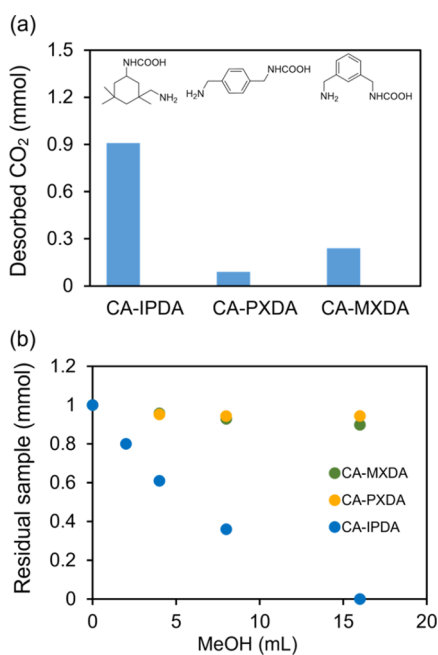
Figure 5. (a) CO_2 desorption capacity of CAs of diamines (IPDA, PXDA, and MXDA) in MeOH at 50 °C under a N_2 flow. Conditions: CA of diamines, 1.0 mmol of F_{gas} of N_2, 100 mL/min; solution, 2 mL; temperature, 50 °C; time, 60 min. (b) Residual quantity of 1 mmol of carbamic acid in a certain amount of MeOH. CA-IPDA, dissolution limit: 60.61 mmol/L (blue); CA-PXDA, dissolution limit: 6.10 mmol/L (yellow); CA-MXDA, dissolution limit: 3.00 mmol/L (green). The samples after dissolution were filtrated and washed with acetone.

was maintained at 45−50 °C during the measurement. The electricity consumption to maintain the temperature during the CO_2 desorption was monitored (Figure S8). The difference in the electricity consumption between CA-IPDA/MeOH and MeOH (blank) was 82.8 kJ during 120 min of desorption, which was derived from the heat duty for desorbing 71.8 mmol of CO_2 (Figure 6). Thus, the heat duty for CO_2 desorption was estimated to be 1153 kJ/mol$_{CO_2}$. The required electric power was compared with that for 5 M MEA aq. (100 mL) at 80−90 °C (heater set to 100 °C) after the absorption of pure CO_2. MEA aq. at 5 M did not completely release the absorbed CO_2 at 80−90 °C and the desorbed CO_2 was 205.8 mmol. The required electric power was 309.6 kJ. The heat duty for CO_2
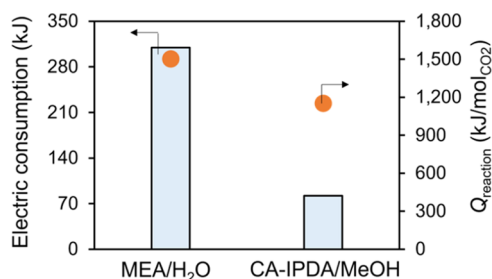
Figure 6. Consumed energy (blue bar) and heat duty ($Q_{reaction}$, orange bar) for CO_2 desorption and from CA-IPDA in MeOH and 5 M MEA aq. Conditions for CA-IPDA/MeOH: CA-IPDA, 100 mmol; MeOH, 100 mL; temperature, 65 °C; and N_2 flow rate, 500 mL/min. Conditions for 5 M MEA/H_2O: 500 mmol MEA, H_2O, 69.8 mL; temperature, 100 °C; N_2 flow rate, 500 mL/min, CO_2 absorption, 100% CO_2.

desorption for 5 M MEA aq. was estimated to be 1504 kJ/mol$_{CO_2}$, which is similar to the reported value (1856 kJ/mol$_{CO_2}$).[21] These findings indicate that the CA-IPDA/MeOH system can save more than 24% heat duty with the MEA aq system, although when determining the net heat duty, the heat loss by heat capacity of N_2 gas or cooling of the reactor should be taken into account. Obviously, a low temperature for CO_2 desorption has advantages in an industrial application where there is not always a sufficient heat source.

2.3. CO_2 Desorption in MeOH without Gas Flow. Notably, we found that CA-IPDA could readily and spontaneously dissolve in MeOH (Movie S1). This IPDA/MeOH system could desorb CO_2 without a N_2 flow. The amount of desorbed CO_2 was determined by measuring the H_2O displacement (Figure S10b). Although there is some ambiguity regarding the quantification by this method due to CO_2 and MeOH dissolving into the H_2O, notably the H_2O displacement increased upon the addition of CA-IPDA. We also confirmed that a part of CO_2 was not desorbed after heating without N_2 flow and that the CO_2 dissolution into H_2O was negligible (Figure S9). In principle, thus, pure CO_2 could be obtained from CA-IPDA by using a MeOH solvent. We optimized the conditions of the heating temperature and MeOH volume for CO_2 desorption using this method. As for the temperature dependence (Figure 7a), the amount of desorbed CO_2 peaked at 0.68 mmol at 80 °C. As for the MeOH volume dependence at 60 °C (Figure 7b), the amount of desorbed CO_2 increased in a small MeOH region and then decreased with increasing MeOH volume. Specifically, a small amount of MeOH was insufficient to dissolve CA-IPDA, resulting in low CO_2 desorption capacity, whereas an excess amount of solvent might have caused residual CA in the liquid phase, preventing CO_2 desorption. The repeatability of absorption and desorption under the optimized conditions using 5 mL of MeOH at 60 °C was also confirmed, and IPDA/MeOH absorbed a comparable amount of desorbed CO_2 from the air (Figure 8). Thus, we concluded that the IPDA/MeOH system can be used to condense the ambient CO_2 concentration to that of pure CO_2.

2.4. Reason for Efficient Desorption of CO_2 from CA-IPDA in MeOH. MeOH solvent decreased the temperature required to desorb CO_2 from CA-IPDA compared with the DMSO or H_2O solvent (Figure S5). We confirmed that the solubility of CA-IPDA in MeOH was 8.7 and 2.5 times higher than those in DMSO and H_2O, respectively. The high solubility of CA-IPDA resulted in a high concentration of liquid carbamic acid $[NH_2-R-C_6H_4-NH-COOH(l)]$ or intermolecular carbamate species $[NH_3^+-R-C_6H_4-NH-COO^-(l)]$ in MeOH. Among the reported absorbents, alcohol solvents accelerated the CO_2 desorption to increase the desorption capacity or reduce the required temperature. It was previously described that the desorption capacity of MEA aqueous solution at 75 °C was increased by 6.8 times with a high desorption rate by the addition of 40% EtOH.[17] In addition, the regeneration temperature was decreased to below 100 °C for MEA aqueous solution upon the addition of MeOH, while MEA aq. generally required more than 120 °C to achieve highly efficient CO_2 desorption.[18] Elsewhere, it was reported that the CO_2 desorption capacity of piperazine/diethylenetriamine aq. at 80 °C was improved by adding diethylene glycol or MeOH.[19] EtOH was also found to promote the decomposition of CO_2 from the carbamate of *N*-
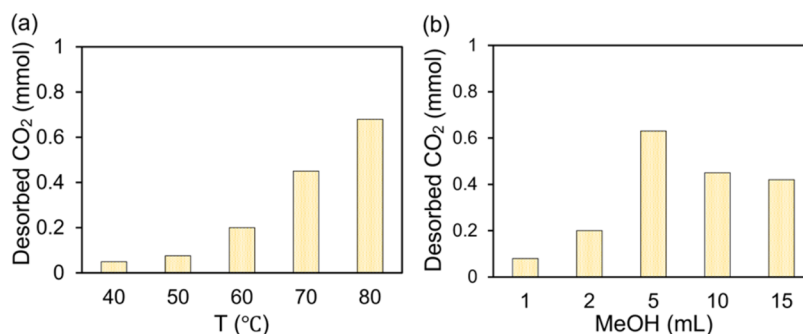
Figure 7. (a) Amount of CO_2 desorbed from CA-IPDA at various temperatures. Conditions: CA-IPDA, 1.0 mmol; volume of MeOH, 2 mL; temperature, 40−80 °C; heating time, 10 min. (b) Amount of CO_2 desorbed from CA-IPDA in various volumes of MeOH. Conditions: CA-IPDA, 1.0 mmol; MeOH, 1−15 mL; temperature, 60 °C; heating time, 10 min.
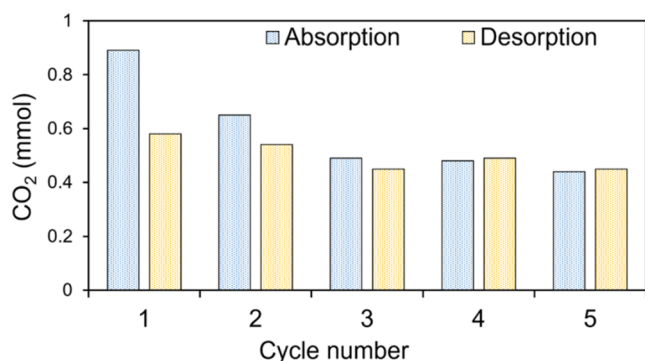
Figure 8. Cycling test for the absorption of CO_2 from air and desorption of CO_2 without gas flow over IPDA in MeOH. IPDA, 1 mmol; MeOH, 5 mL; F_{gas} of air, 500 mL/min; temperature, ambient. For desorption: temperature, 60 °C; heating time, 10 min.

aminoethylpiperazine and convert it into ethyl carbonate $(C_2H_5OCOO^-)$.[23] Based on the effect of alcohol reported previously, we consider the reason for the efficient desorption of CO_2 from CA-IPDA in MEOH as follows. The dissolved CA-IPDA $[NH_2−R−C_6H_4−NH−COOH(l)]$ converted into the intermolecular carbamate species $[NH_3^+−R−C_6H_4−NH−COO^-(l)]$ at a certain proportion according to the equilibrium under the applied conditions. MeOH solvent interacts with them to form the methyl carbonate ion $[CH_3OCOO^-(l)]$, while the ammonium cation is formed $[NH_2−R−C_6H_4−NH_3^+(l)]$. The methyl carbonate ion readily releases CO_2 accompanied by regeneration of carbamic acid $[NH_2−R−C_6H_4−NH−COOH(l)]$. This proposed mechanism is reinforced by the previous findings that CO_2 is more readily desorbed from methyl carbonate ions than from carbamate.[24,25] Thus, we consider that (1) the high solubility of CA-IPDA in MeOH and (2) the transfer of CO_2 between carbamic acid and MeOH to form methyl carbonate ions resulted in the efficient desorption of CO_2 from CA-IPDA in MeOH.

3. CONCLUSIONS

We investigated the CO_2 desorption performance of CA-IPDA in various solvents and found that the MeOH solvent efficiently promoted the desorption of CO_2. CA-IPDA desorbed >99% of the absorbed CO_2 in MeOH under a N_2 flow at 50 °C, while DMSO and H_2O solvents required higher temperatures for the CO_2 desorption under these conditions. The MeOH solution of IPDA absorbed low-concentration

CO_2 from the air at a 1:1 ratio of IPDA to CO_2, and the absorption and desorption cycles could be repeated. Remarkably, >50% of the absorbed CO_2 could be desorbed simply by adding MeOH and heating at 80 °C without any gas flow, suggesting that this system could be used to obtain pure CO_2 from atmospheric CO_2 in air. Needless to say, the required heat energy of the IPDA/MeOH system for CO_2 desorption was much lower than that of the MEA aq. system because a low temperature could be applied. Therefore, we developed a promising system based on liquid diamine−solid carbamic acid phase-change adsorbent, which could widen the availability of DAC.

4. EXPERIMENTAL SECTION

4.1. Materials. All chemicals were used without any purification, as purchased. 3-(Aminomethyl)-3,5,5-trimethylcyclohexylamine, (IPDA, cis- and trans-mixture, >99.0%); *p*-xylylenediamine (PXDA, >99%); *m*-xylylenediamine (MXDA, >99%); 1,3-cyclohexanediamine (cis/trans mixture, CHA, >95%); 1,3-bis(aminomethyl)cyclohexane (cis/trans mixture, CAMA, >98%); dimethyl sufoxide (DMSO, >99.0%); and 2-aminoethanol (MEA, monoethanolamine; >99.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Methanol (MeOH) were purchased from Kanto Chemical Co., Inc.

4.2. CO_2 Desorption with N_2 Bubbling. The carbamic acid of diamine was prepared by bubbling 1 M diamine in a MeOH solvent under a flow of 100% CO_2 at 20 mL/min. The solid yield was filtrated and washed with acetone, followed by drying under vacuum at room temperature for 24 h.

The CO_2 desorption capacity of carbamic acid was evaluated using a flow-type reactor equipped with a CO_2 probe (GMP 252; Vaisala GmbH) downstream of the sorbent (Figure S10a). The tip of the stainless-steel tube as a gas inlet was immersed in the sample solution to efficiently remove desorbed CO_2 by N_2 bubbling. The flow rate of N_2 was controlled by a mass flow controller (HORIBA Precision Instruments Co., Ltd.). The sorbent temperature for desorption was controlled in a range from ambient temperature (∼25 °C) to 100 °C using an aluminum heater. To suppress the volatilization of solvents during evaluation, a saturator filled with the solvent was placed upstream of the sorbent and heated at the same temperature. The contents of CA and solvent were 0.2 and 4.0 mmol and 2 mL, respectively. The amount of desorbed CO_2 $(S_{dsp,flow})$ was quantified by detecting the CO_2 accumulated in the downstream gas, calculated by the following equation:

$$S_{dsp,flow} = \int_0^t C_{CO_2}(t)dt \times F_{gas} \tag{1}$$

where C_{CO_2} and F_{gas} are the concentration of CO_2 and the flow rate of desorption gas (N_2), respectively. We also evaluated the CO_2 desorption capacity of diamines in terms of the CO_2 desorption rate and CO_2 desorption efficiency, calculated by dividing F_{gas} by the initial CO_2 content.

The absorption−desorption cycles in the flow system were tested over 1 mmol of IPDA in 2 mL of MeOH. Absorption was performed under 500 mL/min of compressed air at ambient temperature (25 °C), for which the amount of absorbed CO_2 was quantified in the same way as with the desorption test. For the desorption experiment, MeOH was added to a volume of 2 mL, and then the gas was switched to 100 mL/min N_2 and an aluminum heater at 50 °C for 60 min. The absorption and desorption were repeated for five cycles.

4.3. CO$_2$ Desorption without Flowing. The desorption of CO_2 without any gas flow was tested in a water-displacement-type reactor (Figure S10b). The desorbed CO_2 was collected in a glass cylinder and quantified by the volume of H_2O replacements, taking into account the CO_2 solubility in H_2O and solvent volatilization. The blank test to estimate the solvent volatilization was performed with the same volume of solvent. The amount of desorbed CO_2 (S_{dsp}) was calculated using the following equation:

$$S_{dsp} = \frac{V_{total} - V_{black}}{22.4} \tag{2}$$

where V_{total} and V_{blank} are the volumes of H_2O replacements under sample and blank conditions, respectively. Cycle capacity was also investigated using 1 mmol of IPDA in 5 mL of MeOH. Absorption was performed under 500 mL/min of compressed air at ambient temperature. Upon adding MeOH to a volume of 5 mL, the desorption test was carried out with a water-displacement-type reactor at 60 °C for 10 min. The absorption and desorption were repeated for five cycles.

4.4. Calculation of Energy Consumption for Desorption. The energy required for the desorption of CO_2 was estimated (Figure S11). The cumulative electrical energy for the heating mantle during the desorption process was recorded using an electrical energy meter (DEMO-W7; Namikoshi Electronics Co., Ltd.; ±0.001 kW h). The CO_2 desorption was performed for 120 min under a N_2 flow at 500 mL/min. The MeOH solution of carbamic acid of IPDA (IPDA, 100 mmol; MeOH, 100 mL) was heated at 65 °C with an aluminum heater. Owing to the large scale and the heat loss by the gas flow, the internal temperature in the bottle was maintained at 45−50 °C during the test. Taking into account the heat of vaporization, the heat consumed for heating the vessel, and the heat loss by N_2 flow, a blank test was performed in the same volume of solvent under the same conditions. In this study, 5 M MEA aq. was used as a standard CO_2 sorbent and heated at 100 °C (the internal temperature was 80−90 °C) under 500 mL/min N_2 to release the absorbed CO_2 under a flow of 100% CO_2.

The total regeneration energy consumption is defined as the energy consumed per mmol of regenerated CO_2 and is composed of sensible heat, latent heat, and desorption reaction heat. In this work, we estimated the desorption heat by measuring the consumed electricity to maintain the reactor temperature.

$$Q_{reaction} = (E_{sample} - E_{blank})/n_{CO_2} \; (kJ/mol_{CO_2})$$

where E_{sample} and E_{blank} are the consumed electricity for the CO_2 desorption process with amine and w/o amine, respectively, and n_{CO_2} is the amount of desorbed CO_2.

4.5. Analysis. The contents of C, H, and N atoms in the CA compounds were determined by CHN elemental analysis (UNICUBE; Elementer Japan Co., Ltd.). Fourier transform infrared (FT-IR) spectra were collected using an FT-IR spectrometer (FT/IR-4700; JASCO) equipped with an attenuated total reflectance infrared (ATR-IR) unit (ATR-PRO ONE; JASCO) in the wavenumber range from 400 to 4000 cm^{-1} where 1024 scans were accumulated. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were measured on the CA compounds by using a thermogravimetric analyzer (TG-DTA2000SA; Bruker). The temperature was increased from 25 to 240 °C at a rate of 10 °C/min under N_2 supplied at a flow rate of 50 mL/min.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c05978.

> Pictures of the experimental setup for CO_2 desorption, CA solid compounds' solubility, ^{13}C NMR and FT-IR spectra, and TG profile (PDF)
> Rapid dissolution of CA-IPDA with CO_2 desorption in MeOH (Movie S1) (MP4)

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Author Contributions

All authors have given approval to the final version of the manuscript. S.K. and S.Y. designed this study. F.C. and S.K. contributed to all experimental setup, experimental works, characterizations, and data analysis. All authors discussed the analyzed data, and H.Y. proposed the desorption mechanism. S.Y. supervised this study. All authors took part in the writing of this manuscript.

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