

Sequestration of carbon dioxide by *m*-xylylenediamine with forming a crystalline adduct

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Abstract—The reaction of *m*-xylylenediamine (mXD) with carbon dioxide was examined and its feasibility as a sequestration material of carbon dioxide was discussed. The reaction was monitored by using the FT-IR and gravitational methods, while the crystalline structure of the reaction product was investigated with elemental analysis, powder X-ray diffraction, single crystallography, and ¹³C MAS NMR spectroscopy. Even at ambient temperature, mXD reacted with carbon dioxide of low partial pressure in the atmosphere and produced a 1 : 1 molar adduct which appeared as a white crystalline material. The hydrogen bonds that formed between the adduct molecules resulted in the formation of a stable crystal. The sequestration capacity of mXD was very great, ~280 mg g_{mXD}⁻¹ below 50 °C. An adsorbent prepared by dispersing mXD on silica was capable of capturing carbon dioxide, but it could be regenerated by evacuating at 25 °C.

Key words: *m*-Xylylenediamine, Carbon Dioxide, Adduct, Crystal Structure, Sequestration

INTRODUCTION

Global warming has been accelerated due to the increase in the concentration of carbon dioxide in the atmosphere. Since fossil fuels, which emit carbon dioxide as a combustion product, are widely used in electricity power plants and transportation [1], reducing the emission of carbon dioxide in industrialized societies is a considerable challenge. Although the global warming index of carbon dioxide is not as high as other greenhouse gases, it is considered to be the most important greenhouse gas because of its high levels of emission. The recycling of carbon dioxide is very limited in terms of technology and economics, and thus carbon capture and storage (CCS) technologies have become more important in reducing carbon dioxide concentration in the atmosphere [2-5].

Materials that can sequester carbon dioxide with a great capacity are essential for the successful CCS, and the capture of carbon dioxide at an ambient temperature under a low partial pressure enhances its performance. Since no suitable sequestration material is available, carbon dioxide is usually separated using various methods such as cryogenic distillation, membrane separation, adsorption, and absorption, and is then stored in a liquid or supercritical state [6-9]. While absorption using an aqueous solution of monoethanolamine (MEA) is considered to be the most feasible method for separating carbon dioxide, the high cost of regeneration, the loss of absorbing species by evaporation, and the corrosion of the apparatuses have been the main drawbacks preventing its widespread application [10]. While on the other hand, solid alkali metal oxides do not cause any corrosion, high-temperature operations are needed to capture carbon dioxide [11].

Although zeolites, hydrotalcites, and metal-organic frameworks adsorb carbon dioxide, solid adsorbents prepared by dispersing basic

materials on porous solid supports have been considered more feasible in terms of their high adsorption capacity and relatively easy regeneration [8,9,11-14]. For example, polyethyleneimine (PEI) dispersed in KIT-6 mesoporous material was shown to have a high adsorption capacity for carbon dioxide, 135 mg g_{adsorbent}⁻¹, and could be regenerated at 75 °C and under 1 atm. However, it is not known if this system can sequester carbon dioxide at a low concentration of about 400 ppm and persist in the adsorbed state at an ambient condition permanently.

m-Xylylenediamine (mXD) is a basic material with two substituted aminomethyl groups in the benzene ring. Although mXD is not a widely used material, it is environmental-friendly because it can be converted to polyurea by reacting with carbon dioxide at 180 °C without the need to use phosgene [15]. The reaction of mXD with carbon dioxide at a supercritical condition results in the formation of polyamide with a high gas shielding property [16]. While an aqueous solution of 20-50% mXD has been patented as an absorption solution of carbon dioxide [17], no report exists on its application in practice.

mXD reacts with carbon dioxide at ambient temperatures, even at the atmospheric concentration, and produces a white crystalline solid. Here, we examined the reaction between mXD and carbon dioxide using FT-IR spectroscopy and the gravitational method. The crystal structure and physico-chemical properties of the product were also investigated using elemental analysis, single X-ray crystallography, and ¹³C MAS NMR to better understand the ability of mXD to sequester carbon dioxide. The feasibility of a solid adsorbent prepared by dispersing mXD on silica is also high in selective adsorption and regeneration for carbon dioxide.

EXPERIMENTAL

1. Preparation of the Adduct between mXD and Carbon Dioxide

The adduct between mXD and carbon dioxide was prepared by

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reacting mXD (Aldrich, 99%) charged in a petri dish with a carbon dioxide (Shinil Gas) flow of 5 ml min^{-1} in a quartz tube placed in an electric furnace in the range of temperatures from ambient to $55 \text{ }^\circ\text{C}$.

A solid adsorbent for carbon dioxide was prepared by impregnating mXD dissolved in dichloromethane (Daejung, 99.5%) to silica (Aldrich, Davisil grade 635, 99%, $150\text{--}250 \mu\text{m}$). After stirring for 2 h, the suspension was transferred to a rotary evaporator, and the solvent was removed at $50 \text{ }^\circ\text{C}$ under reduced pressure. The adsorbent was denoted as mXD/silica and the amount of loaded mXD was 22 wt%.

2. Monitoring the Reaction between mXD and Carbon Dioxide

The reaction between mXD and carbon dioxide was monitored with an FT-IR spectrophotometer (Bio-Rad, FTS-175C). A small amount of mXD was coated on a KBr wafer to form a thin film, and it was set on a sample holder of an in situ IR cell (Graseby Specac). IR spectra were recorded in a flow of carbon dioxide at the rate of 5 ml min^{-1} .

The amount of carbon dioxide captured by mXD was measured by using the gravimetric adsorption system equipped with a quartz spring [18]. mXD charged in a small quartz basket was exposed to the carbon dioxide flow of 5 ml min^{-1} and the temperature of the system was maintained at 35, 45, and $55 \text{ }^\circ\text{C}$ by circulating water in a double-walled jacket that surrounded the sample. After reaching uptake equilibrium, the flow of carbon dioxide was closed. The uptake of carbon dioxide on mXD/silica and its regeneration under evacuation were also examined using the same system.

3. Analyses of the Adduct

The shape and size of the reaction product were examined by a scanning electron microscope (SEM, Jeol, JSM-5400) and an optical microscope (Nikon, Eclipse LV-100). An automatic element analyzer (Thermo Fisher, Flash-2000) was used to determine the content of carbon (C), hydrogen (H), and nitrogen (N). The oxygen (O) content was determined with another analyzer (Thermo Quest, EA-1110). The TG/DTA curves of the product were recorded on a thermogravimeter (Seiko, TG/DTA 200). The loss of weight according to the increase of temperature was measured in the air flow at the ramping temperature of $10 \text{ }^\circ\text{C min}^{-1}$.

Powder XRD patterns of the adduct were obtained using an X-ray diffractometer (PANalytical, X'Pert) with a $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) filtered by a nickel filter. The diffractometer was operated at 60 kV and 15 mA. The X-ray intensities of the single crystal of the adduct were collected on a single X-ray diffractometer (Bruker, SMART 1000 CCD) by using a graphite $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $-73 \text{ }^\circ\text{C}$.

The ^{13}C NMR spectrum of the adduct was recorded on a CP/MAS (cross-polarization/magic angle spinning) NMR spectrometer (Agilent Technologies, UNITY INOVA). The adduct charged in a zirconia rotor was rotated at 9 kHz and irradiated with a microwave pulse (150.877 MHz). The pulses were repeated at an interval of 8 s, and averaged signals were obtained from 1024 recordings. Chemical shifts were referenced indirectly through the methyl group of the hexamethylbenzene peak (17.3 ppm relative to TMS).

4. Theoretical Calculation

All density functional theory (DFT) calculations were carried out by using a suite of Gaussian 09 programs [19]. Among the tested hybrid meta exchange-correlation functionals, M06-2X provides

good results for the combination of main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states [20,21]. Hence, as a useful DFT method that shows the best performance in main-group thermochemistry and noncovalent interactions, M06-2X would be sufficient to evaluate the interactions between mXD and carbon dioxide. All structure optimizations were performed using M06-2X with a 6-31+G** basis set. Integral=ultrafine option was utilized to minimize the integration grid errors that may arise from using an inadequate grid in the current M06-2X suite of functional [22], even though the default grid in Gaussian 09 is a fine grid which is sufficient. We compared the two different interaction modes: covalently bonded zwitterion form and non-covalent interaction. In comparing the charged and non-charged systems, the solvent effect would be crucial. Thus, we employed a polarizable continuum model to include the solvent effect. To reveal the electron population and the bonding feature, natural bond orbital (NBO) has been analyzed [23].

RESULTS AND DISCUSSION

1. The Reaction of mXD with Carbon Dioxide

The IR spectra recorded during the reaction of mXD with carbon dioxide exhibit definite changes in the absorption bands of C-H and N-H, as shown in Fig. 1. The band at $3,300\text{--}3,250 \text{ cm}^{-1}$ for mXD was attributed to two N-H stretching vibrations of the primary amine, that at $3,100\text{--}3,050 \text{ cm}^{-1}$ to the sp^2 C-H stretching vibration of the benzene ring, and that at $2,950\text{--}2,850 \text{ cm}^{-1}$ to the C-H stretching vibration of a methylene group [24]. The complicated bands at $1,600\text{--}1,450 \text{ cm}^{-1}$ are also associated with the stretching vibration of the benzene ring. The reaction between mXD and carbon dioxide resulted in the disappearance of two bands that corresponded to the primary amine groups and the appearance of a single band at $3,300\text{--}3,250 \text{ cm}^{-1}$ that corresponded to a secondary amine. In addition, a wide band associated with carboxylic acid appeared at $3,200\text{--}2,400 \text{ cm}^{-1}$, and a band corresponding to carbon dioxide combined with mXD was observed at $2,200 \text{ cm}^{-1}$. In contrast, the bands associated with the benzene ring remained even after exposing mXD to carbon

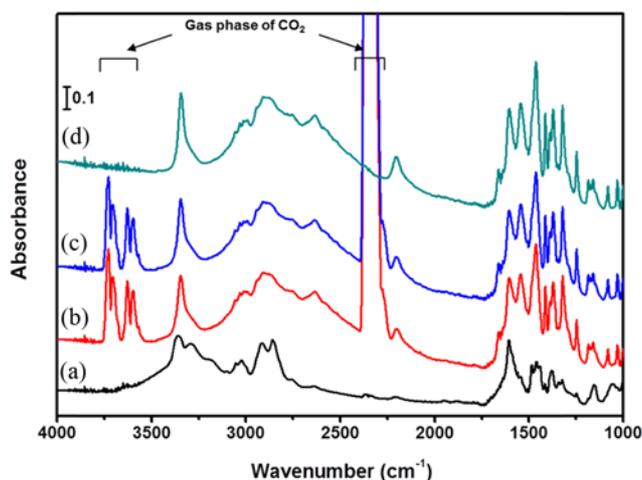


Fig. 1. IR spectra of mXD: (a) as received, (b) exposed to a flow of carbon dioxide for 3 min, (c) exposed to the flow for 15 min, and (d) purged with N_2 flow.

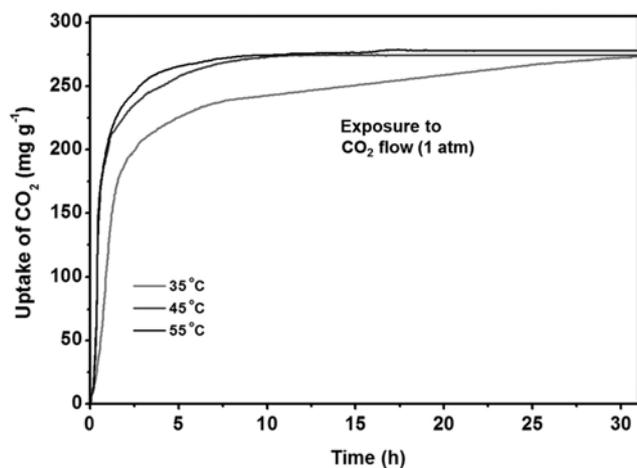


Fig. 2. Uptake curves of CO₂ onto mXD at various temperatures.

dioxide. These IR spectra revealed that carbon dioxide was combined with mXD and the conversion of primary amine groups into secondary amine groups by the reaction, indicating that the formation of an adduct resulted from the bonding between a primary amine group and carbon dioxide.

Fig. 2 shows the increase of mass after exposure of mXD to carbon dioxide. The uptake was initially very rapid but then gradually decreased. Although the uptake rate was more rapid at elevated temperatures, the amounts of carbon dioxide captured were almost the same in the range of 275–280 mg g_{mXD}⁻¹, regardless of temperature. These amounts of uptake corresponded to the combination of 0.87

Table 1. Elemental analysis of the adduct of mXD and CO₂

Material	Composition (wt%)			
	N	C	H	O
mXD (theoretical)	20.6	70.6	8.9	0
mXD:CO ₂ (theoretical) ^a	15.5	60.0	6.7	17.8
mXD:CO ₂ (experimental)	15.8	59.2	6.7	18.3

^aCalculated based on the 1 : 1 molar adduct of mXD and carbon dioxide

carbon dioxide molecules to one mXD molecule. Since the adduct formation occurred on the external surface of liquid mXD and the surface was covered with the adduct as the reaction proceeded, a long time was required for the slow mass transfer through the solid external surface to achieve uptake equilibrium.

The shapes of the adduct varied with the preparation methods, as shown in Fig. 3. The solid was either crystalline or amorphous (Fig. 3(a)). The recrystallization of adduct from its aqueous solution produced thin plate crystals with a width of 100–300 μm (Fig. 3(b)).

Table 1 lists the composition of the adduct produced from mXD and carbon dioxide. The compositions of mXD itself and a 1 : 1 (molar ratio) mixture of mXD and carbon dioxide were also shown for comparison. The composition of the reaction product was almost identical to that of the 1 : 1 molar adduct of mXD and carbon dioxide. The elemental analysis of the adduct suggested that 96.9% of mXD combined with carbon dioxide, indicating a small part of mXD was not converted to the adduct because it was encompassed with solid product.

Fig. 4 shows the X-ray diffraction (XRD) patterns of the mXD:

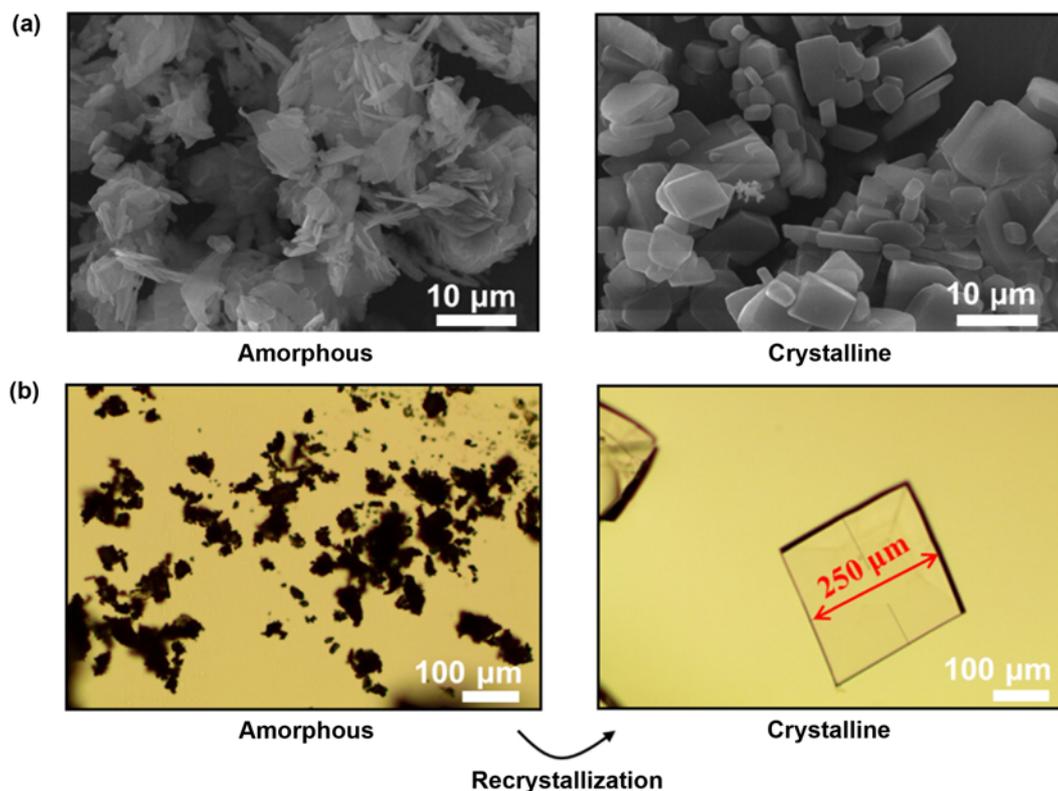


Fig. 3. (a) SEM and (b) optical microscope images of the mXD:CO₂ adduct.

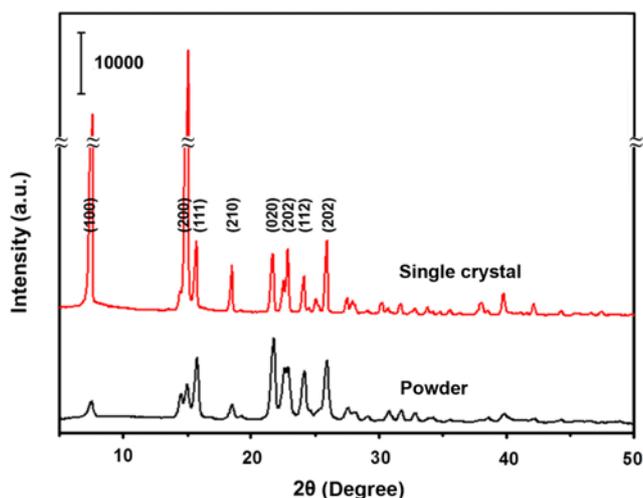


Fig. 4. XRD patterns of the mXD:CO₂ adducts in powder and a single crystal.

CO₂ adducts in powder form and single crystal. The diffraction peaks at $2\theta=15.0^\circ$, 15.7° , 21.7° , 22.9° , and 26.0° revealed that the adduct was crystalline. The sharp peaks $2\theta=7.6^\circ$ and 15.5° from the single crystal were attributed to the intensified planes of (100) and (200) in the plate-type single crystal.

The crystal structure of the adduct obtained from X-ray diffraction analysis is depicted in Fig. 5. The crystallographic data are summarized in Table 2. The compound crystallized in the monoclinic space group $P2_1/c$ and was found as a zwitterion in the solid state. A molecule of carbon dioxide was combined with an amino group of mXD, and a proton of the amino group then moved to another amino group. The zwitterions are connected by relatively strong intermolecular N-H \cdots O hydrogen bonds with $d(\text{N}\cdots\text{O})=2.772(2)$ – $3.162(2)$ Å, to generate a two-dimensional network extending parallel to (100).

The ¹³C NMR spectrum of the adduct confirmed the covalently bonded mXD:CO₂ structure, as shown in Fig. 6. A tertiary carbon

Table 2. Crystallographic data for the mXD:CO₂ adduct

Empirical formula	C ₉ H ₁₂ N ₂ O ₂
Formula weight	180.21
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{Å}$	11.883(2)
$b/\text{Å}$	8.1592(14)
$c/\text{Å}$	9.2806(15)
α/deg	90
β/deg	97.416(4)
γ/deg	90
Volume/Å ³	892.3(3)
Z	4
$D_x/\text{g cm}^{-3}$	1.341
μ/mm^{-1}	0.096
Reflns collected	6375
θ range/deg	3.0, 28.3
Indep. reflns, R_{int}	2195, 0.043
Goodness-of-fit	1.006
R_1 , wR_2 [$I > 2\sigma(I)$]	0.0433, 0.0904
R_1 , wR_2 [all data]	0.0975, 0.1180
Max, min difference/e Å ⁻³	0.239, -0.245

peak originating from the carboxylate (A) was observed at 168 ppm, and three carbon peaks corresponding to the benzene ring (B) were observed at 125–145 ppm [24]. The carbon peaks of the methylene groups (C) with different groups were observed near 45 ppm.

To determine the role of the methylene group of mXD with a great sequestration capacity of carbon dioxide, NBO charges on the nitrogen atoms of various aromatic amines were calculated by DFT calculations using M06-2X functional [19,22] (See Table 3). The NBO charge of nitrogen atom is less negative, hence less basic, when the nitrogen atom is attached directly to a benzene ring (e.g., aniline and benzenediamines) than when it is linked to a benzene

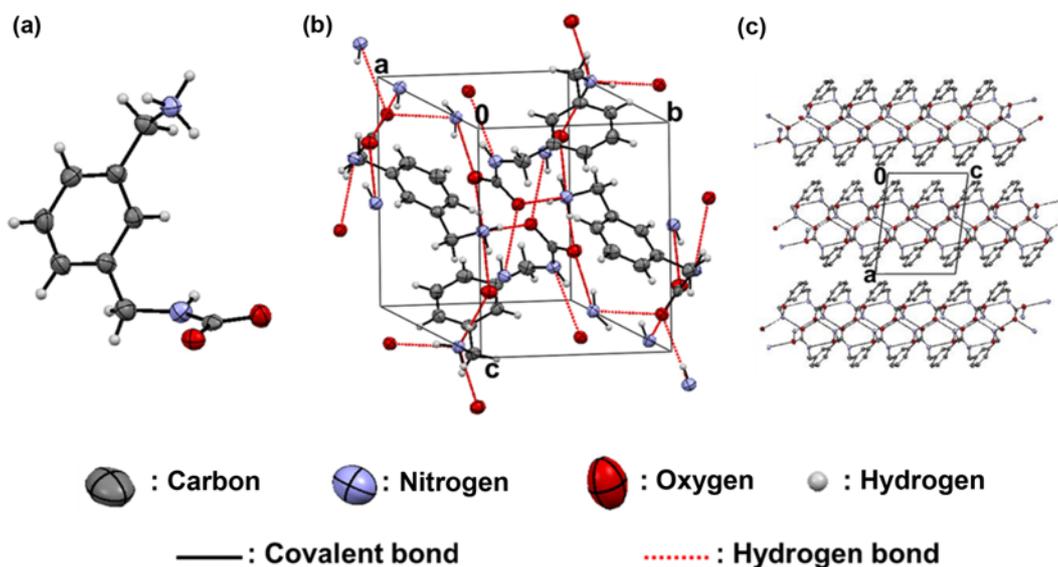


Fig. 5. Crystal structure of mXD:CO₂: (a) molecular structure, (b) unit cell, and (c) layer structure.

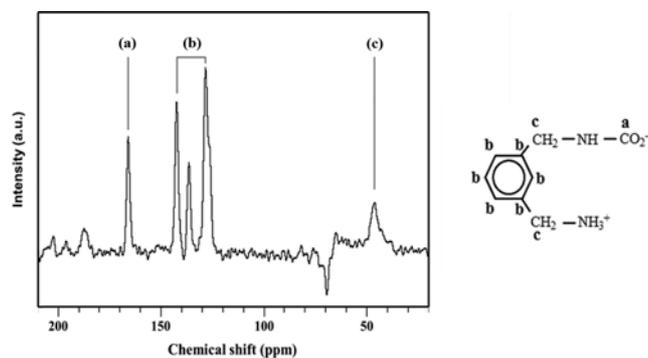


Fig. 6. ^{13}C MAS NMR spectrum of the $\text{mXD}:\text{CO}_2$ adduct.

ring through a methylene spacer (e.g., benzylamine and xylylenediamines). The methylene group between the benzene ring and amine group may disturb the π -conjugation, hence making the charge of the nitrogen atom more negative and thus more basic. Very negative charges (ca. 0.95e) on the nitrogen atoms of benzylamine and xylylenediamines enable them to act as good nucleophiles to attack the carbon atom of carbon dioxide. Although benzylamine and xylylenediamines have similar basicity (electron density of the nitrogen atom), mXD showed much higher sequestration capacity of carbon dioxide than benzylamine. Two benzylamine molecules are required to take one carbon dioxide molecule, but only one mXD molecule is enough to form a 1 : 1 adduct with carbon dioxide [2].

Among the *o*-, *m*-, and *p*-xylylenediamine, mXD is the most efficient, and this is mainly due to the best orientation for bonding. In the binding of mXD with carbon dioxide, mXD can be covalently connected or physically linked through intermolecular interactions. In our quantum calculations considering the solvent effect, the covalently bonded adduct is slightly more stable (by $\sim 2.7 \text{ kJ mol}^{-1}$) than the physically associated adduct. However, since the accuracy of current DFT calculations should be about $8.4\text{--}12.6 \text{ kJ mol}^{-1}$, such a small stability difference could not give a definite preference. Nevertheless, the covalently bonded adduct lies in a zwitterionic form and can be expected to more easily form a crystal structure than a physically associated structure.

2. Adsorption-desorption of Carbon Dioxide on mXD/Silica

The state of impregnated mXD on silica considerably differed from its bulk liquid. Fig. 7 shows the thermogram (TG) and differential thermal analysis (DTA) curves of the $\text{mXD}:\text{CO}_2$ adduct and mXD/silica. The weight losses of $\text{mXD}:\text{CO}_2$ in air occurred in two steps: the first endothermic peak was observed at about 140°C and the second peak at about 180°C . Although the details of weight loss with temperature were not clarified, the endothermic peaks even in air flow clearly demonstrated that $\text{mXD}:\text{CO}_2$ was removed by evaporation with absorbing heat. However, mXD/silica showed a considerably different weight loss profile. Since the silica only showed a weight loss below 100°C due to desorption of water, the further

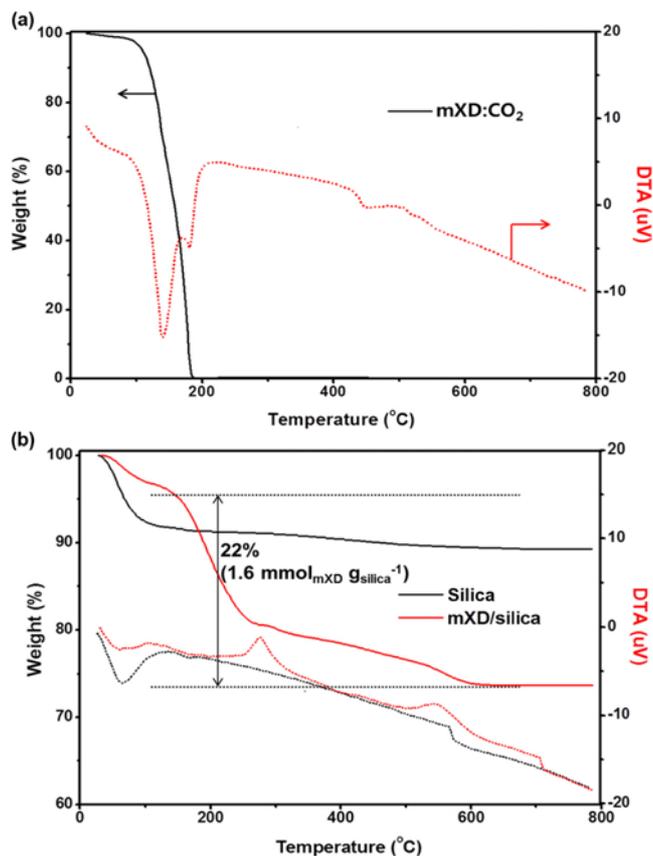


Fig. 7. TG/DTA curves of (a) $\text{mXD}:\text{CO}_2$ and (b) silica and mXD/silica. Solid lines are TG curves and dot lines are DTA curves.

losses of weight were responsible for the mXD dispersed on the silica. The two exothermic peaks at 280 and 550°C suggested that the mXD burned in air and emitted heat. The mXD dispersed on silica was removed while generating heat, indicating that its combustion occurred at considerably high temperatures. The stabilization of mXD by dispersion on the silica may be due to the strong hydrogen bonding between the amine groups of the mXD and the hydroxyl groups of silica.

Fig. 8 shows the adsorption-desorption of carbon dioxide on mXD/silica. Carbon dioxide adsorbed very rapidly and achieved an adsorption equilibrium within 60 min. The desorption of carbon dioxide under evacuation occurred within a similar time scale. However, the amount of carbon dioxide adsorbed was reduced when the adsorption-desorption process was repeated. The amount of carbon dioxide adsorbed was $69 \text{ mg g}_{\text{adsorbent}}^{-1}$ at the first cycle. This amount corresponded to $317 \text{ mg g}_{\text{mXD}}^{-1}$ and was very close to the amount of carbon dioxide required to form the 1 : 1 adduct, $323 \text{ mg g}_{\text{mXD}}^{-1}$. Therefore, carbon dioxide was adsorbed on the mXD dispersed on silica and formed a 1 : 1 adduct at 25°C . However, the captured carbon

Table 3. NBO charges of nitrogen atom of various aromatic amines

Compound	Aniline	Benzylamine	Benzenediamine			Xylylenediamine		
			ortho-	meta-	para-	ortho-	meta-	para-
NBO charge of N atom	-0.893	-0.949	-0.913	-0.891	-0.901	-0.959	-0.951	-0.953

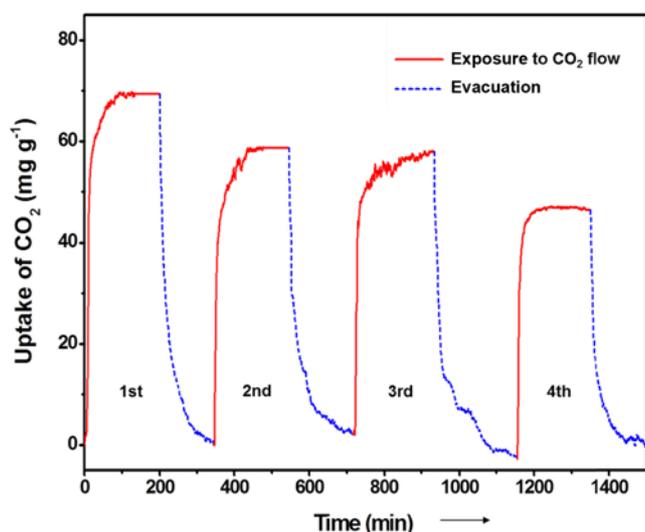


Fig. 8. Uptake and removal of CO₂ on mXD/silica at 25 °C.

dioxide was removed under vacuum at the same temperature. The partial decrease in the amount of carbon dioxide adsorbed might be due to the formation of the crystalline adduct, which could be decomposed under simple evacuation. The mXD, which was dispersed as a monolayer, exhibited a reversible adsorption-desorption behavior, while a lump of liquid mXD formed a stable mXD:CO₂ adduct and displayed an inevitable loss in its adsorption capacity for carbon dioxide. The preparation of mXD on silica with the sufficient amount of carbon dioxide is essential to confirm the suggestion. Although mXD has a great adsorption amount of carbon dioxide, the application of mXD as an adsorbent for the sequestration of carbon dioxide requires the preparation of mXD by supporting it on various supports with different pore characteristics and surface properties. Careful control of mXD coverage and an appropriate interaction between mXD and support improve the adsorption amounts of carbon dioxide and enable the high reversible performance in its adsorption/regeneration.

Table 4 shows the adsorption and sequestered amounts of carbon dioxide on various materials [2,11,13,25,26]. Liquid mXD sequestered carbon dioxide more largely because its two amine groups cooperated for the formation of the 1 : 1 adduct. The amount of sequestered carbon dioxide by the removers with one primary amine group will be less because two molecules are needed to capture one carbon dioxide molecule. Although the molecular weight of MEA is

much smaller than mXD, the amount of sequestered carbon dioxide was small by MEA because MEA contains only one amine group. The most important merit of mXD as a sequestration material is its ability to capture carbon dioxide even at ambient temperatures under very low concentration forming a stable solid. The amount of adsorbed carbon dioxide on mXD incorporated on silica, mXD/silica, 69 mg g_{adsorbent}⁻¹, was slightly smaller than PEI/KIT-6, which had the largest amount of adsorbed carbon dioxide, 80 mg g_{adsorbent}⁻¹. The adsorption capacity of the mXD/silica decreased with repeated use, and thus its feasibility as an adsorbent of carbon dioxide may be low. However, easy removal of carbon dioxide by simple evacuation at 25 °C is an advantage, because the regeneration of other solid adsorbents required elevated temperatures.

CONCLUSIONS

m-Xylylenediamine (mXD) reacted with carbon dioxide at 15–55 °C and formed a crystalline adduct even under low concentration of carbon dioxide in the atmosphere. One proton of one amine group shifted to another amine group in the reaction and formed the 1 : 1 adducts, which was found as a stable zwitterion. The hydrogen bonds among the adduct molecules constituted a stable crystal structure. The sequestration capacity of mXD to carbon dioxide was great, that of 275–280 mg g_{mXD}⁻¹, which corresponded to about 90% of the theoretical capacity of mXD. The two amine groups of mXD with high basicity maximized the sequestration capacity and produced the stable solid. The mXD dispersed on silica acted as an adsorbent of carbon dioxide and could be regenerated under simple evacuation. A small portion of liquid-state mXD dispersed on silica produced a crystalline mXD:CO₂ adduct and lowered the adsorption capacity.

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REFERENCES

1. M. F. Akorede, H. Hizam, M. Z. A. Ab Kadir, I. Aris and S. D. Buda, *Renew. Sust. Energy Rev.*, **16**, 2747 (2012).

Table 4. Amount of CO₂ absorption/adsorption of removers

Remover	Temperature (°C)	CO ₂ pressure (atm)	Amount of CO ₂ removal (mg g _{remover} ⁻¹)	References
mXD	25	1	280	This study
mXD (22 wt%)/silica	25	1	69	This study
MEA	25	1	170	[25]
MEA (50 wt%)/MCM-41	40	1	57.1	[24]
PEI	25	1	79	[11]
PEI (50 wt%)/KIT-6	75	1	135	[11]
Jeffamine (EDR-148)	45	1	150	[13]
Zeolite (Natural)	25	1	35.2	[2]

2. S. Choi, J. H. Drese and C. W. Jones, *ChemSusChem*, **2**, 796 (2009).
3. B. Beck, J. Garrett, I. Havercroft, D. Wagner and P. Zakkour, *Energy Procedia*, **4**, 5933 (2011).
4. J. Lipponen, K. Bumard, B. Beck, J. Gale and B. Pegler, *Energy Procedia*, **4**, 5752 (2011).
5. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, **112**, 724 (2012).
6. C. A. Scholes, S. E. Kentish and G. W. Stevens, *Recent Pat. Chem. Eng.*, **1**, 52 (2008).
7. T. Jockenhoevel, R. Schneider and H. Rode, *Energy Procedia*, **1**, 1043 (2009).
8. A. Samanta, A. Zhao, G. K. H. Shimizu, P. Sarkar and R. Gupta, *Ind. Eng. Chem. Res.*, **51**, 1438 (2012).
9. C. F. Song, Y. Kitamura and S. H. Li, *Appl. Energy*, **98**, 491 (2012).
10. Y. Cho, S.-C. Nam, Y.-I. Yoon, S. Moon and I. H. Baek, *Appl. Chem. Eng.*, **21**, 195 (2010).
11. W.-J. Son, J.-S. Choi and W.-S. Ahn, *Micropor. Mesopor. Mater.*, **113**, 31 (2008).
12. A. L. Chaffee, G. P. Knowles, Z. Liang, J. Zhang, P. Xiao and P. A. Webley, *Int. J. Greenhouse Gas Con.*, **1**, 11 (2007).
13. O. M. Al-Azzawi, C. M. Hofmann, G. A. Baker and S. N. Baker, *J. Colloid Inter. Sci.*, **385**, 154 (2012).
14. Y. Zhao, Y. Shen and L. Bai, *J. Colloid Inter. Sci.*, **379**, 94 (2012).
15. C. Wu, J. Wang, P. Chang, H. Cheng, Y. Yu, Z. Wu, D. Dong and F. Zhao, *Phys. Chem. Chem. Phys.*, **14**, 464 (2012).
16. S. Midatera and Y. Kanda, *Japan Patent*, 2005-272535 (2005).
17. B. Sylvain, D. Bruno, C. P. Louis, J. Marc, M. Sandrine and M. Regis, *French Patent*, 2957268 (2010).
18. J. S. Jung, J. W. Park and G. Seo, *Appl. Catal. A*, **288**, 149 (2005).
19. *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT (2009).
20. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, **120**, 215 (2008).
21. Y. Zhao and D. G. Truhlar, *Accounts Chem. Res.*, **41**, 157 (2008).
22. S. E. Wheeler and K. N. Houk, *J. Chem. Theory Comput.*, **6**, 395 (2010).
23. B. K. Rao, P. Jena, S. Burkart, G. Ganteför and G. Seifert, *Phys. Rev. Lett.*, **86**, 692 (2001).
24. D. L. Pavia, G. M. Lampman, G. S. Kriz and J. A. Vyvyan, *Introduction to Spectroscopy*, 4th Ed., Cengage Learning, Canada (2010).
25. Y.-W. Park, I.-H. Baek, S.-D. Park, J.-W. Lee and S.-J. Park, *Korean J. Chem. Eng. Res.*, **45**, 573 (2007).
26. T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong and J. R. Long, *J. Am. Chem. Soc.*, **134**, 7056 (2012).