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Low- and High-Temperature Solid Sorbents for Carbon Capture and Storage (CCS)

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Low- and High-Temperature Solid Sorbents for Carbon Capture and Storage (CCS)

A thesis/dissertation submitted to the Graduate School of UNIST in partial fulfillment of the requirements for the degree of Master of Science

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07. 14. 2015

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Abstract

Increasing concentration of carbon dioxide (CO$_2$), one of greenhouse gases (GHGs), results in accelerating global warming. The development of carbon capture and storage or sequestration (CCS) technologies came to the fore to alleviate this environmental issue. In order to capture CO$_2$, post-combustion techniques have been focused due to their competitive price and practical applicability. Recently, solid sorbents for CO$_2$ capture have been studied because they have a wide operating temperature from ambient temperature to high temperature (700 - 800 °C). According to the working temperature of the flue gases to apply, the solid sorbents can be categorized as low-temperature (< 200 °C), intermediate-temperature (200 - 400 °C) and high-temperature (> 400 °C) sorbents.

Herein, amine-functionalized metal-organic framework (MOF) is introduced as one of the low-temperature adsorbents. Amine functionalization of their pore surfaces has been studied extensively to enhance the CO$_2$ uptake of MOFs and amine-functionalized MOFs have been synthesized via post-synthetic modifications in general. In this thesis, a one-step construction of a MOF ([NiL$_{ethylamine}$](BPDC)) = MOF$_{NH2}$; [NiL$_{ethylamine}$]$^{2+}$ = [Ni(C$_{12}$H$_{32}$N$_8$)]$^{2+}$; BPDC$^{2-}$ = 4,4’-biphenyldicarboxylate) possessing covalently tethered alkylamine groups without post-synthetic modification was introduced. In order to investigate the effect of amino groups for CO$_2$, an isostructural MOF with propyl pendant chain ([NiL$_{propyl}$](BPDC)) = MOF$_{CH3}$; [NiL$_{propyl}$]$^{2+}$ = [Ni(C$_{14}$H$_{34}$N$_6$)]$^{2+}$ was provided. Unlike MOF$_{CH3}$ showing decrease CO$_2$ uptake as increasing temperatures, MOF$_{NH2}$ showed enhanced CO$_2$ uptake at elevated temperatures, attributed to active chemical interactions between the amine groups and the CO$_2$ molecules. Due to the narrow channels of MOF$_{NH2}$, the accessibility to the channel of CO$_2$ is the limiting factor in its sorption behavior and only crystal size reduction of MOF$_{NH2}$ led to much faster and greater CO$_2$ uptake at low pressures. The chemical interaction between the primary amine chains tethered to the macrocyclic complex and CO$_2$ molecules resulted in the formation of ammonium carbamate, which was reversibly dissociated at mild temperatures, 100 °C, by releasing CO$_2$ molecules. MOF$_{NH2}$ was found to be one of low-temperature adsorbents with good stability over repeated cycling.

In addition, lithium orthosilicate (Li$_4$SiO$_4$) is studied as one of high-temperature absorbents. Among some high-temperature absorbents, Li$_4$SiO$_4$ is lighter and has excellent theoretical capacity (36.7 wt%). Above all, it operates at relatively lower regeneration temperature (~750 °C), which leads to active investigations in recent. Here, the optimal method for synthesizing pristine lithium orthosilicate (p-Li$_4$SiO$_4$) with excellent properties was found by changing various factors and the way to treat the precursors is important to have better sorption properties of p-Li$_4$SiO$_4$. Also, lithium metasilicate (Li$_2$SiO$_3$) and potassium carbonate (K$_2$CO$_3$) as additives can help to improve the sorption properties.
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### Nomenclatures

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<tr>
<th>Abbreviation</th>
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<tr>
<td>CCS</td>
<td>Carbon Capture and Storage or Sequestration</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-Organic Framework</td>
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<tr>
<td>OMS</td>
<td>Open metal site</td>
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<td>EA</td>
<td>Elemental analysis</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<td>Infrared</td>
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I. Introduction

Global warming is an environmental issue resulting in the extreme climate change and ocean acidification. One of the reasons for global warming is the rapidly increasing level of atmospheric carbon dioxide (CO₂) predominantly resulting from the combustion of fossil fuels in the power-plant.¹ Therefore, it is important to decrease the emission of CO₂, but it is expected that the concentration of CO₂ continue to increase until fossil fuels are replaced with alternative energy sources such as wind, hydroelectric, solar, and biomass and so on. Thus, Carbon Capture and Storage or Sequestration (CCS) technologies are essential for decreasing the concentration of CO₂ in the atmosphere. CCS is a series of techniques of capturing CO₂ from industries before releasing in the air and converting it into other materials or transporting and depositing CO₂ underground. CCS is composed of three steps; CO₂ capture, transport and storage. Among three steps, carbon dioxide capture is completed through three combustion methods, (1) pre-combustion capture, (2) post-combustion capture and (3) oxy-fuel combustion capture.²

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**Figure 1.1.** Three combustion methods of CO₂ capture. Post-, pre- and oxy-fuel combustion capture.³
As compared with other two methods, post-combustion capture can be retrofitted to already existing power plants and it can remove over 90% of CO₂ from the emitted flue gas. Therefore, post-combustion techniques (sorbents used for post-combustion) have been recently developed by focusing on improving performance of sorbents and developing the process. Post-combustion is classified into three categories: absorption by using scrubbing solutions, adsorption by using solid sorbents and membranes, which are used for capture and separation of CO₂ from the flue gas stream. Recently, the research on solid sorbents is being carried out as post-combustion technology among these three techniques, because solid sorbents can be operated by covering a wide range of temperature from ambient temperature to high temperature (700 °C). Therefore, solid sorbents can be classified by the operating temperature; low-temperature (< 200 °C), intermediate-temperature (200 - 400 °C) and high-temperature (> 400 °C) sorbents.

I.1 Low-temperature CO₂ adsorbents (< 200 °C)

Low-temperature CO₂ adsorbents is classified when their working temperature is below 200 °C. Low-temperature CO₂ These adsorbents are divided into two groups. One group is the materials adsorbing CO₂ by physical interaction and another is the materials adsorbing CO₂ by chemical interaction. The physisorbents are porous materials with nano-sized pore and their high surface area including MOF-based, zeolite-based, carbon-based, silica-based materials. However, their poor selectivity due to weak affinity leads to the introduction of amino functional group, which is one of strategies for improving selectivity and capacity. This is because amino groups are famous for interacting with CO₂ through the chemical bond formation between nitrogen of amino groups and carbon of CO₂, which leads to the formation of carbamates or carbamic acid and sometimes bicarbonate under water vapor.⁴,⁵ Therefore, many researches have been undertaken for amine-grafted materials and MOFs have great potential in this field.

MOFs are well-ordered coordination polymer constructed from metal-containing clusters and bridging organic linkers, which are a new class of porous materials. They can be designed and assembled to control the size and shape of pores by choosing the appropriate metal building blocks and organic linkers. Recently, metal-organic frameworks (MOFs) have received attention for gas separation and storage³ because of their controllable porosity. MOFs with large surface area have been used for CO₂ adsorption, but it has a problem that selectivity and capacity are not outstanding, so they are not fully applied at low pressure, especially < 0.15 bar. To improve this problem, amino groups, some polar groups including amines are introduced when synthesizing and modifying the MOFs. There are three representative methods for preparing amine-functionalized MOFs.
Figure 1.2. Schematic view for a series of Mg$_2$(dobpdc) and their N$_2$ isotherms. (a) Mg$_2$(dobpdc)$^7$ (b) mmen-Mg$_2$(dobpdc)$^7$ (c) en-Mg$_2$(dobpdc)$^5$.

Firstly, incorporating alkylamine into open metal sites (OMSs) of MOFs$^{5,7}$ can facilitate the CO$_2$ adsorption properties at low pressure. One amine group of the alkylamines coordinates with OMSs and the rest is exposed to the internal pore surfaces to capture CO$_2$ molecules. In 2012, McDonald et al.$^7$ investigated alkylamine-appended metal-organic framework, mmen-Mg$_2$(dobpdc) (mmen = $N,N'$-dimethylethylenediamine; dobpdc$^{4-}$ = 4,4'-dioxido-3,3'-biphenyldicarboxylate), by modifying Mg$_2$(dobpdc) without amine functional group. Mg$_2$(dobpdc) is an expanded version of MOF-74$^8$ and has a number of open metal sites.
After evacuating this MOF at 420 °C for 65 min, coordinated DEF molecules were removed and the open metal (Mg$^{2+}$) sites were revealed on the pore surface, resulting in Mg$_2$(dobpdc). Alkylamine, mmen, were grafted on the open metal sites by immersing in the mixture of hexane and mmen solution leading to the formation of mmen-Mg$_2$(dobpdc). Subsequently, Hong’s group constructed en-Mg$_2$(dobpdc)$^5$ by introducing the primary amine, en (ethylenediamine) to Mg$_2$(dobpdc), instead of mmen as the secondary amine. N$_2$ isotherms of these materials were collected and surface area decreased after grafting amine functional group (Figure 1.2.) because amine functional groups occupied the pore. Due to a large amount of amine taken up the pore, CO$_2$ uptake of Mg$_2$(dobpdc) is mostly larger than amine-grafted Mg$_2$(dobpdc). (Table 1.1.) However, mmen-Mg$_2$(dobpdc) adsorbed 2.0 mmol g$^{-1}$ of CO$_2$, which is 15 times larger than the CO$_2$ uptake of Mg$_2$(dobpdc) at 25 °C and 0.39 mbar of CO$_2$ concentration in the air. This result indicated that amine functional group efficiently enhanced the interaction with CO$_2$, especially at low pressure. CO$_2$ uptake of en-Mg$_2$(dobpdc) at 0.39 mbar is 2.83 mmol g$^{-1}$, which is the highest value among MOFs. Though similar behavior was found in the CO$_2$ isotherms of en-Mg$_2$(dobpdc) and mmen-Mg$_2$(dobpdc), en-Mg$_2$(dobpdc) had more outstanding adsorption capacity than mmen-Mg$_2$(dobpdc). Additionally, the CO$_2$ uptake decreased as the temperature increased. (Figure 1.3.)

Table 1.1. Surface area and CO$_2$ uptake of Mg$_2$(dobpdc), en-Mg$_2$(dobpdc), mmen-Mg$_2$(dobpdc).

<table>
<thead>
<tr>
<th>N$_2$ isotherm</th>
<th>CO$_2$ uptake ( mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface area (m$^2$ g$^{-1}$)</td>
</tr>
<tr>
<td>Mg$_2$(dobpdc)$^7$</td>
<td>3270</td>
</tr>
<tr>
<td>en- Mg$_2$(dobpdc)$^5$</td>
<td>1253</td>
</tr>
<tr>
<td>mmen- Mg$_2$(dobpdc)$^7$</td>
<td>70</td>
</tr>
</tbody>
</table>

At low pressure, the prominent steps are shown in the CO$_2$ isotherms (Figures 1.3.(a)-1 and (b)-1) and they interrupted with calculating isosteric heat ($Q_u$) of adsorption with commonly used Langmuir-Freundlich equation (Eq.1.1)) over the entire ranges. The steps occurred by the CO$_2$-triggered rearrangement of alkylamine groups with making interaction between neighboring amine groups in c-axis for reacting with CO$_2$,$^{12}$ which makes CO$_2$ adsorb at weak-interacted adsorption sites at low pressure. Therefore, dual-site Langmuir-Freundlich equation (Eq.1.1) and modified dual-site Langmuir-Freundlich equation (Eq.1.2) were used to fit the CO$_2$ curves before and after steps, respectively.
\[ q = \frac{q_{\text{sat},A} b_A}{1 + b_A p^{\alpha_A}} + \frac{q_{\text{sat},B} b_B}{1 + b_B p^{\alpha_B}} \] (Eq. 1.1)

\[ q = \frac{q_{\text{sat},A} b_A (p - p^*)^{\alpha_A}}{1 + b_A (p - p^*)^{\alpha_A}} + \frac{q_{\text{sat},B} b_B (p - p^*)^{\alpha_B}}{1 + b_B (p - p^*)^{\alpha_B}} + \frac{q_{\text{sat},C} b_C (p - p^*)^{\alpha_C}}{1 + b_C (p - p^*)^{\alpha_C}} \] (Eq. 1.2)

\[ (\ln p)_q = \left( \frac{q_{\text{sat}}}{R} \right) \left( \frac{1}{T} \right) + C \] (Eq. 1.3)

Figure 1.3. CO$_2$ adsorption isotherms ((a) mmen-Mg$_2$(dobpdc)$_7$ (b) en-Mg$_2$(dobpdc)$_5$) at various temperature.
After modeling the CO$_2$ curves, the isosteric heats of the adsorbents are calculated by using Clausius-Clapeyron equation (Eq.1.3.). The results are shown in Figure 1.4. and 1.5. Both adsorbents had small $Q_u$ at low coverage and isosteric heat of mmen-Mg$_2$(dobpdc) and en-Mg$_2$(dobpdc) increase up to -71 and -41 to -51 kJ mol$^{-1}$, respectively, in the normal range of the chemical adsorption.

Additionally, adsorption-desorption cyclic performance of both adsorbents was tested under simulated air and flue gas flow. Under simulated air, mmen-Mg$_2$(dobpdc) adsorbed 4.4 wt% of CO$_2$ at 25 °C and fully desorbed at 150 °C under N$_2$ flow, while en-Mg$_2$(dobpdc) also adsorbed 11.8 wt% of CO$_2$ at 25 °C in accordance with its CO$_2$ isotherm and fully regenerated at 150 °C under simulated gas. When both adsorbents were exposed under simulated flue gas, mmen-Mg$_2$(dobpdc) adsorbed 9.9 wt% of CO$_2$ at 40 °C and the desorption was completed at 120 °C under N$_2$. In case of en-Mg$_2$(dobpdc), the CO$_2$ capacity is 14.6 wt% and it fully desorbed at 150 °C under Ar flow. The saturated CO$_2$ amount of en-Mg$_2$(dobpdc) increased 1.5 times relative to mmen-Mg$_2$(dobpdc), which is comparable to other porous materials.
The second method is the physical impregnation of poly-alkylamines into MOFs. Lin et al.\textsuperscript{9} prepared polyethyleneimine (PEI)-incorporated MIL-101 with different loadings (50, 75, 100, 125 wt%). As the loading amount of PEI increased, N\textsubscript{2} uptake, surface area and pore volume decreased significantly. For CO\textsubscript{2} adsorption isotherms, the sample of MIL-101 with 100 wt% PEI loading showed the best CO\textsubscript{2} adsorption property in spite of reduced surface area by 80% relative to MIL-101. With 100 wt% PEI loading, the CO\textsubscript{2} uptake is 4.2 mmol g\textsuperscript{-1} at 25 °C and 3.4 mmol g\textsuperscript{-1} at 50 °C at 0.15 bar and no decreased CO\textsubscript{2} uptake even under moisture, showing the water stability of the adsorbents. In addition, PEI incorporated MOF had excellent adsorption kinetics and selectivity for CO\textsubscript{2} over N\textsubscript{2} under the flue gas condition (15% CO\textsubscript{2} 75% N\textsubscript{2}). The selectivity for CO\textsubscript{2} over N\textsubscript{2} is 770 at 25 °C and 1200 at 50 °C, which indicated that the introduction of amine enhanced CO\textsubscript{2} adsorption properties.
Lastly, the organic ligands with covalently grafted amine groups onto the aromatic rings are utilized to prepare amine-functionalized MOFs. Xiang et al.\textsuperscript{10} provided three isostructural MOFs with different polar functional groups. They prepared MOF-A without any functional group (UMCM-1), MOF-B with amine functional group (UMCM-1-NH\textsubscript{2}) and MOF-C with free acid functional group (UMCM-1-NH\textsubscript{2}-MA) and UMCM-1-NH\textsubscript{2}-MA was synthesized via post-modification on the basis of UMCM-1-NH\textsubscript{2}.

\textbf{Figure 1.9.} Schematic view for synthetic methods and post-modification process of three different MOF. (A = UMCM-1, B = UMCM-1-NH\textsubscript{2}, C = UMCM-1-NH\textsubscript{2}-MA, *MA = maleic anhydride).\textsuperscript{10}
Table 1.2. Results of N\textsubscript{2} isotherm and CO\textsubscript{2} uptake of MOF-A, MOF-B and MOF-C.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET SSA (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Pore size (Å)</th>
<th>Pore volume (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>CO\textsubscript{2} uptake (mg g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4092</td>
<td>13.6, 27.3</td>
<td>2.15</td>
<td>696</td>
</tr>
<tr>
<td>B</td>
<td>4064</td>
<td>13.6, 27.3</td>
<td>2.11</td>
<td>869</td>
</tr>
<tr>
<td>C</td>
<td>3887</td>
<td>13.6, 25.2</td>
<td>1.82</td>
<td>651</td>
</tr>
</tbody>
</table>

With those samples, they examined the effects of functional groups on CO\textsubscript{2} capture based on experimental result and calculations. As the length of functional groups is longer, BET surface area, pore size and pore volume decreases, which can confirm the success of introducing the functional group. Based on the CO\textsubscript{2} adsorption isotherms collected at 25 °C up to 18 bar, the MOF-B with amine functional group show the highest CO\textsubscript{2} uptake (869 mg g\textsuperscript{-1}), which proves that the amine enhanced the CO\textsubscript{2} adsorption property. Contrary to the expectation based on the CO\textsubscript{2} adsorption isotherms, calculated isosteric heats (\(Q_{st}\)) of adsorption shows that MOF-C has the highest \(Q_{st}\), which leads to adsorb CO\textsubscript{2} more efficiently than MOF-B at very low pressure. (Figure 1.10.) These experimental results were supported by the first-principle calculation theoretically to compare the binding energy between the adsorption sites and CO\textsubscript{2}. The binding energy of polar acidic functional group are larger than that of amino functional group with benzene rings, which agrees with the previous reports.\textsuperscript{9,11} As a result, it is efficient to use covalent grafting on the organic building blocks to prepare stable amine-functionalized solid adsorbents. However, aromatic amine groups do not interact strongly with CO\textsubscript{2} due to the electron withdrawing effect of benzene rings.

Figure 1.10. (a) CO\textsubscript{2} adsorption isotherms of at 25 °C and P < 18 bar. Insert graph refers to the enlargement of the CO\textsubscript{2} adsorption isotherms at P < 0.3 bar range. (b) Calculated isosteric heat (\(Q_{st}\)) of adsorption at 25 °C.\textsuperscript{10}
Figure 1.11. The calculated binding energy (B.E.) of three different building blocks from (a) MOF-A (b) MOF-B (c) MOF-C. The measured distances are presented in angstroms, and the measured angle is presented in degrees. (C, dark cyan; O, red; H, white; and N, blue).10

In summary, preparation to amine-functionalized MOFs is usually adopted to post-synthetic modification, which are: (1) Coordination of alkylamine to open-metal sites (OMSs) generated by the activation of as-synthesized MOFs results from coordinating one amine group of the alkylamine molecules to OMSs and the rest is exposed to the internal pore surfaces to capture CO₂ molecules. (2) Physical impregnation of poly-alkylamines like polyethyleneimine (PEI) into pore-activated MOFs introduces active amine groups to the pore surfaces. (3) Covalently grafted amine groups to the aromatic organic ligands of MOFs interact with CO₂. These synthetic methods allow the MOFs to enhance CO₂ uptake behavior. However, they have some major disadvantages. The construction and activation of MOFs and incorporation of amine moieties are quite long and complicated. Moreover, the synthesis of robust MOFs that retain their structures even after OMS generation is challenging. Leaching of the impregnated poly-alkylamines during multiple regeneration cycles is another serious problem in their practical utilization. Covalent grafting on the organic building blocks is very efficient in achieving stable amine-functionalized solid adsorbents. However, aromatic amine groups do not interact strongly with CO₂ due to the electron withdrawing effect of benzene rings. Therefore, herein I suggested a covalently alkylamine-tethered MOF constructed by a one-step self-assembly method without post-modification and investigated the effect of amine by comparing the isostructural MOF with propyl chains instead of amine.
I.2 High-temperature CO₂ absorbents (< 400 °C)

Working temperature of CO₂ sorbents is above 400 °C, which is classified as high-temperature CO₂ absorbents. CaO and alkali ceramics are well-known high-temperature CO₂ absorbents.

**Calcium Oxide (CaO)**

Firstly, CaO-based absorbents are good candidates for capturing CO₂ because of their high reactivity with CO₂ and high theoretical sorption capacity and low cost of material. The reaction between CaO and CO₂ is reversible, which is shown in reaction (1.4) and temperature range of absorption (carbonation) is 600-700 °C and that of regeneration is above 950 °C.\(^{14-18}\)

\[
\text{CaO (s) + CO}_2 (g) \rightleftharpoons \text{CaCO}_3 (s) \quad (1.4)
\]

The CO₂ capture by CaO takes place in two steps. The first step is a rapid and kinetically-controlled reaction by absorbing CO₂ chemically on the surface of the absorbent. The second step is a transition controlled by slow diffusion of CO₂ into the bulk of the absorbent.\(^{19}\) Regeneration of absorbent occurs much faster and is completed in minutes.

There is a critical problem for this materials, which is poor reversibility due to the sintering of the absorbents attributed to three major reasons: the absorption is highly exothermic, the volume changes significantly from CaO (16.9 cm³ mol⁻¹) to CaCO₃ (34.1 cm³ mol⁻¹), and Tammann temperature of CaCO₃ (533 °C) is lower than the temperature of absorption.\(^{20-23}\) Lysikov et al.\(^{24}\) provided a mechanism of textural transformation of the absorbent in recarbonation (absorption)-decomposition (regeneration) cycles (Figure 1.12.). The first decomposition of the calcium carbonate makes the CaO particles shrink resulting in highly reactive and nanosized particles that are well dispersed. The following recarbonation is incomplete due to the pore blocking and the diffusion-controlled reaction with CO₂ slowly during carbonation.\(^{18}\) The amount of unreacted CaO increases resulting in large particle size from cycle to cycle until preventing the sintering of the absorbent by forming a rigid interconnected CaO skeleton. This rigid backbone is less reactive absorbent relative to the highly dispersed CaO. There are some other restrictions to such processes related to the kinetics and thermodynamics of the reactions, along with undesirable side reactions such as sulfation and processes such as attrition. In order to improve the sintering properties of this absorbent, numerous efforts have been devoted including improvement of synthetic method, surface modification, transformation of morphology and incorporation of other materials\(^{23}\), and so on.
Lithium zirconate (Li$_2$ZrO$_3$)

Li$_2$ZrO$_3$ is another material for high-temperature CO$_2$ absorbents due to excellent CO$_2$ sorption capacity (28 wt%) and a small volume change during absorption and regeneration. Nakagawa and Ohashi published the CO$_2$ sorption ability of Li$_2$ZrO$_3$ which has been studied as an additive for MCFC (molten carbonate fuel cell) for the first time. Li$_2$ZrO$_3$ reacts with CO$_2$ at 400-600 °C, which is described in (1.5) and the regeneration happens at 750-800 °C.

$$\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \rightleftharpoons \text{Li}_2\text{CO}_3 + \text{ZrO}_2$$  \hspace{1cm} (1.5)

Ida et al. proposed reaction mechanism (Figure 1.13.) occurring due to the lithium mobility in the absorbents. During the absorption of CO$_2$, the lithium ions diffuse from the core to the surface and react with CO$_2$ resulting in the formation of Li$_2$CO$_3$, and then, CO$_2$ diffuse through the solid Li$_2$CO$_3$ to react with Li$_2$ZrO$_3$ located at the core, which is the rate limiting step. They also introduced K$_2$CO$_3$, which was formed as liquid phase by reacting to Li$_2$CO$_3$ resulting in improvement of CO$_2$ sorption property. (Figure 1. 13) Despite this potentially advantages, it is difficult to use practically (for practical application) due to its kinetic limitation. Various efforts have been undertaken to improve its ability, which are controlling particle size or crystal phase and substituting Li$^+$ by other alkali ion (Na$^+$, K$^+$) leading to transform the structure.
Figure 1.13. Schematic illustration of (a) CO₂ absorption (carbonation) and (b) CO₂ desorption process for pure and modified Li₂ZrO₃.

Lithium orthosilicate (Li₄SiO₄)

Recently, a series of alkali silicates have been studied as high-temperature CO₂ absorbents. Among many kinds of alkali silicates, Li₄SiO₄ have received attention as a promising sorbents because of some advantages. Firstly, Li₄SiO₄ is lighter and composed of much cheaper raw materials (SiO₂) than Li₂ZrO₃, therefore it has a competitive price when used in real process. It has excellent theoretical CO₂ capacity (36.7 wt%) when the absorbents fully reacts with CO₂. The reaction between the absorbent and CO₂ is shown in (1.6).

\[
\text{Li}_4\text{SiO}_4 (s) + \text{CO}_2 (g) \rightleftharpoons \text{Li}_2\text{CO}_3 (s) + \text{Li}_2\text{SiO}_3 (s)
\] (1.6)

Li₄SiO₄ reacts with CO₂ at near 450-500 °C and the absorbents regenerate at below 750 °C which is lower regeneration temperature relative to other high-temperature CO₂ absorbents like CaO. The changes of Gibbs free energy (ΔG) for absorption-regeneration (emission) of Li₄SiO₄ and CaO are calculated based on thermodynamic data and the result are shown in Figure 1.14. The calculated
equilibrium temperature ($\Delta G=0$) for two absorbents have difference of approximately 200 °C. In reality, the regeneration temperature of Li$_4$SiO$_4$ is near 800 °C, while the regeneration of CaO takes place at approximately 950 °C under pure CO$_2$ at 1 atm. Li$_4$SiO$_4$ also has good CO$_2$ absorption rate, which depends on the temperature and concentration of CO$_2$. Kato et al. showed that the rate of Li$_4$SiO$_4$ is 30 times faster than that of Li$_2$ZrO$_3$. (Figure 1.15.)

![Figure 1.14. Gibbs free energy changes for Li$_4$SiO$_4$ and CaO.](image)

![Figure 1.15. Thermogravimetric curves for Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ obtained at 500 °C in (a) 20% CO$_2$ and (b) 2% CO$_2$.](image)
Some literature proposed the mechanism for the CO2 sorption/desorption process on Li4SiO4. Kato et al.\textsuperscript{33} and Essaki et al.\textsuperscript{34} suggested double-shell mechanism appropriate for adsorbing and desorbing CO2 process on Li4SiO4, which did not analyze the kinetic behaviors of the proposed mechanism. Qi et al.\textsuperscript{35} compared three kinetic models, the shrinking core model, the double exponential model and Avrami-Erofeev model, to investigate the CO2 absorption process. They concluded the Avrami-Erofeev model was suitable for explaining the process within a wide range of temperature. Therefore, they applied the kinetic model to describe the mechanism of the CO2 absorption and desorption process on Li4SiO4. More specifically, the Avrami-Erofeev model is related to the reaction mechanism for the crystal formation and growth, so it is usually applied to the materials having high crystalline structures. This model is established on the model (Eq. 1.7) for gas-solid reactions

\[
\frac{da}{dt} = KF(\alpha) \tag{Eq.1.7}
\]

where
\[
F(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{(n-1)/n} \tag{Eq.1.8}
\]

(\(\alpha\) : degree of conversion, \(K\) : kinetic constant, \(n\) : kinetic parameter, \(t\) : time)

The kinetic constant, \(K\), depends on the temperature and is expressed by the following Arrhenius equation (1.9).

\[
K = K_0\exp[-E/R(1/T - 1/T_0)] \tag{Eq.1.9}
\]

When \(k = K^n\), substituting (Eq. 1.8) in to (Eq. 1.7) leads to (Eq. 1.10).

\[
\ln(-\ln(1 - \alpha)) = \ln k + n \ln t \tag{Eq.1.10}
\]

The magnitude of \(n\) is related to the reaction rate depending on the rate of the formation and growth of the crystals when \(n > 1\) and the diffusion control when \(n\) is about 0.5.\textsuperscript{36}

Associating this kinetic model and double-shell mechanism, the process of CO2 absorption on Li4SiO4 can be explained in detail. The mechanism of CO2 absorption is described as following procedure. (Figure 1.16)

1. CO2 reacts Li4SiO4 on the surface leading to the formation of Li2CO3 and Li2SiO3 nuclei. In this step, the reaction rate depends on the rate of the formation of nuclei, which is very short.
2. Li$_2$SiO$_3$ nuclei starts to grow and cover the unreacted Li$_4$SiO$_4$ while Li$_2$CO$_3$ nuclei also starts to grow and cover the Li$_2$SiO$_3$ shell, resulting in the formation of double-shell. Li$^+$ and O$_{2^-}$ from the unreacted Li$_4$SiO$_4$ diffuse through the Li$_2$SiO$_3$ shell and CO$_2$ diffuse through the Li$_2$CO$_3$ shell, and then the reaction continue to take place. In this step, the diffusion starts to occur, but the reaction rate still depends on the rate of the formation of nuclei.

3. As the reaction progresses, the shell thickness of Li$_2$CO$_3$ and Li$_2$SiO$_3$ increases and the reaction rate becomes slower because it is difficult for Li$^+$, O$_{2^-}$ and CO$_2$ to diffuse through the thick shell. Therefore, the reaction rate starts to be controlled by the diffusion in this step.

Figure 1.16. Scheme of double-shell mechanism for the CO$_2$ absorption/desorption process on Li$_4$SiO$_4$.\textsuperscript{35}
As a result, the CO₂ absorption depends on the chemical reaction rate until based on the double-shell mechanism and the kinetic model. In additional, the CO₂ absorption of Li₄SiO₄ was controlled by chemical reaction rate, which is dominated until the absorbents were converted up to 84.23%. It was also found that the kinetics depends on the temperature and it becomes slow when the temperature is lower than 650 °C. Therefore, authors advised that the future work should be done to improve the sorption behavior by adding hetero elements to Li₄SiO₄, which helps to design a regeneration reactor and improve in the rapid reaction step.

To improve the CO₂ absorption properties of Li₄SiO₄, several efforts have been made including introduction of alkali carbonate, metal doping, which mentioned above, and microstructural modification, likewise other absorbents. Seggiani et al.³¹,³⁷ and Puccini et al. ³⁸ introduced various alkali carbonates. Each alkali carbonate (K₂CO₃, Na₂CO₃), binary (K₂CO₃/Li₂CO₃, Na₂CO₃/Li₂CO₃) and ternary (K₂CO₃/Na₂CO₃/ Li₂CO₃) eutectic mixtures were added to Li₄SiO₄ and all the additives enhanced the CO₂ absorption rate and capacity.³¹

Table 1.3. Composition and melting point of binary and ternary eutectic mixtures.

<table>
<thead>
<tr>
<th>Composition of eutectic mixture (mol%)</th>
<th>Melting point (°C)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃ (57.3%)/Li₂CO₃ (42.7%)</td>
<td>498</td>
</tr>
<tr>
<td>Na₂CO₃ (48%)/Li₂CO₃ (52%)</td>
<td>500</td>
</tr>
<tr>
<td>K₂CO₃ (26.8%)/Na₂CO₃ (30.6%)/Li₂CO₃ (42.5%)</td>
<td>393</td>
</tr>
</tbody>
</table>

¹ Data from NSRDS (1978).

As a result of this paper, Li₄SiO₄ with 30 wt% K₂CO₃ or Na₂CO₃ showed the best performance with capacity of 5.2 mmol g⁻¹ sorbent at 580 °C under 4 vol% CO₂. (theoretical capacity of Li₄SiO₄ with 30 wt% additive : 5.8 mmol g⁻¹ sorbent and theoretical capacity of Li₄SiO₄ without any additive : 8.3 mmol g⁻¹ sorbent)¹ Moreover, the cyclic stability of these samples was confirmed through a series of 25 CO₂ absorption/regeneration cycles. (Figure 1.17.) They absorption was carried out under 4 vol% in N₂ at 580 °C for 60 min and the absorbents regenerated under pure N₂ at 700 °C for 15 min. Unlike Li₄SiO₄ with 30 wt% K₂CO₃, the sorption capacity of the absorbent with 30 wt% Na₂CO₃ decreased within 6th cycle and maintained. They explained this phenomena with the SEM images before and after cycles. In SEM images, Li₄SiO₄ with 30 wt% Na₂CO₃, aggregated leading to change morphology significantly, which supported by the Li₂CO₃-Na₂CO₃ phase diagram. Li₂CO₃-Na₂CO₃ phase diagram shows that only solid phase was existed in the end of the regeneration, resulting in more dense structures during the cycles while Li₄SiO₄ with 30 wt% K₂CO₃ had partially liquid phase at the end of the regeneration.
Figure 1.17. 4 vol% CO$_2$ isotherms at 580 °C of (a) $p$-Li$_4$SiO$_4$, K-Li$_4$SiO$_4$ and LiK-Li$_4$SiO$_4$ (b) Na-Li$_4$SiO$_4$ and LiNa-Li$_4$SiO$_4$ (c) LiNaK-Li$_4$SiO$_4$.

Figure 1.18. Multiple cycles of CO$_2$ sorption (30 min at 580 °C in 4 vol.% CO$_2$) and desorption (15 min at 700 °C in pure N$_2$) on the (a) K3 and (b) Na3 samples.
II. Experimental Section

Materials and Methods. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. 4,4-biphenyldicarboxylic acid (H₂BPDC), >97% were purchased from TCI and fumed silica, lithium hydroxide monohydrate (LiOH·H₂O), lithium carbonate (Li₂CO₃), and tetraethyl orthosilicate (TEOS) were purchased from Sigma Aldrich. ([Ni₄ethylamine](ClO₄)₂) and ([Ni₄propyl](ClO₄)₂) were prepared by a reported method with minor modifications. Infrared spectra were measured on a Thermo Fisher Scientific Nicolet 6700 FT-IR spectrometer. Thermogravimetric analyses (TGA) were performed under N₂(g) atmosphere at a scan rate of 5 °C/min and under pure CO₂ at a scan rate of 1 °C/min using Q50 from TA instruments. XRPD data were collected using a Bruker D2 PHASER automated diffractometer at 30 kV and 10 mA for Cu Kα (λ = 1.54050 Å), with a step size of 0.02° in 2θ. Scanning electron microscope (SEM) images were taken using a Quanta 200 microscope (FEI) operating at 18 kV. The gas sorption data were collected by using a BELsorp-MAX. UV/Vis diffuse reflectance spectra were recorded with a Cary 5000 UV/Vis spectrophotometer. Elemental analyses were conducted by UNIST Central Research Facilities center (UCRF) in Ulsan National Institute of Science and Technology (UNIST).

Syntheses

[Ni(C₁₂H₂₃N₃)](ClO₄)₂ ([Ni₄ethylamine](ClO₄)₂). ([Ni₄ethylamine](ClO₄)₂) was prepared by minor modifications of the previously reported method. Ni(OAc)₂·4H₂O (9.0 g, 0.04 mol) was dissolved in MeOH (50 mL) and placed in an ice-bath. Then, 99% ethylenediamine (13.5 mL, 0.20 mol) was added to it in drops with stirring. Paraformaldehyde (6.1 g, 0.20 mol) was then added and dissolved with stirring at room temperature. Then, the solution was refluxed for 12 h. After 12 h reaction, the solution was placed in an ice-bath and 70% HClO₄ was added very slowly to adjust pH 5–6 with stirring, and excess amount of NaClO₄ (ca. 2 g) was dissolved to the solution. The mixture solution was kept in room temperature over 1 week until the yellow powder was fully precipitated. The yellow powders was filtered and reduced by triethylamine (TEA) in distilled acetonitrile (MeCN). The final product was filtered and dried under vacuum. Yield: ~ 23 %. FT-IR (KBr, ν max/cm⁻¹): 3304 and 3225 (NH), 1093 (ClO₄⁻); UV/Vis (diffuse reflectance spectrum, λ max): 450 nm; Elemental analysis calc. for Ni₄C₁₂H₂₃N₃O₈Cl₂: C, 26.40; H, 5.91; N, 20.52. Found: C, 26.73; H, 5.89; N, 20.46%.

Figure 2.1. [Ni₄ethylamine](ClO₄)₂.
[Ni(C$_{14}$H$_{34}$N$_6$)][(ClO$_4$)$_2$] ($[\text{NiL}_{\text{propyl}}](\text{ClO}_4)_2$). $[\text{NiL}_{\text{propyl}}](\text{ClO}_4)_2$ was prepared by the reported methods with a little modification.$^{40}$ NiCl$_2$·6H$_2$O (23.7 g, 0.10 mol) was dissolved in MeOH (100 mL) placed in an ice-bath, and 99% ethylenediamine (13.6 mL, 0.20 mol) was added to it in drops with stirring. Paraformaldehyde (15.0 g, 0.50 mol) and propylamine (14.8 mL, 0.20 mol) were then added at room temperature, with stirring slowly. The remaining paraformaldehyde was dissolved by heating and the solution was refluxed for 12 h. The dark green solution was filtered under hot to remove by-products such as nickel hydroxide, and the filtrate was placed in an ice-bath. Then, 10 mL of 70% HClO$_4$ was added very slowly with stirring and NaClO$_4$ (4.2 g) was added. Then yellow solid product was formed, which were filtered off, washed with MeOH, and dried under vacuum. Yield: 21.5%.

Recrystallization: It was recrystallized from MeCN/H$_2$O mixture by heating. Then, orange-yellow crystalline product was formed, filtered, washed with MeOH, and dried under vacuum condition. Yield: 41.5%. FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$): 3206 (NH), 1117 (ClO$_4^-$); UV/Vis (diffuse reflectance spectrum, $\lambda_{\text{max}}$): 454 nm; Elemental analysis calc. for Ni$_3$C$_{14}$H$_{34}$N$_6$O$_8$Cl$_2$: C, 30.91; H, 6.30; N, 15.44. Found: C, 30.74; H, 6.27; N, 15.67%.

![Figure 2.2. $[\text{NiL}_{\text{propyl}}](\text{ClO}_4)_2$.](image)

4,4'-Biphenyldicarboxylate sodium salts (Na$_2$BPDC). The aqueous solution (7 mL) of NaOH was added to the stirred aqueous suspension (25 mL) of 4,4'-biphenyldicarboxylic acid (H$_2$BPDC) (2.42 g, 0.01 mol) at room temperature. After the reaction was completed, the small amount of solid was filtered by syringe filters. To help further precipitation of products, 20 mL of ethanol (EthOH) was put into the solution and the solution was kept in refrigerator more than 3 hours. The white powder was filtered, washed with EthOH, and dried in air. Yield: ~71.0%. FT-IR (ATR, $\nu_{\text{max}}$/cm$^{-1}$): 1578(s), 1394(s) (O–C=O(carboxylate)); Elemental analysis calc. for Na$_2$C$_{14}$H$_8$O$_{4}$: C, 58.76; H, 2.82%. Found: C, 57.48; H, 2.84%.

![Figure 2.3. Na$_2$BPDC.](image)
{{[Ni\textsubscript{(ethyamine)})(BPDC)\cdot3H\textsubscript{2}O}} (MOF\textsubscript{NH\textsubscript{2}-as}).  
{[Ni\textsubscript{(ethyamine)}](ClO\textsubscript{4})\textsubscript{2}} (0.04 g, 0.07 mmol) and Na\textsubscript{2}BPDC (0.02 g, 0.07 mmol) were dissolved in 4 mL of N,N-diethylformamide (DEF) and in mixed solution of acetonitrile (MeCN) and H\textsubscript{2}O (MeCN:H\textsubscript{2}O = 2 mL:1 mL), respectively. The solution of Na\textsubscript{2}BPDC was diffused onto the former solution of {[Ni\textsubscript{(ethyamine)}](ClO\textsubscript{4})\textsubscript{2}}. Powder was formed at the boundary of the layered solution. The stacked solution allowed to stand at room temperature for 1 day until the pale purple crystals were formed along with powder. Only crystals were used for analyses. Yield: 22.7 %. FT-IR (KBr, \nu\textsubscript{max}/cm\textsuperscript{-1}): 3363 and 3291 (NH), 3062 (CH), 1587 and 1379 (COO\textsuperscript{-}); UV-Vis (diffuse reflectance spectrum, \lambda\textsubscript{max}): 517 nm (Ni (II) d-d transition); Elemental analysis calc. for Ni\textsubscript{1}C\textsubscript{26}H\textsubscript{46}N\textsubscript{8}O\textsubscript{7}: C, 48.69; H, 7.23; N, 17.47. Found: C, 49.36; H, 7.10; N, 17.52%.

Preparation of MOF\textsubscript{NH\textsubscript{2}}:crystal and MOF\textsubscript{NH\textsubscript{2}}:powder.  The as-synthesized compounds MOF\textsubscript{NH\textsubscript{2}-as} was heated in round bottom flasks at 90 °C under vacuum for 7 h. Then, cooled the sample and refilled the gas with Ar. FT-IR (KBr, \nu\textsubscript{max}/cm\textsuperscript{-1}): 3368 and 3293 (NH), 3055 (CH), 1594 and 1376 (COO\textsuperscript{-}); UV-Vis (diffuse reflectance spectrum, \lambda\textsubscript{max}): 512 nm; Elemental analysis calc. for Ni\textsubscript{1}C\textsubscript{26}H\textsubscript{40}N\textsubscript{8}O\textsubscript{4}: C, 53.17; H, 6.86; N, 19.08. Found: C, 52.47; H, 6.91; N, 18.78%.

MOF\textsubscript{NH\textsubscript{2}}. The as-synthesized compounds MOF\textsubscript{NH\textsubscript{2}-as} was heated in round bottom flasks at 90 °C under vacuum for 7 h. Then, cooled the sample and refilled the gas with Ar. FT-IR (KBr, \nu\textsubscript{max}/cm\textsuperscript{-1}): 3363 and 3291 (NH), 3062 (CH), 1587 and 1379 (COO\textsuperscript{-}); UV-Vis (diffuse reflectance spectrum, \lambda\textsubscript{max}): 517 nm (Ni (II) d-d transition); Elemental analysis calc. for Ni\textsubscript{1}C\textsubscript{26}H\textsubscript{46}N\textsubscript{8}O\textsubscript{7}: C, 48.69; H, 7.23; N, 17.47. Found: C, 49.36; H, 7.10; N, 17.52%.

Preparation of MOF\textsubscript{NH\textsubscript{2}-as}.  The as-synthesized compounds, MOF\textsubscript{NH\textsubscript{2}-as}, were heated at 90 °C under vacuum for 7 h, and then cooled to an ambient temperature and refilled with Ar (MOF\textsubscript{NH\textsubscript{2}-crystal}), which is same as MOF\textsubscript{NH\textsubscript{2}}. To prepare the powder samples (MOF\textsubscript{NH\textsubscript{2}}:powder), MOF\textsubscript{NH\textsubscript{2}-as} was pulverized for 10 s using a sample grinder with a stainless steel vial and ball (ShakIR sample grinder, PIKE), which is usually used for preparation of infrared spectroscopy samples. The resultant powder was also activated at 90 °C for 7 h, yielding MOF\textsubscript{NH\textsubscript{2}}:powder.

{{[Ni\textsubscript{(propyl)})(BPDC)\cdot2.5H\textsubscript{2}O}} (MOF\textsubscript{CH\textsubscript{3}-as}).  
{[Ni\textsubscript{(propyl)}](ClO\textsubscript{4})\textsubscript{2}} (0.02 g, 0.07 mmol) and Na\textsubscript{2}BPDC (0.01 g, 0.07 mmol) were dissolved in mixture solution of acetonitrile (MeCN) and H\textsubscript{2}O (MeCN:H\textsubscript{2}O = 0.5 mL : 0.5 mL) and 1 mL of H\textsubscript{2}O, respectively. The solution of {[Ni\textsubscript{(propyl)}](ClO\textsubscript{4})\textsubscript{2}} was diffused onto the latter solution. Pale purple crystals started to form immediately and the stacked solution allowed to stand at room temperature for 3 days until the solution was diffused completely. Yield: 89.0 %. FT-IR (KBr, \nu\textsubscript{max}/cm\textsuperscript{-1}): 3294 (NH), 3154 (CH), 1589 and 1543 (COO\textsuperscript{-}); UV-Vis (diffuse reflectance spectrum, \lambda\textsubscript{max}): 507 nm (Ni\textsuperscript{2+} d-d transition).
[(Ni₃-propyl)(BPDC)] (MOFCH₃). The as-synthesized compounds MOFCH₃-as was heated in round bottom flasks at 90 °C under vacuum for 7 h. Then, cooled the sample and refilled the gas with Ar. FT-IR (KBr, νmax/cm⁻¹): 3279 (NH), 3137 (CH), 1545 and 1370 (COO⁻); UV-Vis (diffuse reflectance spectrum, λmax): 510 nm.

**Pristine Li₄SiO₄** (p-Li₄SiO₄). LiOH·H₂O (0.29 g, 6.80 mmol) and fumed silica (0.10 g, 1.66 mmol) (Li:Si = 4.1:1) were put into a 20 mL vial and H₂O (10 mL) was added. The solution was sealed by cap and stirred at 45 °C until it becomes transparent. The temperature increased up to 65 °C and the solution was evaporated at 65 °C with stirring. After the solution was fully dried, the white powder was collected and calcined at 700 °C for 4h under N₂ flow (500 mL/min) in the tube furnace.

**Lithium ion deficiency-induced Li₄SiO₄.** Lithium ion deficiency-induced Li₄SiO₄ were prepared by controlling the ratio of precursors (LiOH·H₂O and fumed silica). LiOH·H₂O and fumed silica were prepared with different ratio (Li:Si = 4.0:1, Li:Si = 3.8:1, Li:Si = 3.6:1) and the precursors were put into a 20 mL vial and distilled H₂O (10 mL) was added. The solution was sealed by cap and stirred at 45 °C until it becomes transparent. The temperature increased up to 65 °C and the solution was evaporated at 65 °C with stirring. After the solution was fully dried, the white powder was collected and calcined at 700 °C for 4h under N₂ flow (500 mL/min) in the tube furnace.

**CO₂ absorption-induced Li₄SiO₄.** When p-Li₄SiO₄ was changed to 7.7 wt% Li₂SiO₃ resulted from absorbing 15% CO₂, introduction of 15% CO₂ was stopped leading to the Li₄SiO₄ with 7.7 wt% Li₂SiO₃ on the surface of the absorbent.

**Li₄SiO₄ physically mixed with 7.7 wt% of Li₂SiO₃.** p-Li₄SiO₄ and 7.7 wt% Li₂SiO₃ were put into stainless vial with stainless ball. After sealing this vial, the mixture was pulverizing for 10s, resulting in physically mixed Li₄SiO₄ with 7.7 wt% Li₂SiO₃.

**Li₂SiO₃ (Lithium metasilicate).** LiOH·H₂O (0.17 g, 4.0 mmol) was dispersed in methanol (5.0 mL) in a teflon autoclave. TEOS (0.42 mL, 2.0 mmol) was added to the mixture, which heated in muffle furnace at 180 °C for 24 h. After the solution was filtered, washed with MeOH and dried in air.
Li$_4$SiO$_4$ physically mixed with X wt% of K$_2$CO$_3$ (or Na$_2$CO$_3$). (X = 5, 10, 20, 30)

$p$-Li$_4$SiO$_4$ and X wt% K$_2$CO$_3$ (or Na$_2$CO$_3$) were put into stainless vial with stainless ball. After sealing this vial, the mixture was pulverizing for 10s, resulting in physically mixed Li$_4$SiO$_4$ with X wt% K$_2$CO$_3$ (or Na$_2$CO$_3$).

Li$_4$SiO$_4$ physically mixed with 10 wt% of K$_2$CO$_3$ and 7.7 wt% of Li$_2$SiO$_3$. (10K+7M)

$p$-Li$_4$SiO$_4$, 10 wt% K$_2$CO$_3$ and 7.7 wt% Li$_2$SiO$_3$ were put into stainless vial with stainless ball. After sealing this vial, the mixture was pulverizing for 10s, resulting in physically mixed Li$_4$SiO$_4$ with 10 wt% K$_2$CO$_3$ and 7.7 wt% Li$_2$SiO$_3$.

Li$_4$SiO$_4$ physically mixed with 3 wt% of K$_2$CO$_3$ and 3 wt% of Li$_2$SiO$_3$. (3K+3M)

$p$-Li$_4$SiO$_4$, 3 wt% K$_2$CO$_3$ and 3 wt% Li$_2$SiO$_3$ were put into stainless vial with stainless ball. After sealing this vial, the mixture was pulverizing for 10s, resulting in physically mixed Li$_4$SiO$_4$ with 3 wt% K$_2$CO$_3$ and 3 wt% Li$_2$SiO$_3$.

**Gas sorption measurement.** The gas sorption isotherms were measured by using BELsorp-MAX. To prepare the samples for gas sorption measurements, MOF$_{CH_3}$-as was added to the gas sorption apparatus, and was heated at 90 °C under vacuum for 7 h, resulting in MOF$_{CH_3}$. MOF$_{NH_2}$ (MOF$_{NH_2}$:crystal) and MOF$_{NH_2}$:powder were filled into the apparatus and heated at 120 °C for 1 h under vacuum. After that, the gas sorption was measured. The N$_2$ and H$_2$ gas sorption isotherms were collected at 77 K. In addition, CO$_2$ gas sorption isotherms of MOF$_{CH_3}$ were measured at 195, 273 and 298 K. CO$_2$ gas sorption isotherms of MOF$_{NH_2}$ (MOF$_{NH_2}$:crystal) and MOF$_{NH_2}$:powder were measured at 195, 273, 298, 323, 348 and 373 K and those were heated at 120 °C for 1h between the measurements.

**X-ray Powder Diffraction (XRPD) Analysis.** The XRPD data of MOF$_{CH_3}$-as, MOF$_{CH_3}$ were collected with Bruker D8 Advance at 40 kV and 40 mA with copper radiation (K$_{\alpha 1}$ = 1.5406 Å and K$_{\alpha 2}$ = 1.54439 Å). For the MOF$_{NH_2}$ related to experiments of thermal and water stability, the XRPD data were collected using a Bruker D2 PHASER automated diffractometer at 30 kV and 10 mA for Cu K$\alpha$ ($\lambda$ = 1.54050 Å), with a step size of 0.02° in 2θ. Samples were grinded finely by mortar and were put on low background sample holder. Data were recorded with 0.02° step. The scan rate of 0.2 s/step was applied for other measurements.
Synchrotron XRPD measurement. For MOF$_{\text{NH2-as}}$ and MOF$_{\text{NH2}}$, the XRPD patterns were measured at 100 K with synchrotron radiation ($\lambda = 1.20029$ and $1.20024$ Å, respectively). The mother liquor of MOF$_{\text{NH2-as}}$ crystals were decanted by filtration, and the resulting solids were finely ground and packed in capillary (diameter, 0.3 mm; wall thickness, 0.01 mm). To prepare the sample MOF$_{\text{NH2}}$, the filtered crystals of MOF$_{\text{NH2-as}}$ were dried at 90 °C under vacuum for 7 h, they were finely ground and packed in capillary under Ar atmosphere in glove box (diameter, 0.3 mm; wall thickness, 0.01 mm). The diffraction data were measured with transmission-mode as Debye-Scherrer Pattern with the 180 mm of sample-to-detector distance in 60 s exposure on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADX program 41 was used for data collection, and the Fit2D 42 program was used for conversion of integrated 2D to 1D patterns, for wavelength and detector distance refinement and for a calibration measurement of a NIST Si 640c standard sample.

Single-Crystal X-ray crystallography. Single-crystals were coated with paratone-$N$ oil because they lost their crystallinity upon exposure to the air. The diffraction data of MOF$_{\text{NH2-as}}$ measured using synchrotron employing a PLSII-2D SMC an ADSC Quantum-210 detector with a silicon (111) double crystal monochromator (DCM) at Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program 41 was used for both data collection, and HKL3000sm (Ver. 703r) 43 was used for cell refinement, reduction and absorption correction. The diffraction data of MOF$_{\text{CH3-as}}$ were collected at 173 K with Mo K$_\alpha$ radiation on an X-ray diffraction camera system using an imaging plate equipped with a graphite crystal incident beam monochromator. RapidAuto software 44 was used for data collection and data processing. The structures were solved using direct methods with SHELX-XS (Ver. 2013) and refined by full-matrix least-squares calculation with SHELX-XL (Ver. 2013) program package. 45 A summary of the crystals and some crystallographic data are given in Table 3.1, S1 - S2. CCDC 1044896 (MOF$_{\text{NH2-as}}$) contain the supplementary crystallographic data. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 EX, UK.

Crystal Structure Determination of MOF$_{\text{NH2-as}}$ and MOF$_{\text{CH3-as}}$. The diffraction data of MOF$_{\text{NH2-as}}$ and MOF$_{\text{CH3-as}}$ were measured at 100 K and 173 K, respectively. An half of ligands, an half of Ni ions, an half of BPDC and two unligated water molecule were observed as an asymmetric unit. For the structure MOF$_{\text{NH2-as}}$, the alkyl amine pendant group and one unligated water molecule in the ligand was restrained using ISOR during the least-squares refinement. Refinement of the
structure \textbf{MOF}_{\text{NH}_2}-\text{as} converged at a final $R_1 = 0.0709$, $wR_2 = 0.2208$ for 18729 reflections with $I > 2\sigma(I)$; $R_1 = 0.0776$, $wR_2 = 0.2294$ for all reflections. The largest difference peak and hole were 0.959 and -0.543 $e\cdot\text{Å}^{-3}$, respectively. Refinement of the structure \textbf{MOF}_{\text{CH}_3}-\text{as} converged at a final $R_1 = 0.0472$, $wR_2 = 0.1263$ for 20065 reflections with $I > 2\sigma(I)$; $R_1 = 0.0542$, $wR_2 = 0.1321$ for all reflections. The largest difference peak and hole were 0.682 and -0.394 $e\cdot\text{Å}^{-3}$, respectively.

**Thermogravimetric (TG) curves under CO\textsubscript{2} atmosphere.** For the research related to high-temperature absorbent, Li\textsubscript{4}SiO\textsubscript{4}, thermogravimetric (TG) curves were collected under 15\% CO\textsubscript{2} (balanced with N\textsubscript{2}) or 100\% CO\textsubscript{2}(g) atmosphere at a scan rate of 10 °C/min using Q50 from TA instruments.

![TG curve diagram](image-url)
III. Results and Discussion

X-ray structure of MOF\textsubscript{NH\textsubscript{2}-as} and MOF\textsubscript{CH\textsubscript{3}-as}. In order to prove the effect of amino groups for CO\textsubscript{2} adsorption, two isostructural MOFs were prepared except to the pendant chain of nickel (II) macrocyclic complex with propyl and ethylamine group, respectively, because those functional groups have similar molecular weight and size. Two MOFs are composed of the two nickel (II) macrocyclic complex with pendant propyl ([NiL\textsubscript{propyl}]\textsuperscript{2+}) and ethylamine ([NiL\textsubscript{ethylamine}]\textsuperscript{2+}) groups, respectively, as metal building blocks and the same organic ligand (BPDC\textsuperscript{2-}) (Figure 3.1). Self-assembly of an organic ligand (BPDC\textsuperscript{2-}) and [NiL\textsubscript{ethylamine}]\textsuperscript{2+} in DEF/H\textsubscript{2}O/MeCN mixed solution, and [NiL\textsubscript{propyl}]\textsuperscript{2+} in H\textsubscript{2}O/MeCN mixed solution yields rod-shaped purple crystals of \{([NiL\textsubscript{ethylamine})(BPDC)]\cdot3H\textsubscript{2}O\} (MOF\textsubscript{NH\textsubscript{2}-as}) and \{([NiL\textsubscript{propyl})(BPDC)]\cdot2.5H\textsubscript{2}O\} (MOF\textsubscript{CH\textsubscript{3}-as}), respectively.

![Figure 3.1 Nickel macrocyclic complexes and ligand.](image)

Through single-crystal X-ray diffraction analysis, both structures of MOF\textsubscript{NH\textsubscript{2}-as} and MOF\textsubscript{CH\textsubscript{3}-as} were found to have crystallized in the same trigonal space group R-3, but have a little bit difference in unit cell parameters. Both Ni (II) macrocyclic complexes have square planar geometry and acts as a linear linker; its axial sites are coordinated by carboxylate anions from two different BPDC\textsuperscript{2-} ligands in a monodentate fashion, resulting in octahedral centers. Infinite coordination between BPDC\textsuperscript{2-} and Ni (II) macrocyclic complexes results in one dimensional (1D) chains, which are extended in three different directions, which was similar to a previously reported structure\textsuperscript{46} generating honeycomb-like 1D channels (Figure 3.2). Each pendant propyl and ethylamine groups are exposed to the 1D channels, decorating the internal pore surface. The simulated XRPD patterns of both MOFs are similar patterns because they have almost the same structure, but there is a subtle distinction and XRPD patterns of both materials proved that they have the same structure (Figure 3.3.). Detailed single crystal X-ray crystallographic information and selected bond lengths and bond angles for MOF\textsubscript{NH\textsubscript{2}-as} and MOF\textsubscript{CH\textsubscript{3}-as} are listed in Table 3.1 and S1 to S2.
Figure 3.2 X-ray structure of isostructural MOFs for MOF$_{\text{NH}_2}$-as and MOF$_{\text{CH}_3}$-as. (a) Structure of the 1D chain by an ORTEP drawing (thermal ellipsoids at 30% probability, C, black; N, blue; O, red). (b) A view for double network of threefold braids (c) $ab$ plane view of framework.

Figure 3.3 The collected XRPD patterns of MOF$_{\text{NH}_2}$-as (red) and MOF$_{\text{CH}_3}$-as (black).
Table 3.1. X-ray crystallographic data of MOF\textsubscript{NH2}-as and MOF\textsubscript{CH3}-as.

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</tbody>
</table>

\(^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|. \(^b\)wR(F^2) = \[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)\]^{1/2} where \(w = 1/[\sigma^2(F_o^2) + (0.1653P)^2 + (7.425P)]\), \(P = (F_o^2 + 2F_c^2)/3\). \(^c\)wR(F^2) = \[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)\]^{1/2} where \(w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + (16.1542P)]\), \(P = (F_o^2 + 2F_c^2)/3\).
Inside honeycomb-like 1D channels, guest water molecules as well as the pendant chains of macrocyclic complexes are occupied and the guest molecules are confirmed by single-crystal X-ray diffraction, TGA and EA. Thermogravimetric analysis (TGA) of MOF_{NH2-as} and MOF_{CH3-as} revealed weight loss up to temperature of ~ 230 °C, which was concurrent to the total weight percent of guest water molecules (8.6 wt% and 6.6 wt%, respectively) occupying the void spaces. (Figure 3.4) The guest molecules in both structures were removed by evacuating MOFs at 90 °C for 7 h, resulting in guest-free structures MOF_{NH2} and MOF_{CH3}. The macrocyclic complexes of both structure are connected to BPDC_{2-} ligands, which making up the 1D chain. Figure 3.3 showed that there is CH···π interactions between the CH of the macrocyclic complex in the chain and the phenyl ring of BPDC_{2-} ligand in other chain (the average C-H···π distance, 3.2 Å; dihedral angles, 43.5°). Due to the interchain interaction, the framework are rigid. The CH···π interactions provide robustness of the framework and their structure can be maintained during activation. As a result, all XRPD patterns before and after activating MOFs were matched with simulated patterns of each structure. (Figure 3.5)

**Figure 3.4.** TGA traces of (a) MOF_{NH2-as} and (b) MOF_{CH3-as}.

**Figure 3.5** XRPD patterns of (a) MOF_{NH2-as} and MOF_{NH2}, and (b) MOF_{CH3-as} and MOF_{CH3}. (Simulated pattern, red; as-synthesized compound, black; dried compound, blue)
Gas sorption behaviors of \( \text{MOF}_{\text{NH}_2} \) and \( \text{MOF}_{\text{CH}_3} \). After activation of the \( \text{MOF}_{\text{NH}_2}\text{-as} \) and \( \text{MOF}_{\text{CH}_3}\text{-as} \) crystals at 90 °C under vacuum for 7 h, gas sorption isotherms (\( \text{N}_2 \), \( \text{H}_2 \) and \( \text{CO}_2 \)) were collected for \( \text{MOF}_{\text{NH}_2} \) and \( \text{MOF}_{\text{CH}_3} \) to observe the effect of amino groups directly. Based on \( \text{N}_2 \) isotherm, both structures are non-porous. \( \text{H}_2 \) isotherm also supported their non-porous properties and the uptake of \( \text{MOF}_{\text{NH}_2} \) is slightly larger than \( \text{MOF}_{\text{CH}_3} \) due to the larger void space, which corresponds with the calculation of PLATON\textsuperscript{47} (void volume of \( \text{MOF}_{\text{NH}_2}\text{-as} \) and \( \text{MOF}_{\text{CH}_3}\text{-as} \) is 612.8 Å (9.1%) and 489.2 Å (7.1%), respectively). \( \text{CO}_2 \) adsorption isotherms for \( \text{MOF}_{\text{NH}_2} \) and \( \text{MOF}_{\text{CH}_3} \) at several temperatures are depicted in Figure 3.6(b) and 3.6(d), which showed some unexpected results. \( \text{CO}_2 \) isotherm at 195 K shows that the uptake of \( \text{MOF}_{\text{CH}_3} \) is much larger than that of \( \text{MOF}_{\text{NH}_2} \). While the uptake of \( \text{MOF}_{\text{CH}_3} \) decreased as the temperature increased, that of \( \text{MOF}_{\text{NH}_2} \) increased as the temperature increase. In addition, there is a little hysteresis at 195 K and no hysteresis at 273 and 298 K for \( \text{MOF}_{\text{CH}_3} \). On the other hand, the large hysteresis is shown in case of \( \text{MOF}_{\text{NH}_2} \) at 273 and 298 K, and the adsorbed \( \text{CO}_2 \) was not fully desorbed only by evacuation at the temperatures.

**Figure 3.6.** Gas sorption isotherms of \( \text{MOF}_{\text{NH}_2} \) (a, b) and \( \text{MOF}_{\text{CH}_3} \) (c, d). (a, c) \( \text{N}_2 \) (dark pink) and \( \text{H}_2 \) (orange) isotherms measured at 77 K and (b, d) \( \text{CO}_2 \) isotherms measured at 195 K (red), 273 K (green), and 298 K (blue).
Additional CO₂ isotherms for MOF_{NH₂} were collected at 323, 348 and 373 K to see whether the same phenomena could be observed. All CO₂ isotherms of MOF_{NH₂} at several temperatures are depicted in Figure 3.7. At 273 K and 1 bar, MOF_{NH₂} adsorbed a small amount of CO₂ (0.17 mmol g⁻¹). However, as the temperature increased to 373 K, the CO₂ uptake increased to 1.32 mmol g⁻¹ (Table 3.2). This behavior is the opposite of what has been observed for previous amine-grafted MOFs, which show a decrease in CO₂ uptake with increasing temperature.⁵,⁷ In the previous reports, owing to their large pores chemisorption was followed by physisorption, which might be weakened at the higher temperature. On the other hand, MOF_{NH₂} does not have a large enough pore diameter to access multi-layer adsorption, and thus the uptake by physisorption can be exclusively considered. Therefore, at high temperatures the chemisorption in MOF_{NH₂} is much sufficiently occurred to form C-N bonds between amines and CO₂. The CO₂ desorption isotherms at 273-348 K did not trace back to the adsorption curve with large hysteresis even in the low-pressure region. Compared to MOF_{NH₂}, MOF_{CH₃} was scarcely shown hysteresis of CO₂ isotherms and adsorbed CO₂ on MOF_{CH₃} was fully desorbed only by evacuation, which indicated that there is no chemical interaction between CO₂ and MOF_{CH₃}.

![Figure 3.7. CO₂ isotherm of MOF_{NH₂} at the various temperatures.](image)

From the CO₂ isotherm of MOF_{NH₂} at 373 K, the adsorbed CO₂ molecules were completely desorbed by evacuation while the adsorbed CO₂ molecules were not fully desorbed up to at 348 K (Figure 3.8). These different desorption behaviors upon temperatures were verified by the gravimetric
uptake result under 100% CO$_2$ gas flow (Figure. 3.9). It was found that adsorption and desorption are at the equilibrium around 100 °C (373 K), and thus the chemisorbed CO$_2$ molecules in MOF$_{NH_2}$, can be liberated at 100 °C (373 K) upon pressure reduction.

**Figure 3.8.** CO$_2$ gas sorption isotherms of MOF$_{NH_2}$ (a) at 348 K (b) at 373 K.

**Figure 3.9.** Trace of TGA with flowing 100% CO$_2$ gas onto MOF$_{NH_2}$. Desorption of CO$_2$ under 100% CO$_2$ condition occurs at 100.6 °C.
As described previously, MOF$_{\text{NH2}}$ is non-porous based on N$_2$ isotherm and single-crystal X-ray diffraction data also indicated that its pore aperture is 1.59 Å, which is only half of the kinetic diameter of CO$_2$ (3.3 Å). Then, how the CO$_2$ adsorption can occur in this MOF? The flexible movement of the pendant alkylamine groups may allow the uptake of CO$_2$. As single-crystal X-ray data was collected at the low temperature, 100 K, the alkylamine groups did not show significant thermal disorderness. However, as the temperature increases, thermal motion of the alkylamines, which have conformational flexibility, become active. Consequently, at certain moments the thermal disorderness makes the pores accessible to CO$_2$ molecules. Therefore, higher temperatures afford not only stochastically more possibilities to generate a suitable pore size, but also thermal energy to produce chemical bonds between the amino groups and CO$_2$.

**Crystal Size effects on carbon dioxide capture of MOF$_{\text{NH2}}$.** The access of CO$_2$ into the MOF is of critical importance based on the above understanding. Accordingly, we compared the CO$_2$ sorption behaviors of MOF$_{\text{NH2}}$ with the different crystal size, MOF$_{\text{NH2}}$:crystal, which have been treated so far, and well-ground MOF$_{\text{NH2}}$ powder (MOF$_{\text{NH2}}$:powder). MOF$_{\text{NH2}}$:powder was prepared by pulverizing MOF$_{\text{NH2}}$:crystal using a sample grinder with stainless steel vial and ball. As shown in the scanning electron microscope (SEM) images (Figure 3.10a and 3.10b), MOF$_{\text{NH2}}$:crystal are several tens of micrometres long (average 58.7 ± 27.8 μm measured from 71 crystals), whilst the size of MOF$_{\text{NH2}}$:powder (average 15.4 ± 12.0 μm measured from 90 crystals) is mainly distributed in a few micrometre range. Interestingly, the only reduction in crystal size of MOF$_{\text{NH2}}$ resulted in much faster and greater CO$_2$ adsorption (Figures. 3.10c and 3.10d, and Table S3 to S4). The uptake of MOF$_{\text{NH2}}$:powder at 1 bar were greater by a factor of 1.3-7.5 than those of MOF$_{\text{NH2}}$:crystal over all temperatures. This might be attributed to a decrease of the channel length in each grain of the adsorbent, which results in high accessibility under the same condition. In contrast with MOF$_{\text{NH2}}$:crystal, MOF$_{\text{NH2}}$:powder adsorbed the almost same CO$_2$ uptake at 348 and 373 K (7.6 wt%). This suggests that under the guaranteed condition of the CO$_2$ accessibility, the uptake of ~1.75 mmol g$^{-1}$ might be the maximum value in this MOF. The relatively slow kinetics shown at 100 °C was observed because the adsorption and desorption are at the equilibrium around 100 °C as mentioned previously (Figure. 3.11). At 0.15 bar, comparable to the CO$_2$ partial pressure of a typical post-combustion flue gas, the CO$_2$ uptake of MOF$_{\text{NH2}}$:powder and MOF$_{\text{NH2}}$:crystal are 1.19 and 0.12 mmol g$^{-1}$, respectively (Figure. 3.11.). In other words, the sorption ability at 0.15 bar improved tenfold with a decrease in crystal size. This result shows the good agreement with the previous report related to that of the amine-modified mesoporous silicas. Sayari group found that the adsorption performance of the porous silica with high loading of PEI strongly depended on the pore length. SBA-15PLT silica with very short pore channels showed much enhanced adsorption and desorption kinetics as well as CO$_2$ uptake at low
temperature. Even though it clearly said that high amine loading was required for high CO₂ uptake, it prohibit the diffusion CO₂ which results in accompanying the optimization of the loading amount. In this context, the reduction of the pore length can be the simple but effective way to enhance the sorption behavior, and our study is the first report of this trial using MOFs.

Figure 3.10. SEM images of (a) MOF₉₂:crystal (b) MOF₉₂:powder and CO₂ isotherms of (c) MOF₉₂:crystal (b) MOF₉₂:powder.

Figure 3.11. CO₂ adsorption isotherms for comparison of the CO₂ adsorption behavior of MOF₉₂:crystal and MOF₉₂:powder at 298 K.
Evidence of chemical interaction between MOF$_{\text{NH}_2}$ and CO$_2$. To verify the chemical interaction between CO$_2$ molecules and the pendant amine groups, the IR spectra of MOF$_{\text{NH}_2}$:powder before and after CO$_2$ adsorption were compared (Figure 3.12). Upon CO$_2$ adsorption at 348 K, the stretching bands at 3368, 3293 cm$^{-1}$ and bending band at 1660 cm$^{-1}$, which correspond to the primary amine (N-H) tethered to the MOF mostly disappeared, remaining the small trace. Simultaneously, new peaks were observed at 3444 cm$^{-1}$ and 1478 cm$^{-1}$, assigned to N-H stretching of carbamate (NHCOO$^-$) group and NH$_3^+$ deformation, respectively.$^{49,50}$ This result indicated that the chemical interactions between CO$_2$ and MOF$_{\text{NH}_2}$:powder form ammonium carbamate, which results from a 2:1 amine:CO$_2$ stoichiometric reaction (Eq 3.1.) .

\[2\text{RNH}_2 + \text{CO}_2 \rightarrow \text{RNH}_3^+ + \text{RNHCOO}^- \text{ (carbamate)} \]  
(Eq 3.1)

The secondary amine (N-H) peak from the Ni (II) macrocyclic complex at 3135 cm$^{-1}$ was maintained, showing that CO$_2$ reacts with only the primary amine of the pendant in the MOF. The isosteric heat of adsorption ($Q_d$) by using CO$_2$ adsorption data at 323 and 348 K was calculated by applying a single site Langmuir-Freundlich model (Figure 3.13. and S1), because the chemisorption is major contribution to the total uptake at those temperatures. $Q_d$ is $-59.5$ kJ mol$^{-1}$ at zero coverage (Figure 3.13), which is reasonable range for chemisorption between amine groups and CO$_2$ but relatively small value for the chemisorbed CO$_2$ in MOF.

![Figure 3.12](image-url)

**Figure 3.12.** Infrared spectra for MOF$_{\text{NH}_2}$:powder before (black) and after (red) adsorbing CO$_2$. 

- 35 -
Figure 3.13. Isosteric heat ($Q_{st}$) of adsorption for CO$_2$ for MOF$_{NH_2}$:powder, as calculated from fits to the gas adsorption data collected at 323 and 348 K.

**Thermal and Water stability of MOF$_{NH_2}$-as.** In order to implement the adsorbents in real process, water stability of the adsorbents is important because real flue gas usually contains more than 10% (v/v) water and the adsorbents should be thermally stable up to at least 200 °C, which is an operating temperature of low-temperature adsorbents.

Thermogravimetric analysis (TGA) of MOF$_{NH_2}$-as (Figure 3.4.) revealed weight loss up to a temperature of ~ 230 °C, which was concurrent to the total weight percent of guest water molecules (8.6 wt%) occupying the void spaces. The X-ray powder diffraction (XRPD) pattern of as-synthesized MOF$_{NH_2}$-as showed strong reflections in the region 5–30°, which were commensurated with the simulated pattern from single crystal X-ray diffraction data (Figure 3.14a.). After heating up to 250 °C under pure N$_2$ flow, the MOF retained the same structure, showing high thermal stability (Figure 3.14c.). As mentioned above, since real flue gas usually contains more than 10% (v/v) water and water molecules are very good ligands for metal centers, the water stabilities of MOFs as well as the amine moieties coordinated to the OMSs cannot be assured under humid condition. In the present study, upon suspending the activated MOF in water for 24 h, its structure and the crystallinity were maintained as evidenced by the XRPD pattern (Figure 3.14d.). Re-activation of the hydrated MOF also resulted in the intact structure as shown in Figure 3.14e. Therefore, MOF$_{NH_2}$-as, in which the amine moieties were tethered by covalent bonds, is a potentially good sorbent due to its thermal and water stability.
Figure 3.14. XRPD patterns of (a) simulation from single-crystal XRD data of MOF\textsubscript{NH2-as}, (b) MOF\textsubscript{NH2-as}, (c) MOF\textsubscript{NH2-as} after heating at 250 °C, and (d) activated MOF after immersing in water for 24 h (hydrated MOF). (e) re-activated of the hydrated MOF.

Since durability of CO\textsubscript{2} adsorbents is also very important for practical applications, adsorption-desorption cyclic performance of MOF\textsubscript{NH2-powder} was tested by using TGA with a combined temperature swing and nitrogen purge approach (Figure 3.15.). The sample was activated at 150 °C under pure N\textsubscript{2} flow for 7 h. Then, a simulated flue gas was introduced into the furnace for 2 h at 25 °C, followed by regeneration at 120 °C for 1 h under pure N\textsubscript{2} gas. A CO\textsubscript{2} uptake capacity of 4.80 wt% (1.09 mmol g\textsuperscript{-1}) was recorded on an average over 12 cycles, in accordance with the CO\textsubscript{2} isotherm of MOF\textsubscript{NH2-powder} at 298 K (Figure 3.10b) and there was no decrease in CO\textsubscript{2} uptake, indicating that the CO\textsubscript{2} adsorption ability of MOF\textsubscript{NH2-powder} is maintained over repeated cycling.

Figure 3.15. Adsorption-desorption cycling for MOF\textsubscript{NH2-powder}, showing reversible uptake from simulated flue gas (15% CO\textsubscript{2} balanced with N\textsubscript{2}). CO\textsubscript{2} was introduced at the red points.
Significant factor for lithium orthosilicate (Li$_4$SiO$_4$) with enhanced sorption property. As has been mentioned in the introduction part on the mechanism for CO$_2$, lithium carbonate (Li$_2$CO$_3$) and lithium metasilicate (Li$_2$SiO$_3$) external shell were formed as a result from the reaction between Li$_4$SiO$_4$ and CO$_2$. To enhance the sorption kinetics of Li$_4$SiO$_4$, there have been various methods for preparing Li$_4$SiO$_4$ in different papers,$^{32,51-56}$ for example controlling mixing methods, using different types of SiO$_2$ with different crystallinity and doping with heteroatoms and so on. The sorption property varied from different synthetic methods, but there have been insufficient analyses for the reason and some methods were too complicate to apply in real process. Therefore, we tried to find the factors affecting CO$_2$ sorption ability by controlling some conditions. The ratio of lithium to silicon ion is fixed, Li:Si = 4.1:1, in which excess amount of lithium source was used to prevent from forming different phase of lithium silicate such as Li$_2$SiO$_3$ due to the lithium sublimation during calcination at high temperature. The calcination condition (700 °C for 4 h) is identical for all syntheses. In this experiment, Li$_4$SiO$_4$ have been synthesized by controlling mixing methods, calcinations atmosphere and reacting between various lithium precursors and size of silica precursors.

Table 3.2. Controlled conditions for synthesizing Li$_4$SiO$_4$.

<table>
<thead>
<tr>
<th>Controlled conditions</th>
<th>Details</th>
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| Mixing method         | - physically mixing : precursors were mixed with a mortar and pestle  
                        | - wet-mixing : dispersing precursors in water (10 mL) at 45 °C in closed system and then, the solution was evaporated at 65 °C with stirring. |
| Lithium precursors    | - LiOH·H$_2$O  
                        | - Li$_2$CO$_3$ |
| Size of SiO$_2$       | - fumed silica (6-9 nm)  
                        | - silica sphere (400-600 nm) |
| Calcination atmosphere| - Air  
                        | - N$_2$ flow |

XRPD data and TG curves of all the products were collected for all products under 15% CO$_2$ flow (balanced with N$_2$) and the results from those data were expressed in Table 3.3. The results indicated that calcination atmosphere and the kinds of lithium precursors did not have great effect on the sorption property of the absorbents, especially, lithium hydroxide (LiOH·H$_2$O) reacted with CO$_2$ resulting in lithium carbonate (Li$_2$CO$_3$) (Figure S2).$^{57}$ On the other hand, mixing method and size of SiO$_2$ were notable conditions to affect properties of Li$_4$SiO$_4$. Firstly, the CO$_2$ sorption ability of...
absorbents synthesized by wet-mixing method has better than by mixing precursors physically. Therefore, significant factors would be studied only in case of using wet-mixing method. Wet-mixing method would help precursors to be mixed evenly and the solvent, H2O, would provide the pores when evaporated. Also, the best sorption property was shown when the larger size of SiO2 source was used, which would contribute to make macropores by alleviating aggregation of SiO2 source, which was confirmed by SEM images (Figure S3). As result, the existence of macropores make significantly impact on the sorption property. However, a lack of reproducibility was found through repeated experiment when using SiO2 sphere, whereas similar sorption amount was shown in case of using fumed silica, that is, good reproducibility would be expected when using fumed silica. In order to improve the reproducibility as well as excellent sorption amount, both silica source were used to synthesize Li4SiO4 leading to the best sorption capacity (Figure 3.16.) but still slightly poor reproducibility. As the result of this experiment, it is very important for Li4SiO4 itself with excellent sorption properties to have highly porous structure because pores would help to shorten the diffusion path length leading to enhance Li+ diffusion.

To further study on improving the sorption property of the absorbent, the recommended synthetic condition is that mixing fumed silica and lithium precursors with solvent, H2O, because it is much more important to have better reproducibility than to show the best sorption property. Therefore, p-Li4SiO4 was prepared for further research and the synthetic method was described in experimental section.
Table 3.3. Sorption property of the product from various condition.

<table>
<thead>
<tr>
<th>Physical mixing</th>
<th>Wet mixing</th>
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<tr>
<td><strong>Synthesis of Li$_4$SiO$_4$</strong></td>
<td><strong>Wet mixing</strong></td>
</tr>
<tr>
<td>* Li : Si = 4.1 : 1 (LiOH·H$_2$O : SiO$_2$ = 4.1 : 1/Li$_2$CO$_3$ : SiO$_2$ = 2.05 : 1)*</td>
<td>(Precursors were dispersed in water (10 mL) at 45 °C under stirring them the solution was evaporated at 65 °C under stirring.)</td>
</tr>
<tr>
<td>* Size: Fumed SiO$_2$ (6-9 nm) / SiO$_2$ sphere (400-600 nm)</td>
<td></td>
</tr>
<tr>
<td><strong>Calcination</strong></td>
<td>700 °C (5 °C/min) for 4 h</td>
</tr>
<tr>
<td><strong>Air, 700 °C (5 °C/min), 4 h</strong></td>
<td><strong>N$_2$, 700 °C (5 °C/min), 4 h</strong></td>
</tr>
<tr>
<td><strong>Product</strong></td>
<td><strong>Amoun t (wt%)</strong></td>
</tr>
<tr>
<td>Fumed SiO$_2$ + LiOH·H$_2$O</td>
<td>Li$_4$SiO$_4$ + Li$_2$CO$_3$</td>
</tr>
<tr>
<td>Fumed SiO$_2$ + Li$_2$CO$_3$</td>
<td>Li$_4$SiO$_4$ + Li$_2$CO$_3$</td>
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<tr>
<td>SiO$_2$ sphere + LiOH·H$_2$O</td>
<td>Li$_4$SiO$_4$ + Li$_2$CO$_3$</td>
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<td>SiO$_2$ sphere + Li$_2$CO$_3$</td>
<td>Li$_4$SiO$_4$ + Li$_2$CO$_3$</td>
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Incorporation of additives. Li$_4$SiO$_4$ has excellent sorption capacity theoretically (36.7 wt%), but it is difficult to reach the theoretical capacity because the Li$_2$CO$_3$ and Li$_2$SiO$_3$ shell resulting from the reaction between $p$-Li$_4$SiO$_4$ and CO$_2$ disturb the diffusion of CO$_2$ molecules, as mentioned in the introduction part. Therefore, incorporating additives help to improve the sorption properties of the absorbents. Two kinds of additives were introduced; the first additive is Li$_2$SiO$_3$ and the second is alkali carbonate.

Additives I. Li$_2$SiO$_3$ (Lithium metasilicate). The improvement of sorption properties was found when Li$_2$SiO$_3$ was existed. To investigate the optimal amount and location of Li$_2$SiO$_3$ for enhancing CO$_2$ absorption, $p$-Li$_4$SiO$_4$ was used as a control group and three additional samples were prepared; (1) Li$_2$SiO$_3$-induced Li$_4$SiO$_4$ by using deficient lithium source when synthesizing $p$-Li$_4$SiO$_4$ (Lithium ion deficiency-induced) (2) Li$_2$SiO$_3$-induced Li$_4$SiO$_4$ by reacting $p$-Li$_4$SiO$_4$ with CO$_2$ (CO$_2$ absorption-induced) (3) $p$-Li$_4$SiO$_4$ physically mixed with Li$_2$SiO$_3$ (physically mixed). Those samples were shown as schematic view in Figure 3.17.
The first sample, lithium ion deficiency-induced Li2SiO4, was prepared in order to find the optimal ratio of Li2SiO3, which shows the best sorption property of the absorbent. The absorbents were synthesized through controlling the ratio of lithium source to silica source. The products were confirmed by XRPD and TG curves were collected under 15% CO2 balanced with N2 (Figure 3.18.).

The absorbent with the ratio, Li:Si = 3.8:1, showed the best performance (10.3 wt%) from TG curves (Figure 3.18b.). This absorbent synthesized with Li:Si = 3.8:1, contains 7.7 wt% Li2SiO3 theoretically if lithium source fully reacted with silica source with the ratio of 3.8:1. The ratio of Li2SiO3, 7.7 wt%, will be fixed in order to compare the properties of absorbents according to the distribution of Li2SiO3.

**Figure 3.17.** Schematic view of prepared Li2SiO3-included Li4SiO4. (color: orange, Li2SiO3).

**Figure 3.18** (a) PXRD patterns of products  (b) TG curves under 15% CO2 balanced with N2 (5 °C/min to 800 °C).
The second sample was prepared by adsorbing 15% CO$_2$ balanced with N$_2$ until $p$-Li$_4$SiO$_4$ turned into 7.7 wt% Li$_2$SiO$_3$ and this sample is called as CO$_2$ absorption-induced Li$_4$SiO$_4$. Based on the CO$_2$ absorption mechanism of Li$_4$SiO$_4$, generated Li$_2$SiO$_3$ resulting from CO$_2$ absorption was formed on the surface of $p$-Li$_4$SiO$_4$. The absorbent included Li$_2$SiO$_3$ confirmed by XRPD and TG curves under 15% CO$_2$ balanced with N$_2$ showed that the maximum absorbed amount is 2.9 wt% and change in mass uptake of the absorbent under the same gas condition for 300 min is 15 wt% (Figure 3.19.). Even though there is the same amount of Li$_2$SiO$_3$ in the absorbent, surface-covered Li$_2$SiO$_3$ impediment to absorb CO$_2$.

Figure 3.19. (a) XRPD patterns of the absorbent. (b) TG curves under 15% CO$_2$ balanced with N$_2$ (5 °C/min to 800 °C).
The third sample was prepared by mixing $p$-Li$_4$SiO$_4$ and 7.7 wt% Li$_2$SiO$_3$ physically. Li$_2$SiO$_3$ was synthesized through solvothermal reaction and it was confirmed by PXRD pattern (Figure 3.20a.). TG curves under 15% CO$_2$ balanced with N$_2$ showed that the maximum absorbed amount is 8.1 wt%, which is enhanced value comparing with the CO$_2$ uptake of $p$-Li$_4$SiO$_4$.

Figure 3.20. (a) XRPD patterns of Li$_2$SiO$_3$ and (b) the absorbent (c) TG curves under 15% CO$_2$ balanced with N$_2$ (5 °C/min to 800 °C).

Overall, performance of these three Li$_2$SiO$_3$-added absorbents as a comparison group compared with that of $p$-Li$_4$SiO$_4$ depending on the distribution of additives (Figure 3.21.). TG curves appeared the best performance of lithium ion deficiency-induced Li$_4$SiO$_4$ and CO$_2$ isotherm data indicated that physically mixed Li$_4$SiO$_4$ with Li$_2$SiO$_3$ had fast kinetics and it reaches the theoretical capacity of $p$-Li$_4$SiO$_4$ (The theoretical capacity of 7.7 wt% Li$_2$SiO$_3$-incorporated Li$_4$SiO$_4$ is 33.9 wt%). Unlike CO$_2$ absorption-induced Li$_4$SiO$_4$ with Li$_2$SiO$_3$ shell on the surface, both absorbents had evenly distributed Li$_2$SiO$_3$, which accelerate the sorption ability of $p$-Li$_4$SiO$_4$. 
Figure 3.21. (a) TG curves under 15% CO₂ balanced with N₂ (5 °C/min to 800 °C) (b) 15% CO₂ isotherms for various Li₂SiO₃-included absorbents.

In summary, the sorption properties such as sorption amount and sorption rate of \( p-\text{Li}_4\text{SiO}_4 \) with Li₂SiO₃ were improved, especially Li₂SiO₃ ought to be distributed all over the absorbent. As above mentioned on the mechanism of absorbing CO₂ for Li₄SiO₄, the reaction between Li₄SiO₄ and CO₂ could be continued by lithium ion and oxygen ion were diffused throughout the absorbent. The diffusion of lithium and oxygen ion (or Li₂O) could be accelerated by existing Li₂SiO₃ in the absorbent beforehand.

However, Li₂SiO₃ is formed as result of CO₂ absorption by Li₄SiO₄. Therefore, Li₂SiO₃ could not change the characteristics or attributes of the absorbent, so it could not affect the absorption and regeneration temperature, leading to introduce new additives to change properties of the absorbent.
Additives I. Alkali carbonate (K$_2$CO$_3$ and Na$_2$CO$_3$). Alkali carbonates (K$_2$CO$_3$ or Na$_2$CO$_3$) were chosen because it reacts with Li$_2$CO$_3$, the product of reaction between Li$_4$SiO$_4$ and CO$_2$, resulting in the formation of eutectic mixture, KLiCO$_3$. It is expected that this eutectic mixture will have an effect on the absorption and regeneration temperature, resulting from changing the characteristics of the absorbent.

At first, K$_2$CO$_3$ was chosen as one of alkali carbonate and controlling the amount of K$_2$CO$_3$ relative to $p$-Li$_4$SiO$_4$ was required to find the optimal ratio of K$_2$CO$_3$. TG curves under 15% CO$_2$ (balanced with N$_2$) are shown in Figure 3.22. By introducing K$_2$CO$_3$, the absorbents started to absorb CO$_2$ at near 410 °C, which is lower about 50 °C than that of $p$-Li$_4$SiO$_4$, but K$_2$CO$_3$ cannot lower the desorption temperature. When 10 wt% and 20 wt% of K$_2$CO$_3$ was added to $p$-Li$_4$SiO$_4$, the best adsorption capacity (21.3 wt%) was shown and it was also found that the larger the amount of K$_2$CO$_3$ is, the slower the desorption rate is.

As mentioned above, K$_2$CO$_3$ reacts with Li$_2$CO$_3$ leading to the generation of the eutectic mixture. The mole fraction of K$_2$CO$_3$ to Li$_2$CO$_3$ continued to change because Li$_2$CO$_3$ kept on increasing as $p$-Li$_4$SiO$_4$ reacted with CO$_2$. The trace of changing mole fraction of Li$_2$CO$_3$ was expressed on the phase diagram between Li$_2$CO$_3$ and K$_2$CO$_3$ (Figure 3.23). It is found that the reaction rate was changed when the liquid phase started to be formed at near 500 °C.

Figure 3.22. TG curves and the results of sorption properties for $p$-Li$_4$SiO$_4$ with X wt% K$_2$CO$_3$ under 15% CO$_2$ (balanced with N$_2$) (X = 5, 10, 20, 30).

<table>
<thead>
<tr>
<th>K$_2$CO$_3$ Amount (wt%)</th>
<th>T$_{ad}$</th>
<th>T$_{des}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% ($p$-Li$_4$SiO$_4$)</td>
<td>8.7</td>
<td>458</td>
</tr>
<tr>
<td>5 wt%</td>
<td>19.3</td>
<td>409</td>
</tr>
<tr>
<td>10 wt%</td>
<td>21.3</td>
<td>409</td>
</tr>
<tr>
<td>20 wt%</td>
<td>21.3</td>
<td>403</td>
</tr>
<tr>
<td>30 wt%</td>
<td>19.3</td>
<td>390</td>
</tr>
</tbody>
</table>
Additional experiment with Na$_2$CO$_3$, which were also used to make eutectic mixture by reacting with Li$_2$CO$_3$, was done. Likewise, the amount of Na$_2$CO$_3$ was controlled to investigate the optimal condition and TG curves collected under 15% CO$_2$ (balanced with N$_2$) are shown in Figure 3.24. The curves were pointed out that the absorption started at near 400 °C and the best adsorption capacity is 24.2 wt% when adding 10 wt% Na$_2$CO$_3$. The more the amount of Na$_2$CO$_3$, the slower the desorption rate. The absorbents with smaller than 20 wt% Na$_2$CO$_3$ started to desorb at near 600 °C and the desorption of absorbent with 30 wt% Na$_2$CO$_3$ started at higher than 600 °C, which can be shown in case of K$_2$CO$_3$. Those results are different from the previous report, which described that the larger amount of alkali carbonate help to improve the properties of the absorbent. Also, mole fraction of Li$_2$CO$_3$ kept on changing as the reaction progressed and this trace was also represented on the phase diagram of Li$_2$CO$_3$-Na$_2$CO$_3$. 

**Figure 3.23.** Trace of changing mole fraction of Li$_2$CO$_3$ expressed on the K$_2$CO$_3$-Li$_2$CO$_3$ phase diagram.
Figure 3.24. TG curves and the results of sorption properties for $p$-Li$_4$SiO$_4$ with X wt% Na$_2$CO$_3$ under 15% CO$_2$ (balanced with N$_2$) (X = 5, 10, 20, 30).

<table>
<thead>
<tr>
<th>Na$_2$CO$_3$ Amount (wt%)</th>
<th>$T_{ad}$</th>
<th>$T_{des}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% (p-Li$_4$SiO$_4$)</td>
<td>8.7</td>
<td>458</td>
</tr>
<tr>
<td>&gt; 5 wt%</td>
<td>42.5</td>
<td>400</td>
</tr>
<tr>
<td>10 wt%</td>
<td>24.2</td>
<td>400</td>
</tr>
<tr>
<td>20 wt%</td>
<td>21.1</td>
<td>400</td>
</tr>
<tr>
<td>30 wt%</td>
<td>19.4</td>
<td>399</td>
</tr>
</tbody>
</table>

Figure 3.25. Trace of changing mole fraction of Li$_2$CO$_3$ expressed on the Na$_2$CO$_3$-Li$_2$CO$_3$ phase diagram.
Unlike absorbent with K₂CO₃, XRPD pattern indicated that NaLi₃SiO₄ was formed after Li₄SiO₄ with Na₂CO₃ reacted with CO₂ up to 800 °C, so the absorbent with 10 wt% K₂CO₃ showing the best adsorption capacity was selected for additional experiments.

**Figure 3.26.** XRPD patterns of the absorbent. (purple, before CO₂ sorption; black, after CO₂ adsorption and desorption.)

Figure 3.27. shows isotherms of the CO₂ sorption on Li₄SiO₄ with 10 wt% K₂CO₃ (10K) were collected at 500, 550 and 600 °C under 15% CO₂ balanced with N₂. Theoretical capacity of the absorbent is 33 wt% and adsorption capacity reached to 31.8 wt% at 550 and 600 °C. The rate of absorption at 550 °C was faster than at 600 °C for initial 5 min.

**Figure 3.27.** 15% CO₂ isotherms of p-Li₄SiO₄ with 10 wt% K₂CO₃ measured at 500, 550 and 600 °C.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Amount (wt%)</th>
<th>wt%/S min</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>31.8</td>
<td>17.7</td>
</tr>
<tr>
<td>550</td>
<td>31.6</td>
<td>22.3</td>
</tr>
<tr>
<td>500</td>
<td>28.9</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Theoretical capacity of pure absorbent : 33 wt%
In conclusion, introduction of K$_2$CO$_3$ or Na$_2$CO$_3$ can accelerate CO$_2$ absorption capacity of the absorbent as well as lower absorption temperature as much as 50-60 °C. According to the reaction mechanism by simulation, the first step of the CO$_2$ absorption is the efficient collision between CO$_2$ and lithium-deficient oxygen on the surface of the absorbent. By reacting alkali carbonate with Li$_2$CO$_3$ continuously, the interaction between lithium ion (Li$^+$) and oxygen ion (O$^{2-}$), so lithium-deficient oxygen ion can be actively appeared on the surface, which improves the number of efficient collision between CO$_2$ and the oxygen, leading to start absorbing CO$_2$ at the lower temperature.

**Additive III. Both Li$_2$SiO$_3$ and K$_2$CO$_3$.** Through two experiments, alkali carbonate helps to reduce the interaction between lithium and oxygen and increase the number of active sites (O$^{2-}$) by increasing the interaction between lithium and alkali ion leading to the formation of eutectic mixture. Also, Li$_2$SiO$_3$ helps to increase the diffusion rate of Li$^+$ and O$^{2-}$, which improves the sorption properties of absorbents. In order to obtain the effect of both additives, the absorbent was prepared by adding 10 wt% K$_2$CO$_3$ and 7.7 wt% Li$_2$SiO$_3$ (10K+7M) and another sample with 3 wt% K$_2$CO$_3$ and 3 wt% Li$_2$SiO$_3$ (3K+3M) was also prepared to increase the portion of $p$-Li$_4$SiO$_4$. These absorbents would be tested CO$_2$ sorption ability and compared with $p$-Li$_4$SiO$_4$, $p$-Li$_4$SiO$_4$ with 10 wt% K$_2$CO$_3$ (10K) and $p$-Li$_4$SiO$_4$ with 7.7 wt% Li$_2$SiO$_3$ (7M), respectively.

In real process, the absorption is completed under 15% CO$_2$, and the absorbents are regenerated under 100% CO$_2$ atmosphere. Therefore, TG curves were collected under both atmospheric conditions. Firstly, the result show that additives improve the sorption capacity under 15% CO$_2$ atmosphere, especially, K$_2$CO$_3$-incorporated absorbents (10K, 10K+7M and 3K+3M) started to absorb CO$_2$ at lower temperature. However, additives did not have effect on the desorption temperature. From TG curves collected under 100% CO$_2$, additives did not improve the sorption capacity, but we can find that the absorption temperature decreases similar to the results of 15% CO$_2$ TG curves. Above all, it is notable that the regeneration temperature decreases in case of using both additives regardless of the portion of additives.
Figure 3.28. (a) TG curves under 15% CO₂ balanced with N₂ (b) TG curves under 100% CO₂ (c) 15% CO₂ isotherms at 550 °C (d) 15% CO₂ isotherms at 600 °C. (black, \( p-\text{Li}_4\text{SiO}_4 \); green, \( p-\text{Li}_4\text{SiO}_4 \) with 10 wt% K₂CO₃; blue, \( p-\text{Li}_4\text{SiO}_4 \) with 7.7 wt% Li₂SiO₃; red, \( p-\text{Li}_4\text{SiO}_4 \) with 10 wt% K₂CO₃ and 7.7 wt% Li₂SiO₃; orange, \( p-\text{Li}_4\text{SiO}_4 \) with 3 wt% K₂CO₃ and 3 wt% Li₂SiO₃)
With those samples, the isotherm data were collected under 15% CO₂ balanced with N₂ at 550 °C and 600 °C, respectively. Both results indicated that $p$-Li₄SiO₄ with 10 wt% K₂CO₃ and 7.7 wt% Li₂SiO₃ (10K+7M) had the best sorption capacity and rate.

Based on this data, cyclic absorption-regeneration was tested under 100% CO₂ flow. Figure 3.29 showed the cyclic performance of $p$-Li₄SiO₄ and the absorbent with 10 wt% K₂CO₃ and 7.7 wt% Li₂SiO₃ (10K+7M). Firstly, $p$-Li₄SiO₄ reached the theoretical value (36.2 wt%) at the first cycle, but there is a significant decrease of capacity after the 1st cycle. As the absorption-regeneration cycle was progressed, the capacity was saturated as about 22 wt% even though the rate of absorption and regeneration is slow. On the other hand, 10K+7M have also excellent initial absorption rate as we expected and sorption capacity (33.4 wt%) reaches the theoretical value. Even though the sorption capacity of 10K+7M decreases after the 4th cycle and the regeneration rate also became slower, which would results from the aggregation of the absorbents due to the liquid phase of eutectic mixture, it was found that the sorption property was improved during the initial four cycles.

![Figure 3.29. Cyclic performance of $p$-Li₄SiO₄ and the absorbents with 10 wt% K₂CO₃ and 7.7 wt% Li₂SiO₃ (10K+7M) (Absorption at 600 °C, Regeneration at 750 °C).](image)

To increase the portion of pure absorbent, 3K+3M was prepared and the cyclic performance was collected under the same condition (Figure 3.30.). 3K+3M had tendency to decrease both sorption rate and amount relative to that of 10K+7M, but 3K+3M maintained the sorption amount after 3rd cycle in different from 10K+7M showing decrease of the sorption amount persistently.
Figure 3.30. Cyclic performance of $p$-Li$_4$SiO$_4$ with 10 wt% K$_2$CO$_3$ and 7.7 wt% Li$_2$SiO$_3$ (10K+7M) and $p$-Li$_4$SiO$_4$ with 3 wt% K$_2$CO$_3$ and 3 wt% Li$_2$SiO$_3$ (3K+3M) (Absorption at 600 °C, Regeneration at 750 °C).

On the whole, the regeneration rate of all prepared absorbents is very slow. Therefore, the additional experiment was conducted at different range of temperature in order to change the phase of absorbent when starting regeneration. With 3K+3M, cyclic performance data was collected under 100% CO$_2$ flow at different temperature (absorption at 550 °C and regeneration at 720 °C) and the result was shown in Figure 3.32. The regeneration rate was improved at 720 °C, but degeneration of sorption amount was still observed due to the aggregation of the absorbent by forming liquid phase at the regeneration temperature. Therefore, introduction of additional materials to coat the surface of the absorbent for preventing the aggregation should be required and then, the additive-incorporated absorbents will be applied in real process.
Figure 3.31. Phase diagram of K₂CO₃-Li₂CO₃ and different conditions for cyclic performance.

Figure 3.32. Cyclic performance of $\rho$-Li₄SiO₄ with 3 wt% K₂CO₃ and 3 wt% Li₂SiO₃ (3K+3M). (Blue: Absorption at 600 °C / Regeneration at 750 °C, Orange: Absorption at 600 °C / Regeneration at 750 °C)
IV. Conclusion

In conclusion, an amine-functionalized MOF, **MOF\textsubscript{NH2}**, was successfully synthesized via a one-step construction method. In order to investigate the effect of amino groups for CO$_2$, an isostructural MOF with propyl pendant chain, **MOF\textsubscript{CH3}** was also prepared. The structure of **MOF\textsubscript{CH3}** and **MOF\textsubscript{NH2}** was determined using single-crystal XRD, confirming that two MOF have the same structure. In case of **MOF\textsubscript{NH2}**, the covalently tethered alkylamine groups conserved the loading of amine groups as two per metal centre. Unlike **MOF\textsubscript{CH3}** showing decreasing CO$_2$ uptake, **MOF\textsubscript{NH2}** showed enhanced CO$_2$ adsorption as temperature increases due to the chemical interaction between amine groups and CO$_2$, which confirmed by the results of sorption experiments and IR spectroscopy. Since the narrow channel in the MOF restricts the easy access of CO$_2$ molecules, reducing the crystal size led faster and greater CO$_2$ adsorption under same sorption condition. The chemical interaction between the primary amine groups tethered to the MOF and CO$_2$ molecules formed ammonium carbamate, which was reversibly dissociated at mild temperature, 100 °C, to release CO$_2$ molecules. **MOF\textsubscript{NH2}** was found to be a renewable CO$_2$ adsorbent with good stability over repeated cycling.

In addition, lithium orthosilicate (Li$_4$SiO$_4$), one of high-temperature absorbents, was synthesized through various conditions and the optimal condition was found. From this experiment, the reaction process or treatment of precursors like mixing and reacting method is important factor to obtain Li$_4$SiO$_4$ with excellent properties rather than the kinds of precursors, which was assumed to form macropores during the reaction process. To improve the sorption properties, Li$_2$SiO$_3$ and K$_2$CO$_3$ were incorporated to p-Li$_4$SiO$_4$. Both additives help to enhance the sorption capacity, especially additives were well distributed over the absorbents. K$_2$CO$_3$ helps to reduce the interaction between lithium and oxygen and increase the number of active sites (O$^2-$) by increasing the interaction between lithium and alkali ion leading to the formation of eutectic mixture. Also, Li$_2$SiO$_3$ helps to increase the diffusion rate of Li$^+$ and O$^2-$, which improves the sorption properties of absorbents. Additive-incorporated Li$_4$SiO$_4$ showed enhanced CO$_2$ absorption rate in the cyclic performance data, but the sorption amount was not maintained due to the aggregation by forming liquid phase of eutectic mixture. Therefore, introduction of additional materials as new strategy to prevent the aggregation of absorbents is required and then, additive-incorporated absorbents will be applied in real process.
V. Supporting Information

Table S1. Selected bond distances [Å] and angles [°] of MOF_{NH2-as} (100 K).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Distance/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(1)-N(1A)^#1</td>
<td>2.057(3)</td>
</tr>
<tr>
<td>Ni(1)-N(1A)</td>
<td>2.057(3)</td>
</tr>
<tr>
<td>Ni(1)-N(2A)^#1</td>
<td>2.061(4)</td>
</tr>
<tr>
<td>Ni(1)-N(2A)</td>
<td>2.061(4)</td>
</tr>
<tr>
<td>Ni(1)-O(1B)^#1</td>
<td>2.1085(18)</td>
</tr>
<tr>
<td>Ni(1)-O(1B)</td>
<td>2.1085(18)</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-N(1A)</td>
<td>180.0</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-N(2A)^#1</td>
<td>94.03(18)</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-N(2A)</td>
<td>85.97(18)</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-O(1B)^#1</td>
<td>93.79(10)</td>
</tr>
<tr>
<td>N(1A)-Ni(1)-O(1B)</td>
<td>91.44(11)</td>
</tr>
<tr>
<td>N(1A)-Ni(1)-O(1B)^#1</td>
<td>93.44(11)</td>
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</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
#1 –x+1,-y,-z+1

Table S2. Selected bond distances [Å] and angles [°] of MOF_{CH3-as} (173 K).

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</thead>
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<tr>
<td>Ni(1)-N(1A)^#1</td>
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</tr>
<tr>
<td>Ni(1)-N(1A)</td>
<td>2.066(2)</td>
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<td>Ni(1)-N(2A)^#1</td>
<td>2.064(2)</td>
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<tr>
<td>Ni(1)-N(2A)</td>
<td>2.064(2)</td>
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<td>Ni(1)-O(1B)^#1</td>
<td>2.1081(16)</td>
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<tr>
<td>Ni(1)-O(1B)</td>
<td>2.1080(16)</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-N(1A)</td>
<td>180.00(10)</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-N(2A)^#1</td>
<td>93.69(9)</td>
</tr>
<tr>
<td>N(1A)^#1-Ni(1)-N(2A)</td>
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<td>N(1A)^#1-Ni(1)-O(1B)^#1</td>
<td>93.44(8)</td>
</tr>
<tr>
<td>N(1A)-Ni(1)-O(1B)</td>
<td>91.92(9)</td>
</tr>
<tr>
<td>N(1A)-Ni(1)-O(1B)^#1</td>
<td>93.44(8)</td>
</tr>
<tr>
<td>O(1B)^#1-Ni(1)-O(1B)</td>
<td>180.00(6)</td>
</tr>
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</table>

Symmetry transformations used to generate equivalent atoms:
#1 –x+1,-y+2,-z+2
Table S3. Gas sorption data of MOF$_{\text{NH2}}$:crystal.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$T$ (K)</th>
<th>Surface area ($\text{m}^2/\text{g}$)$^a$</th>
<th>Total pore volume ($\text{cm}^3/\text{g}$)$^b$</th>
<th>Adsorbed gas wt%</th>
<th>mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>77</td>
<td>13</td>
<td>0.017</td>
<td>1.1</td>
<td>0.39</td>
</tr>
<tr>
<td>H$_2$</td>
<td>77</td>
<td></td>
<td>0.037</td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>195</td>
<td></td>
<td>0.73</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273</td>
<td></td>
<td>0.74</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>298</td>
<td></td>
<td>1.40</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>2.72</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>348</td>
<td></td>
<td>4.45</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>373</td>
<td></td>
<td>5.80</td>
<td>1.32</td>
<td></td>
</tr>
</tbody>
</table>

$^a$The specific surface area was calculated by Brunauer-Emmet-Teller method. $^b$Total pore volume was calculated at $P/P_0 = 0.990$.

Table S4. Gas sorption data of MOF$_{\text{NH2}}$:powder.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$T$ (K)</th>
<th>Surface area ($\text{m}^2/\text{g}$)$^a$</th>
<th>Total pore volume ($\text{cm}^3/\text{g}$)$^b$</th>
<th>Adsorbed gas wt%</th>
<th>mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>77</td>
<td>17.2</td>
<td>0.056</td>
<td>4.1</td>
<td>1.5</td>
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<tr>
<td>H$_2$</td>
<td>77</td>
<td></td>
<td>0.051</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>195</td>
<td></td>
<td>2.5</td>
<td>0.56</td>
<td></td>
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<td></td>
<td>273</td>
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<td>5.46</td>
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<td>323</td>
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<td>373</td>
<td></td>
<td>7.69</td>
<td>5.80</td>
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</tbody>
</table>

$^a$The specific surface area was calculated by Brunauer-Emmet-Teller method. $^b$Total pore volume was calculated at $P/P_0 = 0.990$. 
Table S5. Gas sorption data of MOF$_{\text{CH3}}$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$T$ (K)</th>
<th>Adsorbed gas</th>
<th>wt%</th>
<th>mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
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<td>H$_2$</td>
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<td>0.0074</td>
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<td>CO$_2$</td>
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<td></td>
<td>9.3</td>
<td>2.1</td>
</tr>
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<td></td>
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</tr>
<tr>
<td></td>
<td>273</td>
<td></td>
<td>2.0</td>
<td>0.45</td>
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</table>
Calculation of isoseric heat of adsorption ($Q_{st}$)

A single-site Langmuir-Freundlich equation (eq 1) was employed to fit the experimental data for CO$_2$ adsorption in MOF$_{NH2}$:powder.

$$q = \frac{q_{sat} \cdot b \cdot p^\alpha}{1 + b \cdot p^\alpha}$$  \hspace{1cm} (1)

$q$ is the CO$_2$ uptake (mmol g$^{-1}$), $p$ is the pressure (bar), $q_{sat}$ is the saturated capacity (mmol g$^{-1}$), $b$ is the Langmuir-Freundlich constant and $\alpha$ is the Langmuir-Freundlich exponent.

Utilizing single-site Langmuir adsorption model, the exact pressures was obtained with the CO$_2$ adsorption data at 50 and 75 °C. The Clausius-Clapeyron formula (eq 2) was used to calculate the isosteric heats of adsorption ($Q_{st}$).

$$(\ln p)_q = \left(\frac{Q_{st}}{R} \right) \left(\frac{1}{T}\right) + C$$  \hspace{1cm} (2)

**Figure. S1.** Experimental CO$_2$ adsorption data in MOF$_{NH2}$:powder at 50 and 75 °C., and corresponding single-site Langmuir-Freundlich (SSLF) isotherm fit.
**Figure. S2.** XRPD patterns of the mixture after evaporation of the solvent when using LiOH·H₂O as Lithium precursor before calcination.

**Figure. S3.** SEM images of Li₄SiO₄ synthesized by wet-mixing (a) using fumed silica (b) SiO₂ sphere.
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Appendix
4,4’-Biphenyldicarboxylate sodium coordination compounds as anodes for Na-ion batteries†

Aram Choi,‡ Yun Kyeong Kim,‡ Tae Kyung Kim, Mi-Sook Kwon, Kyu Tae Lee* and Hoi Ri Moon*‡

Novel 4,4’-biphenyldicarboxylate (bpdc) sodium salts with different compositions were evaluated for the first time as anodes for Na-ion batteries, and their crystal structures and corresponding electrochemical performances were analyzed. The structure of the bpdc-sodium salts was modified using precipitation and solvothermal methods to afford three different crystal structures with different degrees of deprotonation of the carboxylic acid (COOH) groups and different coordination of the water molecule, as determined by single crystal X-ray diffraction. The extent of deprotonation in bpdc-sodium salts not only affects their electrochemical performance, but also affects the corresponding reaction mechanisms. The fully deprotonated bpdc-disodium salt exhibits a promising electrochemical performance with a reversible capacity of about 200 mA h g⁻¹ at ca. 0.5 V vs. Na/Na⁺, stable cycle performance over 150 cycles, and an excellent rate performance of 100 mA h g⁻¹ even at a 20 C rate, which are better than those of the partially deprotonated bpdc-sodium salt. The sodiation–desodiation of bpdc-sodium salts proceeds in a two-phase reaction, regardless of the degree of deprotonation. However, unlike the fully deprotonated bpdc-disodium salt, which shows a reversible phase transition during sodiation and desodiation, the partially deprotonated bpdc-sodium salt exhibits an irreversible phase transition during cycling.

1. Introduction

Sodium-ion batteries are considered a promising alternative for next-generation batteries that can replace Li-ion batteries in large-scale energy storage systems and electric vehicles, because of their potential cost advantages owing to the natural abundance of Na resources and geographically constrained Li resources.†–‡ A variety of electrode materials such as non-graphitic carbons, alloys (e.g., Sn and Sb), metal oxides, and phosphorus‡⁻²⁸ have been shown to exhibit promising electrochemical performances as anodes for Na-ion batteries. Recently, a few organic compound-based materials such as conjugated and aromatic compounds containing carbonyl groups or N-heterocycles have been reported as promising anode materials because of their attractive features such as good electrochemical performance, low-cost production, recyclability, and structural diversity. For example, organic electrode materials can be produced from commonly used recycled materials such as polyethylene terephthalate (PET). Several sodium terephthalate derivatives with amino- and bromo-groups have been easily synthesized owing to the structural diversity of organic architecture, resulting in controllable redox potential changes through inductive and resonance effects. However, only a small number of organic compounds have been examined as electrode materials for rechargeable batteries such as Li-ion and Na-ion batteries. In particular, only a few organic compounds have been examined as electrode materials for Na-ion batteries. Herein, we evaluated novel bpdc-sodium salts as anodes for Na-ion batteries for the first time and elucidated the correlation between the structural properties of organic anodes and their electrochemical performances. The bpdc-sodium salts were obtained using three different synthetic methods: precipitation at low and room temperatures, and solvothermal methods. Based on the degree of deprotonation of the carboxylic acid (COOH) groups and the coordination of water molecules, three different crystal structures for the bpdc-sodium salts were obtained. The crystal structures were determined and compared using single-crystal X-ray diffraction (XRD) and powder XRD (PXRD) patterns. The bpdc-sodium salts exhibit a promising electrochemical performance depending on the degree of deprotonation.

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‡ Electronic supplementary information (ESI) available: Table of X-ray data and voltage profiles. CCDC 944127 and 944128. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ta02424a
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2. Experimental section

Synthesis

\([\text{Na}[\text{Na(H}_2\text{O)}][\text{bpdc}]n] (\text{hyd-Na}_2\text{bpdc})\). To an aqueous suspension (3.2 mL) of 4,4'-biphenyldicarboxylic acid (H\(_2\)bpdc) (0.258 g, 1.06 mmol), an aqueous solution (0.8 mL) of NaOH (0.137 g, 3.43 mmol) was added. After the completion of the reaction, the solution was filtered, and the clear pale yellow filtrate was exposed to ethanol vapor inside a refrigerator (2 °C) to crystallize the products. After two days, block-shaped pale yellow single crystals of \([\text{Na}[\text{Na(H}_2\text{O)}][\text{bpdc}]n] (\text{hyd-Na}_2\text{bpdc})\) started to form at the surface of the solution. The crystals were filtered after seven days, washed with ethanol, and dried in air. Yield: 0.17 g (53%). FT-IR (ATR): \(\nu\) (carboxylic acid) 1672 cm\(^{-1}\); \(\nu\) (O(carboxylic acid) = O(carboxylic acid)) 1579(s); \(\nu\) (Na\(_2\)bpdc) 1390(s); \(\nu\) (Na(NO\(_3\)) 1309(s); \(\nu\) (H\(_2\)O) 1609 cm\(^{-1}\). Anal. calced for Na\(_2\)C\(_{14}\)H\(_{9}\)O\(_4\): C, 63.64; H, 3.43%. Found: C, 64.07; H, 3.31%. Found: C, 57.26; H, 3.27%.

\([\text{Na}_{2}\text{bpdc}] (\text{Na}\_2\text{bpdc})\). To a stirred aqueous suspension (25 mL) of H\(_2\)bpdc (2.42 g, 0.01 mol), an aqueous solution (7 mL) of NaOH (1.20 g, 0.03 mol) was added at room temperature. A suspension (3.2 mL) of Na\(_2\)bpdc was added. The completion of the reaction, the solution was filtered, and ethanol (20 mL) was added to the filtrate, resulting in white precipitates. The white precipitate obtained was filtered, washed with ethanol, and dried in air. Yield: 2.04 g (71%). FT-IR (ATR): \(\nu\) (Na\(_2\)bpdc) 1578(s); \(\nu\) (Na\(_2\)bpdc) 1394(s) cm\(^{-1}\). Anal. calced for Na\(_2\)C\(_{14}\)H\(_{8}\)O\(_4\): C, 58.76; H, 2.82%. Found: C, 57.48; H, 3.88%.

\([\text{NaHbpdc}] (\text{NaHbpdc})\). NaN\(_3\) (0.026 g, 0.30 mmol) was dissolved in methanol (2 mL) and H\(_2\)bpdc (0.036 g, 0.15 mmol) was dissolved in DMA–H\(_2\)O (5.1 mL, 4 : 1 v/v). The two solutions were placed in a glass jar and sealed together, and the mixture was heated at 100 °C for 48 h. The solution was then cooled to room temperature. The plate-shaped colorless crystals obtained were filtered, washed briefly with methanol, and dried in air. Yield: 0.029 g (74%). FT-IR (ATR): \(\nu\) (H\(_2\)bpdc) 1672 cm\(^{-1}\); \(\nu\) (O(carboxylic acid) = O(carboxylic acid)) 1605 and 1399 cm\(^{-1}\). Anal. calced for Na\(_2\)C\(_{14}\)H\(_{8}\)O\(_4\): C, 57.26; H, 3.34%. Found: C, 64.07; H, 3.88%.

Characterization

All chemicals and solvents used in the syntheses were of reagent grade and they were used as received without further purification. The IR spectra were recorded using a ThermoFisher Scientific Nicolet 6700 FT-IR spectrophotometer. Elemental analyses (EA) were performed at the UNIST Central Research Facilities (UCRF) in the Ulsan National Institute of Science and Technology (UNIST). Thermogravimetric analyses (TGA) were performed under a N\(_2\) (g) atmosphere at a scan rate of 5 °C min\(^{-1}\) using a Q50 (TA instruments). PXRD data were recorded using a Bruker D2 PHASER automated diffractometer at 30 kV and 10 mA for Cu K\(_\alpha\) (\(\lambda = 1.54050\) Å), with a step size of 0.02° in 2θ. Scanning electron microscopy was carried out using a cold FE-SEM (Hitachi). Single crystals of hyd-Na\(_2\)bpdc and NaHbpdc, coated with Paratone-N oil, were mounted on a loop, and the diffraction data were collected with synchrotron radiation (\(\lambda = 0.64999\) Å at 95 K for hyd-Na\(_2\)bpdc; 0.69999 Å at 100 K for NaHbpdc) using an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at Pohang Accelerator Laboratory, S. Korea. The ADSC Q210 A
d program was used for the data collection, and HKL3000 (Ver. 703r) was used for the cell refinement, reduction, and absorption correction. The structures of hyd-Na\(_2\)bpdc and NaHbpdc have been deposited in the CCDC database, reference numbers 944127 and 944128, respectively.

Electrochemical measurements

The samples of electrochemically active materials (57.1 wt%) were mixed with carbon black (Super P, 28.6 wt%) and carboxymethyl cellulose (CMC, 14.3 wt%). The loading amount of electrode materials is about 1 mg cm\(^{-2}\). The electrochemical performance was evaluated using 2032 coin cells with a Na metal anode and 0.8 M NaClO\(_4\) in a mixture of ethylene carbonate and diethyl carbonate (1 : 1 v/v) electrolyte solution. The galvanostatic experiments were performed at 30 °C, and specific current densities of 18.7 mA g\(^{-1}\) (ca. 0.1 C) and 20.3 mA g\(^{-1}\) (ca. 0.1 C) were applied to evaluate the cycle performances of NaHbpdc and Na\(_2\)bpdc, respectively. For the rate performance evaluation, the discharging (desodiation) current density was fixed at 0.1 C, and the charging current was varied. The GITT experiments were performed between 0.1 and 2.5 V vs. Na/Na\(^+\) by applying a current corresponding to a C/20 rate in intervals of 1 h, separated by a rest period of 1 h. The electrochemical impedance spectroscopy (EIS) study was performed using a BIO Logic SP 150. The AC impedance measurements were recorded using a signal with an amplitude of 5 mV and a frequency range of 300 kHz to 1 mHz.

3. Results and discussion

The H\(_2\)bpdc ligand and sodium cations were reacted under three different reaction conditions to afford three different types of bpdc-sodium salts. Disodium bpdc monohydrate (hyd-Na\(_2\)bpdc), \([\text{Na}[\text{Na(H}_2\text{O)}][\text{bpdc}]n]\), was synthesized by the reaction of NaOH with H\(_2\)bpdc in water, and single crystals of the product were obtained by slow diffusion of ethanol at ca. 2 °C. NaOH was employed in this reaction as a source of Na ions and a strong base for deprotonating the carboxylic acid (COOH) groups of H\(_2\)bpdc. On the other hand, interestingly, non-hydrated disodium bpdc (Na\(_2\)bpdc) was synthesized as a microcrystalline solid by the rapid reaction of NaOH with H\(_2\)bpdc in a mixture of water and ethanol at room temperature. The partially deprotonated sodium salt, monosodium bpdc (NaHbpdc), \([\text{Na}[\text{Hbpdc}]n]\), was synthesized by the solvolithothermal reaction of NaNO\(_3\) and H\(_2\)bpdc in a mixture of methanol, NN-dimethylacetamide (DMA), and water at 100 °C. Under these conditions, only one of two carboxylic acid (COOH) groups of H\(_2\)bpdc was deprotonated. Thus, the three bpdc-sodium salts were composed of the same organic (bpdc) and inorganic (Na\(^+\)) building blocks, but had different compositions and crystal structures.

Because hyd-Na\(_2\)bpdc and NaHbpdc could be obtained as single crystals, their crystal structures were directly determined

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and compared via single-crystal X-ray diffraction results. The lattice parameters, agreement factors, and detailed structural information of hyd-Na$_2$bpdc and NaHbpdc are listed in Table S1.† hyd-Na$_2$bpdc crystallized in the monoclinic P$2_1$/c space group. As shown in Fig. 1a, the structure of hyd-Na$_2$bpdc consisted of Na–O layers as the secondary building units (SBUs), and the bridging ligands, bpdc$^{2-}$, formed a three-dimensional (3D) network. The Na–O layers resulted from the coordination between Na$^+$ ions and O atoms of carboxylate groups (COO$^-$) and water molecules. The crystal structure of hyd-Na$_2$bpdc possessed two Na$^+$, two halves of the bpdc$^{2-}$ ligand, and one coordinating water molecule, which are crystallographically independent. Fig. 1c reveals the coordination modes of carboxylates (COO$^-$) in hyd-Na$_2$bpdc to be as follows: the O1–C1–O2 group acts as a tetradentate ligand forming a four-membered chelate ring, and the O3–C8–O4 group coordinates to four Na ions without chelation. Na1 and Na2 exhibited a distorted trigonal bipyramidal and an octahedral coordination geometry, respectively. The bpdc$^{2-}$ ligand was planar with a dihedral angle of 0° between the two phenyl rings.

NaHbpdc crystallized in the triclinic P1 space group. The crystal structure of NaHbpdc showed two crystallographically independent Na$^+$ ions and one bpdc$^{2-}$ ligand. The Na$^+$ ions were bridged by carboxylate groups (COO$^-$) to form one-dimensional (1D) Na–O chains as SBUs, which were linked by bpdc$^{2-}$ ligands to form a 3D network (Fig. 1b). Na1 and Na2 showed distorted octahedral and square planar geometry, respectively. Unlike hyd-Na$_2$bpdc, the phenyl rings in the bpdc$^{2-}$ ligand of NaHbpdc were tilted by 30.69(5)°. Because the carboxylic acid (COOH) groups in NaHbpdc were partially deprotonated, the deprotonated O1–C1–O2 group coordinated to three Na ions using both the oxygen atoms. In contrast, only the O3 atom in O3–C8–O4–H44 acted as a bidentate ligand (Fig. 1d).

The PXRD patterns of the as-synthesized hyd-Na$_2$bpdc and NaHbpdc powders were compared to the simulated patterns based on the single crystal XRD data, respectively. As shown in Fig. 2a–d, the XRD patterns of both the bulk powders showed good agreement with the corresponding simulated patterns, indicating that the phase pure powders have the same crystal structure as the single crystals. On the other hand, because Na$_2$bpdc was obtained as microcrystals, which are not suitable for single crystal XRD analysis, its PXRD pattern (Fig. 2e) was compared to those of hyd-Na$_2$bpdc and NaHbpdc. Na$_2$bpdc showed a different PXRD pattern, indicating that the crystal structure of Na$_2$bpdc was different from those of hyd-Na$_2$bpdc and NaHbpdc. However, the structure of Na$_2$bpdc was found to be the same as that of hyd-Na$_2$bpdc after the coordinating water.
molecules were removed (Fig. 2f). hyd-Na₂bpdc was dehydrated by heating at 120 °C under vacuum. The dehydration results in a weight loss of 5.98% below 100 °C in the thermogravimetric analysis (TGA) curves of hyd-Na₂bpdc (Fig. 3). The amount of weight loss corresponded to one water molecule per molecular formula. The incorporation of water molecules in the structure of Na₂bpdc may depend on the reaction temperature as well as the reaction rate.

Further, the structural similarity between hyd-Na₂bpdc and Na₂bpdc is indirectly supported by the TGA curves because they show the same thermal behavior except for the water loss in hyd-Na₂bpdc below 100 °C (Fig. 3). Although both hyd-Na₂bpdc and Na₂bpdc are decomposed at ca. 600 °C, Na₂bpdc did not show any weight loss around 100 °C indicating that this compound is not hydrated. On the other hand, NaHbpdc exhibited no weight loss around 100 °C, which is consistent with the single-crystal XRD data of NaHbpdc, which is not hydrated. The structure of NaHbpdc is rapidly decomposed above 300 °C. The lower thermal stability of NaHbpdc compared to hyd-Na₂bpdc and Na₂bpdc is attributed to the weak coordination between Na⁺ ions and the carbonyl group of carboxylic acid (COOH) groups, which were not deprotonated. This indicates that a higher degree of deprotonation is required to improve the thermal stability of organic electrode materials.

The acid–base reactions of H₂bpdc with sodium precursors to produce hyd-Na₂bpdc, Na₂bpdc and NaHbpdc were further verified by Fourier transform infrared (FT-IR) spectroscopy. As shown in Fig. 4, the spectrum of H₂bpdc showed typical C=O stretching and O–H bending vibrations of carboxylic acid (COOH) groups at 1668 and 922 cm⁻¹, respectively. However, after the formation of the metal–carboxylate coordination (COO–Na) compounds via complete deprotonation by NaOH, the carbonyl (C=O) stretching vibration of the carboxylate groups (COO⁻) in hyd-Na₂bpdc was shifted and split into two bands at 1579 and 1390 cm⁻¹, which were assigned to asymmetric (νas) and symmetric (νs) stretching vibrations, respectively (Fig. 4). Moreover, the characteristic O–H bending vibrations for the carboxylic acid groups around 920 cm⁻¹ disappeared. The weak peak at 1690 cm⁻¹ in the spectrum of hyd-Na₂bpdc corresponds to the O–H bending vibration of water.

This observation agrees with the existence of guest water molecules, as suggested by single-crystal XRD and TGA data. Na₂bpdc showed the same FT-IR spectrum as hyd-Na₂bpdc, except for the peak around 1690 cm⁻¹. As expected from the XRD and TGA results, the FT-IR spectrum of NaHbpdc, containing both of the protonated and deprotonated form of carboxylic acid groups, showed peaks characteristic of both COOH and COO⁻ groups, i.e., C=O stretching and O–H bending vibrations of carboxylic acid at 1672 and 923 cm⁻¹, respectively, and νas and νs of the carboxylate groups at 1605 and 1399 cm⁻¹, respectively (Fig. 4).

As shown in Fig. 5, Na₂bpdc and NaHbpdc, which have different crystal structures and degrees of deprotonation of the organic ligands, were examined as anode materials for Na-ion batteries. The cycle performance of hyd-Na₂bpdc was not examined separately because it transforms into Na₂bpdc during the preparation of the electrodes. The electrodes were dried at 120 °C under vacuum to remove the adsorbed water molecules.
on the surface of powders that is related to electrolyte decomposition during charging/discharging. This drying process leads to the dehydration of hyd-Na$_2$bpdc to afford Na$_2$bpdc. Both Na$_2$bpdc and NaHbpdc electrodes showed similar reversible capacities of approximately 200 mA h g$^{-1}$ at ca. 0.5 V vs. Na/Na$^+$, which is larger than the theoretical specific capacity of 187 mA h g$^{-1}$ corresponding to the storage of two Na$^+$ ions, as shown in Scheme 1. The excess capacity (about 10 mA h g$^{-1}$) is attributed to carbon additive (super P) that can reversibly store Na$^+$ ions and deliver about 100 mA h g$^{-1}$ (Fig. S2†). The gravimetric specific capacity of bpdc-sodium salts is relatively small compared to other anode materials. Moreover, the densities of Na$_2$bpdc and NaHbpdc are 1.566 g cm$^{-3}$ and 1.657 g cm$^{-3}$, respectively, based on X-ray single crystallographic data, which causes a low volumetric energy density. However, these organic electrode materials are inexpensive, indicating that organic electrode materials have an advantage of low cost/energy density. Above all, organic electrode materials are environmentally benign and reproducible, and this makes organic electrode materials attractive in spite of their relatively low energy density. Also, they showed a stable cycle performance over 150 cycles. Notably, unlike Na$_2$bpdc, NaHbpdc showed a large amount of irreversible capacity at the first cycle. The coulombic efficiencies of Na$_2$bpdc and NaHbpdc at the first cycle were 81% and 47%, respectively. The poor coulombic efficiency of NaHbpdc (large sodiation capacity at the first cycle) is attributed to its irreversible electrolyte decomposition on the surface of NaHbpdc possessing carboxylic acid groups. The same behavior, i.e., a large amount of irreversible capacity at the first cycle, was also observed in a partially deprotonated monosodium terephthalate,

while a fully deprotonated disodium terephthalate showed good coulombic efficiency similar to Na$_2$bpdc.

The rate performances of Na$_2$bpdc and NaHbpdc were also compared, as shown in Fig. 6 and S1.† Na$_2$bpdc showed a better rate performance than NaHbpdc, and even at a 20 C rate (3.74 A g$^{-1}$), Na$_2$bpdc sustained 50% of the reversible capacity delivered at a 0.2 C rate. This superior rate performance of Na$_2$bpdc is definitely attributed to the smaller particle size (diffusion length) of Na$_2$bpdc compared to NaHbpdc, as shown in Fig. 7. The particle sizes of Na$_2$bpdc and NaHbpdc are a few μm and approximately 10 μm, respectively. However, even the dehydrated hyd-Na$_2$bpdc, which has a size similar to NaHbpdc, exhibited a better rate performance than NaHbpdc, indicating that the rate performance is affected by both the degree of deprotonation and the particle size of the bpdc-sodium salts. Note that little change of particle sizes of NaHbpdc and Na$_2$bpdc was observed after water-treatment under the same conditions of electrode preparation, because only a very small amount of water was used for the electrode preparation despite the fact that they are slightly soluble in water, indicating that the particle sizes of NaHbpdc and Na$_2$bpdc were not changed after the electrode preparation.

Fig. 6 Rate performance of hyd-Na$_2$bpdc, Na$_2$bpdc and NaHbpdc.

Fig. 7 SEM images of bare (a) NaHbpdc, (b) Na$_2$bpdc, and (c) hyd-Na$_2$bpdc powders, and water-treated (d) NaHbpdc and (e) Na$_2$bpdc powders under the same conditions of electrode preparation.
cells comprised of the same working electrode (bpdc salt)/working electrode (bpdc salt). The working electrodes were half-sodiated charging state after pre-cycling. As shown in Fig. 8, the semicircle of NaHbpdc is larger than that of hyd-Na2bpdc, indicating that the charge-transfer resistance of NaHbpdc is larger than that of hyd-Na2bpdc because the semicircle corresponds to charge-transfer resistance that is dependent on SEI layers. Also, the smaller charge-transfer resistance of Na2bpdc than hyd-Na2bpdc is attributed to the larger surface area caused by smaller particle size. Moreover, while both the Na cations present in the structure of Na2bpdc can act as charge carriers for the solid state diffusion of Na ions, the proton present in the structure of NaHbpdc cannot act as a charge carrier because it is strongly bound to the carbonyl group through covalent bonding. This indicates that the reduced amount of charge carriers in NaHbpdc compared to Na2bpdc causes slower ionic diffusivity of Na+ ions, resulting in poorer rate performance.

To observe the structural changes upon sodiation/desodiation, ex situ XRD analysis of Na2bpdc was performed, and it showed that the reversible sodiation/desodiation of Na2bpdc proceeds in a two-phase reaction, as shown in Fig. 9. Upon sodiation, the intensity of PXRD peaks corresponding to Na2bpdc decreased, and new peaks corresponding to the sodiated phase of Na2bpdc gradually appeared at ca. 11, 20, 23 and 31° (and vice versa for the desodiation). Despite two plateau steps in the voltage profile of desodiation during the first cycle, the ex situ XRD patterns showed that only one type of two-phase reaction occurred during the desodiation. This agrees well with the galvanostatic intermittent titration technique (GITT) curves, as shown in Fig. 10. Although two plateaus were observed during the first cycle, the second plateau is attributed to larger polarization because of a higher mass transfer resistance in Na-deficient compositions. This type of polarization behavior gradually disappeared on cycling, and may be closely related to the amorphization of Na2bpdc during the cycling. As shown in the ex situ XRD patterns of the electrodes during cycling (Fig. 9c), broader PXRD peaks were observed after the cycling, indicating that the amorphization of Na2bpdc occurred during cycling. In general, materials that are more amorphous show less polarization owing to the faster ionic diffusion at grain boundaries.

Unlike Na2bpdc, NaHbpdc showed an irreversible phase transformation during the sodiation and desodiation, as shown in Fig. 11. NaHbpdc proceeds in a two-phase reaction during the sodiation and desodiation; however, the mixture phases of NaHbpdc and Na2bpdc were observed after the desodiation. This indicates that the ion exchange occurred between the proton of the carboxylic acid group in NaHbpdc and sodium ions in electrolytes during cycling. Similar behavior has been observed in the partially deprotonated monosodium terephthalate, which was

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**Fig. 8** Nyquist plots of bpdc electrode/bpdc electrode symmetric cells.

**Fig. 9** Ex situ XRD analysis of Na2bpdc: (a) voltage profiles, (b) corresponding XRD patterns, and (c) XRD patterns of desodiated electrodes during the various cyclings.

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transformed into the fully deprotonated disodium terephthalate due to the ion exchange between the proton and sodium during sodiation and desodiation. The ion exchange of NaHbpdc powders was not observed when NaHbpdc powders were stored in electrolytes for 3, 5, and 10 days without passage of current, as shown in Fig. S3,† and thus, the ion exchange is merely related to electrochemical sodiation and desodiation. The ion-exchange behaviour of NaHbpdc on cycling is further supported by the comparison between the differential capacity (dQ/dV) plots of NaHbpdc and Na2bpdc. As the cycle number increases, the intensity of oxidative peaks of NaHbpdc at 0.5 V and 0.6 V vs. Na/Na⁺ decreases and increases, respectively (Fig. 12a). The oxidative peak at 0.6 V corresponds to the oxidative peak of Na2bpdc, as observed in the dQ/dV plots of Na2bpdc (Fig. 12b). Therefore, this indicates that some of the NaHbpdc was transformed into Na2bpdc during cycling.

4. Conclusions

In conclusion, the crystal structures and electrochemical performance of bpdc-sodium salts as anode materials for Na-ion batteries have been evaluated for the first time. The different degrees of deprotonation and differently coordinated water molecules in the bpdc-sodium salts were obtained through deliberate synthesis such as precipitation and solvothermal methods, resulting in the formation of bpdc-sodium salts with three different crystal structures. Their crystal structures were determined using single-crystal XRD. The bpdc-sodium salts exhibited a promising electrochemical performance with a reversible capacity of 200 mA h g⁻¹ at ca. 0.5 V vs. Na/Na⁺,
negligible capacity fading over 150 cycles, and an excellent rate performance of approximately 100 mA h g$^{-1}$ even at a 20 C rate. The sodiation/desodiation of bpdc-sodium salts proceeds in a two-phase reaction. In addition, the degree of deprotonation in bpdc-sodium salts not only affected the electrochemical performance, but also affected the corresponding reaction mechanisms. The fully deprotonated bpdc-disodium salt (Na$_2$bpdc) showed better coulombic efficiency and rate performance than the partially deprotonated bpdc-monosodium salt (NaHbpdc). Unlike Na$_2$bpdc, which showed irreversible phase transition during sodiation and desodiation, NaHbpdc exhibited an irreversible phase transition during the cycling.

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**Notes and references**

Guest-driven structural flexibility of 2D coordination polymers: Synthesis, structural characterizations, and gas sorption properties

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Two coordination polymers, \{[(NiLallyl)2(BuTC)]·2DEF·H2O\}, \{[(NiLallyl)2(BuTC)]·3H2O\} (1), and \{[(NiLallyl)2(BuTC)]·3H2O\} (2), \{[(NiLallyl)](CO3)2 = [Ni(C14H30N6) + ClO4\2. BuTC = 1,2,3,4-butane-tetracarboxylic acid, DEF = N,N'-diethylformamide\}, were prepared by the self-assembly of [NiLallyl][ClO4]2 and H2BuTC in DEF/H2O and acetone tri-nitrite/H2O, respectively. Single crystal X-ray diffraction and X-ray powder diffraction (XRPD) results revealed that 1 and 2 have two-dimensional layered structures, and the layers were intercalated between the layers. Since both of coordination polymers 1 and 2 were constructed from the same building blocks, the structure of each layer was identical. However, depending on the size and the nature of guest molecules, layer packing and the interlayer distances were different for each coordination polymer. Interestingly, due to the instability of DEF guest molecules intercalated in the coordination polymer 1, these guest molecules could be easily liberated from the host, consequently resulting in the same XRPD pattern as that of 2 with slightly different relative intensities. Dried compounds of 1 and 2 (1' and 2', respectively) also showed the same result as evidenced by the XRPD patterns. The similar but non-identical XRPD patterns were revealed that the dried structure 1' had the same interlayer distance and the same intralayer structure as 2 and 2' did, whereas its layer packing remained the same as that of 1. This subtle structural difference of 1' and 2' resulted in their different CO2 uptake behaviors at 195 K.

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Multidimensional coordination polymers are constructed by the reaction between metal building blocks and coordinating organic ligands. Coordination polymers have attracted much attention due to their vast potential for applications in various fields such as gas storage [1,2], catalysis [3–5], molecular separation [6,7], and sensing [8–10]. Since the interesting properties of the coordination polymers for practical applications are greatly influenced by their structures [11,12], intensive efforts have been devoted to the design of new architectures for coordination polymers. Among them, an interesting approach is the formation of various coordination polymer structures by varying the guest molecules with different functional groups of diverse shapes and sizes [13,14]. In this approach, the structural control of the coordination polymers is based on an understanding of the interaction between the host framework and the guest molecules, and of the influence of the guest molecules on the coordination behavior of the metal ions and the organic linker. Previously, the structural diversities of several coordination polymers upon the interaction of guest molecules have been observed. For example, [Zn2(adb)2(dabco)] (adb = 9,10-anthracene dibenzoate, dabco = 1,4-diazabicyclo[2.2.2]octane) showed translation from kinetic phase to thermodynamic phase as guest molecules were removed [15]. The desolvation and resolution of [M2(2.6-ndc)2(dabco)] (M = Ni, Co, and Zn; ndc = 2,6-naphthalenedicarboxylate) caused closing and opening the pore [16]. [Zn2(bdc)2(tea)] (bdc = terephthalate, tea = triethylamine) showed reversible structural changes with pore opening and closing, which were induced by changing the shape of guest molecules [11].

Two-dimensional (2D) coordination polymers offer a good example for demonstrating the flexible change in their structures depending on the amount as well as the size and shape of the intercalated guest molecules. Herein, we report the synthesis and single-crystal structures of two 2D coordination polymers, \{[(NiLallyl)2(BuTC)]·2DEF·H2O\} (1) and \{[(NiLallyl)2(BuTC)]·3H2O\} (2), which are self-assembled in two different kinds of solvent systems, and their interesting structural flexibility and the CO2 sorption behavior depending on guest molecules.

To construct the guest-responsive coordination polymers, the host frameworks need to possess the functional groups required to effectively interact with the guest molecules, and need to have structural flexibility. Thus, we employed a flexible aliphatic ligand, 1,2,3,4-butanetetracarboxylic acid (H2BuTC), and a Ni(II) macrocyclic complex with two allyl pendant arms, [NiLallyl]2+ ([NiLallyl]2+ = [Ni(C14H30N6)], during the self-assembly reaction, [NiLallyl]2+ is present in a square planar geometry and acts as a linear linker because its two
axial positions could be accessed by the carboxylate of BuTC$^{4-}$ ligand for coordination. BuTC$^{4-}$ ligand has four carboxylate groups, which can freely rotate and can be stretched along four different directions. As shown in Scheme 1, the coordination between the square planar Ni(II) ions incorporated in the macrocyclic complex and the tetradentate carboxylate ligand yielded the 2D layered structures resulting in six-coordinated octahedral Ni(II) centers. For the self-assembly, we utilized two kinds of solvent systems; for the coordination polymer 1, DEF and H$_2$O (4/1.9, v/v, mL/mL) mixture was used, and for 2, acetonitrile and H$_2$O (2/0.4, v/v, mL/mL) mixture was used [17]. After reacting for 7 days, pale purple crystals of 1 and 2 were formed in the reaction mixture, which were suitable enough for single-crystal X-ray analysis [18]. Detailed single crystal X-ray crystallographic information and selected bond lengths and bond angles for 1 and 2 are listed in Table S1 to S3.

Fig. 1a shows a fundamental building unit of 1, which is the same as the fundamental building unit of 2 (Fig. S1). The axial positions of the Ni(II) macrocycle are occupied by carboxylate anions from the two BuTC$^{4-}$ ligands in a monodentate fashion with the average Ni–O distance of 2.105(2) Å for 1 and 2.108(2) Å for 2. Since each carboxylate group in a BuTC$^{4-}$ ligand binds to four different macrocycles and the tetradentate ligands extend in a square grid fashion, the infinite coordination between Ni(II) macrocycles and BuTC$^{4-}$ ligands forms the 2D layer (ab plane) composed of the rectangular compartments (Fig. 1b). The asymmetric unit contains two crystallographically independent Ni(II) macrocycles, which are coordinated with the carboxylate groups located on two different environments, 1 and 4 versus 2 and 3 positions on the butane chain of 1,2,3,4-BuTC$^{4-}$ ligand. In both structures, the allyl pendant arms of macrocycles coordinated with the carboxylates on 2 and 3 positions show the disorderness in the structure. Due to the flexibility of the aliphatic chain of BuTC$^{4-}$ ligand, the conformation of BuTC$^{4-}$ ligand in 2 is slightly different from that in 1, but it does not affect the entire layer structure of 2 (Fig. S2). The guest molecules, two DEF and two water molecules for 1 and three water molecules for 2 per formula, are intercalated between the layers as evidenced by elemental analyses as well as thermogravimetric analysis (TGA) (Fig. S3). Despite the high boiling point of DEF molecules, those are easily liberated from 1 at a relatively low temperature (~100 °C), which might be attributed to the week molecular interaction between the guest molecules and the host framework. For that reason, even under the careful treatment of the crystal, disordered DEF molecules were not refined properly in the X-ray structure of 1, and thus the data was necessarily squeezed.

Scheme 1. Synthetic scheme of 2D coordination polymers 1 and 2.
Since the guest water molecules in 1 and 2 are located close to the secondary amine group of the macrocycles with very strong hydrogen bonds (N4–OW1 3.015(5) Å and N4–H4···OW1 148.6 ° for 1; N5–OW1 2.968(13) Å and N5–H5···OW1 148.9 ° for 2), those were confirmed by single crystal X-ray crystallography. While the composition of the reaction solvent mixtures does not affect the local structure on each layer, it greatly affects the infinite structure made by stacking of the 2D layers in both coordination polymers. Coordination polymer 1 possesses the triclinic system with space group P –1, whereas 2 is crystallized in monoclinic system with the space group P2/1. In the coordination polymer 1, equivalent layers are stacked in the −A–A–A– manner (Fig. 1c). However, in the coordination polymer 2, due to the existence of a twofold screw axis between the layers, two different kinds of layers are packed alternatively through the c axis in the −A–B–A–B– fashion (Fig. 1d). In addition, because of the bulkiness of DEF molecules, the layer-layer distance in 1 (12.96 Å) is much larger than that in 2 (9.47 Å) as shown in Fig. 1c and d.

To examine structural changes in compounds driven by the removal of guest molecules, both compounds 1 and 2 were dried by heating at 100 °C under vacuum for 7 h, generating the dried compounds 1’ and 2’, respectively. The structural diversities in 1’ and 2’ compared with 1 and 2, respectively, were proved by the X-ray powder diffraction (XRPD) patterns. The measured XRPD pattern for 1 shows good agreement with the simulated pattern based on the single crystal X-ray diffraction data except for 2θ = 9.76, 11.9, 14.7, 16.1 ° peaks (Fig. 2a). The mismatched peaks of 1 agree with the peaks from the XRPD pattern of dried compound 1’. Those mismatched peaks might have been generated during the sample preparation and data collection, and those peaks slightly appeared even in the measurement of the wet sample in mother liquor with a faster scan rate (Fig. S7). Consequently, they are attributed to the instability of the DEF molecules in structure 1, and DEF molecules were rapidly removed from the interlayer spaces, resulting in the coexistence of the dried structure 1’ with the original structure 1. On the other hand, XRPD pattern of 2 exhibits the same pattern as that of the 2’ as well as that from the simulated data (Fig. 2b). Interestingly, 1’ obtained after evacuating the guest molecules from 1 showed the same pattern as 2 and 2’ with slightly different relative intensities.

Fig. 1. X-ray crystal structures of 1 and 2. (a) An ORTEP drawing of 1 with atomic numbering scheme. Symmetry operations: 1, -x + 1, -y, -z; 2, -x, -y, -z; 3, -x, -y, -z. Grey part is the disordered structure of allyl pendant arms. (b) The 2D layer structure of 1. Ni, yellow; C, gray; N, blue; O, red. Green part correspond to the ORTEP drawing in (a). The stacking of the 2D layers for (c) 1, and (d) 2. Six-coordinated Ni(II) center was described as an octahedron.

Fig. 2. X-ray powder diffraction (XRPD) patterns of (a) 1 and (b) 2. Black, measured patterns of as-synthesized 1 and 2; red, the simulated patterns for 1 and 2 based on the single crystal X-ray data; blue, measured patterns of dried compounds, 1’ and 2’.
might be attributed to the subtle structural differences between desorption curve. These different behaviors for gas molecule uptake are larger than those of $1''$, and 2.7 wt.% for $1', and 2.7 wt.% for $2'$ (Fig. 3b). $1'$ adsorbed CO$_2$ molecules with a two-step adsorption profile as well as a large hysteric desorption curve. On the other hand, $2'$ showed no abrupt increase in adsorption of CO$_2$ in a single-step and it had a moderate hysteric desorption curve. These different behaviors for gas molecule uptake might be attributed to the subtle structural differences between $1'$ and $2'$ as described previously. Although the differences in structures are not distinguishable by XRPD patterns, the different packing modes result in the different inner pore structures [19]. In other words, unlike $2'$ with the $\text{A-A-A-}$ structure, since $1'$ with the $\text{A-A-A-}$ structure has closed pores that cannot accommodate N$_2$ molecules, the BET surface area of $1'$ is only 22% of $2'$. However, because flexible allyl pendant arms are exposed between the layers, open pores can be generated under high pressures especially for adsorbing CO$_2$ molecules, which have a small kinetic diameter (3.3 Å) and high quadrupole moment ($-1.4 \times 10^{-35}$ cm$^2$) [20,21]. Consequently $1'$ shows the second large adsorption step, and the same interlayer distance in $1'$ and $2'$ allows the similar total amount of adsorbed CO$_2$.

In conclusion, two 2D coordination polymers, [[Ni(Lallyl)$_2$(BuTC)] 2DEF2H$_2$O] (1) and [[Ni(Lallyl)$_2$(BuTC)] 3H$_2$O] (2), with different structural patterns were synthesized by employing two different solvent mixtures. The structural flexibilities of these coordination polymers upon guest removal were studied by single crystal X-ray analysis and XRPD patterns. In addition, interesting behavior of the two coordination polymers upon gas adsorption was examined.

Acknowledgments

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Appendix A. Supplementary material

Crystallographic data for the complex have been deposited with the Cambridge Crystallographic Data Centre (CCDC-922874 for 1 and CCDC-922875 for 2). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/xxx.

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Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate \(\text{M(OH)}_2\) and intrinsic dynamics in the \(\text{M}_2(2,6\text{-ndc})_2(\text{dabco})\) (\(\text{M} = \text{Ni, Cu, Co, Zn}\)) framework, J. Mater. Chem. 22 (2012) 10303–10312.

(b) Synthesis of 1: A solution of DEF/H_2O/TEA (2 mL/1 mL/0.125 mL) dissolving H_4BuTC (0.028 g, 0.1 mmol) was slowly added to a solution of DEF/H_2O (1.0 mL) and H_2O (0.4 mL), and an acetonitrile solution (1 mL) of H_4BuTC (0.027 g, 0.1 mmol) was diffused into the former solution at room temperature for 7 days until pale purple crystals were formed. Yield: 32.8%. Anal. Calcd for Ni_2C_{46}H_{92}N_{14}O_{12}: C, 48.01; H, 7.51; N, 17.71. FT-IR for 1 (KBr pellet): \(\nu\text{ (max.)}: 510 \text{ nm}, 332 \text{ nm}, 210 \text{ nm}\). (b) Synthesis of 2: [NiL_{allyl}(ClO_4)_2] (0.120 g, 0.2 mmol) was dissolved in a mixture of acetonitrile (1.0 mL) and H_2O (0.4 mL), and an acetonitrile solution (1 mL) of H_4BuTC (0.027 g, 0.1 mmol) and TEA (0.120 mL) was diffused into the former solution at room temperature for 7 days until pale purple crystals were formed. Yield: 63.5%. Anal. Calc. For Ni_2C_{46}H_{92}N_{14}O_{12}: C, 47.29; H, 8.25; N, 16.96. FT-IR for 1 (KBr pellet): \(\nu\text{ (max.)}: 1558, \nu\text{ (C=O (DEF))}: 1643, \nu\text{ (C=O (BuTC))}: 1556, \nu\text{ (C=O (dabco))}: 1640, \nu\text{ (C=H (3083 cm^{-1}))}: 3075 \text{ cm}^{-1}\). UV–Vis (diffuse reflectance spectrum, \(\lambda_{\text{max}}\)): 511 nm, 331 nm, 215 nm.

Data collection were performed on a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) with synchrotron radiation (\(\lambda = 0.74999 \text{ Å for 1 and } \lambda = 0.75902 \text{ Å for 2}\) at the Pohang Accelerator Laboratory, Korea. The crystal structures of 1 and 2 was solved by the direct method and refined by full-matrix least-squares calculations with the SHELX-TL program package. Data of 1: C_{16}H_{35}NiO_5Ni, triclinic, space group P-1, \(a = 12.276(3) \text{ Å, } b = 9.7320(19) \text{ Å, } c = 12.961(3) \text{ Å, } \alpha = 106.74(3) \text{ °, } \beta = 76.14(3) \text{ °, } \gamma = 86.62(3) \text{ °. } V = 1426.0(5) \text{ Å}^3, Z = 2, \rho_{\text{crys}} = 1.104 \text{ g/cm}^3, \mu = 0.781 \text{ mm, GOF} = 1.107, 7882 reflections were measured, 3991 independent \(R\text{(int}) = 0.0150\) with \(I > 2\sigma(I)\). Final \(R\text{fl} = 0.0758\). Crystal Data of 2: C_{26}H_{68}Ni_2O_{10}Ni_2, monoclinic, space group P2_1/c, \(a = 12.243(2) \text{ Å, } b = 9.5330(19) \text{ Å, } c = 18.947(3) \text{ Å, } \alpha = 90\text{ °, } \beta = 101.88(3) \text{ °, } \gamma = 90\text{ °. } V = 2168.5(7) \text{ Å}^3, Z = 2, \rho_{\text{crys}} = 1.449 \text{ g/cm}^3, \mu = 1.028 \text{ mm, GOF} = 1.101, 17306 reflections were measured, 4754 independent \(R\text{(int}) = 0.0280\) with \(I > 2\sigma(I)\). Final \(R\text{fl} = 0.0579\). Crystal Data of 1 and 2 was solved by the direct method and refined by full-matrix least-squares calculations with the SHELX-TL program package. Crystal Data of 1: C_{16}H_{35}NiO_5Ni, triclinic, space group P-1, \(a = 12.276(3) \text{ Å, } b = 9.7320(19) \text{ Å, } c = 12.961(3) \text{ Å, } \alpha = 106.74(3) \text{ °, } \beta = 76.14(3) \text{ °, } \gamma = 86.62(3) \text{ °. } V = 1426.0(5) \text{ Å}^3, Z = 2, \rho_{\text{crys}} = 1.104 \text{ g/cm}^3, \mu = 0.781 \text{ mm, GOF} = 1.107, 7882 reflections were measured, 3991 independent \(R\text{(int}) = 0.0150\) with \(I > 2\sigma(I)\). Final \(R\text{fl} = 0.0758\).

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