Effects of Alkali Metal (Li, Na, and K) Incorporation in NH₂–MIL125(Ti) on the Performance of CO₂ Adsorption

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Received: 9 January 2019; Accepted: 8 March 2019; Published: 13 March 2019

Abstract: A series of titanium-based, metal–organic framework (MOF) materials, xM@NH₂–MIL125(Ti) (x is the alkali metal loading percentage during the synthesis; M = Li, Na, K), have been synthesized solvothermally. Alkali metal doping in the NH₂–MIL125(Ti) in situ solvothermal process demonstrated a vital modification of the material structure and surface morphology for the CO₂ adsorption capacity at ambient conditions. By changing the reactants’ precursor, including different kinds of alkali metal, the morphology of xM@NH₂–MIL125(Ti) can be adjusted from a tetragonal plate through a circular plate to a truncated octahedron. The variation of the alkali metal loading results in substantial differences in the CO₂ adsorption. The properties of xM@NH₂–MIL125(Ti) were evaluated via functional group coordination using FT-IR, phase identification based on X-ray diffraction (XRD), surface morphology through scanning electron microscopy (SEM), as well as N₂ and CO₂ adsorption by physical gas adsorption analysis. This work reveals a new pathway to the modification of MOF materials for high-efficiency CO₂ adsorption.

Keywords: alkali metal; CO₂ adsorption; metal-organic frameworks; NH₂–MIL125

1. Introduction

With rapid economic growth, excessive carbon consumption correlated with enhanced CO₂ emission into the atmosphere has caused involved environmental problems, such as global warming and climate change [1]. Carbon capture and storage (CCS) has been considered a prospective technological strategy to slow down gas emissions and alleviate the climate [2]. Up to now, there are multifarious approaches to CO₂ storage and separation, such as solvent absorption, physicochemical adsorption, membrane separation, cryogenic distillation, and so on [3]. Among the technologies applied for this purpose, adsorption of CO₂ into porous solid materials, such as zeolites, mesoporous silicas, porous carbon, and metal–organic frameworks (MOFs), has been gaining increasing attention due to its low energy requirements, cost-effectiveness, high adsorption capacity, and regeneration [4–7].

MOFs, exhibiting large internal surface area, controllable porosity and pore walls, and affinity for particular valuable gases, have been regarded as potential CO₂ adsorption and separation materials under mild conditions. Usually, MOFs are constructed through metal ions or clusters as connected centers, and polyfunctional organic ligands as connected linkers. As a matter of fact, the extended framework can be controlled by selecting the appropriate metal centers and organic linkers to obtain the desired structural features and physicochemical properties. In order to promote the CO₂ adsorption capacity and the separation selectivity over other gases, various strategies have been reported, such as metal cation incorporation [8,9], pore size and shape tuning [10], and ligand functionality [11–13].
The alkali metal incorporation strategy has been widely utilized in the field of hydrogen storage, which has been confirmed to be effective. However, the influence of alkali metal incorporation into MOF materials on CO\textsubscript{2} capture has been relatively less investigated. Lan et al. and Cao et al. showed clearly, by multiscale simulation, that the CO\textsubscript{2} uptake of lithium-doped covalent organic frameworks (COFs) was enhanced by four to eight times compared with the pristine COFs at 298 K and 1 bar [14,15]. Mu et al. studied the effect of different metal doping on the gas adsorption performance of MOFs through a grand canonical Monte Carlo (GCMC) simulation [16]. They found that CO\textsubscript{2} preferentially adsorbs at the alkali metal doping position. Babarao et al. studied Mg-IRMOF-1 and Be-IRMOF-1 (Isoreticular metal-organic frameworks, IRMOF), indicating that alkaline earth metal ion substitution improves adsorption capacity [17]. Xiang et al. analyzed the CO\textsubscript{2} adsorption results of Li@Cu\textsubscript{3}(BTC)\textsubscript{2}, CNT@Cu\textsubscript{3}(BTC)\textsubscript{2}, and Li@CNT@Cu\textsubscript{3}(BTC)\textsubscript{2}, and they found that lithium doping actually improved CO\textsubscript{2} adsorption capacity, and increased by 305% for Li@CNT@Cu\textsubscript{3}(BTC)\textsubscript{2} [18].

Doping metal ions into an MOF can improve adsorption performance, as metal ions can increase the interaction energy between CO\textsubscript{2} and MOFs. Virtually most of the reports on alkali metal incorporation in MOFs are established on theoretical models and computer simulations. Actually, direct verification of this effect through lab experiments is still a challenge. Surveying the effect of alkali metal doping in MOFs on CO\textsubscript{2} capture became urgent for us. The in situ incorporation procedure of metal ions into MOFs during the solvothermal process is straightforward compared with the post-synthetic modification procedure.

To further improve the CO\textsubscript{2} adsorption performance of MOFs, the introduction of amino groups (–NR\textsubscript{2}) into the organic linkers are considered to be effective. The amino group can act as a Lewis basic active site, with strong binding to carbon dioxide, and the presence of the lone electron pair enhances the affinity between an MOF and carbon dioxide molecules. Zhu et al. indicated that the basic sites of MOFs can be generated by either direct synthesis or post-synthetic modification. In the case of direct synthesis, the basicity may originate from metal centers, organic ligands, and the interplay between the two. For post-synthetic modification, both metal sites and ligands are available for the introduction of basic species [19]. Kim et al. point out that pore engineering of MOFs utilizing Lewis basic functionalities are beneficial for CO\textsubscript{2} adsorption. Using N-containing, aromatic, ring-based Lewis basic ligands to establish MOFs is one main strategy for the pore engineering [20]. Yang et al. reported that the –NH\textsubscript{2} functional group can exhibit a good effect and provide a strong affinity for CO\textsubscript{2} molecules in adsorption [21]. At the same time, the procedure of introducing a functional group is complicated, and the pore window might be blocked by the functional groups [19,22].

The titanium-based MOF NH\textsubscript{2}–MIL125 (Material of Institute Lavoisier, MIL) has been investigated for different fields, such as gas storage, gas separation, and photocatalysis [23–26]. The amino-functionalization of MOFs is believed to improve CO\textsubscript{2} adsorption, so NH\textsubscript{2}–MIL125 was chosen to be investigated. The structure of NH\textsubscript{2}–MIL125 is quasi-cubic tetragonal system, constructed with octameric Ti\textsubscript{8}O\textsubscript{8}(OH)\textsubscript{4} oxo-clusters connected by amino-dicarboxylate linkers. In addition, the incorporation of alkali metal into Ti-MOF has not been reported. In this study, a sequence of xM@NH\textsubscript{2}–MIL125(Ti) (M = Li, Na, K) was successfully synthesized by in situ cation incorporation, in order to understand the impact of the doping of alkali metals on the CO\textsubscript{2} adsorption capacity of NH\textsubscript{2}–MIL125(Ti).

2. Materials and Methods

2.1. Chemicals

Titanium isopropoxide (98%, AR) and 2-aminoterephthalic acid (H\textsubscript{2}BDC–NH\textsubscript{2}, AR) were purchased from J&K Scientific Ltd. (Beijing, China). Lithium chloride (LiCl, AR), sodium chloride (NaCl, AR) and potassium chloride (KCl, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol (CH\textsubscript{3}OH, AR) and N,N-dimethylformamide (DMF, AR) were
provided by Tianjin Fuchen Chemicals Co. Ltd. (Tianjin, China). All the chemicals were used as received, without further purification.

2.2. Synthesis of NH$_2$-MIL125(Ti)

The synthesis of NH$_2$-MIL125(Ti) was performed by dissolving H$_2$BDC-NH$_2$ (1.449 g, 8 mmol) in 30 mL DMF/methanol (1:1 V/V) and stirred for 10 min at room temperature; then, titanium isopropoxide (1.308 g, 1.39 mL, 4.5 mmol) was added to the above solution and stirred for another 30 min. The mixture was transferred into a Teflon liner inserted in a stainless-steel autoclave. Then the autoclave was sealed and the mixture was heated for 16 h at 150 °C. After cooling slowly to ambient temperature, the obtained yellow powder was filtered and washed with DMF and methanol, and the resultant product was finally vacuum-dried at 60 °C overnight.

2.3. Synthesis of xM@NH$_2$-MIL125(Ti)

The alkali metal-doped NH$_2$-MIL125(Ti) samples were prepared through the in situ synthesis method. MCl (M = Li$^+$, Na$^+$, K$^+$) was milled into fine particles and dissolved in DMF. The above solution containing M$^+$ was then added to the solution containing H$_2$BDC-NH$_2$ and titanium isopropoxide. The synthesis and activation of the alkali metal cation incorporated NH$_2$-MIL125(Ti) followed the same route of NH$_2$-MIL125(Ti). The yellow powder product was denoted as xM@NH$_2$-MIL125(Ti), where M is related to the alkali metal cation (Li$^+$, Na$^+$, K$^+$), and x represents the mass ratio (1% and 2%) of alkali metal chloride to the pure NH$_2$-MIL125(Ti). For the 1% case, as the sum mass of H$_2$BDC-NH$_2$ and titanium isopropoxide were 2.757 g, so 0.028 g of MCl (0.65 mmol for LiCl, 0.47 mmol for NaCl, and 0.37 mmol for KCl) was added. All the obtained samples after final filtration were vacuum-dried at 60 °C overnight. The yield, 90% of the product, is nearly the same as the pristine NH$_2$-MIL125(Ti).

2.4. Sample Characterization

FT-IR spectra were obtained on AXS TENSOR-27 FT-IR spectrometer (Bruker, Karlsruhe, Germany), with KBr pellets at room temperature in the range of 4000–500 cm$^{-1}$, with a resolution of 4 cm$^{-1}$. Powder X-ray diffraction (PXRD) data were performed on an Advance-D8 (Bruker, Karlsruhe, Germany) with Cu K$_\alpha$ radiation operating at 40 kV and 40 mA, in the range of 5° < 2θ < 50°, with a step length of 0.02° (2θ). X-ray photoelectron spectrometer (XPS) data were collected on an Axis Ultra DLD (Kratos Analytical Ltd. of Shimadzu Corporation, Manchester, UK) with Al K$_\alpha$ (h$\nu$ = 1486.7 eV), operating at 15 kV and 10 mA. All curves have been charge-corrected to the main line of the carbon C1’s spectral component (C/C, C/H), set to 284.80 eV. Thermal stability was characterized via TA-SDT Q600 (TA Instruments, NewCastle, DE, USA) from room temperature to 900 °C, under a heating rate of 5 °C·min$^{-1}$ in N$_2$ atmosphere and with a flowing rate of 10 mL·min$^{-1}$. The contents of the metal ions were analyzed by ICP-OES730 (Agilent, Santa Clara, CA, USA). The scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS) were carried out using a Hitachi SU8020 (Hitachi High-Technologies Corporation, Tokyo, Japan). The powder surface was gold that had been metalized previously. N$_2$ and CO$_2$ adsorption isotherms were obtained using Autosorb-1 (Quantachrome Instruments, Boynton Beach, FL, USA). The samples were pre-treated to remove excess water molecules and impurities at 150 °C for 8 h under vacuum, and the CO$_2$ adsorption isotherm was tested at 273 and 293 K.

3. Results

3.1. FT-IR Analysis

The FT-IR spectra of xM@NH$_2$-MIL125(Ti), as shown in Figure 1, shows the characteristic vibration peaks before and after the alkali metal doping. There is no obvious change in the region of the peaks, but the intensity is slightly changed. To be specific, 3420–3452 cm$^{-1}$ shows the contribution
of $\text{-NH}_2$ group in the structure. The vibration bands located at about 1637 and 1500 cm$^{-1}$ belonged to carbonyl asymmetric stretching vibrations, and vibration bands located at 1298 cm$^{-1}$ could be assigned to the C–H symmetric stretching vibrations of the benzene ring. The peak around 760 cm$^{-1}$ is the Ti–O stretching for non-bound oxygen atoms, and 500–755 cm$^{-1}$ is the Ti–O–Ti stretching vibration [27].

![FT-IR spectra](image)

**Figure 1.** FT-IR spectra of H$_2$BDC–$\text{NH}_2$, NH$_2$–MIL125(Ti) and xM@NH$_2$–MIL125(Ti).

### 3.2. X-ray Diffraction Analysis

XRD patterns of NH$_2$–MIL125(Ti) synthesized with different loadings of Li, Na, and K are shown in Figure 2. It can be seen that all samples still maintained the crystal structure of NH$_2$–MIL125(Ti). It shows that xM@NH$_2$–MIL125(Ti) exhibited the distinct characteristic diffraction peaks at $2\theta = 6.8^\circ$, 9.8$^\circ$, 12.1$^\circ$, 17.3$^\circ$, and 18.8$^\circ$, which were consistent with the experimental and calculated patterns of NH$_2$–MIL125(Ti) [27], and no additional peaks were observed; this means that no other crystalline impurity phases formed after the modification, indicating that the crystal structure of NH$_2$–MIL125(Ti) was well maintained. Therefore, we speculate that the doping of alkali metal ions during the solvothermal synthesis would not affect the crystalline structures of NH$_2$–MIL125(Ti). However, the characteristic diffraction peak positions around 6.8$^\circ$ of xK@NH$_2$–MIL125(Ti) have been shifted slightly for the case of potassium ion doping, as shown in Figure 2d, which is owing to the larger ionic radius of K$^+$ than of Li$^+$ and Na$^+$ [28]. The larger ionic radius may cause differences in the construction of the framework during the solvothermal synthesis.

### 3.3. X-ray Photoelectron Spectrometer

XPS measurements were carried out to determine the chemical composition and electronic structure of xM@NH$_2$–MIL125(Ti). As shown in Figure 3, the wide-scan XPS spectra of all the samples show four peaks. The peak of 288.7 eV, corresponding to C 1s, indicates the existence of a C element. Similarly, the peaks of 399.6 eV for N at 1s, 458.9 eV for Ti at 2p, and 288.7 eV for O at 1s, indicate the existence of N, Ti, and O elements. In the 1s spectrum for N, the peak at 399.6 eV belonged to the N of the amine group protruding or stretching out into the cavities. The peak at 403.1 eV can be assigned to the positively charged $-\text{N}=^+$ and $-\text{NH}^+$ [29]. The symmetric peaks in the Ti 2p spectrum located at 458.9 eV and 464.6 eV are attributed for Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively. This means that the oxidation state Ti in the titanium–oxo cluster remains in IV. Combining with the experimental results of XRD and N$_2$ adsorption, it can be inferred that the amine groups are not coordinated with metal ions, but may be protruding into the empty space of the internal porous [29]. The XPS peaks of xM@NH$_2$–MIL125(Ti) are nearly the same as those of NH$_2$–MIL125(Ti), which indicates that the alkali metal doping procedure has little influence on the electronic structures of NH$_2$–MIL125(Ti).
3.4. Thermal Stability

The thermal stability and decomposition temperatures of NH$_2$–MIL125 and xM@NH$_2$–MIL125 were investigated via thermogravimetric analysis (TGA). It can be seen from Figure 4 that there are three stages of weight losses in the TGA curves. NH$_2$–MIL125, xLi@NH$_2$–MIL125, xNa@NH$_2$–MIL125, and xK@NH$_2$–MIL125 showed similar weight-loss behaviors. The first weight loss, between 30 and 130 °C, was caused by the removal of physically adsorbed water, bound water, and free solvent molecules (such as methanol) [27]. At the region of 130 to 300 °C, the weight loss curves of all the samples gradually decreased, which was due to the removal of the DMF and non-coordinated organic linkers of H$_2$BDC–NH$_2$ trapped in the material. When the temperature reached around 300 °C, a sudden weight loss occurred, which corresponds to the degradation of the framework to TiO$_2$.
anatase [11,23]. The thermogravimetric results show that xM@NH2–MIL125 can remain thermally stable at 300 °C.

Figure 4. Thermogravimetric analysis (TGA) curves of NH2–MIL125(Ti) and xM@NH2–MIL125(Ti).

3.5. Scanning Electron Microscopy

The morphology of pristine NH2–MIL125 and xM@NH2–MIL125 are shown in Figure 5. NH2–MIL125 (Figure 5a) and xNa@NH2–MIL125 (Figure 5c) exert thin and circular plate shapes. The NH2–MIL125 involves an average particle size of 6 μm, which is similar to the conventional synthetic method of NH2–MIL125 (5 μm) [23], while xLi@NH2–MIL125 has a tetragonal plate shape with a particle size of 5 μm (Figure 5b). The average particle size of xNa@NH2–MIL125 is 8 μm, with a circular plate shape (Figure 5c). However, xK@NH2–MIL125 has a truncated octahedron shape with the particle size of 15 μm (Figure 5d). The crystal size increases in the sequence of Li, Na, and K, reflecting the different growth rates of the xM@NH2–MIL125. The titanium precursor contains different amount of alkali metal ions during the solvothermal synthesis. As for the case of 1M@NH2–MIL125(Ti), there was 0.65 mmol of LiCl, 0.47 mmol of NaCl, and 0.37 mmol of KCl in the solvothermal precursor, respectively. The titanium precursor containing K ions involves the lowest doping ions molar concentration, which may have less influence on the moving of Ti and the growing rate of Ti–O in the titanium precursor, resulting in the highest particle size.

Figure 5. Scanning electron microscopy (SEM) images of doped and pristine NH2–MIL125(Ti): (a) NH2–MIL125(Ti), (b) xLi@NH2–MIL125(Ti), (c) xNa@NH2–MIL125(Ti), and (d) xK@NH2–MIL125(Ti).

The alkali metal incorporation has an influence on the kinetics of hydrolysis and condensation reactions. The morphology evolution of the crystal has affected the changes of NH2–MIL125. Thus,
special polyhedrons of NH2–MIL125 from the tetragonal plate through the circular plate to a truncated octahedron were obtained. The crystal morphology of NH2–MIL125(Ti) changing in our work is a little different from what Hu et al. previously reported [27]. They controlled the crystal morphology from the circular plate to the octahedron, by altering the concentration of reactants from low to high and by changing the total solvent volume. In our work, the concentration of the reactant was the same when adding different kind of alkali metal salts, but the total ion concentration was decreased in the sequence of Li, Na, and K, which caused the different growth rates. Hu et al. reported that the perfect NH2–MIL125 crystal should be rhombic dodecahedron morphology by Bravais-Friedel-Donnay-Harker (BFDH) theory [30]. It can be concluded that these morphology changes were affected by the total concentration of the ions in the solvothermal precursors.

To verify that the alkali metals were doped into NH2–MIL125 homogeneously, the mapping images of the 1K@NH2–MIL125 through SEM–EDS were performed. As can be seen in Figure 6, the C, N, Ti, K, and Cl elements are uniformly dispersed in the 1K@NH2–MIL125, indicating that the K ions have been well distributed into the framework of the 1K@NH2–MIL125. The same results were found in the 1Na@NH2–MIL125(Ti). The doped alkali metal ions might be well incorporated into the structure, or just dispersed on the surface of the Ti8O8(OH)4–(O2C–C6H5–CO2–NH2)6. The alkali metals presumably exist in the form of chlorides, because the alkali oxide needs a higher temperature to be obtained [31]. The signal intensity of lithium is too weak to determine its dispersion in xLi@NH2–MIL125 by SEM–EDS imaging, due to the high background noises.

![Figure 6. SEM–energy-dispersive spectroscopy (EDS) mapping of 1K@NH2–MIL125(Ti) elements: C, N, Ti, K, and Cl.](image)

3.6. Alkali Metal Content

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP–OES) analyses were performed to examine the presence and quantity of the alkali metal for xLi@NH2–MIL125(Ti), and the results are listed in Table 1. The experimental titanium content for both doped and original NH2–MIL125(Ti) are nearly the same, which is between 15.7–16.9 wt %. This is close to the theoretical calculating value 23 wt % for NH2–MIL125(Ti) and Ti8O8(OH)4–(O2C–C6H5–CO2–NH2)6 [11]. The higher lithium content can be observed by increasing the lithium loading in the precursor. The amount of Li and Na in the framework drops greatly after a series of solvent exchanging treatment, because the alkali metal does not coordinate with the organic ligands and its small atomic radius. For the K case, maybe there are more K ions trapped in the pores or on the surface of the framework, so the ICP results of K are higher than those for Li and Na.
and 1226 m\(^2\)·g\(^{-1}\) for the pristine NH\(_2\)–MIL125(Ti). It is worth pointing out that the BET specific surface area of the pristine NH\(_2\)–MIL125(Ti) in our work is lower than those reported in the reference, including 862–1469 m\(^2\)·g\(^{-1}\) [23], 1203 m\(^2\)·g\(^{-1}\) [21], 1215 m\(^2\)·g\(^{-1}\) [32], and 1041~1268 m\(^2\)·g\(^{-1}\) [27]. The pristine NH\(_2\)–MIL125(Ti) and the xM@NH\(_2\)–MIL125 are using the same synthetic procedure and calcination temperatures in this work, to investigate the tendency of the alkali metal doping effects.

The enhancement of 1Li@NH\(_2\)–MIL125 was greater than that observed for 1Na@NH\(_2\)–MIL125 and 1K@NH\(_2\)–MIL125. The increasing trend of surface area correlates excellently with the conclusions from the SEM and XRD investigations, as described previously. However, the specific surface area dropped rapidly when the alkali metal doping amount increased to 2 wt %. Perhaps a doping amount 2 wt % of the dopants themselves (Li, Na, and K) is too much, and the channels or pores of NH\(_2\)–MIL125 might be blocked [8]. Therefore, the alkali metal doping can promote the specific surface area and pore volumes of the NH\(_2\)–MIL125(Ti), but excessive doping will block the pores of metal organic framework, consequently reducing its performance. It is very important to select suitable alkali metal type and doping dosage for the purpose of improving the gas adsorption performance of MOFs.

### 3.7. \(\text{N}_2\) Adsorption Isotherms

Nitrogen adsorption isotherms were measured to obtain the porosity of xM@NH\(_2\)–MIL125, and the results are shown in Figure 7. All obtained \(\text{N}_2\) adsorption isotherms of the xM@NH\(_2\)–MIL125 series exhibited a type I isotherm curve. The Brunauer Emmet Teller (BET) surface area was calculated in the relative pressure (\(P/P_0\)) range of 0.05 to 0.3, and the detailed adsorption data were summarized in Table 1. The NH\(_2\)–MIL125(Ti) structure involves octahedral cages of 12.5 Å and tetrahedral cages of 6.1 Å, and are accessible through triangular windows of 5–7 Å. At low relative pressure, the significant adsorption amount indicates that the materials involve microporosity [22,28].

![Figure 7. \(\text{N}_2\) adsorption isotherms at 77 K for NH\(_2\)–MIL125(Ti) and xM@NH\(_2\)–MIL125(Ti).](image)

| Samples | \(S_{\text{BET}}\) (m\(^2\)·g\(^{-1}\)) | \(\text{CO}_2\) Adsorption (mmol g\(^{-1}\)) | Alkali Metal Introduced in the Synthesis (wt %) | Metal Analysis (ICP, wt %) |
|---------|---------------------------------|---------------------------------|---------------------------------|------------------|
| NH\(_2\)–MIL125(Ti) | 1038 | 2.13 | 0 | 16.3 |
| 1Li@NH\(_2\)–MIL125(Ti) | 1470 | 4.60 | 0.164 | 16.7 |
| 1Na@NH\(_2\)–MIL125(Ti) | 1115 | 2.31 | 0.327 | 16.1 |
| 2Na@NH\(_2\)–MIL125(Ti) | 1451 | 4.57 | 0.393 | 15.7 |
| 1K@NH\(_2\)–MIL125(Ti) | 985 | 2.50 | 0.787 | 16.9 |
| 2K@NH\(_2\)–MIL125(Ti) | 1226 | 3.55 | 0.524 | 15.6 |
| 2K@NH\(_2\)–MIL125(Ti) | 872 | 2.08 | 1.049 | 15.6 |
3.8. CO₂ Adsorption Isotherms Measured

CO₂ adsorption isotherms of NH₂–MIL125(Ti) and xM@NH₂–MIL125(Ti) at 293 K and 1 atm are shown in Figure 8. All the samples show a steep initial increase at low pressures, which is characteristic of a high-CO₂-adsorption material with microporosity. In the research system for carbon dioxide adsorption, the presence of amino functionalization provides more active sites, NH₂–MIL125 showed a higher quantity of CO₂ adsorption, as summarized in Table 2.

![Figure 8. CO₂ adsorption isotherms of NH₂–MIL125(Ti) and xM@NH₂–MIL125(Ti) at 293 K.](image)

| MOFs          | Condition | CO₂ Adsorption (mmol g⁻¹) | References |
|---------------|-----------|---------------------------|------------|
| PEHA-MIL-101  | 298 K, 10 bar | 1.30                      | [33]       |
| MIL-101(Cr)   | 298 K, 10 bar | 0.85                      | [33]       |
| NH₂-UiO-66    | 298 K, 1 bar  | 3.15                      | [34]       |
| UiO-66-AD6    | 298 K, 1 bar  | 2.63                      | [35]       |
| Mg-MOF-74     | 298 K, 1 bar  | 7.95                      | [36]       |
| MIL125(Ti)    | 298 K, 1 bar  | 3.00                      | [11]       |
| NH₂–MIL125(Ti)| 298 K, 1 bar  | 2.18                      | [11]       |
| NH₂–MIL125(Ti)| 293 K, 1 bar  | 2.13                      | This work  |
| 1Li@NH₂–MIL125(Ti)| 293 K, 1 bar | 4.60                      | This work  |
| 1Na@NH₂–MIL125(Ti)| 293 K, 1 bar | 4.57                      | This work  |
| 1K@NH₂–MIL125(Ti)| 293 K, 1 bar | 3.55                      | This work  |

It can be seen from the CO₂ adsorption isotherms that the CO₂ adsorption amount of xM@NH₂–MIL125(Ti) increased when the 1 wt% alkali metal was introduced during the solvothermal synthesis. The adsorption amounts are 4.60, 4.57, and 3.55 mmol g⁻¹ for 1Li@NH₂–MIL125(Ti), 1Na@NH₂–MIL125(Ti), and 1K@NH₂–MIL125(Ti), respectively. The CO₂ adsorption capacity of 1M@NH₂–MIL125 is in the sequence of Li > Na > K, which is consistent with the order of the decreasing ionic radius, and in agreement with the N₂ adsorption performance. Of these compounds, 1Li@NH₂–MIL125(Ti) showed the highest CO₂ adsorption capacity, but the amount is still much lower than that of Mg-MOF-74 [36].

One reason why alkali metal doping increases the carbon dioxide adsorption capacity is the influence of the framework structure. The enhancement is maybe due to the defect site of the frameworks caused by the alkali metal doping tuning the crystallite framework (interpenetrated level), surface (surface area, pore etc.), and adsorptive site (dipole interaction) [28]. As we discussed before, the alkali metal doped xM@NH₂–MIL125(Ti) has a larger specific surface area, and the morphology of the MOFs changed. The specific surface area of NH₂–MIL125(Ti) increases due to the decrease of the particle size, which leads to a large amount of CO₂ adsorption. The CO₂ adsorption capacity has a positive correlation with the Sₜₜ, as shown in Figure 9. The surface area of the 1Li@NH₂–MIL125(Ti) is much higher than that of the NH₂–MIL125(Ti) and 2Li@NH₂–MIL125(Ti), so the higher CO₂
adsorption of 1Li@NH$_2$–MIL125(Ti) is understandable. The approximate CO$_2$ adsorption capacity for 1Li@NH$_2$–MIL125(Ti) and 1Na@NH$_2$–MIL125(Ti) may because the surface area of them are closed.

![Figure 9](image_url)

**Figure 9.** The relationship of CO$_2$ uptake on x@NH$_2$–MIL125(Ti) with $S_{ BET}$ at 293 K and 1 atm.

The results of the CO$_2$ adsorption on x@NH$_2$–MIL125(Ti) is not only relevant to the specific surface area, but also to the alkali metal dispersed in the framework of the x@NH$_2$–MIL125(Ti). Another reason why alkali metal doping increases the carbon dioxide adsorption capacity is that carbon dioxide preferentially adsorbs around the alkali metal ions, and computer simulations by Mu et al. confirm this view [16]. They found that the first ionization energies and the electron donating ability of the alkali metal atoms are much lower than the boron group metal and alkaline earth metal atoms, thereby causing more ion partial charges. The first ionization energy is the minimal energy required to remove an electron from the atom or molecule isolated in free space and in its ground electronic state. The electrostatic interaction between CO$_2$ and MOFs increases with increasingly induced charges. The 2Na@NH$_2$–MIL125(Ti) has a bit of a smaller surface area than NH$_2$–MIL125, but a larger CO$_2$ adsorption, which may contribute to its smaller pore size and the doping of alkali metals. Therefore, the doping of alkali metal helps to improve the CO$_2$ adsorption properties of NH$_2$–MIL125(Ti).

The heat of CO$_2$ adsorption for NH$_2$–MIL125 and 1Li@NH$_2$–MIL125 were calculated using the Clausius–Clapeyron equation, based on the CO$_2$ adsorption isotherms at 273 and 293 K, as shown in Figure 10. Of those tested, 1Li@NH$_2$–MIL125 showed a higher heat of CO$_2$ adsorption (42–26 kJ mol$^{-1}$) than NH$_2$–MIL125 (21–17 kJ mol$^{-1}$). However, the value is lower than that of MIL-100 (63–23 kJ mol$^{-1}$) [23]. The heat of CO$_2$ adsorption at a CO$_2$ coverage of 2.0 wt % for 1Li@NH$_2$–MIL125 is estimated to be 28.2 kJ mol$^{-1}$, which is much higher than that of NH$_2$–MIL125 (17.1 kJ mol$^{-1}$), suggesting a much stronger interaction between adsorbed CO$_2$ and 1Li@NH$_2$–MIL125.

![Figure 10](image_url)

**Figure 10.** (a) The CO$_2$ adsorption isotherms at 273 and 293 K. (b) The heats of CO$_2$ adsorption of 1Li@NH$_2$–MIL125 and NH$_2$–MIL125.
3.9. CO₂ Adsorption Regenerability

The recycle test of 1Li@NH₂–MIL125(Ti) on CO₂ adsorption was performed to test its regenerability for gas capture applications, because of it having the highest capacity for CO₂ adsorption in xM@NH₂–MIL125(Ti). Figure 11 shows the static CO₂ adsorption capacity of 1Li@NH₂–MIL125(Ti) at 293 K. The sample was desorbed by vacuum before the new test. The readsorption amount is nearly stable for six cycles, with no obvious loss in activity. This indicates that the adsorption mechanism of CO₂ is mainly based on physical adsorption [8].

![Figure 11. Recycle test of CO₂ adsorption on 1Li@NH₂–MIL125(Ti) at 293 K.](image)

4. Conclusions

A series of xM@NH₂–MIL125(Ti) has been synthesized by in situ incorporation of alkali metal, which is straightforward and can tune the morphology of MOFs, compared with post-modification procedures. The effect of in situ alkali metal incorporation into the structure was demonstrated through the experimental data of N₂ and CO₂ adsorption of MOFs. The CO₂ adsorption is mainly affected by the van der Waals forces between the framework and CO₂ molecules. The smaller pore size, the Lewis basic active site – NH₂ groups, and the alkali metals in our work are all beneficial for CO₂ adsorption. The introduction of alkali metal mainly affects the CO₂ adsorption in two respects. On the one hand, it impacts the crystal growth rate of MOFs, resulting in the different morphology and size of grains, thus leading to the differences in specific surface area and pore size, which has a significant impact on the CO₂ adsorption. On the other hand, the alkali metals, existing in the final framework after a series of solvent exchanging treatments, have an influence on the CO₂ adsorption. This enhancement is due to the increased specific surface area and alkali metal coordinated on the defects of the cage construction. It was found that 1Li@NH₂–MIL125(Ti) is the most efficient CO₂ adsorbent among xM@NH₂–MIL125(Ti). Although the amount is still lower than the reported MOFs, such as Mg-MOF-74, alkali metal doping has proven to be an effective modification strategy. This preliminary study is a practical attempt to improve the performance of MOF materials on CO₂ adsorption, which will promote related research on CO₂ conversion reactions.

Author Contributions: L.S. (Lifang Song) designed the experiments and drafted the manuscript; C.X. participated in the experiments and measurements; H.X. and S.Q. contributed to the analysis of the data; L.S. (Lixian Sun) and H.C. participated in the discussion of the results.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 51502021, the State Scholarship Fund from the China Scholarship Council, grant number 201706565013, the Natural Science Basic Research Plan in Shaanxi Province of China, grant number 2017JQ2025, and the Guangxi Key Laboratory of Information Laboratory Foundation, grant number 151001-K.

Acknowledgments: The authors would like to thank Yongpeng Xia for SEM and gas adsorption measurements.

Conflicts of Interest: The authors declare no conflict of interest.
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