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UiO-66-NH₂/GO Composite: Synthesis, Characterization and CO₂ Adsorption Performance

Yan Cao 1,*, Hongmei Zhang 1, Fujiao Song 1, Tao Huang 1, Jiayu Ji 1, Qin Zhong 1,2, Wei Chu 3 and Qi Xu 1

1 School of Environmental Science and Engineering, Yancheng Institute of Technology, Yancheng 224000, China; hjxyzhm@ycit.cn (H.Z.); song_fjiao2006@126.com (F.S.); huangtaoasd@126.com (T.H.); wm12142005@163.com (J.J.); xqsteve@ycit.cn (Q.X.)
2 School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China; zhongqin304@163.com
3 Department of Chemical Engineering, Sichuan University, Chengdu 610065, China; chuwei1965@foxmail.com
* Correspondence: caoyan823@163.com

Received: 26 March 2018; Accepted: 9 April 2018; Published: 11 April 2018

Abstract: In this work, a new composite materials of graphene oxide (GO)-incorporated metal-organic framework (MOF)(UiO-66-NH₂/GO) were in-situ synthesized, and were found to exhibit enhanced high performances for CO₂ capture. X-ray diffraction (XRD), scanning electron microscope (SEM), N₂ physical adsorption, and thermogravimetric analysis (TGA) were applied to investigate the crystalline structure, pore structure, thermal stability, and the exterior morphology of the composite. We aimed to investigate the influence of the introduction of GO on the stability of the crystal skeleton and pore structure. Water, acid, and alkali resistances were tested for physical and chemical properties of the new composites. CO₂ adsorption isotherms of UiO-66, UiO-66-NH₂, UiO-66/GO, and UiO-66-NH₂/GO were measured at 273 K, 298 K, and 318 K. The composite UiO-66-NH₂/GO exhibited better optimized CO₂ uptake of 6.41 mmol/g at 273 K, which was 5.1% higher than that of UiO-66/GO (6.10 mmol/g). CO₂ adsorption heat and CO₂/N₂ selectivity were then calculated to further evaluate the CO₂ adsorption performance. The results indicated that UiO-66-NH₂/GO composites have a potential application in CO₂ capture technologies to alleviate the increase in temperature of the earth’s atmosphere.

Keywords: graphene oxide (GO); metal-organic framework (MOF); UiO-66-NH₂; carbon dioxide adsorption

1. Introduction

Metal-organic frameworks (MOFs) are formed by the coordination between metal clusters and organic linkers. Due to their large capacity for the adsorption of gases and structural and chemical tenability, they have gained much attention to the potential applications of CO₂ capture [1,2]. The UiO-66 sample with good thermal stability (>500 ℃) and water resistance shows some improved CO₂ adsorption performance [3–5]. Moreover, when compared with the performance of industrial adsorbent (zeolite 13x, for example), the adsorption capacity of UiO-66 demonstrates an improved value [1,6]. In order to enrich this type MOFs, some functional groups were introduced to the skeleton to synthesize the functional series UiO-66 type of MOFs, which could maintain the topology of the original constant [7–10]. However, after functionalization, although the series UiO-66 type of MOFs still displayed the same skeletal structure, the thermal stability, chemical stability, etc., exhibited degradation to some extent. Kandiah et al. [11,12] compared the thermal stability and the chemical stability of three kinds of UiO-66 types of MOFs (UiO-66-NH₂, UiO-66-NO₂, and UiO-66-Br), and the
results showed that, for UiO-66-NH$_2$ and UiO-66-NO$_2$, the thermal stability fell at 350–400 °C, which was due to the ligand decomposition. Moreover, UiO-66-NH$_2$, UiO-66-NO$_2$, and UiO-66-Br prepared in water and HCl solution with pH = 1 displayed the stability of the structure, while UiO-66-NH$_2$ and UiO-66-Br that were prepared in the NaOH solution with pH = 14 exhibited the collapsed structure partially or completely at the above experimental condition. Yang et al. [13,14] reported that, when compared to UiO-66, the CO$_2$ adsorption capacity of UiO-66-NH$_2$ increased, which was due to the existence of amino. However, the stability of UiO-66-NH$_2$ was inferior to that of UiO-66. Therefore, it is necessary to find a new kind of UiO-66 type of MOFs, which can display outstanding performance on thermal stability, chemical stability, and gas adsorption.

Simultaneously, as reported in the literature, the introduction of NH$_2$ could improve the CO$_2$/N$_2$ selectivity in the coal-fired flue gas [15,16]. MOFs have plenty of porosities, but the large pore space in MOFs was not in favor of gas molecules storage. GO has a layered structure and its surface has some groups (–OH, –C–O–C, –C=O). The incorporation of GO to MOFs could effectively reduce the MOFs pore space [17,18].

Hence, in this paper, UiO-66-NH$_2$/GO composites were in-situ synthesized with the addition of graphene oxide (GO) into UiO-66-NH$_2$. Moreover, the CO$_2$ adsorption performances for the UiO-66-NH$_2$/GO and UiO-66-NH$_2$ samples were investigated in order to discuss the influence factor effects on the structure and chemical properties, which could be beneficial for the development of high stability, high gas adsorption materials.

2. Experimental

2.1. Synthesis of UiO-66-NH$_2$/GO Composites

UiO-66-NH$_2$ was solvothermally synthesized based on the method of Abid et al. [19]. Zirconium chloride (ZrCl$_4$, 1.47 g) and 2-aminoterephthalic acid (H$_2$BDC-NH$_2$, 1.06 g) were dissolved in N,N-dimethylformamide (DMF, 150 mL). Then, the mixture was transferred into a 200 mL Teflon lined stainless-steel autoclave for homogeneous reaction, which was maintained at 393 K for 24 h. The mixture was cooled to ambient temperature and repeatedly washed three times with DMF and ethanol, respectively. Yellow crystal was obtained by drying at 393 K.

The composites of UiO-66-NH$_2$/GO were synthesized as the following procedure. Firstly, graphene oxide (GO) was prepared according to Hummers’ technique [17,18]. A given mass of dry scattered GO was added to 150 mL DMF solvent with ultrasonic treatment for 5 h to obtain a GO suspension. Then, ZrCl$_4$ (1.47 g) and H$_2$BDC-NH$_2$ (1.06 g) were added to the GO suspension to synthesize UiO-66-NH$_2$/GO. The expected amount of GO is 5 wt % in UiO-66-NH$_2$/GO, which is the most appropriate ratio that is found in our previous studies of UiO-66/GO samples [17]. The obtained gray mixture was transferred into a 200 mL Teflon lined stainless-steel autoclave for homogeneous reaction, which was maintained at 393 K for 24 h. The mixture was cooled to ambient temperature and repeatedly washed three times with DMF and ethanol, respectively. Finally, gray crystal was obtained by drying at 393 K.

2.2. Characterizations

For X-ray diffraction (XRD) measurements, the samples were grounded with DMF (MOF series) or ethanol (GO series) in a small agate mortar, then, the mixture was smear-mounted onto a glass slide and was air-dried. The samples were analyzed by using a Philips X’Pert X-ray diffractometer (Cu K$_x$ radiation, with a voltage of 40 kV and current of 40 mA, Philips (China) Investment Co. Ltd, Shanghai, China)

Infrared spectrum (FT-IR) was performed by using a MB154S-FTIR spectrometer (Bomem, Quebec City, QC, Canada) according to the attenuated total reflectance method (ATR).
Thermogravimetric analysis (TGA) was analyzed by using a SDTQ600 thermal analyzer (Perkin-Elmer Pyris Diamond, Waltham, MA, USA). Experiments were carried out under a N\textsubscript{2} atmosphere (30 mL/min flow rate) at a heating rate of 10 °C/min from room temperature to 800 °C.

ASAP 2010 analyzer (Micromeritics, Norcross, GA, USA) was applied to evaluate the N\textsubscript{2} adsorption isotherms at −196 °C. Before the experiment, the samples were decorated 12 h at 393 K. The surface area S\textsubscript{BET}, the total pore volume V\textsubscript{pore}, the micropore volume V\textsubscript{mic}, and the mesopore volume V\textsubscript{mes} were obtained from the isotherms.

Scanning electron microscope (SEM) was performed on a S-4800 field emission scanning electron microscope (Hitachi High-Technologies corporation, Tokyo, Japan). Scanning was ran on a powder sample that was previously dried and also should be coated with a thinness of gold to avoid charging in the case of MOFs and the composites.

2.3. CO\textsubscript{2} Adsorption Experiment

CO\textsubscript{2} adsorption measurements under 0~1.2 bar were performed by an apparatus for physical adsorption (V-Sorbet 2008S, Beijing Jinaipu Science & Technology Co., Ltd., Beijing, China). The experiments were operated at 273 K, 298 K and 318 K. The sample tube was immersed in a heated dewar flask filled with water to control the adsorption temperature. Before the experiment, the samples (0.1–0.2 g) in the analysis chamber were subjected to a vacuum at ambient temperature for 12 h. The reversibility of the CO\textsubscript{2} adsorption process on the samples was studied by multiple CO\textsubscript{2} adsorption cycles. Regeneration experiments were conducted at 393 K for 12 h in vacuum, and then the corresponding adsorption isotherms were collected.

2.4. Chemical Stability Test

At room temperature, newly synthesized UiO-66-NH\textsubscript{2}/GO (0.2 g) was exposed to air humidity (70–90%) for 30 days, or 20 mL pH = 1 HCl solution (or pH = 14 in NaOH solution for 2 h. XRD testing was carried out on samples after filtration drying.

3. Results and Discussion

3.1. Structure Characterization

X-ray diffraction (XRD) of different samples is illustrated in Figure 1. As shown in Figure 1, the main diffraction peaks of UiO-66-NH\textsubscript{2} are similar to those of UiO-66, revealing that the introduction of –NH\textsubscript{2} groups did not change the crystal structure of matrix UiO-66, which is consistent with the results of previous reports [20–22]. UiO-66-NH\textsubscript{2}/GO composites have the same diffraction peak position and a slightly stronger peak intensity when compared with UiO-66-NH\textsubscript{2}. It proved that UiO-66-NH\textsubscript{2} is the main component of UiO-66-NH\textsubscript{2}/GO composites and UiO-66-NH\textsubscript{2}/GO composites still maintained a good crystal structure. The main diffraction peak of GO (2θ = 10°) does not appear in UiO-66-NH\textsubscript{2}/GO composites, which is consistent with the situation of UiO-66/GO. The reason could be concluded that the very low content (5%) of GO in the composites, the high dispersion of GO with polar solvents (DMF), which were known to disperse GO very well, and the interaction of GO with UiO-66-NH\textsubscript{2}.

SEM images of different samples were showed in Figure 2. As seen from Figure 2a,b, UiO-66-NH\textsubscript{2} has the same cubic structure as UiO-66 crystal. Owing to the influence of synthesis condition, the particle size of UiO-66-NH\textsubscript{2} is around 150 nm, which is smaller than that of UiO-66 (300 nm). The result is in accordance with the previous reported in the literature [22]. UiO-66-NH\textsubscript{2} and UiO-66/GO composites have similar cubic crystals with a much smaller particle size of approximately 80–100 nm and are of irregular appearance (as shown in Figure 2c,d), which could be attributed to the introduction of GO. It can be explained that the oxygen-containing functional groups in GO combined with Zr\textsuperscript{4+}, inhibiting the crystal growth of UiO-66-NH\textsubscript{2}. 

Materials 2018, 11, 589
Figure 1. X-ray diffraction patterns of the different samples.

Figure 2. Scanning electron microscope (SEM) images of UiO-66 (a) [17]; UiO-66-NH$_2$ (b); UiO-66/GO (c) [17]; and UiO-66-NH$_2$/GO (d).

Figure 3 presents the N$_2$ adsorption-desorption isotherm of different materials. N$_2$ adsorption-desorption isothermal of all the synthetic samples reveal a typical type I isotherm. Pore structure parameters and Density Functional Theory (DFT) pore size distribution are presented in Figure 4 and Table 1.
Figure 3. $N_2$ adsorption-desorption isotherms of the different samples at 77 K.

Figure 4. Pore size distribution of the different samples.

Table 1. Data of porous structure of the different samples.

| Sample          | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{pore}}$ (cm$^3$/g) | $V_{\text{mic}}$ (cm$^3$/g) | $V_{\text{mic}}/V_{\text{pore}}$ (%) |
|-----------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------------|
| UiO-66          | 838                         | 0.245                         | 0.224                       | 91                                  |
| UiO-66-NH$_2$   | 822                         | 0.236                         | 0.214                       | 90                                  |
| UiO-66/GO       | 1184                        | 0.384                         | 0.304                       | 79                                  |
| UiO-66-NH$_2$/GO| 1052                        | 0.345                         | 0.286                       | 83                                  |

As can be seen from Table 1, the $S_{\text{BET}}$ and $V_{\text{pore}}$ of UiO-66-NH$_2$ is 822 m$^2$/g and 0.236 cm$^3$/g respectively, which is similar to that of UiO-66, in conformity with the results that were reported by Nik et al. [22], but slightly lower those that were reported by Garibay et al. [8]. This slight difference may result from the different activation temperatures. GO has no adverse effect on composite materials. Properly adding GO significantly improves the $S_{\text{BET}}$ and $V_{\text{pore}}$ of UiO-66/GO. For $S_{\text{BET}}$, $V_{\text{pore}}$, and $V_{\text{mic}}$ of UiO-66-NH$_2$/GO are 1052 m$^2$/g, 0.345 cm$^3$/g, and 0.286 cm$^3$/g, respectively, which increases by 28%, 46%, and 46% than UiO-66-NH$_2$. The incorporation of GO does not negatively affect the porosity of UiO-66-NH$_2$, it is in accordance with the previous report. The new pores could generate on the interface between the GO layers and the MOF “blocks”, which could improve the surface area.
As shown in Figure 4, the pore size of the composite material is 8~12 Å. In this range, the pore size distribution of UiO-66/GO and UiO-66-NH$_2$/GO is more than the corresponding parent material UiO-66 and UiO-66-NH$_2$, which is good for CO$_2$ adsorption. It can also be seen that the pore sizes of these materials are partly distributed between 16 Å and 22 Å. During this interval, the pore size distribution of UiO-66-NH$_2$ and UiO-66 is similar, and that of UiO-66/GO and UiO-66-NH$_2$/GO is similar. The pore volume of the composite materials is higher than that of the parent material, which is also good for CO$_2$ adsorption.

3.2. Chemical Characteristics

Figure 5 is the FT-IR spectra of different samples. In the spectrum of UiO-66-NH$_2$, new peaks appeared at 3461 cm$^{-1}$ and 3361 cm$^{-1}$, respectively, when compared with UiO-66, corresponding to the symmetric and asymmetric vibration peak of –NH$_2$ [23]. The peak at 1621 cm$^{-1}$ corresponds to the N–H bending vibration. The peaks at 1482 cm$^{-1}$ and 1382 cm$^{-1}$ can be attributed to the N–H bending vibration and C–N stretching vibration, respectively [12]. The IR spectrum of UiO-66/GO was almost the same as that of UiO-66, with a slight decrease in strength.

When comparing to the UiO-66-NH$_2$, the spectrum of UiO-66-NH$_2$/GO composites was relatively unchanged, while the peak strength decreased slightly. The main peaks of GO also do not appear in the composite materials. The oxygen functional groups on the GO layers could bond with the open metal sites of UiO-66-NH$_2$, resulting in the band disappearance of GO over UiO-66-NH$_2$/GO composites in the FTIR spectra. In addition, small changes in the composite materials were observed at 1158 cm$^{-1}$, 893 cm$^{-1}$, 961 cm$^{-1}$, and 698 cm$^{-1}$. The reason for this is that the introduction of functional groups that are carried by the GO surface and carboxyl coordinated with metal ion slightly changed the chemical environment of the Terephthalic acid ligand.

3.3. Stability Analysis

Figure 6 shows the TG curves of the different samples. The thermal stability of UiO-66-NH$_2$ decreased when compared with that of UiO-66. The terephthalic acid ligand in UiO-66 skeleton materials decomposed above 480 °C, but the decomposition of amino terephthalic acid ligand occurred from 380 °C, which is 100 °C lower than that of UiO-66 materials. This is consistent with the UiO-66-NH$_2$ collapse of skeleton temperature, as reported by the literature [8]. The decomposition temperature of other types of amine-MOF is also lower than that of the matrix [24,25]. Finally, when the temperature reaches 650 °C, the UiO-66-NH$_2$ has the largest quality loss of approximately 65 wt %,
and the quality loss of the UiO-66 is about 52 wt %. This shows that the thermostability of the latter is better. In addition, the thermostability of UiO-66-NH$_2$/GO composites is better than UiO-66, which is similar to UiO-66/GO composites. Their decomposition temperature is in the range of 500–650 °C, with a similar quality loss of 47 wt %. To sum up, the thermal stability of UiO-66-NH$_2$/GO composites is obviously higher than that of UiO-66-NH$_2$. The addition of the right amount of GO clearly improved the thermostability of UiO-66-NH$_2$.

Figure 6. Thermo-gravimetric analysis for the different samples.

In addition to the above investigation of the thermal stability, we also studied the chemical stability of the UiO-66-NH$_2$/GO. The stability of UiO-66-NH$_2$/GO in the air, water, acid, and alkali qualitative is characterized by XRD. As can be seen from Figure 7b,c, after the UiO-66-NH$_2$/GO exposed in the air for 30 days, or is soaked in water for 10 days at room temperature, the crystal structure did not change, which proved that the UiO-66-NH$_2$/GO has a high water stability that is the same as that of matrix UiO-66 and UiO-66/GO [17]. The introduction of GO means that the UiO-66-NH$_2$ can improve the stability of the network structure under the condition of humidity.

Figure 7. XRD patterns for UiO-66-NH$_2$/GO: (a) as-prepared; (b) desolvated; (c) in air for 30 days; (d) soaked in water for 10 days; (e) immersed in in HCl solution (pH = 1) for 2 h; and, (f) NaOH solution (pH = 14) for 2 h.

As shown in Figure 7d,e, after the UiO-66-NH$_2$/GO was soaked in HCl solution (pH = 1) and NaOH solution (pH = 14) for 2 h, the strength of the main peak got slightly smaller, but was still able to
maintain crystal structure. According to the literature, after soaking in the same condition of the NaOH solution, the skeleton of UiO-66-NH$_2$, UiO-66-NO$_2$, and UiO-66-Br completely collapsed, whereas the UiO-66 structure was damaged, and it was converted into a state of lower crystallinity [11]. A chemical stability test showed that UiO-66-NH$_2$/GO have excellent water resistance, acid resistance, and alkali resistance. Among them, the alkali resistance has a significant increase when compared with the other reported UiO-66 type of MOFs.

3.4. Low Pressure CO$_2$ Adsorption

The CO$_2$ adsorption performance of the samples was elevated using a physical adsorption instrument under the condition of low voltage static. Before the gas adsorption test, all of the samples were dried under vacuum for 12 h at 393 K to completely remove the solvent molecules from inorganic metal element Zr [13]. CO$_2$ adsorption isotherms of different samples are shown in Figure 8. The tests were carried out at 273 K, 298 K, and 318 K, respectively, and 0–1.2 bar.

![Figure 8. Cont.](image-url)
Materials 2018, 11, 589

Figure 8. CO\(_2\) adsorption isotherms measured at 273 K (A); 298 K (B); and, 318 K (C).

The CO\(_2\) adsorption capacities of all of the samples decrease with the increase of temperature. The CO\(_2\) uptakes of all the samples under three temperatures followed the same order: UiO-66-NH\(_2\)/GO > UiO-66/GO > UiO-66-NH\(_2\) > UiO-66. As can be seen from the isotherms, the CO\(_2\) adsorption capacity of UiO-66 and UiO-66/GO clearly increased with the decrease of temperature, which proved that the adsorption mechanism can be assigned to physical adsorption. The incorporation of GO to UiO-66 led to the increase of the mesopore volume and micropore volume. The mesopore was in favor of the transmission of CO\(_2\) to the adsorption site with high energy and the micropore was in favor of the strong retention of CO\(_2\) molecules. As showed in Figure 8, the adsorption capacity of UiO-66-NH\(_2\) at 273 K below 1.0 bar is 3.93 mmol/g, which is 7.3% higher than that of UiO-66 (3.66 mmol/g). A similar situation occurs when the adsorption temperature increases to 318 K. The UiO-66-NH\(_2\) adsorption capacity is 1.60 mmol/g, which is 16.0% higher than that of UiO-66 1.38 mmol/g. The UiO-66-NH\(_2\)/GO adsorption capacity at 273 K is 6.41 mmol/g, which is 5.1% higher than that of UiO-66/GO (6.10 mmol/g), while the UiO-66-NH\(_2\)/GO adsorption capacity at 318 K is 2.26 mmol/g, which is 20.2% higher than that of UiO-66 1.88 mmol/g. As known in Table 1, the \(S_{BET}\) of UiO-66-NH\(_2\) is a bit smaller than that of UiO-66. Similarly, the specific surface area of UiO-66-NH\(_2\)/GO is slightly smaller than that of UiO-66/GO. Moreover, in terms of CO\(_2\) adsorption capacity, the opposite is true: UiO-66-NH\(_2\) is above UiO-66, and UiO-66-NH\(_2\)/GO is higher than UiO-66/GO. This phenomenon shows that, for UiO-66-NH\(_2\) and UiO-66-NH\(_2\)/GO, in addition to the physical adsorption sites of CO\(_2\) adsorption, there are other adsorption sites, and the adsorption reaction between CO\(_2\) and amino groups improves the CO\(_2\) adsorption capacity. Moreover, the high temperature is advantageous in terms of the reaction on the adsorption sites and being conducive to the physical adsorption at low temperature, high temperature reaction adsorption sites when strength is more obvious. The existence of reaction adsorption sites results in strong interaction and better adsorption selectivity between the adsorbate and adsorbent, which favors the important factors of gas purification.

In Table 2, several traditional adsorbent and synthetic samples for CO\(_2\) adsorption capacity under 1.0 bar are listed. As can be seen from the Table 2, when compared with other typical porous materials, such as 13 x molecular sieve, activated carbon adsorption, and some common MOFs, the UiO-66-NH\(_2\)/GO composite has a higher CO\(_2\) adsorption capacity. Therefore, the UiO-66-NH\(_2\)/GO composite has certain industrial application prospects.
Table 2. Adsorption capacity of the prepared composite and some other adsorbents for selected CO\textsubscript{2} reported from the literature at 1 bar.

| Sample          | Chemical Formula | Q (mmol/g) | Temperature (K) | Ref.  |
|-----------------|------------------|------------|-----------------|-------|
| MOF-5           | Zn\textsubscript{4}O(BDC)\textsubscript{3} | 2.10       | 296             | [26]  |
| IRMOF-1         | Zn\textsubscript{4}O(BDC)\textsubscript{3} | 1.92       | 208             | [2]   |
| MOF-177         | Zn\textsubscript{4}O(HTB)\textsubscript{2} | 0.8        | 298             | [27]  |
| Zeolite 13X     | -                | 1.77       | 293             | [28]  |
| Activated carbon | -                | 1.5        | 298             | [29]  |
| UiO-66          | Zr\textsubscript{6}O\textsubscript{4}(OH)(BDC)\textsubscript{6} | 1.77       | 298             | [4]   |
| UiO-66-NH\textsubscript{2} | Zr\textsubscript{6}O\textsubscript{4}(OH)(BDC-NH\textsubscript{2})\textsubscript{6} | 3.05       | 298             | [4]   |
| UiO-66          | Zr\textsubscript{6}O\textsubscript{4}(OH)(BDC)\textsubscript{6} | 2.27       | 298             | present work |
| UiO-66/GO       | -                | 3.37       | 298             | present work |
| UiO-66-NH\textsubscript{2} | Zr\textsubscript{6}O\textsubscript{4}(OH)(BDC-NH\textsubscript{2})\textsubscript{6} | 2.59       | 298             | present work |
| UiO-66-NH\textsubscript{2}/GO | -                | 3.80       | 298             | present work |

Q is CO\textsubscript{2} adsorption capacities.

In order to determine the reason for the difference in CO\textsubscript{2} adsorption capacity, the calculation of CO\textsubscript{2} adsorption heat was carried out. When compared with UiO-66, UiO-66-NH\textsubscript{2}, and UiO-66/GO, the CO\textsubscript{2} adsorption capacity of UiO-66-NH\textsubscript{2}/GO has an excellent performance. The reason for this may be related to the adsorption heat $\Delta$H.

Langmuir isotherm equation had been proposed to describe the experimental data, according to the following Langmuir equation:

$$Q_e = \frac{Q_m b P_e}{1 + b P_e}$$  \hspace{1cm} (1)

where $Q_e$ and $P_e$ are equilibrium adsorption and pressure, respectively. $Q_m$ is the monolayer capacity and b is the Langmuir equilibrium constant. Isotherm parameters at all of the temperatures are summarized in Table 3.

Table 3. Data of Langmuir isotherm for CO\textsubscript{2} adsorption on the different samples.

| Sample          | 273 K        | 298 K        | 318 K        |
|-----------------|--------------|--------------|--------------|
|                 | $Q_m$  | $b$    | $R^2$ | $Q_m$  | $b$    | $R^2$ | $Q_m$  | $b$    | $R^2$ |
| UiO-66          | 11.78  | 0.45   | 0.999 | 15.49  | 0.17   | 0.999 | 4.42   | 0.45   | 0.999 |
| UiO-66-NH\textsubscript{2} | 12.63  | 0.45   | 0.999 | 8.28   | 0.45   | 0.999 | 3.82   | 0.71   | 0.998 |
| UiO-66/GO       | 10.83  | 1.26   | 0.997 | 6.03   | 1.20   | 0.997 | 3.37   | 1.22   | 0.997 |
| UiO-66-NH\textsubscript{2}/GO | 10.92  | 1.39   | 0.996 | 6.38   | 1.41   | 0.996 | 4.39   | 1.06   | 0.998 |

From the isothermal measurements performed at three different temperatures (Figures 8 and 9), it is possible to calculate the net isosteric heat of adsorption from Clausius-Clapeyron equation [30]:

$$\ln P = -\frac{\Delta H}{RT} + C$$  \hspace{1cm} (2)

where $\Delta H$ is the amount of adsorption heat (kJ/mol), p is the pressure (MPa), T is the temperature (K), R is the gas constant, and C is integration constant. The lnP plot of 1/T is a straight line with slope—($\Delta H$/R). According to the low voltage (0.01 MPa to 0.1 MPa), under the 273 K, 298 K and 318 K adsorption isotherm, we obtain relevant data generation according to the type, and CO\textsubscript{2} isothermal adsorption heat is calculated. The isosteric heat of adsorptions for CO\textsubscript{2} were 24.3–22.9 kJ/mol for UiO-66, 24.6–23.2 kJ/mol for UiO-66-NH\textsubscript{2}, 28.9–27.8 kJ/mol for UiO-66/GO, and 30.5–29.4 kJ/mol for UiO-66-NH\textsubscript{2}/GO, depending on the degree of CO\textsubscript{2} loading. There was no significant difference in Q values and the maximum variation between the highest and lowest values did not exceed 5%. Therefore, an average Q was calculated. The average isosteric heat of adsorption for CO\textsubscript{2} on the samples studied. UiO-66, UiO-66-NH\textsubscript{2}, UiO-66/GO, and UiO-66-NH\textsubscript{2}/GO CO\textsubscript{2} isothermal adsorption.
heat is, respectively, 23.5 kJ/mol, 24.2 kJ/mol, 28.3 kJ/mol, and 29.9 kJ/mol. Among them, the UiO-66 and UiO-66-NH$_2$ CO$_2$ isothermal adsorption heat is the same as the literature. Hui et al. [31] measured CO$_2$ UiO-66 when the high coverage adsorption heat is 22 kJ/mol. Aprea et al. [32] reported that the 13x molecular sieve CO$_2$ isothermal adsorption heat is 32.5 kJ/mol. Generally, the smaller the adsorption heat of the materials, the lower renewable energy. However, for low adsorption heat, the adsorption selectivity will decrease, leading to the capture of the lower gas purity. The UiO-66-NH$_2$/GO CO$_2$ isothermal adsorption heat is 29.9 kJ/mol, which is higher than the UiO-66-NH$_2$ CO$_2$ isothermal adsorption heat of 24.2 kJ/mol. The UiO-66/GO CO$_2$ isothermal adsorption heat is 28.3 kJ/mol, which is higher than that of UiO-66 isothermal adsorption heat 23.5 kJ/mol. This is mainly due to holes or defects in the interface between the MOF and the GO in the crystal structure, boosting the interaction between the skeleton and CO$_2$, and thus increasing the CO$_2$ adsorption capacity. At the same time, CO$_2$ intermolecular interactions in the channel may also increase $\Delta H$. The UiO-66-NH$_2$ CO$_2$ isothermal adsorption heat is 24.2 kJ/mol, which is slightly higher than that of the UiO-66 CO$_2$ isothermal adsorption heat of 23.5 kJ/mol. The UiO-66-NH$_2$/GO CO$_2$ isothermal adsorption heat is 29.9 kJ/mol, which is slightly higher than the UiO-66/GO isothermal adsorption heat of 28.3 kJ/mol. This can be attributed to the existence of -NH$_2$ and the reaction adsorption sites between CO$_2$, raising the heat of adsorption. The interaction between CO$_2$ is enhanced, the CO$_2$ adsorption capacity increases, and thus, eventually, there was a corresponding conformity.

Figure 9. N$_2$ adsorption isotherms measured at 298 K on the sample.

3.5. Adsorption Selectivity of CO$_2$/N$_2$

UiO-66-NH$_2$/GO may be a potential adsorbent for flue gas containing CO$_2$/N$_2$ in view of its high stability and CO$_2$ adsorption capacity. In order to get N$_2$ adsorption isotherms, the sample is tested at 298 K in the pressure range from 0 to 1 bar. As shown in Figure 9, the adsorption capacity order of N$_2$ on the sample is: UiO-66/GO > UiO-66-NH$_2$/GO > UiO-66 > UiO-66-NH$_2$. This is different from that of CO$_2$ on the sample, the latter is: UiO-66-NH$_2$/GO > UiO-66/GO > UiO-66-NH$_2$ > UiO-66. When compared with parent materials, the N$_2$ adsorption capacity of UiO-66-NH$_2$ and UiO-66-NH$_2$/GO composites decreases, which is helpful for improving the CO$_2$/N$_2$ adsorption selectivity of the sample.

According to the CO$_2$ and N$_2$ adsorption isotherm of the samples in Figures 8B and 9, CO$_2$/N$_2$ selectivity can be calculated. The initial slope (Henry’s constant) of the CO$_2$ and N$_2$ adsorption isotherm at the low pressure section can be used to calculate the selectivity factor and the single-component adsorption isotherm can be used to estimate the selectivity factor. The selectivity factor is defined as the ratio of the initial slope of CO$_2$ and N$_2$ [33]. Figure 10 shows the result according to the initial slope of CO$_2$ and N$_2$ adsorption isotherm.
The selectivities of UiO-66, UiO-66/GO, UiO-66-NH₂, and UiO-66-NH₂/GO to CO₂/N₂ were 14.78, 18.84, 22.83, and 28.45. The selectivity of UiO-66 to CO₂/N₂ is 14.78. The selectivity of UiO-66-NH₂ to CO₂/N₂ is 22.83, which has increased by 54.5%. The selectivity of UiO-66/GO to CO₂/N₂ is 18.84 and UiO-66-NH₂/GO to CO₂/N₂ is 28.45. The latter has increased by 51.0%. Similar to the MOFs of the amine ligand, the selectivity of both UiO-66-NH₂ and UiO-66-NH₂/GO composites clearly improve. This is because the adsorption of UiO-66-NH₂ and UiO-66-NH₂/GO to CO₂ contain chemical reaction adsorption sites, in addition to physical adsorption sites because of -NH₂, which makes their adsorption capacity to CO₂ increase significantly. Furthermore, the adsorption capacity of UiO-66-NH₂ and UiO-66-NH₂/GO to N₂ decrease. The selectivity order of the sample to CO₂/N₂ is: UiO-66-NH₂/GO > UiO-66-NH₂ > UiO-66/GO > UiO-66. Saha et al. [34] reported that the selectivity of MOF-5 and MOF-177 to CO₂/N₂ is 17.48 and 17.73, respectively, at 298 K and 1 bar. When compared with MOF-5 and MOF-177, the selectivity of UiO-66-NH₂ and UiO-66-NH₂/GO synthesized to CO₂/N₂ is much higher. To sum up, UiO-66-NH₂/GO and UiO-66-NH₂ have good prospects for industrial applications.

![Graph A](image1)

![Graph B](image2)

**Figure 10.** Initial slopes calculation for CO₂ (A) and N₂ (B) collected at 298 K.

### 3.6. Multiple Cycles of CO₂ Adsorption–Desorption

Figure 11 depicts the reversibility of the CO₂ adsorption process on UiO-66-NH₂/GO at 298 K from 0 bar to 1.2 bar. The isotherms in the diagram have been obtained after 12 h heating at 393 K in the vacuum condition. The adsorption capacity of the UiO-66-NH₂/GO was lowered by only 4% after six cycles, from 3.80 to 3.64 mmol/g at 298 K and 1.0 bar. The six isotherms overlapped partly.
The cyclical data reveals that the new UiO-66-NH$_2$/GO material that is synthesized in this work is a more stable adsorbent after six adsorption/desorption cycles under mild regeneration conditions.

![Figure 11. Six cycles of CO$_2$ adsorption isotherms on UiO-66-NH$_2$/GO at 298 K.](image)

4. Conclusions

In this work, new composite materials of graphene oxide (GO)-incorporated metal-organic framework (MOF)(UiO-66-NH$_2$/GO) were in-situ synthesized, and exhibited enhanced high performances for CO$_2$ capture. The sample stabilities of this new sample were also investigated in the presence of water attack or acid treatment or base treatment. In terms of stability, the results were good. UiO-66-NH$_2$/GO have been characterized by kinds of technical indicators and have been tested for CO$_2$ adsorption, with comparison of counterparts UiO-66-NH$_2$, UiO-66/GO, and UiO-66 samples. $S_{BET}$, $V_{pore}$, and $V_{mic}$ of UiO-66-NH$_2$/GO are, respectively, 1052 m$^2$/g, 0.345 cm$^3$/g, and 0.286 cm$^3$/g larger than UiO-66-NH$_2$ but slightly smaller than UiO-66/GO. The CO$_2$ absorbance of UiO-66-NH$_2$/GO achieves 6.41 mmol/g at 273 K, which is 5.1% higher than that of UiO-66/GO (6.10 mmol/g). In addition to physical adsorption sites, chemical adsorption sites (amino groups) also improved the CO$_2$ adsorption capacity. CO$_2$ adsorption heat and CO$_2$/N$_2$ selectivity was 29.9 kJ/mol and 28.45, which is higher than the selectivity of UiO-66-NH$_2$ and UiO-66/GO. UiO-66-NH$_2$/GO exhibited better optimized CO$_2$ adsorption and CO$_2$/N$_2$ selectivity. So, UiO-66-NH$_2$/GO composites has a potential application in CO$_2$ capture technologies to alleviate the increase in temperature of the earth’s atmosphere.

Acknowledgments: This work was supported by the funding of Ecological Building Materials and Environmental Protection Equipment Collaborative Innovation Center Project of Jiang Su Province (1142658).

Author Contributions: Yan Cao provided the experimental methods, analyzed the experimental data and wrote this manuscript. Fujiao Song, Hongmei Zhang, Tao Huang and Jiayu Ji participated in experimental work. Qin Zhong gave some advice of experimental methods. Wei Chu and Qi Xu made some guides to the use of instruments, reviewed the manuscript.

Conflicts of Interest: There is no conflicts of interest.

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