CO₂ Capture on Metal-Organic Framework and Graphene Oxide Composite Using a High-Pressure Static Adsorption Apparatus

Yunxia Zhao, Yan Cao, and Qin Zhong

Abstract—Metal-organic frameworks (MOFs) have attracted much attention as adsorbents for the separation of CO₂ from flue gas or natural gas. A copper-based metal-organic framework and graphite oxide composite (HKUST-1/GO) was synthesized and characterized using X-ray diffraction, sorption of nitrogen and scanning electron microscopy. The composite improved the CO₂ adsorption capacity and CO₂/N₂ selectivity. The composite obtained exhibited about a 38 % increase in CO₂ storage capacity than the parent MOF HKUST-1 at 305 K and 5 atm.

Index Terms—Carbon dioxide adsorption, composites, high-pressure adsorption apparatus, metal-organic frameworks.

I. INTRODUCTION

As electricity consumption and oil use have increased enormously, carbon dioxide emissions are larger than in the past, which exacerbates greenhouse effect as a class of greenhouse gases. Among all the anthropogenic emission sources, fuel-burning power plants are long-term, immobile and centralized, accounting for approximately one-third of CO₂ emissions. [1] Consequently, the removal of carbon dioxide from coal-fired plants is a problem that is exigent to be solved. Pressure swing adsorption technology is one of the advanced techniques with high gas consumption. [2] It requires pressure generally in 0.1 ~ 2.5 MPa, allowing a wide pressure range. Nevertheless, excellent adsorbent materials are the prerequisite of completing the operation smoothly and realizing high CO₂ load.

Metal-organic frameworks (MOFs), as a class of physisorbents, possess remarkable gas adsorption ability. [3] They are self-assembled of metal ions and organic ligands that involve O and N. [4] Size, volume and physical-chemical conditions of pore of MOFs could realize orient design by changing or modifying organic ligands, widely used in gases storage and separation of mixture gases in recent years. [5], [6] CO₂ capture and separation from mixtures is one of the focuses of research.

Many kinds of MOFs with high CO₂ capacity and CO₂/N₂ selectivity have been reported. Omar M. Yaghi and his coworkers [7] synthesized MOF-210 with BET and Langmuir surface area 6240 and 10400 m²/g respectively, which is a kind of MOF with the highest surface area so far. The CO₂ capacity is attained to 2870 mg/g at 5 MPa under 298K. However, the large void space in MOFs is not completely utilized for gas storage because of weak interactions between the walls of MOFs and usually small gas molecules. [8] In order to utilize effectively the MOF pore space, other materials with ordinary structure like microporous [9] and layered [10], [11] can be incorporated as composite components. Bandosz group are well experienced in synthesis of MOF-5/GO and HKUST-1/GO composites as well as their application for either acidic (NO₂ [12], H₂S [13]) or basic (NH₃ [14], [15]) gases adsorption. Such composites led to an improved gas adsorption capacity.

In this work, adsorption of CO₂ on synthetic HKUST-1 and its composite with graphite oxide was investigated. Single-component CO₂ or N₂ adsorption properties were measured by static volumetric method on a homemade high-pressure adsorption apparatus and cycle stabilities of CO₂ adsorption/desorption were examined. Moreover, adsorption mechanism was discussed briefly.

II. EXPERIMENTAL SECTION

A. Materials

HKUST-1 was synthesized following the procedure in the literature about low temperature synthesis [16]. Graphite oxide (GO) was prepared by oxidation of graphite using improved Hummers’ method [17]. The synthesis of HKUST-1 and graphite oxide composite referred to as HKUST-1/GO was similar to the preparation of HKUST-1. The difference was that GO and HKUST-1 precursors were simultaneously dispersed/dissolved in the solvent by sonication. The content of GO in the composite was 10 wt. % of the parent MOF. Cu(NO₃)₂·3H₂O (2.077 g), trimesic acid (H₃BTC) (1 g) and graphite oxide (0.05g) was dissolved in N,N-dimethylformamide (DMF, 15 ml), ethanol (15 ml) and H₂O (15 ml). The mixture was sonicated for 30 min, then transferred into 100 ml teflon lined stainless-steel autoclave, reacted for 10 h under 100 °C in thermostatic drying oven. After cooling to room temperature, the mother liquor was decanted. The product was washed by ethanol repeatedly, and then dried at room temperature.

B. Characterization

X-ray powder diffraction (XRD) patterns were taken on a XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China) using Cu Kα radiation (λ=0.15406 nm). The
tube voltage was 35 kV, and the current was 20 mA. The XRD diffraction patterns were taken in the 2θ range of 5°–80° at a scan speed of 8°/min. V-Sorbet 2008S ratio surface area analyzer (Beijing Jinaipu General Instrument Co., Ltd, China) was used to measure the Brunauer–Emmet–Teller (BET) surface area by nitrogen adsorption. Prior to the experiment, the samples were degassed at 120°C overnight. Scanning Electron Microscope (SEM) images were obtained with a JEOLJSM-6380LV instrument. The samples were previously coated with a thin layer of gold to avoid charging.

C. Gas Adsorption Measurement

To measure high-pressure CO2 uptake a homemade adsorption apparatus was developed as shown in Fig. 1 using a static volumetric system. The reactor section made of stainless steel was tailored by Yatai marine engineering co., LTD (Nantong, Jiangsu, China). The pressure sensor was capacitance type high precision absolute pressure sensor. Helium was used to calibrate dead volume and volume of sample cell with sample. High vacuum pump was used for desorption of adsorbents by vacuum to achieve the measurement of adsorption capacities under different pressures. Samples were run at 305K and up to about 550 KPa. The detailed operation and calculation process was learned from the reference [18]. Finally the values of gas adsorption capacity were calculated by MATLAB software.

III. RESULTS AND DISCUSSIONS

The isotherms for CO2 and N2 on HKUST-1 and HKUST-1/GO at 305 K and up to 520 KPa are shown in Fig. 2. The CO2 adsorption capacity rapidly increases with increasing pressure. The N2 adsorption capacities of the two samples are not that different, but they are much lower than the CO2 uptake values. The higher selectivity for CO2 adsorption than that for N2 on MOFs is owing to the larger quadrupole moment of CO2 than that of N2. [19] In Fig.2, the CO2 adsorption capacity for HKUST-1 is much higher than that of HKUST-1 at 305K and about 5 atm. The CO2 storage capacity reaches 2.5 mmol/g, higher than that of HKUST-1 1.8 mmol/g at the same pressure. The value of HKUST-1 is a little lower than that obtained by Chowdhury [16]. This may be due to the insufficient activation of the samples. Nevertheless, HKUST-1 and HKUST-1/GO here were prepared and tested in the same way, so the effect on them was similar. When GO was incorporated, the CO2 storage capacity of HKUST-1/GO was enhanced by 38 %. Due to the close N2 capacities of the two samples, clearly, the CO2/N2 selectivity of HKUST-1/GO is higher than that of HKUST-1.

To examine the cycling performance of the adsorbents, re-adsorption experiments were carried out after desorption by vacuum. Corresponding results are shown in Fig. 3. For HKUST-1, the re-adsorption isotherm is similar to the first adsorption, indicating good structure stability. CO2 is reported to physically adsorbed on HKUST-1 [20], [21], so the desorption is effective and results in good reproducibility of HKUST-1. For HKUST-1/GO, the re-adsorption property is a little higher than that of the first adsorption. This may be attributed to that the some pores in the composite are activated under the first adsorption, such as the pores at the interface between graphene oxide and MOF units. Then CO2 gas molecular will be more easily transported.

To figure out the difference between the parent MOF and the composite, some characterizations were carried out and analyzed. The X-ray powder diffraction patterns of GO, HKUST-1 and HKUST-1/GO are shown in Fig. 4. For HKUST-1, the diffraction pattern is in accordance with the literature data [16], [22], showing good crystallinity. The diffraction pattern of the composite material HKUST-1/GO is similar to that of HKUST-1 without peak position change, which indicates that the presence of GO does not prevent the formation of linkages between the copper dimmers and the organic bridges. The octahedral crystal structure is preserved. However, the peak intensity significantly decreases, indicating a small disturbance of the main framework and decrease in crystallinity associated with the incorporation of GO. It is worth noting that the peak of GO is not found for the composite. One reason is that the content of the GO is very low. Another more important reason is the exfoliation of GO.
and graphene oxide dispersed among HKUST-1 crystals. In addition, compared with the parent MOF, the peaks of the composite slightly towards right, which means its particle size is smaller.

![Graph](image)

**Fig. 4.** X-ray powder diffraction patterns of GO, HKUST-1 and HKUST-1/GO.

**TABLE I: PARAMETERS OF THE SURFACE AREA AND POROUS STRUCTURE FOR HKUST-1 AND HKUST-1/GO**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m²/g)</th>
<th>(S_{\text{Langmuir}}) (m²/g)</th>
<th>(V_{\text{pore}}) (cm³/g)</th>
<th>(V_{\text{mic}}/V_{\text{pore}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1.27</td>
<td>1.67</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1048.43</td>
<td>1387.54</td>
<td>0.5144</td>
<td>0.92</td>
</tr>
<tr>
<td>HKUST-1/GO</td>
<td>1015.25</td>
<td>1352.16</td>
<td>0.4996</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Even though the porosity seems to be the main factor governing the \(\text{CO}_2\) retention, the huge increase in the amount of \(\text{CO}_2\) adsorbed on the composite suggests that some specific interaction exists between the composite and \(\text{CO}_2\) molecule. GO may not be completely dispersed because ultrasonic time was not enough or GO amount was excessive, which can cause too much distortion and many defects in the structure of the composite, confirmed by the decreased intensities in the XRD patterns of the composite. Thus these defects partly account for the improvement of the \(\text{CO}_2\) adsorption performance [26], just as \(\text{CO}_2\) adsorption happens on the defective graphene, the physisorption energy is much stronger than that on a perfect defect-free graphene surface [27]. Moreover, the incorporation of GO can bring out steric hindrance effect and prevent BTC organic ligands coordinating with copper sites, result in more unsaturated Cu sites. Zhou [20] and Wu [21] reported that \(\text{CO}_2\) primary adsorption sites include the open Cu site and the cage window. So the extra unsaturated Cu site is responsible for the increased \(\text{CO}_2\) uptake. In addition, GO itself can adsorb \(\text{CO}_2\) due to the interaction between the delocalized \(\pi\) aromatic system of GO and the molecule quadrupole of \(\text{CO}_2\) [28] and polar interaction of \(\text{CO}_2\) with the oxygen groups on the basal planes. Furthermore, \(\text{CO}_2\) is more strongly adsorbed in defective GO [27].

### IV. Conclusion

A high-pressure static adsorption apparatus was manufactured in this work to measure the \(\text{CO}_2\) adsorption capacity on HKUST-1 and its composite with graphene oxide. The obtained \(\text{CO}_2\) adsorption capacity and \(\text{CO}_2/\text{N}_2\) selectivity indicate that the composite HKUST-1/GO is efficient for \(\text{CO}_2\) capture and separation, better than the parent MOF HKUST-1. And both of them have good cycling performance. The incorporation of GO brings differences for the composite on porosity, open metal sites, and defective GO and so on. These factors can have a strong effect on improved \(\text{CO}_2\) capture property of HKUST-1/GO. The measurement under high pressure has great guidance value to the engineering practice.
REFERENCES


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