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 CO_2 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 outcome and lower energy consumption. [2] It requires pressure generally in $0.1 \sim 2.5$ MPa, allowing a wide pressure range. Nevertheless, excellent adsorbent materials are the prerequisite of completing the operation smoothly and realizing high CO_2 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 CO_2 capacity and CO_2/N_2 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 CO_2 on synthetic HKUST-1 and its composite with graphite oxide was investigated. Single-component CO_2 or N_2 adsorption properties were measured by static volumetric method on a homemade high-pressure adsorption apparatus and cycle stabilities of CO_2 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 (H_3BTC) (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 K α radiation (λ =0.15406 nm). The

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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 CO_2 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.



Fig. 1. Schematic diagram of the apparatus used to measure single-component adsorption performance.

III. RESULTS AND DISCUSSIONS

The isotherms for CO_2 and N_2 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 CO_2 uptake values. The higher selectivity for CO_2 adsorption than that for N_2 on MOFs is owing to the larger quadrupole moment of CO_2 than that of N_2 . [19] In Fig.2, the CO₂ adsorption capacity for HKUST-1/GO 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 CO_2 storage capacity of HKUST-1/GO was enhanced by 38 %. Due to the close N2 capacities of the two samples, clearly, the CO_2/N_2 selectivity of HKUST-1/GO is higher than that of HKUST-1.



Fig. 2. Single component high-pressure adsorption isotherms of CO₂ and N₂ at 305K on HKUST-1 and HKUST-1/GO.

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. CO_2 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 CO_2 gas molecular will be more easily transported.



Fig. 3. High-pressure adsorption and re-adsorption isotherms of CO₂ at 305K for HKUST-1 and HKUST-1/GO.

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 graphenen 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.



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



Fig. 5. SEM images of GO, HKUST-1 and HKUST-1/GO.

The scanning electron microscopy images of GO, HKUST-1, HKUST-1/GO are shown in Fig. 5. GO is seen as paper with the layers stacked together. The crystals of HKUST-1 are typically octahedral-shaped with smooth surfaces. However, the composite is not so "perfect". Defects like fracture and corner breakage are obvious. Moreover, the particle size of the composite is smaller than that of HKUST-1, which coincides with the XRD results. The incorporation of GO impeded the growth of MOF crystallites, which resulted in the crystallites of the composites with small size. The formation of the composite is hypothesized to occur via the reaction between the copper sites of HKUST-1 and the oxygen-containing groups on GO, which has been deduced by Bandosz group [23]. Thus the graphene oxide layers can be embedded in the MOF "blocks". As can be seen in Fig. 5, the surface of the composite is not very smooth and some textures on the surfaces exist.

Porosity is an important parameter that has effect on gas adsorption. Results of surface area and porous structure obtained from nitrogen adsorption measurements are listed in Table I. GO used for surface area and pore volume test here was just GO powders and not treated by any exfoliation way like thermal expansion and so on. So its surface area is very low. In Table I, HKUST-1 has a BET surface area about 1048 m^2/g , which is higher the values obtained by Chui *et al.* [24] but lower than those obtained by Millward [3] and Decoste [25]. However, the surface area of the composite is a little lower than the parent MOF HKUST-1, but it's higher than the hypothetical value when the two phases are only a physical mixture. This reveals the presence of a synergy between the two components, just as mentioned above the attachment of graphene oxide layers on the MOF units by the interaction of oxygen groups on GO and Cu²⁺ dimers. A new porosity can be created at the interface between the graphene layers and the MOF "blocks" [23].

 \mathbf{S}_{BET} SLangmuin V_{mic}/V_{pore} Sample Vpore(cm3/g) (m^2/g) (m^2/g) GO 1.27 1.67 HKUST-1 1048.43 1387.54 0.5144 0.92 HKUST-1/GO 1015.25 0.92 1352.16 0.4996

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

Even though the porosity seems to be the main factor governing the CO_2 retention, the huge increase in the amount of CO₂ adsorbed on the composite suggests that some specific interaction exists between the composite and 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 CO₂ adsorption performance [26], just as CO₂ 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 cordinating with cooper sites, result in more unsaturated Cu sites. Zhou [20] and Wu [21] reported that CO₂ primary adsorption sites include the open Cu site and the cage window. So the extra unsaturated Cu site is responsible for the increased CO₂ uptake. In addition, GO itself can adsorb CO_2 due to the interaction between the delocalized π aromatic system of GO and the molecule quadrupole of CO_2 [28] and polar interaction of CO₂ with the oxygen groups on the basal planes. Furthermore, CO2 is more strongly adsorbed in defective GO [27].

IV. CONCLUSION

A high-pressure static adsorption apparatus was manufactured in this work to measure the CO_2 adsorption capacity on HKUST-1 and its composite with graphene oxide. The obtained CO_2 adsorption capacity and CO_2/N_2 selectivity indicate that the composite HKUST-1/GO is efficient for 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 CO_2 capture property of HKUST-1/GO. The measurement under high pressure has great guidance value to the engineering practice.

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