In-situ HKUST-1 growth into inner pores of activated carbon granule for CO₂ efficient capture

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Abstract. Metal-organic frameworks (MOFs) are efficient adsorption materials for carbon capture and storage. We proposed a strategy of solid-liquid in-situ reaction method to grow MOFs in activated carbon granule (AC), preparing high efficient CO₂ adsorbent. At first, metal salts were solidified in the pores of AC granule carriers by 445 K treating. Then the organic ligands were introduced into the pores of AC. The MOF can be successfully prepared by solid-liquid reaction method. By this method, MOFs uniformly disperse in AC pores, making it possible for MOFs used in fixed bed adsorption separation. The CO₂ adsorption was tested by conducting breakthrough experiments in a fixed bed. When organic ligand concentration increased from 0 to 6%, the CO₂ uptake value increased from 0.2868 mmol·g⁻¹ to 0.3324 mmol·g⁻¹ in the CO₂/Air atmosphere with CO₂ concentration of 10%. The CO₂ uptake value increased 67% at 5000 PPM compared to original AC.

1. Introduction
Carbon capture is vital both in industry and controlled ecological life support system (CELSS). In industry, carbon capture was used in three aspects: pre-combustion, post-combustion and oxygen-enriched combustion. The general CO₂ concentration of these process ranges from 5 to 15%. In CELSS application, the CO₂ concentration must be controlled in relatively low concentration, which is usually under 0.5%. [1]

Carbon capture methods can be divided into three categories: chemical absorption, membrane separation and adsorption separation. Adsorption separation can be applied in wide range of temperature and pressure, which is facility for various carbon capture requirements. Moreover, adsorption separation will cause little environmental footprint compared to chemical absorption, because adsorbents will not decompose, avoiding the toxic compounds producing. [2] Many indicators points to the cost reduction of adsorption.

Activated carbon, molecular sieves, metallic oxides, mesoporous silicon, MOFs and POPs are main porous materials for CO₂ adsorption. [3] Due to rich surface area, uniform pore structure, adjustable pore size and strong interaction force with CO₂ molecule, the MOFs attracted much attention. In current studied MOFs, Zr-Uio-66, fcu-MOF and HKUST-1 show superior CO₂ adsorption performance. Cavka et al. [4] prepared a zirconium MOF called Zr-Uio-66, which is extremely stable in relatively high temperature, alkaline and acidic condition. The CO₂ capacity is 2.39 mmol·g⁻¹ at 298 K, 1 bar. Xue et al. [5] studied the tunable rare-earth fcu-MOFs as CO₂ adsorbent, and the CO₂ adsorption capacity reached 4.1 mmol·g⁻¹ at 298 K, 1 bar.

HKUST-1 reveals outstanding performance on CO₂ adsorption because of its possessing exposed metal cation sites in the pores. HKUST-1 showed 4.2 mmol·g⁻¹ CO₂ capacity at 298 K, 1 bar. Notably,
CO₂ uptake of HKUST-1 at post-combustion partial pressure (0.15 bar) is 2.63 mmol·g⁻¹.[6] which is superior to most current MOFs.

However, the MOFs are all in powder forms, which is barrier for their application in industrial application. Because the micro/sub-micro particles would be blew away by fluids easily, and usually agglomerate, causing pipe blocking and slow mass transfer kinetics. In order to solve this problem, we propose solid-liquid reaction method to grow HKUST-1 in porous carrier. The optimum condition of solid-liquid reaction was first invested by changing reaction temperature, reaction time and precursor concentration. Furthermore, the CO₂ adsorption separation performance was investigated.

2. Experimental section

2.1. Materials
Copper(II) nitrate trihydrate (Cu(NO₃)₂ꞏ3H₂O) and Cupric carbonate basic (Cu₂(OH)₂CO₃) were purchased from Shanghai Macklin Biochemical Co. Ltd. Trimesic acid (H₃BTC) was purchased from J & K Scientific Ltd. Activated carbon (AC, cylindrical monoliths) was purchased from Beijing Tong Guang Fine Chemical Ltd. 99.99% CO₂, simulated air (21% O₂, 79% N₂) and 99.99% N₂ for adsorption measurements were purchased from Shaanxi Wang Wei Gas Technology Co. Ltd, China.

2.2. Preparation and loading of HKUST-1

2.2.1. HKUST-1 preparation using solvothermal method. In this paper, we use typical solvothermal method to prepare HKUST-1.[7] In brief, 0.435 g Cu(NO₃)₂ꞏ3H₂O was dissolved in 5 g deionized water. 0.22 g H₃BTC was dissolved in 1.5 g ethanol. These two solutions were mixed in Teflon reaction kettle and sealed. The reaction kettle was placed in a high temperature oven at 110 °C for 12 hours, then it was naturally cooled to room temperature. The obtained product was centrifuged at 10⁴ r·min⁻¹ in a high-speed centrifuge, and the blue precipitate was washed with ethanol and centrifuged three times. Finally, the HKUST-1 product was dried and activated at 100 °C.

2.2.2. HKUST-1 preparation using Solid-liquid method. We propose a method of solidifying metal salts to prepare HKUST-1. The specific operation is as follows: Cu(NO₃)₂ꞏ3H₂O (3.0 g) was decomposed in a blast-type high temperature oven at 172 °C for 2 h to obtain Cu₂(OH)₂CO₃. After cooling, 0.199 g of Cu₂(OH)₂CO₃ was added into a 100 mL beaker. H₃BTC (0.252 g) was dissolved in mixed solution of ethanol (5.0 g) and deionized water (1.5 g). The solution was poured into the beaker containing Cu₂(OH)₂CO₃. Then the beaker was sealed and placed in a constant temperature oscillator (at 60 °C, shaking speed of 90 r·min⁻¹) to start the reaction. After 3–24 h of reaction, the suspension in the beaker was poured into a 50 mL centrifuge tube and centrifuged at 10⁴ r·min⁻¹. It was then washed with 30 mL of ethanol three times. The product was final dried at 100 °C and the mass was weighed.

2.2.3. HKUST-1 loading in AC. The solid-liquid in-situ growth schematic diagram was shown in figure 1. The specific steps are as follows: Cu(NO₃)₂ꞏ3H₂O (1.266 g) was dissolved in deionized water (30 g). Then the Cu(NO₃)₂ solution was absorbed by activated carbon granules (20 g) in a 1.00 L beaker. After 15 min, the beaker was placed in a blast-type high-temperature oven and decomposed at 172 °C for 2 h. Cu₂(OH)₂CO₃@AC composite was obtained.

H₃BTC (0.587 g) was dissolved in 30 g 76% ethanol aqueous, and then absorbed by Cu₂(OH)₂CO₃@AC. It was placed in an oven at 60 °C for 24 h and then dried at 100 °C for 2 h. The HKUST-1 immobilized activated carbon composite material was obtained. Since the pyrazine concentration was 2%, the composite material was recorded as HKUST-1@AC-2%, and the composite material prepared at the higher concentration ligand was named the same way. The molar ratio of Cu(NO₃)₂ꞏ3H₂O to H₃BTC in all the experiments in this work is 3:2.
2.3. Characterization of the HKUST-1 and HKUST-1@AC

The morphologies of prepared materials were evaluated by high resolution scanning electron microscopy (ZEISS SUPRA™ 55, German). Samples were sputtered by Au with an auto fine coater (JFC-1600, JEOL, Japan), 23 mA, 60 s, under the vacuum of 5 Pa to ensure the conductivity.

The textural characteristics of SIFSIX-3-Cu and SIFSIX-3-Cu@MFS were carried out by X-ray diffraction (XRD) using a diffractometer (Ultima IV, Japan) under Cu-Kα radiation (λ = 0.15418 nm, 40 kV, 40 mA).

3. Result and discussion

3.1. Characterization of the adsorbents

3.1.1. Morphology of HKUST-1 and HKUST-1@AC. The SEM image of HKUST-1 prepared by solvothermal method and solid-liquid reaction method were shown in figure 2. Octahedron crystals were prepared by both methods. Within the same reaction time, the crystal size of solvothermal prepared HKUST-1 was 3–10 μm, which is larger than that of solid-liquid prepared HKUST-1 (0.5–5 μm).

The SEM image of HKUST-1@AC prepared at different precursor concentration can be seen from figure 3(a)–(d). With the concentration of the precursor increasing, the number of HKUST-1 crystals immobilized in activated carbon increased. It was worth noting that HKUST-1 crystals were rarely seen in HKUST-1@AC-2%. Sporadic HKUST-1 crystals appear in HKUST-1@AC-4%. The HKUST-1 crystals in HKUST-1@AC-6% were rich and uniformly dispersed. In addition, there were micron gaps between the crystals. The HKUST-1 crystals in the HKUST-1@AC-8% was dense, stacking tightly. Theoretically, the more loading amount of HKUST-1 crystal is, the more adsorption sites of HKUST-1@AC are. This will contribute to larger CO₂ adsorption capacity. However, from the perspective of mass transfer, the tightly stacked HKUST-1 crystals were not beneficial to mass transfer during the adsorption process.
Figure 3. SEM image of HKUST-1@AC prepared at different precursor concentrations. Organic ligand concentration: (a) 2%; (b) 4%; (c) 6%; (d) 8%; The reaction temperature was 60 °C, and reaction time was 24 h.

3.1.2. XRD patterns of HKUST-1 and HKUST-1@AC. As shown in figure 4(a), the XRD patterns of HKUST-1 synthesized by solid-liquid reaction method and solvothermal method of HKUST-1 were coincident with the diffraction peaks of simulated HKUST-1. Among them, $2\theta = 6.68^\circ$ was the [200] crystal plane diffraction peak, $2\theta = 9.42^\circ$ was the [220] crystal plane diffraction peak, $2\theta = 11.59^\circ$ was the [222] crystal plane diffraction peak [8]. It can be seen that the solid-liquid reaction method proposed in this paper successfully prepared HKUST-1 crystal. In addition, the full width at half maxima (FWHM) of the HKUST-1 diffraction peak prepared by the solid-liquid reaction method is larger than that prepared by the solvothermal method. According to the Scherrer formula[9], the crystal size prepared by the solid-liquid reaction method is smaller than that of solvothermal prepared, which coincide with SEM images.

Figure 4(b) shows the XRD patterns of HKUST-1@AC prepared at different precursor concentrations. As can be seen, these HKUST-1@AC composite showed activated carbon hump in the $2\theta$ region of 20–30°. The HKUST-1 characteristic peak appeared at the same time, indicating that
HKUST-1 was successfully immobilized in activated carbon. Moreover, with the precursor concentration increasing, the characteristic peak of HKUST-1 becomes more and more obvious.

3.2. Effect of loading conditions on adsorption performance

Figure 5(a) showed the breakthrough curve of HKUST-1@AC prepared at different precursor concentrations. The feed CO₂ concentration was 10 vol%, the temperature was 293 K, the pressure was 1 atm, and the quality of the filled AC carrier in the adsorption column was the same. The breakthrough time, saturation time and CO₂ uptake value was shown in table 1. When organic ligand concentration increased from 0 to 6%, the CO₂ uptake value increased from 0.2868 to 0.3324 mmol·g⁻¹.

![Figure 5](image)

**Figure 5.** The breakthrough curve of HKUST-1@AC and AC tested at 1 atm, 293 K. (a) 10 vol% CO₂ concentration in CO₂/Air, (b) 5000 PPM CO₂ concentration in CO₂/Air.

| Adsorbent       | Breakthrough time / s | Saturation time / s | CO₂ uptake / mmol·g⁻¹ | CO₂ uptake per gram carrier / mmol·g⁻¹ |
|-----------------|-----------------------|---------------------|-----------------------|--------------------------------------|
| AC              | 100                   | 235                 | 0.2868                | 0.2868                               |
| HKUST-1@AC-4%   | 95                    | 245                 | 0.2876                | 0.2663                               |
| HKUST-1@AC-6%   | 116                   | 281                 | 0.3324                | 0.2916                               |
| HKUST-1@AC-8%   | 84                    | 300                 | 0.2937                | 0.2448                               |

* Reaction condition: temperature was 60 °C, organic ligand concentration was 4%, 6%, 8%, the ratio of Cu(NO₃)₂·3H₂O and H₂BTC was 3:2. Fixed bed breakthrough condition: the CO₂ concentration was 10 vol%, the temperature was 293 K.

* CO₂ uptake value per gram of HKUST-1@AC composite.

* CO₂ uptake value per gram of AC carrier.

Furthermore, breakthrough curve tested at low CO₂ concentration (5000 PPM) was shown in figure 5(b). The adsorption results were shown in table 2. Compared to the original activated carbon, CO₂ uptake value of HKUST-1@AC-6% composites increased 67%.

| Adsorbent       | Breakthrough time / s | Saturation time / s | CO₂ uptake / mmol·g⁻¹ | CO₂ uptake per gram carrier / mmol·g⁻¹ |
|-----------------|-----------------------|---------------------|-----------------------|--------------------------------------|
| AC              | 56                    | 160                 | 0.0668                | 0.0668                               |
| HKUST-1@AC-6%   | 112                   | 231                 | 0.1116                | 0.0979                               |

* Adsorption condition: 293 K, 1 atm.

* CO₂ uptake value per gram of HKUST-1@AC composite.

* CO₂ uptake value per gram of AC carrier.
4. Conclusions
In this paper, a method of solidifying metal salt was proposed to prepare MOFs. The solid-liquid in-situ reaction was used to uniformly immobilize HKUST-1 in the internal pores of activated carbon granule, which realized the application of HKUST-1 in fixed bed CO2 adsorption separation. The temperature required for the reaction was reduced from 110 °C to 60 °C. Furthermore, in the CO2/Air breakthrough test, the CO2 uptake value of the HKUST-1@AC composite increased from 0.2868 to 0.3324 mmol·g⁻¹ at 10% CO2 concentration. The CO2 uptake value increased 67% at 5000 PPM compared to original AC.

Acknowledgements
This study was financially supported by the National Natural Science Foundation of China (No. 21736001 and 21576024). We also acknowledge the research support from the Analysis & Testing Center of Beijing Institute of Technology.

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