Synthesis of Metal–Organic Framework material Cu–BTC and its application for CO₂ adsorption

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Abstract
A copper-based metal organic framework (MOF) named Cu–BTC, also known as HKUST-1, was successfully synthesized by using a solvothermal method. The properties of the Cu–BTC sample were characterized with Powder X-ray diffraction (XRD) for phase structure, Thermogravimetric analysis (TGA) for thermal stability, Scanning electron microscopy (SEM) for crystal structure, and Nitrogen adsorption–desorption for pore textural structure. The analysis results displayed that the Cu–BTC sample exhibited a good crystal structure with uniform size of octahedral particles. The BET data revealed a high surface area of 1457 m²/g and a pore volume of 0.60 cm³/g. The Cu–BTCs ample was also studied for CO₂ adsorption and exhibited a maximum CO₂ adsorption capacity of 170 mg/g of the sorbent (3.8 mol/kg) at 25 °C.

1. Introduction
Scenarios of global warming have projected a rise in global temperature up to 2 - 4 °C by 2050 due to increasing CO₂ concentrations in the atmosphere [1]. Selective trapping of CO₂ from the emissions of coal–fired power plants is an important goal, which, if achieved in an economical fashion, could significantly contribute to the reduction of CO₂ emissions [2]. Developing new materials for CO₂ capture and separation is critically important. Metal–organic frameworks (MOFs) are emerging as promising materials for selectively adsorbing CO₂ [3]. MOFs have been recognized as a new class of nanoporous materials that have many potential advantages over the traditional adsorbents [4]. They are synthesized using organic ligands and metal clusters that self-assemble to form crystalline materials with well-defined structures, controlled pore size, high surface area, and desired chemical functionalities [5–9]. These attractive properties make MOFs promising materials for gas separation and storage [10–15]. Cu–BTC [Cu₆(BTC)₃, BTC = 1,3,5-benzenetricarboxylate] also known as HKUST-1 is a widely studied MOF, which was first reported by Chui et al. [16], and has been widely studied for gas adsorption and diffusion [17–19], especially for hydrogen storage. In this work, we synthesized Cu–BTC by using a traditional solvothermal method at 393 K, and studied its CO₂ adsorption characteristics.

2. Experimental
2.1. Synthesis of Cu–BTC
The Cu–BTC material studied in this work was harvested from the reaction of cupric nitrate hydrate [Cu(NO₃)₂·3H₂O] and trimesic acid (BTC:1,3,5-benzenetricarboxylate) by using a solvothermal method [20]. In a typical synthesis,
1.75 g Cu(NO$_3$)$_2$·3H$_2$O was dissolved into 24 ml DI water, and 0.84 g BTC was dissolved into 24 ml ethanol under stirring at room temperature. Then the copper solution was added to the BTC solution and keep in stirring for 1 hour. The mixture was transferred to a Teflon lined stainless steel and kept at 393 K for 12 hours. The reaction vessel was cooled to ambient temperature and the product mixture were separated by centrifugation and the solid product was vacuum dried at room temperature. The obtained blue color powder was named as Cu-BTC [Cu$_3$(BTC)$_2$].

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Miniflex diffractometer with Cu-K$\alpha$ radiation ($\lambda$=0.154 nm). The diffraction data were recorded in the 20 range 5-60 $^\circ$ at step of 0.02$^\circ$ /s. Thermogravimetric analysis (TGA) was performed by means of a SCINCO thermal gravimeter N-1000, the sample was heated from room temperature to 800 $^\circ$C under N$_2$ at a scan rate of 5 $^\circ$C/min. The nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 200 $^\circ$C under vacuum (p<10$^{-5}$ mbar) for 6 hours in the degas port. The specific surface area, $S_{BET}$ was determined from the linear part of the BETequation, and the pore volume was calculated using a BET plot based on the amount of nitrogen gas adsorbed at the last adsorption point (P/P$_0$=0.98) and the pore size distribution using the Barrett-Joyner-Halenda (BJH) method. SEM images were captured on JEOL JSM 5600 scanning electron microscope.

3. Results and Discussions

3.1 Characterization

3.1.1. XRD analysis

Fig. 1 shows the XRD patterns of Cu–BTC. It is in well agreement with the pattern calculated from crystallographic data [20], indicating high purity of the crystalline phases.

![XRD pattern of Cu–BTC](image)

3.1.2 TGA analysis

The thermal stability of the Cu-BTC sample as analyzed by TGA is presented in Fig.2. The TGA results show that there is a weight loss from 100 $^\circ$C to 300 $^\circ$C. The first weight loss is due to water molecules. The second weight loss around 300 $^\circ$C is due to the decomposition of the organic network [1].
3.1.3. BET analysis

The N₂ adsorption/desorption isotherms of Cu-BTC sample is displayed in Fig.3. The Cu-BTC exhibits a typical type I isotherm with a very sharp uptake at P/P₀ from 10⁻⁵ to 10⁻¹, a signature characteristic of microporous materials. The BET surface area was estimated to be 1457 m²g⁻¹. The total pore volume was calculated to be 0.60 cm³g⁻¹. The BET surface area and pore volume of the Cu-BTC sample are comparable to the values obtained by Liang et al.[1], which is much higher than those reported by Chui et al. [16] and Wang et al. [21]. The average pore diameter calculated from BET data was 1.66 nm.

3.2 CO₂ adsorption

Fig. 4 shows CO₂ adsorption/desorption profiles of Cu-BTC sample carried out at 25, 50 and 75 °C under the pressure of 1 bar. The CO₂ sorption/desorption profiles illustrates the initial weight loss of approximately 14 wt% after preliminary activation at 200 °C in N₂ atmosphere is due to loss of moisture content and physisorbed CO₂ on exposure to atmosphere. The maximum CO₂ adsorption capacity of Cu-BTC is 170 mg/g of the sorbent (3.8 mol/kg) at 25 °C, which is similar to the values reported by Liang et al [1].

3.1.4. SEM analysis

The SEM analysis result of the Cu-BTC sample is presented in Fig. 3. The Cu-BTC crystal is composed by uniform size of octahedral particles, which is identical to that reported in literature [22].
4. Conclusions

A copper–based metal–organic framework (MOF) material named as Cu–BTC was successfully synthesized from the solvothermal reaction of cupric nitrate hydrate \([\text{Cu(NO}_3\text{)}_2\cdot\text{3H}_2\text{O}]\) and trimethylacetic acid (BTC:1,3,5–benzenetricarboxylate). The obtained Cu–BTC sample was characterized by XRD, TGA, SEM and BET analysis, and the results illustrate the crystal structure and the porosity properties of Cu–BTC. The surface area and total pore volume of Cu–BTC are 1457 m\(^2\)g\(^{-1}\) and 0.60 cm\(^3\)g\(^{-1}\), respectively. The Cu–BTC exhibits microporous with a pore size of 1.66 nm. The Cu–BTC sample was tested for CO\(_2\) gas adsorption and it showed a maximum CO\(_2\) adsorption capacity of 170 mg/g of sorbent (3.8 mol/kg) at 25 °C.

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