Synthesis of Metal-Organic Framework material Cu-BTC and its application for CO_2 adsorption

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유기 금속 Framework Cu-BTC의 합성 및 이산화탄소 분리 응용

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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 m^2g^{-1} and a pore volume of 0.60 cm^3g^{-1}. The Cu-BTCs ample was also studied for CO_2 adsorption and exhibited a maximum CO_2 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 ºC by 2050 due to increasing CO_2 concentrations in the atmosphere [1]. Selective trapping of CO_2 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 CO_2 emissions [2]. Developing new materials for CO_2 capture and eparationis critically important. Metal-organic frameworks (MOFs) are emerging as promising materials for selectively adsorbing CO_2 [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 [$Cu_3(BTC)_2$, 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 CO_2 adsorption characteristics.

2. Experimental

2.1. Synthesisof Cu-BTC

The Cu-BTC material studied in this work was harvested from the reaction of cupric nitrate hydrate [$Cu(NO_3)_2 \cdot 3H_2O$] and trimesic acid (BTC;1,3,5-benzenetricarboxylate) by using a solvothermal method [20]. In a typical synthesis,

1.75 g $Cu(NO_3)_2 \cdot 3H_2O$ 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-Kα radiation (λ=0.154 nm). The diffraction data were recorded in the 2Θ range 5-60 ° at step of 0.02° /s. Thermogravimetric analysis (TGA) was performed by means of a SCINCO thermal gravimeter N-1000, the sample was heated from room temperature to 800 °C under N_2 at a scan rate of 5 °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 °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.

2.3. CO_2 adsorption

CO_2 adsorption-desorption measurements for Cu-BTC were performed using Thermo Gravimetric Analyzer. A sample weight of approximately 10 mg was loaded into an alumina sample pan in a TG unit (SCINCO thermal gravimeter N-1000) and tested for CO_2 adsorption-desorption performance. The initial activation of the samples was carried out at 200 °C for 1 h in a nitrogen atmosphere. Then adsorption run was conducted using high purity CO_2 (99.999%) gas, and the desorption run was conducted in N_2 flow.The adsorption runs were conducted at 25, 50 and 75 °C under atmospheric conditions, and desorption was determined at 200 °C. Both the gases, CO_2 and N_2 were passed through an automatic valve, assisted with a timer for continuous adsorption and desorption profiles.

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.

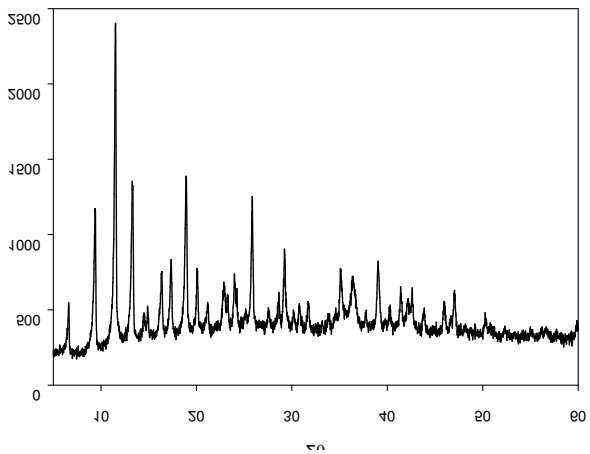


Fig. 1. XRD pattern of Cu-BTC

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 °C to 300 °C. The first weight loss is due to water molecules. The second weight loss around 300 °C is due to the decomposition of the organic network [1].

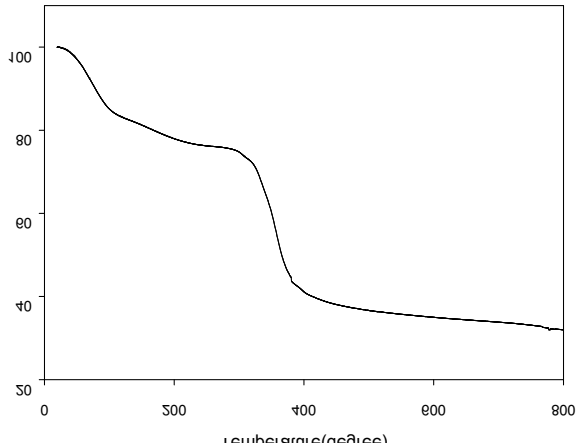


Fig.2. TGA curve of Cu-BTC sample.

3.1.3. BET analysis

The N_2 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/P_0 from10^{-5}to10^{-1}, a signature characteristic of microporous materials. The BET surface area was estimated to be 1457 m^2g^{-1}. The total pore volume was calculated to be 0.60 cm^3g^{-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.

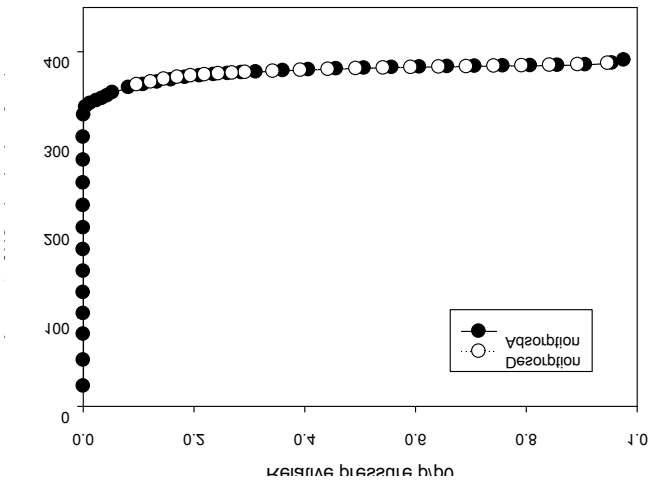
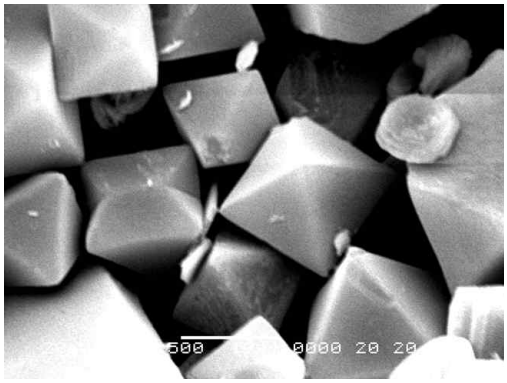


Fig. 3. N_2 adsorption/desorption isotherm of Cu-BTC.

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].



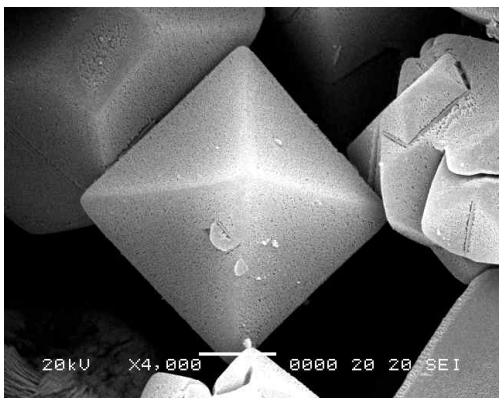


Fig.3. SEM images of Cu-BTC.

3.2 CO_2 adsorption

Fig. 4 shows CO_2 adsorption/desorption profiles of Cu-BTC sample carried out at 25, 50 and 75 °C under the pressure of 1 bar. The CO_2 sorption/desorption profiles illustrates the initial weight loss of approximately 14 wt% after preliminary activation at 200 °C in N_2 atmosphere is due to loss of moisture content and physisorbed CO_2 on exposure to atmosphere. The maximum CO_2 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].

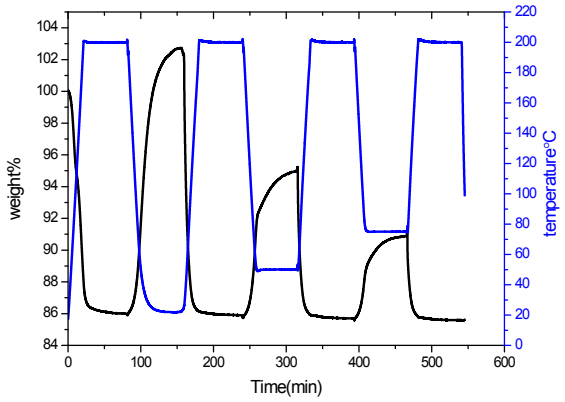


Fig. 4. CO_2 adsorption/desorption profiles of Cu-BTC.

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 [$Cu(NO_3)_2 \cdot 3H_2O$] andtrimesicacid(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^2g^{-1} and 0.60 cm^3g^{-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 amaximum CO_2 adsorption capacity of 170 mg/g of sorbent (3.8 mol/kg) at 25 °C.

Acknowledgements

This study was supported by a grant (code CD3-201) from Carbon Dioxide Reduction & Sequestration Research Center, one of the 21st Century Frontier funded by the Ministry of Science and Technology of Korean Government.

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