Optimization of synthesis conditions and CO_2 capture capability of Cu-BTC Metal-Organic Framework

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이산화탄소 흡착용 Cu-BTC MOF 합성 최적화

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Abstract

A copper-based metal organic framework (MOF) named Cu-BTC, also known as HKUST-1, was synthesized by using a solvothermal method at various synthesis temperature, time and pressure. The obtained samples were characterized with Powder X-ray diffraction (XRD) for phase structure, scanning electron microscopy (SEM) for crystal structure, and nitrogen adsorption-desorption for pore textural structure. The Cu-BTC sample was also studied for CO_2 adsorption. The analysis results displayed that the sample synthesized at the condition of temperature: 120 °C, synthesis time: 12 hours, pressure: 1 bar exhibited a good crystal structure with uniform size of octahedral particles. The BET data revealed a high surface area of 1741.7 m^2g^{-1} and a pore volume of 0.7137 $cm^3g^{-1}$and exhibiteda maximum CO_2 adsorption capacity of 170 mg/g of the sorbent at 25 °C.
Key words: MOFs, Cu-BTC, CO_2 adsorption, porous materials.

1. Introfuction

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 separationis 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]. In this work, we synthesized Cu-BTC by using a traditional solvothermal method at various synthesis temperature, time and pressure to investigate the optimal synthesis condition of Cu-BTC.

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 [$Cu(NO_3)_2{\cdot}3H_2O$] and trimesic acid (BTC;1,3,5-benzenetricarboxylate) by using a solvothermal method [17]. 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 autoclaved and kept at 120 °C for 12 hours. The reaction vessel was cooled to ambient temperature and the product mixture was separated by centrifugation and the solid product

was vacuum dried at room temperature. The effect of synthesis temperature, pressure and time was studied in order to obtain Cu-BTC crystals with fewer defects.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2200+Ultima diffractometer with Cu-Kα radiation (λ=0.154 nm). The diffraction data were recorded in the 2Θ range 5-60 ° at step diffraction data were recorded in the 2Θ range 5-60 ° at step of 0.02/s. The nitrogen adsorption-desorption isotherms were measured at 77 K on a BEL-Belsorp II volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 105 °C under vacuum ($p<10^{-5}$ mbar) for 6 hours in the degas port. The specific surface area, a/BET was determined from the linear part of the BET equation, 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 gravimetric (TG) analyzer. A sample weight of were performed using Scinco TGA N-1000 thermo approximately 10 mg was loaded into an alumina sample pan in a TG unit and tested for CO_2 adsorption-desorption performance. The initial activation of the samples was carried out at 110 °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_2flow.The adsorption runs were conducted at 25,50 and 75 °C under atmospheric conditions, and desorption was determined at 110 °C. Both the gases, CO_2 and N_2were passed through an automatic valve, assisted with a timer for continuous adsorption and desorption profiles.

3. Results and discussions Synthesis temperature effect

In order to study the influence of synthesis temperature for the formation of Cu-BTC crystals, the synthesis was carried out at various temperatures (90, 105, 120, 135, 150, 165 and 180 °C). The XRD patterns of Cu-BTC (1-7) are presented in Fig. 1. For comparison the XRD patterns of Cu_2O are also given in the same figure. During the synthesis, along with the formation of Cu-BTC crystals, trace amount of Cu_2O phases were also formed. This is evident by the peak reflections at 36.25 and 42.5° (2q). The intensity of these peaks increased with increase in the synthesis temperature. Hence, high temperature synthesis results in crystals with more Cu_2O phase. The Cu-BTC crystals synthesized at 120 °C was found to be more crystalline than the others.

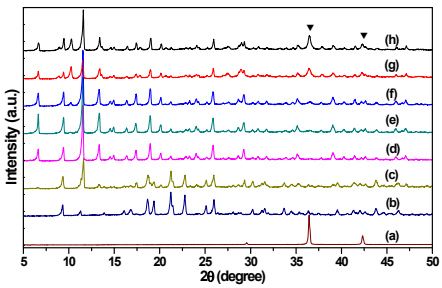

Fig.1, XRD patterns of Cu-BTC synthesized at different temperatures, (a) Cu_2O,(b)90°C, (c) 105 °C, (d) 120 °C, (e) 150 °C, (f) 165 °C, (g) 180 °C.

Table 1, Nitrogen Adsorption-Desorption data of Cu-BTC synthesizedat different temperatures

name	Synthesis temperature(°C)	a/BET(㎡ g⁻¹)	Total pore volume (cm³ g⁻¹)	Average pore diameter(nm)
Cu-BTC-1	90	7.9254	0.016616	8.3864
Cu-BTC-2	105	942.38	0.3968	1.6844
Cu-BTC-3	120	1741.7	0.7137	1.6391
Cu-BTC-4	135	1527.8	0.6395	1.6743
Cu-BTC-5	150	1384.6	0.5668	1.6373
Cu-BTC-6	165	778.5	0.3346	1.7191
Cu-BTC-7	180	761.88	0.3302	1.7335

(Synthesis condition: time 12 hours, pressure 1 bar)

The specific surface area characteristics and pore volume of materials synthesized at different temperatures are summarized in Table 1. Herein, both surface area and pore volume of Cu-BTC increased with increase in temperature up to 120 °C. At 120 °C (Cu-BTC-3) the specific surface area and pore volume were 1741.7 m^2g^{-1} and 0.7137 cm^3g^{-1} respectively. The information of pore size given in Table 1 display that Cu-BTC synthesized in the temperature range 120 - 180 °C exhibited an average pore size of about 1.7 nm.

The SEM images of the Cu-BTC (1-7) are presented in Fig.2. The morphology of the crystals is influenced by the temperature. At the synthesis temperature (120 °C), the crystals displayed an octahedral structure with smooth edges while at lower temperatures the morphology of the crystals was quite different. The formation of the elongated crystals reveals incomplete crystallization. While at temperature above 150 °C, the octahedral structure became irregular leading to different morphology.

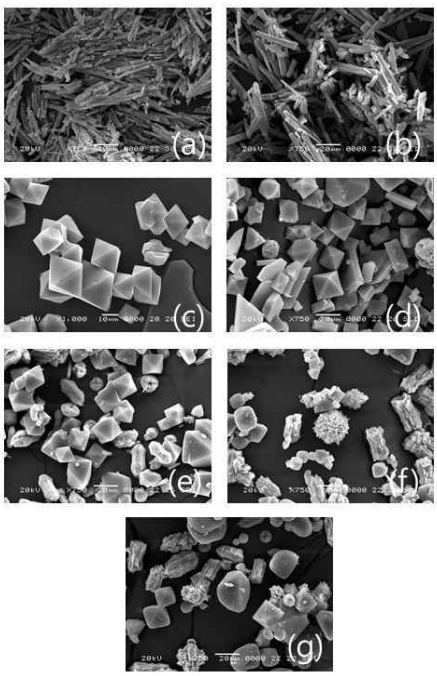

Fig. 2, SEM images of Cu-BTC synthesized at different temperatures, (a) 90 °C, (b) 105 °C, (c) 120 °C, (d) 135 °C, (e) 150 °C, (f) 165 °C, (g) 180 °C.

The CO_2 adsorption capacities at25 °C of the Cu-BTC (1-7) are presented in Fig. 21. The adsorption capacity increased with increase in synthesis temperature up to 120 °C. The CuBTC-3 exhibited a maximum CO_2 adsorption capacity of 17 wt% (170 mg/g of the sorbent). (Table 2), thereafter the adsorption capacity decreased. The decrease at lower synthesis temperature is due to incomplete crystallization of the Cu-BTC crystals while at higher synthesis temperature of Cu-BTC decreases with increasing synthesis temperature, which was in a good agreement with BET results.

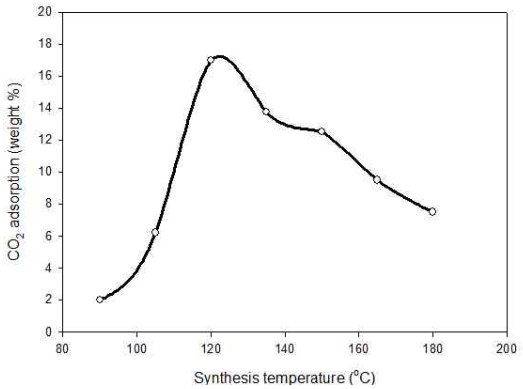

Fig. 3, The CO_2 adsorption of Cu-BTC sample synthesized at different temperatures

Table 2, CO_2 adsorption data of Cu-BTC synthesized at different temperatures.

Sample name	Synthesis temperature(°C)	CO_2 adsorption Weight %
Cu-BTC-1	90	2.00
Cu-BTC-2	105	6.20
Cu-BTC-3	120	17.00
Cu-BTC-4	135	13.75
Cu-BTC-5	150	12.50
Cu-BTC-6	165	7.50
Cu-BTC-7	180	9.50

(Synthesis condition: time 12 hours, pressure 1 bar)

Synthesis time and pressure effect were also studied in this research (3.2 and 3.3). The effect of synthesis time was studied by varying the crystallization time by 8, 10, 12, 14, 16 and 24 hours respectively and the synthesis pressure of 4 values (4, 5, 6 and 7 bar, respectively) were conducted in the synthesis process of Cu-BTC to

investigate the effect of synthesis pressure to the characteristics of Cu-BTC.

4. Conclusions

A copper-based metal-organic framework (MOF) material named as Cu-BTC was synthesized from the solvothermal reaction of cupric nitrate hydrate and trimesic acid (BTC). In the process of synthesis, three parameters synthesis temperature, time and pressure were investigated. The obtained Cu-BTC sample was characterized by XRD, SEM and BET analysis, and the results displayed that the sample synthesized at the condition of temperature: 120 °C, synthesis time: 12 hours, pressure: 1 bar exhibited a good crystal structure with uniform size of octahedral particles. The BET data revealed a high surface area of 1741.7 $m^2g^{-1}$and a pore volume of0.7137cm^3g^{-1} and exhibited a maximum CO_2 adsorption capacity of 170 mg/g of the sorbent at 25°C.

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