Synthesis, characterization and experimental investigation of Cu-BTC as CO$_2$ adsorbent from flue gas

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Abstract

Porous Cu-BTC material was synthesized by the solvothermal method. Powder X-ray diffraction (PXRD) was used to test the phase purity of the synthesized material and investigate its structural stability under the influence of flue gas components. The thermal stability of the material was determined through thermal gravimetric (TG) analysis. Scanning electron microscopy (SEM) was employed to study the microstructure of the material. Cu-BTC was demonstrated not only to have high CO$_2$ adsorption capacity but also good selectivity of CO$_2$ over N$_2$ by means of packed bed tests. The adsorption capacity of Cu-BTC for CO$_2$ was about 69 mL/g at 22°C. The influence of the main flue gas components on the CO$_2$ capacity of the material were discussed as well.

Key words: Cu-BTC; CO$_2$ capture; structural stability; influence of flue gas components

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Introduction

With the rapid development of modern industries and the huge demand for energy, global warming caused by the excessive emission of greenhouse gases has attracted more and more attention from the public and governments (Oh, 2010). How to control CO$_2$ emission economically and effectively has become an urgent issue. Power plants using fossil fuel have contributed most of the CO$_2$ emission to the atmosphere. According to the IPCC report (IPCC, 2005), CO$_2$ emission to the atmosphere could be reduced by 80%–90% for a conventional power plant equipped with carbon capture and storage technology (CCS). Therefore, CO$_2$ capture in these large power plants is of great significance in the effort to reduce greenhouse gas effects and alleviate global warming problems (D'Alessandro et al., 2010).

Various methods have been attempted to separate CO$_2$ from flue gas, including chemical absorption such as with conventional amine scrubbers, but such processes can increase the energy consumption of a plant by 25%–40% (Haszeldine, 2009). For this reason, physical adsorption methods such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) have attracted much more research attention and interest.

For the optimal operation of a PSA or TSA process, it is very important to find a high capacity adsorbent for CO$_2$ adsorption. However, general-purpose adsorbents such as zeolites appeared to be ineffective for this purpose due to

the high energy consumption required for their regeneration (often requiring temperatures above 300°C) and low selectivity against water vapor (Harlick and Sayari, 2006). Therefore, the design and preparation of high-capacity adsorbents for CO$_2$ capture have attracted the interest of research both in advanced material and environmental areas.

Recently, emerging materials called metal-organic frameworks (MOFs), which are self-assembled from metal ions and organic ligands, have shown higher potential for CO$_2$ separation due to their high specific surface area, regular pore distribution and facile modification ability. Up to now, many MOF materials have been synthesized and tested for CO$_2$ adsorption, such as those with hexagonally packed cylindrical channels (MOF-74) (Rosi et al., 2005; Davison and Thambimuthu, 2009), functional group modified pores (IRMOF-3) (Eddaoudi et al., 2002), high porosity frameworks (MOF-5 and MOF-177) (Millward and Yaghi, 2005), square channels (MOF-2) (Li et al., 1998) and pores with exposed metal sites (Cu-BTC) (Yazaydin et al., 2009a). These materials have shown the potential for CO$_2$ capture (Yazaydin et al., 2009b), but most of them have displayed a fragility toward humidity that inhibits their application (Kaye et al., 2007). Interestingly, the MOFs containing exposed metal sites displayed high CO$_2$ capacity at relatively lower pressures due to their high heat of adsorption (Britt et al., 2009). Among the reported materials, Cu-BTC (BTC = 1,3,5-benzenetricarboxylate), which consists of paddlewheel Cu$_2$(COO$^-$)$_4$ units, belongs to this series and has been attracting more attention in both experimental research and

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theoretical simulation (Yazaydin et al., 2009a; Chui et al., 1999; Yang et al., 2007).

In addition, not only high CO$_2$ capacity but also the resistance to flue gas components (such as SO$_2$, NO or moisture) is quite important for a good sorbent for industrial application purposes. But only a few studies of the endurance of MOFs to humidity (Cychosz and Matzger, 2010) and the effect of NO on CO$_2$ adsorption (Xiao et al., 2007) have been reported so far. Meanwhile, studies on the influence of SO$_2$ and NO in flue gas on MOFs structure and CO$_2$ adsorption performance have hardly been reported yet. It should be of great importance to develop high-capacity CO$_2$ adsorbents and test the influence of flue gas components on their structure and adsorption capacity.

Among the investigated MOFs, Cu-BTC (also called MOF-199 or HKUST-1) has been reported to show higher CO$_2$ capacity after pre-adsorbing a small amount of water (Yazaydin et al., 2009a), which makes it a material with the potential to work in actual flue gas containing moisture. However, the influence of the main components in flue gas on its CO$_2$ adsorption behavior still needs investigating. Therefore, Cu-BTC was synthesized and characterized in this study, and the influence of moist air, SO$_2$ and NO on its structural stability was investigated. The influence of moist air, SO$_2$ and NO on the CO$_2$ capacity of the material was also studied through adsorption analysis. The adsorption selectivity of CO$_2$ over N$_2$ on Cu-BTC was demonstrated through a packed bed experiment.

1 Experimental

1.1 Synthesis and activation of Cu-BTC

Cu-BTC was synthesized and activated by means of a reported procedure with appropriate modification (Chui et al., 1999). Briefly, the procedure was as follows: a solid mixture of 0.725 g of Cu(NO$_3$)$_2$·3H$_2$O and 0.42 g of H$_3$BTC (1,3,5-benzene tricarboxylic acid), and 40 mL of DMF was added to a 50-mL jar, and the suspension was mixed and stirred until homogeneous. The reaction vial was capped tightly and placed in an oven at 140°C. After 24 hr, the sample was removed from the oven to cool down to room temperature. After removal of the mother liquor, the light blue crystalline product was washed with DMF (three times) and methanol (three times). Then, the crystals were immersed in methanol overnight, and dried at 140°C for activation, after which the crystals changed to dark blue. All reagents were used as received (AR grade).

1.2 Characterization

Powder X-ray diffraction (PXRD) patterns were collected at room temperature using a Rigaku diffractometer (D/max-2200/PC, Japan) with graphite-monochromated Cu radiation (40 kV, 20 mA). The scanning range of 2θ was from 5 to 50 degrees at 5 degrees/min speed.

To study the structural stability in moist air, three samples each with about 100 mg of Cu-BTC were enveloped in an air atmosphere (containing about 2.6% of water vapor, *V/V*) for 1, 3 and 5 days, respectively, after which a PXRD pattern of each sample was collected to identify their structural stability.

To study the structural stability in SO$_2$, three samples each with 100 mg of Cu-BTC were enveloped in a SO$_2$/N$_2$ (10/90, *V/V*) atmosphere for 1, 3 and 5 days, respectively. Then, a PXRD pattern of each sample was collected to determine their structural stability.

To study the structural stability in NO, three samples each with about 100 mg of Cu-BTC were enveloped in a NO/N$_2$ (10/90, *V/V*) atmosphere for 1, 3 and 5 day(s), respectively, after which a PXRD pattern of each sample was collected to identify their structural stability.

To characterize the microstructure, images of the Cu-BTC crystals were taken with a scanning electron microscope (Hitachi S-2150, Japan) after gold deposition.

To test the thermal stability of Cu-BTC, thermal gravimetric analysis was performed on a Netzsch STA 409PC Instrument. A powder sample was weighed and heated in a corundum crucible from 30 to 580°C at the heating rate of 5°C/min under a high purity N$_2$ atmosphere (60 mL/min), and the curve of weight loss over temperature was collected.

The BET surface area of Cu-BTC was measured with a Quantachrome Nova 2200e Surface & Pore Size Analyzer (USA) using high purity nitrogen as adsorbate. After being weighed, samples were degassed at 155°C for 3 hr in the activation chamber and then were transferred into the measurement chamber to collect multi-point BET data in a liquid nitrogen bath.

CO$_2$ adsorption measurements were also performed on the Quantachrome Nava 2200e Surface & Pore Size Analyzer by submerging the sample holder in an isothermal water bath. After the same activation procedure as in the BET measurement, adsorption and desorption isotherms of CO$_2$ were recorded using high purity CO$_2$ as adsorbate.

To test the selectivity toward CO$_2$ over N$_2$ of the material, a Cu-BTC packed bed was built for a breakthrough experiment. A CO$_2$/N$_2$ (50/50, *V/V*) mixture was driven through the packed bed intermittently using a syringe at the end of the bed (0.2 mL at a time), and then the pumped gas (0.2 mL) was injected into a gas chromatograph to detect the concentration of CO$_2$ and N$_2$ in the pumped gas.

2 Results and discussion

2.1 PXRD characterization

To identify the structure of the material, PXRD analysis was performed for the synthesized Cu-BTC, and its PXRD pattern was matched well with that reported in the literature, indicating both the successful preparation of Cu-BTC and its good crystallinity (Xiao et al., 2007).

2.2 SEM characterization

In order to observe its surface morphology, images of Cu-BTC were taken with a scanning electron microscope after gold deposition. As illustrated in Fig. 1, the crystals of Cu-BTC in the SEM image had a double-sided pyramidal shape with about 10 to 20 μm width. Such a
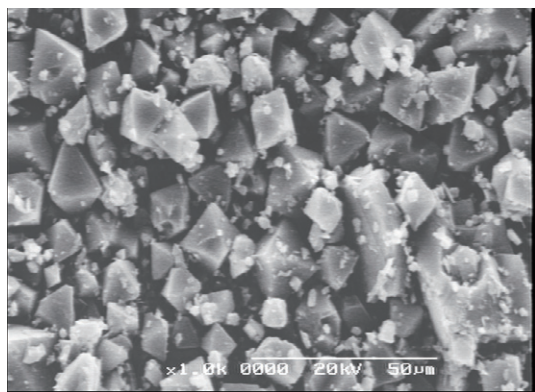
Fig. 1 SEM image of Cu-BTC.

regular structure confirmed the good crystallinity of the material, which was already demonstrated by powder X-ray diffraction.

2.3 TG characterization

Once employed in flue gas conditions, material should have the ability to maintain structural stability at temperatures higher than that encountered in flue gas. TG analysis for Cu-BTC was conducted to test its thermal stability (shown in Fig. 2): about 25% weight loss could be seen from the beginning temperature to 110°C, which could be attributed to the removal of solvent molecules adsorbed on the surface. After that point, a plateau was observed
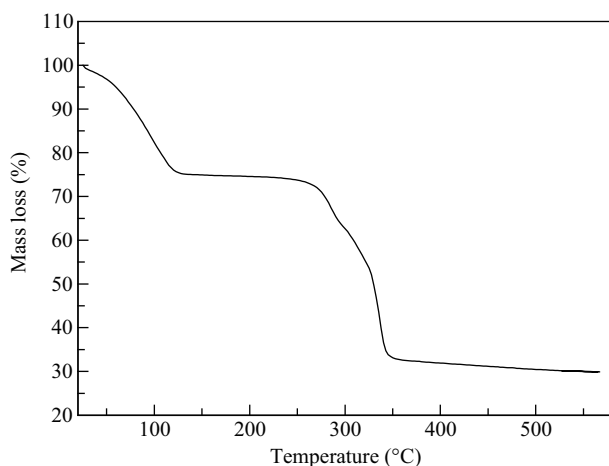

Fig. 2 TG curve of Cu-BTC.

from 110 to 270°C indicating the maintenance of the structure within this temperature range; with further rise in the temperature, a sharp weight loss could be observed from the curve, which demonstrated the collapse of the structure. Considering common flue gas temperatures, Cu-BTC has enough thermal stability to be employed in CO_2 capture from flue gas.

2.4 Influence of flue gas components on structural stability of Cu-BTC

Both thermal stability and chemical stability of the MOFs are very important for the material. In these experiments, the stability of Cu-BTC was tested in moist air, SO_2 and NO with the PXRD method. As shown in Fig. 3a, after Cu-BTC crystals were exposed to moist air for 1, 3 and 5 days, no significant peak changes could be observed from the PXRD patterns, which indicated that the framework of Cu-BTC was well-maintained in the presence of moist air. Notably, the crystals changed their color from dark blue to light blue after exposure to moisture; this change demonstrated that water had recoordinated to the coordinatively unsaturated metal centers in the activated material. After activation through heat or vacuum, its color could reversibly turn back to dark blue, indicating that water could be adsorbed and desorbed on Cu-BTC expediently.

Similarly, to determine the stability of the material in the presence of SO_2, the crystals were enveloped and kept in the SO_2/N_2 mixture. As shown in Fig. 3b, PXRD patterns of Cu-BTC were almost the same before and after being exposed to the SO_2/N_2 mixture (10/90, V/V) for 1, 3 and 5 day(s). This indicated that Cu-BTC could well maintain its structure in the presence of SO_2.

NO is also one of the common components in flue gas, and its effect on the stability of the material was tested. As expected, no pattern change could be observed from PXRD patterns before and after being exposed to the NO/N_2 mixture (10/90, V/V) for 1, 3 and 5 day(s) (Fig. 3c). This implied that the crystal structure of Cu-BTC was very stable in the presence of NO, such that its structure would not be destroyed by the NO/N_2 mixture (10/90, V/V).

2.5 Measurement of CO_2 capacity

In addition to structural stability, high CO_2 capacity is also an important criterion for a sorbent for carbon capture.
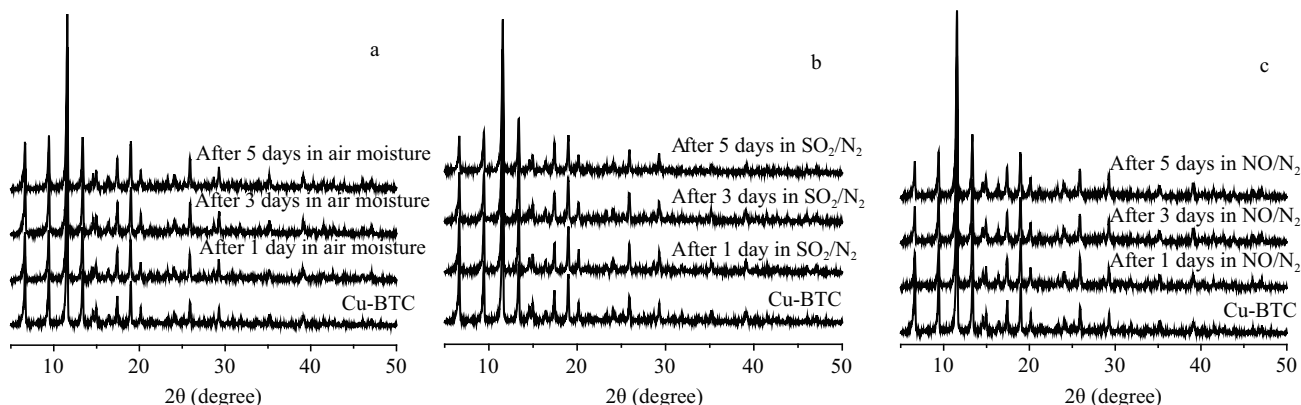

Fig. 3 PXRD patterns of Cu-BTC before and after being kept in moist air (a), SO_2/N_2 mixture (b) and NO/N_2 mixture (c) for 1, 3 and 5 day(s), respectively.

In the experiment, not only the specific surface area of the material but also its CO_2 capacity was measured. As illustrated in Fig. 4, its BET surface area was about 934 m^2/g and its CO_2 capacity was about 69 mL/g CO_2 (at 22°C and 0.98 P/P_0) which leads the list of reported CO_2 capture materials (Yazaydin et al., 2009b). Such a high performance for CO_2 capture could be attributed to the strong interaction between the exposed metal sites in the framework and the CO_2 molecule (Yazaydin et al., 2009a). In addition, the material could be completely regenerated under vacuum conditions, which may be employed in the PSA process (Fig. 4).

2.6 Influence of flue gas components on CO_2 adsorption capacity

Moreover, for industrial applications, the influence of flue gas components such as SO_2 and NO on the CO_2 capacity of the adsorbent should be considered. As shown in Fig. 5a, after exposure to moisture for 5 days, no significant influence could be observed on the Cu-BTC CO_2 adsorption capacity; a similar result was also found after exposing Cu-BTC to the SO_2/N_2 mixture (10/90, V/V) for 5 days (Fig. 5b). Therefore, both moist air and the SO_2/N_2 mixture (10/90, V/V) would not reduce the CO_2 adsorption capacity of Cu-BTC, indicating the promising potential of this material for application in flue gas conditions.

However, when Cu-BTC was exposed to the NO/N_2 mixture (10/90, V/V) for 5 days, its CO_2 adsorption

capacity significantly decreased from 69 to 39 mL/g. This could be attributed to competition between NO and CO_2 molecules for adsorption on the pore surface. With NO molecules pre-adsorbed in the pores, the CO_2 capacity of Cu-BTC decreased significantly with the decrease of adsorption sites on the pore surface. To test the performance of the material at much lower NO concentrations, we exposed Cu-BTC to a different NO/N_2 mixture (1/1000, V/V, which is close to the actual NO concentration in flue gas) for 5 days, and then tested its CO_2 adsorption capacity. As shown in Fig. 5c, no significant decrease of capacity was displayed after this treatment.

2.7 Selectivity of CO_2 over N_2 on Cu-BTC

To determine the CO_2 selectivity of the material, a packed bed with Cu-BTC particles was built for a breakthrough experiment. A CO_2/N_2 (50/50, V/V) mixture was driven through the packed bed intermittently using a syringe at the end of the bed (0.2 mL at a time), and then the pumped gas was injected (0.2 mL) into a gas chromatograph to detect the concentration of CO_2 and N_2 in the pumped gas. As shown in Fig. 6, the first sampling was the CO_2 and N_2 (50/50, V/V) mixture that bypassed the Cu-BTC packed bed, and the subsequent six samplings represented the component concentration of the second to the seventh 0.2 mL gas pumped through the packed bed. It could be seen that no CO_2 peak could be detected in the second sampling, indicating that CO_2 was preferably retained over N_2. That
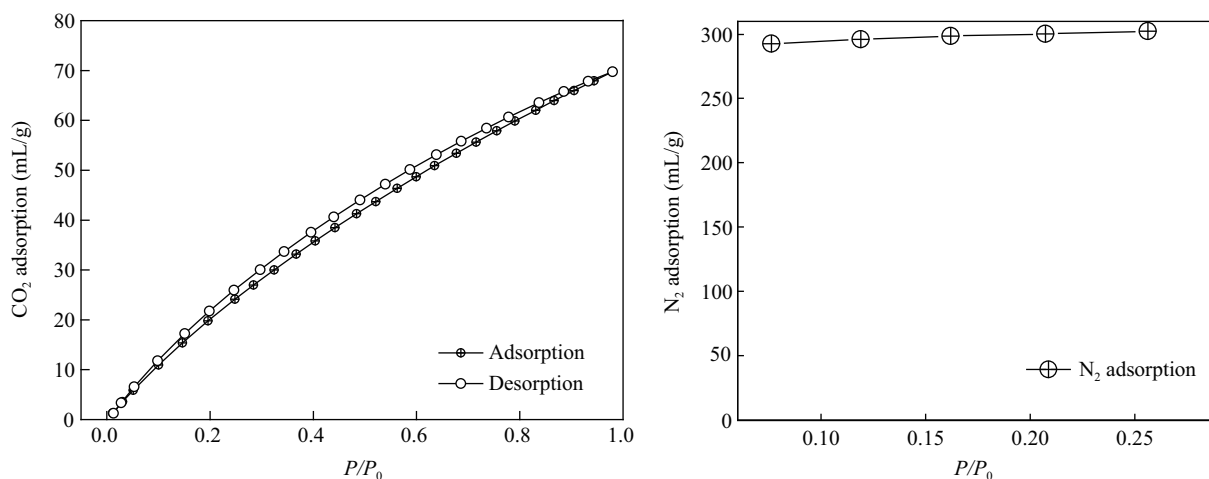

Fig. 4 CO_2 adsorption and desorption curves on Cu-BTC (a), and N_2 adsorption curve on Cu-BTC (b).
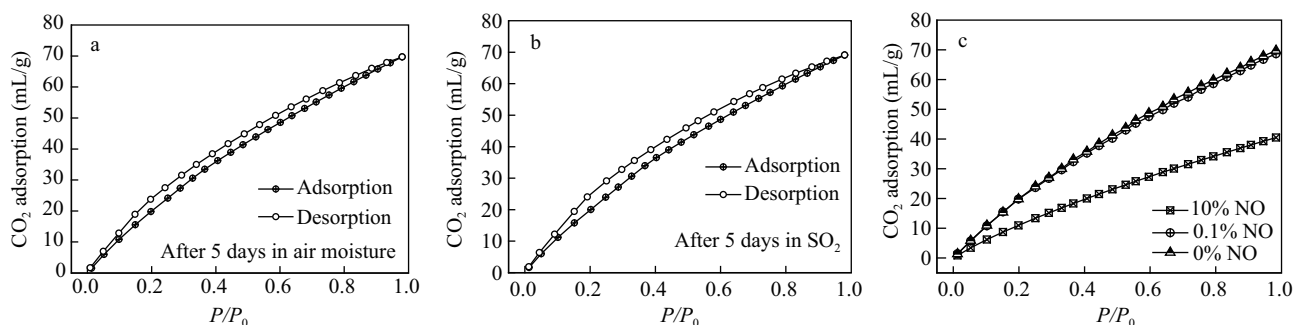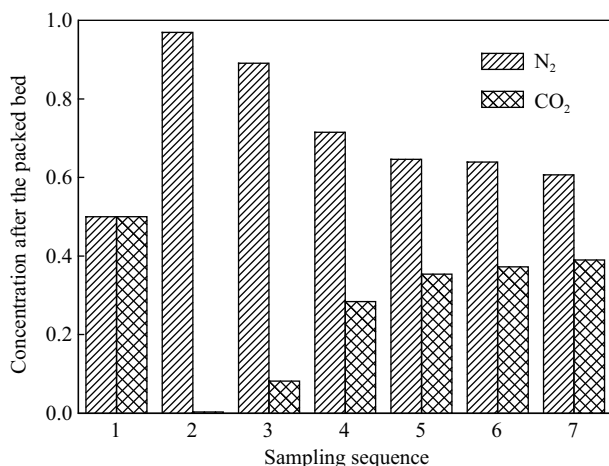

Fig. 5 CO_2 adsorption and desorption curves on Cu-BTC after being exposed to moist air (containing about 2.6% of vapor, V/V) for 5 days (a), SO_2/N_2 mixture for 5 days (b), and adsorption curves after exposure to different concentration NO/N_2 mixtures for 5 days (c).

Fig. 6 CO_2 and N_2 concentration detected by gas chromatography before (1) and after (2–7) passing through Cu-BTC packed bed at room temperature (0.2 mL of CO_2/N_2 mixture was pumped through the bed each time with a syringe and injected into a gas chromatograph, and then the peak area was translated into concentration).

meant Cu-BTC had a large CO_2 selectivity over N_2 at the beginning. Thereafter, with the increase of amount of gas mixture passing through the packed bed, the CO_2 component increased step by step with the simultaneous decrease of the N_2 component, which demonstrated that CO_2 broke through the packed bed gradually. According to this experiment, Cu-BTC displayed an excellent CO_2 selectivity over N_2, which could be utilized to separate CO_2 from CO_2/N_2 and other components in flue gas.

3 Conclusions

Cu-BTC was synthesized and characterized, and its structural stability in the presence of flue gas components SO_2 and NO was tested through powder X-ray diffraction analysis. Its BET specific surface area was about 934 m^2/g and CO_2 capacity at low pressure was about 69 mL/g (at 22°C and 0.98 P/P_0), which ranks Cu-BTC among the top performers of previously reported CO_2 capture materials. Moreover, this capacity did not show any significant decrease in the presence of common flue gas components. Due to its high thermal stability, structural stability in flue gas components and its excellent selectivity for CO_2 over N_2, Cu-BTC material displayed substantial potential for application in CO_2 capture from flue gas.

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