Influence of water vapor and acid gases on CO₂ adsorption using *N,N*-dimethylethylenediamine decorated Cu-BTC

Fujiao Song¹ · Yan Cao¹ · Ruiyu Jiang² · Yunxia Zhao³ · Jinlong Yan¹ · Tianming Chen¹ · Qi Xu¹ · Bairen Yang¹

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Abstract

N,N-Dimethylethylenediamine (mmen) was incorporated as a ligand on the Cu²⁺ of Cu-BTC by a protophilic solvent-assisted solvothermal method for improved performance. X-ray diffraction, scanning electron microscopy and low temperature N₂ adsorption were used to investigate the structural stability of the synthesized material under the influence of flue gas components, such as water vapor, NO and SO₂. The thermal stability was determined through thermal gravimetric (TG) analysis. The influence of the main flue gas components on the CO₂ adsorption capacity of the material were discussed as well. Finally the SO₂/NO resistance mechanism were deduced. Both Cu-BTC-raw and Cu-BTC-mmen were very stable in the presence of H₂O, while the former could be destroyed by the continuous NO/N₂ and SO₂/N₂ mixture flow significantly. This situation has been improved on Cu-BTC-mmen sample, probably because the mmen on the surface of Cu-BTC react with SO₂/NO preferentially and protect the Cu²⁺ sites to some extent. Cyclic regeneration test of the CO₂ adsorption process on fresh and disposed adsorbents was also investigated.

Keywords Cu-BTC · *N,N*-Dimethylethylenediamine · CO₂ adsorption · Water vapor · Acid gases

1 Introduction

At present, postcombustion carbon capture and sequestration from power plant flue gas is considered to be an effective way to mitigate the impact of CO₂ emissions on climate change [1–4]. Capturing CO₂ from flue gas is extremely challenging due to the high flow rates, the low partial pressure of CO₂ and the need to consider the separation costs [5]. Adsorption CO₂ with solid media is considered to be a more energy efficient technology for CO₂ capture than traditional absorption method with alkaline solvents [6, 7].

Since coal is commonly burned in air, N₂ is the highest content in the flue gas. The typical composition of the coal-fired flue gas was 12.5–12.8% CO₂, 6.2% H₂O, 4.4% O₂, 50 ppm CO, 420 ppm NO_x, 420 ppm SO₂, and 76–77% N₂

[8]. Therefore, the CO₂/N₂ selectivity is as important as the CO₂ adsorption capacity for CO₂ adsorbents [9, 10]. In the past decades, selective adsorption of CO₂ over N₂ has been extensively studied, both theoretically and experimentally. In particular, other components in flue gas, such as H₂O, SO₂ and NO, are crucial for the applications of a sorbent in CO₂ capture due to the considerable content and particular interaction with the adsorbents [11]. The effect of H₂O on CO₂ adsorption depends on specific situation. When water molecules compete with CO₂ for the adsorption sites, it has an inhibiting effect on CO₂ adsorption. Contrarily, water vapor in the flue gas promotes the CO₂ adsorption on the amine-based sorbents because the formation of bicarbonate under a wet condition can enhance the amine efficiency [12]. What's more, the effect of moisture on CO₂ adsorption also

✉ Fujiao Song, Song_fj2006@126.com; Yan Cao, caoyan823@163.com; Ruiyu Jiang, jiangry@ycit.edu.cn; Yunxia Zhao, nlgyzx@163.com; Jinlong Yan, yjlyt@ycit.cn; Tianming Chen, ycchentm@163.com; Qi Xu, ycxqsteve@163.com; Bairen Yang, ybairan@163.com | ¹School of Environmental Science and Engineering, Yancheng Institute of Technology, Yancheng 224051, People's Republic of China. ²Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, People's Republic of China. ³School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, People's Republic of China.

depends on moisture content [13]. In general, SO_2 inhibit CO_2 adsorption in amine-based sorbents due to the formation of the heat-stable and irreversible amine salts [14]. NO_x on the other hand was predicted to have a significantly smaller effect on limiting CO_2 adsorption [15].

Metal–organic frameworks (MOFs) are a novel type of porous crystal materials with ultrahigh porosity, enormous internal surface areas and the extraordinary degree of variability for both the organic and inorganic components of their structures [16–18]. Due to these properties, MOFs have proved to be the hottest material for CO_2 capture in recent years and displayed superior CO_2 adsorption performance [19–21]. The influence of the impurities, such as water, SO_2 , and NO_x , in flue gases on CO_2 separations in MOFs were also explored by some researchers. Decoste reported the water resistance property by characterizing the crystal structure and morphology of Cu-BTC before and after exposure to 90% relative humidity at 25 °C [22]. Xie investigated the PXRD patterns of Cu-BTC before and after being kept in moist air, SO_2/N_2 mixture and NO/N_2 mixture [23].

In this work, the *N,N*-dimethylethylenediamine (mmen) was incorporated as a ligand on the Cu^{2+} cation sites of Cu-BTC for improved performance. A thorough investigation of the effects of the impurities in flue gas on the structure, such as crystal structure, morphology, surface area, as well as CO_2 capture was carried out.

2 Experimental methods

2.1 Synthesis of adsorbents

Cu-BTC adsorbents were synthesized by a protophilic solvent-assisted solvothermal method. Briefly, the procedure was as follows: a solid mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (5.000 g, 0.021 mol) and H_3BTC (1,3,5-benzene tricarboxylic acid, 2.500 g, 0.012 mol) were dissolved in 42.5 mL of DMF, then 42.5 mL ethanol and 42.5 mL deionized water was added into the solution successively after stirring for 15 min. The solution was filled in a 200 mL Teflon liner placed in an autoclave and heated to 85 °C for 20 h. Then 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 and ethanol. Then, the crystals were dried at 120 °C in a vacuum oven until the crystals changed to dark blue. With these process parameters, we obtained Cu-BTC-raw. Before the hydrothermal reaction, *N,N*-dimethylethylenediamine (mmen) (0.11 mL, 1 mmol) was added into the solution with other process changeless, then the protophilic solvent-assisted synthesized Cu-BTC was obtained and named as Cu-BTC-mmen, in which the molar ratio of mmen to Cu-BTC is about 0.15 (Fig. 1).

The quantity of *N,N*-dimethylethylenediamine used for Cu-BTC-mmen synthesis referred to Long JR's study [24].

2.2 Characterization

The power X-ray diffraction (XRD) (Beijing Purkinje General Instrument Co., Ltd., China) pattern were recorded using nickel-filtered Cu K α radiation at 36 kV and 40 mA (2θ ranging from 5° to 80°, $\lambda = 0.15418$ nm and 0.02° step size). The morphologies and composition of samples were observed on the JSM 6380 SEM (Japanese Electronics Co., Ltd., Japan) at an acceleration voltage of 30 kV. The BET surface areas (S_{BET}) and pore volumes (V_{pore}) of given samples were determined by surface area and porosimetry analyzer (V-Sorb 2008P).

To study the structural stability in water vapor, 300 mg of each sample was disposed with a saturation water vapor at 60 °C for 2 days. To study the structural stability in NO and SO_2 , 300 mg of each sample was disposed with a binary-gas flow of 400 ppm NO and SO_2 in N_2 for 2 days, respectively.

CO_2 adsorption isotherms were measured using a surface area and porosimetry analyzer (V-Sorb 2008P) under low pressure (0–1.1 bar). The experiments were conducted at 0 °C and 20 °C by the dewar flask using ice water or circulated water in which the sample tube was immersed. Prior to each adsorption experiment, the samples were degassed at 120 °C overnight. The reversibility of the CO_2 adsorption process on the samples studied was tested by multiple CO_2 adsorption cycles. The corresponding adsorption isotherms have been acquired after heating at 120 °C for 12 h in vacuum in sequence.

3 Results and discussion

3.1 Structural characterization (XRD, SEM, BET)

The power XRD was performed to investigate the effect of impurities on the crystal structure of the adsorbents.

Fig. 1 Schematic illustration of solvothermal method to synthesize Cu-BTC-mmen

And the XRD patterns were collected in Fig. 2. As can be seen in Fig. 2a, the diffraction pattern of fresh Cu-BTC-raw was in accordance with the published literature data (Fig. 2c, d) [25, 26]. (111), (220), (222), (400), (311), (333) and (440) were reflecting planes of Cu-BTC, which were labeled in Fig. 2a. The samples disposed with water vapor and NO/N₂ mixture flow almost replicated the pattern of the fresh one, accompanied by a slight decrease in peak intensity. However, significant changes occurred on the sample disposed with SO₂/N₂ mixture flow. The intensity of all peaks decreased dramatically and the peak around 6.7° (attributed to (111) plane) almost disappeared. Because SO₂/N₂ mixture flow destroyed the Cu-BTC crystal structures (detailed explanation was analyzed in the Sect. 3.4). In Fig. 2b, the XRD patterns of fresh

Cu-BTC-mmen and the samples dealt with H₂O/NO/SO₂ resemble that of Cu-BTC-raw. Xie et al. [23] reported that Cu-BTC could well maintain its structure in the presence of not only H₂O and NO but also SO₂ impurities, which was not completely identical with our results. It could be attributed to different gas treatment conditions. Xie et al. disposed Cu-BTC in a certain amount of binary gas containing H₂O, NO or SO₂, while we disposed the adsorbents with a continuous binary-gas flow. Therefore, the crystal structure of Cu-BTC-raw and Cu-BTC-mmen was very stable in the presence of H₂O and NO, but could be destroyed by the continuous SO₂/N₂ mixture flow.

Scanning electron microscopy was carried out to reveal the effect of impurities on the crystal morphology and the results were collected in Fig. 3. The untreated two samples

Fig. 2 XRD patterns of Cu-BTC-raw (**a**) and Cu-BTC-mmen (**b**): before and after disposed with water vapor, NO/N₂ mixture flow and SO₂/N₂ mixture flow for 2 days, respectively; **c** XRD patterns of (top) a coating compared with (bottom) the one obtained for Cu₃(BTC)₂ crystals (Reflections marked by (o) in the coating cor-

respond to the alumina support); **d** XRD patterns of the simulated (black) and experimental Cu-BTC (red), compared against experimental Mn (blue), Fe- (magenta), and Co- (green) substituted versions of the CuBTC

(A1 and B1) show an octahedral shape and smooth surface, with average size of 30 and 15 μm respectively. A large quantity of irregular particles is also found beside the Cu-BTC-mmen crystal, which can be attributed to Cu_2O impurities [27]. Interestingly, Cu_2O impurities can be observed in SEM but could not be detected by XRD, which had been reported by De Vos DE [28]. After Cu-BTC-raw were exposed to water vapor and 400 ppm NO for 2 days, no significant peak changes could be observed from the morphologies (A2 and A3), Cu-BTC-mmen was also well-maintained in the presence of NO (B3). However, the Cu_2O impurities reunited and adhered to the surface of the crystals (B2) due to the effect of vapor condensation. After exposed in 400 ppm SO_2 for 2 days, the crystals of the two samples maintained the octahedral shape (A4 and B4), while the surface were corroded and turned from smooth to rough (inset of A4 and B4).

N_2 adsorption isotherms at -196°C of the sorbents are shown in Fig. 4. The isotherm of fresh Cu-BTC-raw revealed typical I behavior as expected for microporous materials, corresponding to that reported in literatures [29, 30]. Type H4 loops occurred in the isotherms of the sorbents disposed with water vapor and NO, indicative of existence of mesopores [31]. The hysteresis loop of the latter was broader than the former, indicating that sorbents disposed with NO enjoy more slit-like pores. After the Cu-BTC-raw was disposed with SO_2 , the isotherm shape changed from typical I to type-III. SO_2 reacted with the Cu^{2+} sites of the Cu-BTC-raw and formed irreversible salts, which not only blocked microporous structure absolutely, but also bonded the Cu-BTC-raw particles together to form macropore structure. That is why the isotherm shape of Cu-BTC-raw changed from typical I to type-III and the pore volume increased from $0.44\text{ cm}^3/\text{g}$ to $0.61\text{ cm}^3/\text{g}$ after adsorption of SO_2 .

When mmen is incorporated onto the adsorbents, secondary amino groups of mmen react with SO_2 preferentially and protect the Cu^{2+} sites to some extent. As can be seen from Fig. 4b, the isotherm of all the four Cu-BTC-mmen samples remained typical I behavior. Therefore, the behavior of the Cu-BTC-raw is so different compared to the one of Cu-BTC-mmen.

As can be seen from Table 1, the surface area and pore volume of fresh Cu-BTC-raw were $1044.07\text{ cm}^2/\text{g}$ and $0.44\text{ cm}^3/\text{g}$, respectively. After the Cu-BTC-raw was disposed with H_2O and NO, the surface area and pore volume decreased significantly. The sample disposed with H_2O displayed the lowest surface area, but the pore volume was the largest, corresponding to the pore formed by accumulation. Although the surface area and pore volume of fresh Cu-BTC-mmen decreased to $816.72\text{ cm}^2/\text{g}$ and $0.36\text{ cm}^3/\text{g}$ respectively, the sample disposed with SO_2 maintained type-I isotherm, indicating that Cu-BTC-mmen enjoyed a better performance of SO_2 resistance than Cu-BTC-raw.

3.2 TG characterization

The TGA of Cu-BTC-raw and Cu-BTC-mmen is shown in Fig. 5 to evaluate the thermal stability of the sorbents.

In Fig. 5a, the fresh Cu-BTC-raw displayed about 11% weight loss from 100 to 280°C , corresponding to the removal of solvent molecules adsorbed on the surface and water molecules coordinated with Cu (II). With temperature increasing, Cu-BTC showed a sharp weight loss of 41% from 280 to 410°C due to the decomposition of the trimelic acid, which confirmed the structural collapse of the sample [32]. The decomposition temperature of Cu-BTC-raw is close to those of rht-MOF-9 and MOF-74(Co) [33–35]. The TGA curve of Cu-BTC-mmen almost remained that of Cu-BTC-raw but the weight loss increased, which could be attributed to the removal of *N,N*-dimethylethylenediamine. In Fig. 5b, the weight loss of disposed with water vapor was almost equal to that of fresh sample. However, the adsorbents disposed with a binary mixture of NO or SO_2 in N_2 displayed a higher weight loss, corresponding to the decomposition of nitrate and sulfate respectively. And the TGA curves of fresh Cu-BTC-mmen and the ones dealt with $\text{H}_2\text{O}/\text{NO}/\text{SO}_2$ in Fig. 5b resemble that of Cu-BTC-raw.

3.3 Adsorption properties

The CO_2 adsorption capacity is one of paramount importance parameters used to evaluate the suitability of materials for the CO_2 capture. Figure 6 show the CO_2 adsorption isotherms on Cu-BTC-raw and Cu-BTC-mmen at 0°C and 20°C in the pressure range from 0 to 1.1 bar. The CO_2 adsorption capacities at 1 bar are collected in Table 2, which are similar to the results reported in the literature [36–38].

The CO_2 adsorption isotherms on the two samples studied at two temperatures follows the trend that adsorption capacity increased with the pressure increase and decreased with the temperature increase [39]. At the same temperature, CO_2 uptake of Cu-BTC-raw is larger than that of Cu-BTC-mmen, which is consistent with the values of surface area. Therefore, the CO_2 adsorption on the synthesized adsorbents is mainly dependent on physisorption determined by the surface area.

3.4 Influence of flue gas components on CO_2 adsorption capacity

For industrial applications, the influence of flue gas components such as water vapor, SO_2 and NO on the CO_2 capacity of the adsorbent should be considered. As shown in Fig. 7, after exposure to water vapor for 2 days, both Cu-BTC-raw and Cu-BTC-mmen show a little lower

Fig. 3 SEM micrographs of Cu-BTC-raw (**a**) and Cu-BTC-mm (**b**): before (1) and after disposed with water vapor (2), NO/N₂ mixture flow (3) and SO₂/N₂ mixture flow (4) for 2 days, respectively

Fig. 4 Nitrogen sorption isotherms of Cu-BTC-raw (a) and Cu-BTC-mmen (b): before and after disposed with water vapor, NO/N₂ mixture flow and SO₂/N₂ mixture flow, respectively

Table 1 Physical properties of Cu-BTC-raw and Cu-BTC-mmen

Cu-BTC-raw	BET (m ² /g)	Pore volume (m ³ /g)	Cu-BTC-mmen	BET (m ² /g)	Pore volume (m ³ /g)
Fresh	1044.07	0.44	Fresh	816.72	0.36
H ₂ O	837.42	0.37	H ₂ O	657.85	0.33
NO	512.37	0.29	NO	579.42	0.32
SO ₂	59.90	0.61	SO ₂	394.36	0.19

Fig. 5 The TGA curves of Cu-BTC-raw (a) and Cu-BTC-mmen (b). A1 and B1: TGA curves of fresh samples; A2 and B2: TGA curves of samples disposed with water vapor for 2 days; A3 and B3: TGA curves

of samples disposed with NO/N₂ mixture flow for 2 days; A4 and B4: TGA curves of samples disposed with SO₂/N₂ mixture flow for 2 days

CO₂ adsorption capacity than the fresh ones [40]. Therefore, water vapor would not significantly reduce the CO₂ adsorption capacity of the adsorbents. The Cu-BTC-raw

samples (Fig. 7a) disposed with NO/N₂ and SO₂/N₂ mixture flow show a decrease of 46% and 88% respectively, while the Cu-BTC-mmen samples (Fig. 7b) disposed under

Fig. 6 CO₂ adsorption isotherms measured at 0 °C and 20 °C on the samples studied

Table 2 Amount of CO₂ adsorbed at 0 °C and 20 °C

Sample	Amount of CO ₂ adsorbed (mmol/g)	
	At 0 °C	At 20 °C
Cu-BTC-raw	4.03	2.80
Cu-BTC-mmen	3.72	2.59

the same conditions show a decrease of 18% and 45% respectively. Therefore, SO₂ and NO have obvious effect on CO₂ adsorption performance because their strong acidity competes with CO₂ for the Cu²⁺ sites and forms heat-stable and irreversible salts [41]. Take SO₂ adsorption for

example, the Lewis acids SO₂ adsorb at open metal sites (Cu²⁺) of Cu-BTC to form local sulfite (SO₃²⁻)- and sulfate (SO₄²⁻)-like structures in the presence of oxygen and water vapor, which destroyed the crystal structures of Cu-BTC-raw [42]. These salts could block the pore structures of the adsorbents, leading to a decrease in surface area, pore volume and CO₂ uptake. Moreover, this situation has been improved on Cu-BTC-mmen sample. Xie et al. [23] reported that no significant influence could be observed on the Cu-BTC CO₂ adsorption capacity after exposure to SO₂/N₂ mixture, which was not completely identical with our results. It could be attributed to different gas treatment conditions that mentioned in the section of XRD characterization.

3.5 SO₂/NO resistance mechanism

SO₂/NO resistance performance is critical for application of CO₂ adsorbents. The SO₂ resistance mechanism of Cu-BTC-raw and Cu-BTC-mmen is deduced in Fig. 8. SO₂ has obvious effect on CO₂ adsorption performance of Cu-BTC-raw because its strong acidity competes with CO₂ for the Cu²⁺ sites and forms heat-stable and irreversible salts. These salts could cover the Cu²⁺ sites and block the pore structures of the adsorbents, leading to a decrease in surface area, pore volume, Cu²⁺ sites as well as CO₂ uptake. When mmen is incorporated onto the adsorbents, secondary amino groups of mmen react with SO₂ preferentially and protect the Cu²⁺ sites to some extent. The mechanism of NO resistance is similar to that of SO₂. Therefore, the SO₂/NO resistance performance of Cu-BTC-mmen has been improved significantly.

Fig. 7 CO₂ adsorption isotherms of Cu-BTC-raw (a) and Cu-BTC-mmen (b) at 0 °C: before and after disposed with water vapor, NO/N₂ mixture flow and SO₂/N₂ mixture flow, respectively

Fig. 8 SO_2 resistance mechanism of Cu-BTC-raw (a) and Cu-BTC-mmen (b)

3.6 Regenerability and multicycle stability

Regenerability is an important technical parameter in industrial gas adsorption processes. Figure 9 shows the reversibility of the CO_2 adsorption process on fresh adsorbents and adsorbents disposed with water vapor and SO_2 at 0 °C. In both Fig. 9a, b, the five isotherms are acquired after heating at 120 °C for 12 h in vacuum in sequence. The CO_2 uptakes of fresh Cu-BTC-raw and Cu-BTC-mmen decreased by 6.8% and 5.3% after the five cycles, respectively. Therefore, the difference in CO_2 uptake behavior is not that significant between fresh Cu-BTC-raw and Cu-BTC-mmen. All isotherms of the five cycles almost overlap, which reveals a stable CO_2 adsorption performance and excellent regenerability at two samples. The CO_2 uptakes of Cu-BTC-raw and Cu-BTC-mmen disposed with water vapor decreased by 18.3% and 26.7% after the five cycles, respectively. The CO_2 uptakes of Cu-BTC-raw and Cu-BTC-mmen disposed with SO_2 decreased by 90.6% and 50.8% after the five cycles respectively, in which most decay originated from the first disposal with SO_2 .

4 Conclusions

N,N-Dimethylethylenediamine (mmen) was incorporated as a ligand on the Cu^{2+} cation sites of Cu-BTC for improved CO_2 adsorption performance. A thorough investigation of the effects of the impurities in flue gas on the structure, such as crystal structure, morphology, surface area, as well as CO_2 capture was carried out. Cu-BTC-raw and Cu-BTC-mmen was very stable in the presence of H_2O , but could be destroyed by the continuous NO/N_2 and SO_2/N_2 mixture flow in varying degrees. It can be explained that the strong acidity of SO_2 and NO competes with CO_2 for the adsorption sites and forms heat-stable and irreversible salts. These salts could block the pore structures of the adsorbents, leading to a decrease in surface area, pore volume and CO_2 uptake. It is notable that this situation has been improved on Cu-BTC-mmen sample, probably because the mmen on the surface of Cu-BTC react with SO_2/NO preferentially and protect the Cu^{2+} sites to some extent. Cyclic regeneration test also reveals a more stable CO_2 adsorption performance and excellent regenerability of Cu-BTC-mmen.

Fig. 9 Five cycles of the CO₂ adsorption isotherms on Cu-BTC-raw and Cu-BTC-mmen at 0 °C. **A1** and **B1**: fresh adsorbents; **A2** and **B2**: adsorbents disposed with water vapor; **A3** and **B3**: adsorbents disposed with SO₂

Acknowledgements The Work was supported by Joint Open Fund of Jiangsu Collaborative Innovation Center for Ecological Building Material and Environmental Protection Equipments and Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu

Province, Key Laboratory under Construction for Volatile Organic Compounds Controlling of Jiangsu Province.

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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