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# Structure and denitration performance of carbon-based catalysts prepared from Cu–BTC precursor

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**Abstract:** Using Cu–BTC prepared by hydrothermal method as precursor, carbon-based catalysts were obtained as model materials for low-temperature DeNO<sub>x</sub>. These catalysts were characterized by X-ray diffractometry (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). The results showed that all carbon-based catalysts held the octahedron shape of Cu–BTC in most parts, and they mainly consisted of face-centered cubic copper. CuO<sub>x</sub>/C exhibited excellent catalytic activity, and such catalytic activity was further improved with the introduction of Ag. The catalyst with a Cu to Ag mole ratio of 6:1 and an activated temperature of 600 °C showed the best catalytic performance, and its catalytic denitration rate reached 100% at a temperature as low as 235 °C. During the catalytic reaction process, Cu<sup>+</sup> mainly played a catalytic role. **Key words:** metal organic frameworks; Cu–BTC precusor; carbon-based catalyst; low-temperature denitration; CO

# **1** Introduction

As a major kind of air pollutants, nitrogen oxides are very harmful to human health since they may lead to photochemical smog, acid rain, ozone depletion and greenhouse effect [1-3]. The selective catalytic reduction (SCR) of NO has been considered as a promising method for NO reduction due to its significant environmental impact. Currently, one of the leading technologies is selective catalytic reduction by ammonia (NH<sub>3</sub>-SCR) [4-6]. However, the NH<sub>3</sub>-SCR process is typically expensive due to the high capital investment requirement, injection of ammonia, catalytic toxicity, equipment corrosion and NH<sub>3</sub> slip issue [7–9]. As one of the contaminants in exhaust, carbon monoxide is a promising agent showing good reducing effect as well as cost-reduction potential in SCR processes [10,11], thus CO-SCR can be considered as an advantageous technology in the future.

Selective catalytic reduction of NO with CO has been demonstrated over so-called three-way Rh–Pt–Pd catalysts. In the past decade, many studies have been performed to replace noble metal catalysts in view of their high cost and scarce resources [12–14]. Thereafter, various base metal catalysts with high SCR activity at lower temperatures have been found, which are more suitable for coal-fired power plants and industrial application [15-17]. YU et al [18] obtained Cu-catalysts supported with different Ce/Zr mole ratios for the reduction of NO with CO, and their results showed that the dispersion of CuO was influenced by the crystal structure of CeO<sub>2</sub>-ZrO<sub>2</sub> support: once Cu atoms were located in oxygen vacancies, the reduction performance of CuO over NO was improved [18]; though Cu-containing catalysts performed poorly at low temperature, their activity could be enhanced with the addition of other elements, such as Ag atoms. This phenomenon could be a good basis for a new type of bimetallic system if the selectivity of system for NO reduction could be enhanced by the presence of a second metal, such as Ag or Cu.

Metal oxide-supported carbonaceous materials, such as activated carbon (AC), activated carbon fibers (ACFs), carbon nanotubes (CNTs), and ordered mesoporous carbon (OMC), among others, have shown high activity and resistance to  $SO_2$  [19–23]. The performance of carbon-supported catalysts is significantly affected by the pore structure and surface properties of the supports. At present, metal organic frameworks (MOFs) consisted of metal ions and polyfunctional organic ligands have attracted considerable attention due to their splendid

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structures and outstanding properties [24,25], which have been investigated for potential applications in gas storage, separation, catalysis, drug delivery, etc. [26–28]. From the point of crystallology, MOFs may be an affordable approach to generate metal oxides and carbon-based materials [29–31]. For instance, Zn-based MOFs were used to obtain highly porous carbon [32], and Fe-based MOFs were applied as precursor to prepare Fe<sub>2</sub>O<sub>3</sub> as possible anode material for Li-ion batteries [33]. Compared with other means, this synthetic route is advantageous because it is free of surfactant, other template or other complicated additives [34].

Among reported MOFs materials, Cu-benzene-1,3,5-tricarboxylic acid (Cu–BTC) shows better potential. Because it is formed by paddlewheel secondary builing units which contain plenty of Cu<sup>2+</sup> dimers coordinatively, Cu–BTC can not only exhibit high porosity, but also possess a large number of unsaturated metal sites, providing it with powerful catalytic performance in low temperature range [35,36]. WANG et al [37] have studied the potential use of Cu–BTC for gas purification and separation. Recently, Cu–BTC metal-organic framework as a novel catalyst was used for low temperature selective catalytic reduction of NO by NH<sub>3</sub>, and showed a good catalytic activity with operating-temperature below 300 °C [38]. However, there has been no report on Cu–BTC used for low-temperature DeNO<sub>x</sub> by CO.

In this work, we focus our attention on  $CuO_x/C$  and a series of  $Cu-Ag_yO_x/C$  obtained from Cu-BTC. These materials were applied in the selective catalytic reduction of NO with CO. As far as we know, this was the first time that the sample method was used to obtain carbon-based catalysts in the field of denitration. In the present study, carbon-based catalysts were characterized by different instrumental techniques and the effects of reaction conditions (such as mole ratio of Cu to Ag and activated temperature) on the catalytic performance of cabon-based catalysts were also investigated.

# 2 Experimental

#### 2.1 Preparation of catalysts

#### 2.1.1 Cu-BTC precursor

Cu–BTC was synthesized by the hydrothermal method according to literatures [39,40]. Briefly, 4 mmol of benzebe-1,3,5-tricarboxylic acid (H<sub>3</sub>BTC, 98%) was dissolved in 20 mL of ethyl alcohol (CH<sub>3</sub>CH<sub>2</sub>OH, 99%), and 6 mmol of copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>, 99%) was dissolved in 20 mL of ultrapure water. Then, they were mixed together and stirred for 30 min. Afterwards, the mixture was poured into a 50 mL stainless steel reactor with a polytetrafluoroethylene liner, and the autoclave was put into a 120 °C oven for 24 h. The precipitated crystals from the solution were allowed to

settle down as precipitates. After the removal of top solution, the solid precipitates were purified in 50 mL of ethyl alcohol to remove unreacted chemicals and the process lasted for 30 min. The purified products were filtered and washed with ethyl alcohol (50 mL  $\times$  3) and ultrapure water (50 mL  $\times$  3) repetitively, then dried at 100 °C for 12 h before test.

# 2.1.2 CuO catalysts

CuO catalyst was prepared by putting copper nitrate trihydrate at 500 °C in air for 3 h. Cu–BTC was put in a quartz tube and roasted at 500 °C for 3 h in air. The two materials were named as  $CuO_n$  and  $CuO_c$ .

#### 2.1.3 CuO<sub>x</sub>/C catalysts

Cu–BTC was put in a quartz tube and roasted at 500 °C for 3 h in a nitrogen atmosphere and reducing atmosphere (1% of CO in volume), and they were named as  $CuO_x/C_n$  and  $CuO_x/C_r$ , respectively.

2.1.4 Cu–Ag<sub>y</sub>O<sub>x</sub>/C catalysts

Furthermore, Ag element was directly loaded by synthetic exchange solvothermal method. Briefly, 4 mmol of benzebe-1,3,5-tricarboxylic acid (H<sub>3</sub>BTC, 98%) was dissolved in 20 mL of ethyl alcohol (CH<sub>3</sub>CH<sub>2</sub>OH, 99%), 6 mmol of copper nitrate trihydrate (Cu (NO<sub>3</sub>)<sub>2</sub>, 99%) and different amounts (2, 1, 0.5, 0.25 mmol) of silver nitrate (AgNO<sub>3</sub>, 99%) were dissolved in 20 mL of ultrapure water. Then, they were mixed together and stirred for 30 min. The mixture was put in a 50 mL stainless steel reactor with a polytetrafluoroethylene liner, and the autoclave was put into a 120 °C oven for 24 h. The purification process of the precipitation was the same as that of Cu-BTC. The precipitation was decomposed in a reducing atmosphere (1% CO in volume) at 500 °C for 3 h. Then, the four samples were prepared for test, and they were named as  $Cu-Ag_vO_x/C$  (y=2, 1, 0.5, 0.25).

#### 2.2 Catalyst characterization

X-ray diffraction data were collected on a Rigaku D/Max 2200 diffractometer employing Cu K<sub> $\alpha$ </sub> radiation. Raman spectra were recorded by using HR–8 micro Raman spectrometer from French HORIBA Jobin Yvon Company. The 532 nm wavelength laser source was adopted to investigate the M—O bonding situation in MOFs. The scanning electron microscopy (SEM) images were taken on JEOL 3600 electron microscope equipment using a 20 kV energy source under vacuum, coupled with energy dispersive X-ray spectrometry (EDS).

# 2.3 Catalytic tests

The NO reduction reaction in specific stream was carried out at a fixed bed quartz reactor. For every experiment, 0.5 g of catalyst was put in a quartz tube with a diameter of 12 mm. The space velocity was 128000 mL/(h·g). The experimental equipment consists of three sections: a gas feeding system, a reactor, and a gas analyzer. The gas was mixed through a MF–4B flue gas flow meter. The reaction mixture consisted of 0.04% NO, 0.05% CO, 82.85% N<sub>2</sub>, and 17.06% O<sub>2</sub> in volume. The reactant and product mixtures were analyzed by an on-line gas analytical device made by Germanic MRU Company. The NO conversion was calculated as follows:

 $X_{NO} = \{([NO]_{in} - [NO_X]_{out})/[NO]_{in}\} \times 100\%$ (NO<sub>X</sub> includes NO and NO<sub>2</sub>)

#### **3** Results and discussion

# 3.1 Catalyst characterization

3.1.1 XRD analysis

Figure 1 shows the XRD results of Cu-BTC, CuO<sub>n</sub>, CuO<sub>c</sub>, CuO<sub>x</sub>/C<sub>n</sub>, CuO<sub>x</sub>/C<sub>r</sub> and Cu-Ag<sub>1</sub>O<sub>x</sub>/C samples. The characteristic peaks of Cu-BTC were roughly identical characteristic peaks of Cu<sub>3</sub>(BTC)<sub>2</sub>·3H<sub>2</sub>O to the (JCPDS-ICDD 39-1962), confirming the formation of Cu-BTC phase [41]. CuO<sub>n</sub> and CuO<sub>c</sub> exhibited the structure of monoclinic CuO (JCPDS-ICDD 44-0706) with their characteristic peaks at 32.4°, 35.5°, 38.7° and 48.8°. However, the peaks of CuO disappeared since Cu-BTC was decomposed to  $CuO_x/C_n$  and  $CuO_x/C_r$  in nitrogen atmosphere and reducing atmosphere. The new positions of the main reflections at 43.6°, 50.7° and 74.4° corresponded to the structures of (111), (200) and (220) of face-centered cubic copper (JCPDS-ICDD 04-0836). There were no characteristic diffraction peaks of Cu<sub>2</sub>O  $(2\theta \approx 36.4^\circ, 42.3^\circ \text{ and } 43.3^\circ)$  and C in the XRD patterns of  $CuO_x/C_n$  and  $CuO_x/C_r$ , perhaps because the carbon element and Cu2O were well dispersed. No characteristic peaks of Ag appeared in the XRD patterns of Cu-Ag<sub>1</sub>O<sub>x</sub>/C, perhaps because silver atoms were not densely distributed on the surface of carbon structure, but were well dispersed in the carbon structure.



Fig. 1 XRD patterns of catalysts

3.1.2 Raman spectroscopy analysis

In order to further determine the existing states of copper, silver and carbon element in the carbon-based materials, Raman spectra analyses of CuO/C<sub>r</sub> and Cu-Ag<sub>1</sub>O<sub>x</sub>/C were carried out and the results were shown in Fig. 2. The weak Raman peaks of CuO and Cu<sub>2</sub>O [42] appeared in the wavelength ranging from 100 to 1000 cm<sup>-1</sup>, demonstrating that a small amount of Cu<sup>2+</sup> and Cu<sup>+</sup> were well dispersed in the structure of CuO<sub>x</sub>/C<sub>r</sub> and Cu-Ag<sub>1</sub>O<sub>x</sub>/C.



Fig. 2 Raman spectra at wavenumber of  $100-1000 \text{ cm}^{-1}$  (a) and  $100-2000 \text{ cm}^{-1}$  (b)

The D band at 1361 cm<sup>-1</sup> (Fig. 2(b)) is a common feature for the lattice defects of carbon atoms, and the stretching vibrations in sp<sup>3</sup> hybridization surface of carbon atoms with disordered structure belong to amorphous carbon. The G band at 1594 cm<sup>-1</sup> (Fig. 2(b)) provided information on the stretching vibrations in sp<sup>2</sup> hybridization surface of carbon atom with graphitization degree, which belongs to graphite carbon [43]. The calculated  $I_G/I_D$  ratio of carbon in CuO<sub>x</sub>/C<sub>r</sub> was 1.33:1, hence, the carbon material in CuO<sub>x</sub>/C<sub>r</sub> was determined as graphite carbon. The Raman spectra of Cu–Ag<sub>1</sub>O<sub>x</sub>/C showed the same peak positions as those of CuO/C<sub>r</sub>, but the strength of peaks was enhanced obviously. It was easy to find that no Raman spectra peak was associated with Ag appeared in Fig. 2.

#### 3.1.3 SEM analysis

The SEM images of the six catalysts were shown in Fig. 3. Cu–BTC had a uniform octahedron shape. CuO<sub>n</sub> had different sizes of round shapes, which were directly made by Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in the air. The morphology of CuO<sub>c</sub> obtained by using Cu–BTC as precursor maintained the topography of Cu–BTC in some parts, and tended to be octahedron in shape. Carbon-based catalysts, including CuO<sub>x</sub>/C<sub>n</sub>, CuO<sub>x</sub>/C<sub>r</sub> and Cu–Ag<sub>1</sub>O<sub>x</sub>/C, all held the topography of Cu–BTC in more parts. It can be inferred that metal ions and carbon still played a structure supporting role during the disintegration

# process of Cu-BTC.

# 3.1.4 EDS analysis

The results of energy dispersive spectrometer analysis on Cu–Ag<sub>1</sub>O<sub>x</sub>/C and CuO/C<sub>r</sub> were shown in Fig. 4. It can be determined that Ag atoms were doped successfully in Cu–Ag<sub>1</sub>O<sub>x</sub>/C by comparing the EDS results of Cu–Ag<sub>1</sub>O<sub>x</sub>/C with those of CuO/C<sub>r</sub> (Fig. 4). It can be seen that Ag atoms in Cu–Ag<sub>1</sub>O<sub>x</sub>/C did not produce new Raman spectra peaks, thus Ag atoms only played surface enhancing role in the Raman spectra. Therefore, the speculation that Ag atoms were well dispersed in the carbon structure was correct.



Fig. 3 SEM images of catalysts: (a) Cu–BTC; (b) CuO<sub>n</sub>; (c) CuO<sub>c</sub>; (d) CuO<sub>x</sub>/C<sub>n</sub>; (e) CuO<sub>x</sub>/C<sub>r</sub>; (f) Cu–Ag<sub>1</sub>O<sub>x</sub>/C



Fig. 4 SEM images (a, c) and corresponding EDS analyses (b, d) of  $CuO_x/C_r$  (a, b) and  $Cu-Ag_1O_x/C$  (c, d)

#### 3.2 Catalytic performance

# 3.2.1 Catalytic activity of different catalysts

NO reduction reaction was performed by putting these catalysts in the quartz tube and letting specific gas flow through the tube. Through programmed temperature control, the temperature went up to 500 °C from 50 °C at 2.5 °C/min. The on-line gas analytical device took notes of the gas composition minute-by-minute after the catalytic reaction began. The NO conversions over CuO<sub>n</sub>,  $CuO_c$ ,  $CuO_x/C_n$ ,  $CuO_x/C_r$  and  $Cu-Ag_1O_x/C$  were described in Fig. 5. CuOn and CuOc had the similar catalytic performance at 500 °C (87.1% CuOn, 88.6%  $CuO_c$ ). The NO conversions over  $CuO_x/C_n$  and  $CuO_x/C_r$ were obviously better than that over single CuO, and it reached 100% at 317 and 310 °C, respectively. It was clear that carbon-based materials had much better catalytic activity, mainly because carbon, as a carrier, was beneficial for the dispersion of catalytic active sites.



**Fig. 5** NO conversion over  $CuO_n$ ,  $CuO_c$ ,  $CuO_x/C_n$ ,  $CuO_x/C_r$  and  $Cu-Ag_1O_x/C$ 

On the other hand, reducing atmosphere was more prone to produce Cu species in low valence, which was beneficial for forming more oxygen vacancies; hence, the CuO<sub>x</sub>/C<sub>r</sub> synthesized under reducing atmosphere exhibited better catalytic denitration performance when compared with CuO<sub>x</sub>/C<sub>n</sub> synthesized under nitrogen atmosphere. Cu-Ag<sub>1</sub>O<sub>x</sub>/C reached a catalytic denitration rate of 100% at 268 °C, and its catalytic denitration activity was superior to CuO<sub>x</sub>/C<sub>r</sub> and CuO<sub>x</sub>/C<sub>n</sub> in the whole temperature interval. Thus, it can be inferred that the introduction of Ag to carbon-based copper oxide could improve the catalytic denitration activity, which endowed the catalysts with stronger adaptability and better flexibility at the processing temperature of flue gas.

#### 3.2.2 Effect of different mole ratios of Cu to Ag

Cu-Ag<sub>y</sub>O<sub>x</sub>/C (y=2, 1, 0.5, 0.25) was investigated to find the mole ratio of Cu to Ag that offered the best

performance. The Cu/Ag mole ratio (6: *y*) was obtained by direct synthetic exchange solvothermal method. It was demonstrated that the NO conversion could reach 100% at 275, 268, 274, 285 °C for Cu–Ag<sub>y</sub>O<sub>x</sub>/C with the Cu/Ag mole ratios of 6:2, 6:1, 6:0.5, 6:0.25, respectively (Fig. 6). The catalysts with the addition of Ag atoms performed better than single CuO<sub>x</sub>/C<sub>r</sub>, and the catalytic performance was improved with the increase of Ag until the Cu to Ag mole ratio reached 6:2; afterwards, with the increase of Ag, the catalytic performance was depressed, probably because too many Ag atoms may restrain the main structure of Cu–BTC under direct solvothermal method, leading to a worse structure of the precursor. Furthermore, Cu–Ag<sub>1</sub>O<sub>x</sub>/C would be the best catalyst for CO–NO reaction in our work.



**Fig. 6** Denitrification efficiency of Cu–Ag<sub>y</sub>O<sub>x</sub>/C (y=2, 1, 0.5, 0.25)

#### 3.2.3 Effect of activated temperature

As activated temperature plays an important role for catalysts, it was also considered in this study. The activated  $CuO_x/C_r$  catalysts were respectively pretreated at 400, 500, 600 °C for 3 h in advance, and the NO conversions reached 100% at 314, 303, 274 °C, respectively, as shown in Fig. 7. What's more, the NO conversion of activated  $Cu-Ag_1O_x/C$  catalysts reached 100% at 305, 268, 235 °C respectively under the same pretreated conditions as mentioned above. It was noted that high activated temperature contributed to more activate molecules, therefore, 600 °C was considered as the best pretreated temperature for our catalysts.

#### 3.3 Reaction mechanism

In order to further understand the catalytic reaction process,  $CuO_x/C_r$  and  $Cu-Ag_1O_x/C$  with good catalytic denitration activity were selected, and the changes of their surface topography and structure before and after the catalytic reaction were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). There were no obvious changes on the surface topography of  $CuO_x/C_r$  and  $Cu-Ag_1O_x/C$  in Fig. 8, and both of them kept a part topography of Cu-BTC with regular octahedrons. However, the structures of catalysts before and after catalytic reaction had changed a lot, as shown in Fig. 9. Zero valence copper was the main state of copper in the catalysts before the reaction. After the catalytic reaction, Cu in zero valence was reduced and Cu<sub>2</sub>O with cubic structure (JCPDS-ICDD 35-1091) showed XRD peaks at 36°, 38°, 42°, 43°, 61° and 73°, illustrating that Cu<sup>+</sup> mainly played a catalytic role in the CO-NO reaction, in accordance with previous reports [44,45]. The relevant reaction calculations were shown as follows (300 °C):

(1)  $CO(g)+2CuO(s)=Cu_2O(s)+CO_2(g)$ Δ*H*=145.506 kJ/mol

 $2NO(g)+2Cu_2O(s)=N_2(g)+4CuO(s)$ 

 $CO(g)+Cu_2O(s)=2Cu(s)+CO_2(g)$ 

 $\Delta H$ =-456.071 kJ/mol

$$\Delta H$$
=-113.56 kJ/mol

$$2NO(g)+2Cu(s)=N_{2}(g)+2CuO(s)$$
(4)  
$$\Delta H=-488.270 \text{ kJ/mol}$$

$$CO(g) + Ag_2O(s) = 2Ag(s) + CO_2(g)$$

$$\Delta H = -254 379 \text{ kJ/mol}$$
(5)

$$2NO(g)+4Ag(s)=2Ag_2O(s)+N_2(g)$$
(6)  
$$\Delta H=-239.602 \text{ kJ/mol}$$

$$2Cu(s)+Ag_2O(s)=2Ag(s)+Cu_2O(s)$$
 (7)  
 $\Delta H=-140.704 \text{ kJ/mol}$ 

$$Cu(s)+CuO(s)=Cu_2O(s)$$

$$\Delta H=-16.015 \text{ kJ/mol}$$
(8)

(2) 100 (b)



Fig. 7 Denitrification efficiency of CuO<sub>x</sub>/C<sub>r</sub> (a) and Cu-Ag<sub>1</sub>O<sub>x</sub>/C (b) activated at different temperatures



Fig. 8 SEM images of  $CuO_x/C_r$  and  $Cu-Ag_1O_x/C$  before and after reaction: (a)  $CuO_x/C_r$  before reaction; (b)  $CuO_x/C_r$  after reaction; (c)  $Cu-Ag_1O_x/C_r$  before reaction; (d)  $Cu-Ag_1O_x/C_r$  after reaction

(3)



Fig. 9 XRD patterns before and after reaction of catalysts: (a) CuO<sub>x</sub>/C<sub>r</sub>; (b) Cu-Ag<sub>1</sub>O<sub>x</sub>/C



Fig.10 Reaction mechanism of catalytic denitration

The calculations demonstrated that, as an important node in CO-NO reaction, Cu<sup>+</sup> could be obtained and react with CO and NO much more easily. Recent research indicated that the interaction between CO and metal oxides only weakened the metal-oxygen bond, thus the catalyst surface was only partially reduced to form activated CO molecule. CO could be adsorbed by  $Cu^+$  easily and form  $Cu^+(CO)_n$  (n=1-3). Additionally, CO could be adsorbed by  $Ag^+$  to acquire  $Ag^+(CO)_n$ (n=1-4) or Ag<sub>n</sub><sup>+</sup>CO (n=2-4) [46,47]. Infrared ray study had confirmed that NO was adsorbed on the surface of catalyst, in this case, the N-O bond strength was weakened and even dissociated on the surface, yielding adsorbed O and N atoms that led to the formation of N<sub>2</sub> and O<sub>2</sub>. NO was also absorbed by Cu<sup>+</sup> easily to obtain  $Cu^{+}(NO)_{n}$  (n=1-2), producing adsorbed oxygen [48]. While adsorbed oxygen was obtained by NO on the surface of Ag atoms, different activated O species (Oa,  $O_{\beta}$ ,  $O_{\gamma}$ ) would be produced in agreement with intensive activated sites for low temperature  $DeNO_x$  [49]. Hence, the reaction mechanism might be Langmuir-Hinshelwood mechanism, as described in Fig. 10.

# **4** Conclusions

1) Carbon-based catalysts prepared from Cu–BTC precursor mainly consisted of face-centered cubic copper;

a small amount of  $Cu^{2+}$  and  $Cu^+$  were well dispersed in the carbon skeleton that determined as graphite carbon structure. Cu–BTC had a uniform octahedron shape, and carbon-based catalysts, including  $CuO_x/C_n$ ,  $CuO_x/C_r$  and  $Cu–Ag_1O_x/C$ , all held the topography of Cu–BTC in more parts.

2) The NO conversion over  $\text{CuO}_x/\text{C}_n$  and  $\text{CuO}_x/\text{C}_r$ was obviously better than that over single CuO, and it reached 100% at 317 and 310 °C, respectively, illustrating that MOFs Cu–BTC is a better precursor candidate in the catalytic field. The introduction of Ag was beneficial for improving the catalytic activity, and the catalytic denitration rate of Cu–Ag<sub>1</sub>O<sub>x</sub>/C reached 100% only at 268 °C. The mole ratio of Cu to Ag and the activated temperature played important roles on the catalytic performance. The optimized conditions were determined as Cu/Ag ratio of 6:1 and activated temperature of 600 °C, under which the catalytic denitration rate reached 100% at a temperature as low as 235 °C.

3) The reaction mechanism was investigated, and  $Cu^+$  was found to occupy the main activated sites. The reaction of low temperature  $DeNO_x$  was greatly improved with the introduction of Ag atoms, because NO would be rapidly consumed on the surface of Ag atoms to produce more activated O species. The reaction mechanism gave a good model for  $Cu^+$  and Ag-loaded

catalyst in CO–NO reaction. It was noted that MOFs would be a good precursor while investigating multimetal and carbon-based metal oxides used for the future design materials in many applications.

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#### Li ZHANG, et al/Trans. Nonferrous Met. Soc. China 28(2018) 980-988

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# Cu-BTC 前驱体制备碳基催化剂的结构和脱硝性能

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摘 要:以 Cu-BTC 为前驱体,采用水热法制备碳基催化剂,并进行低温脱硝性能研究。通过 X 射线衍射(XRD)、 拉曼光谱(Raman)、扫描电镜(SEM)和能量弥散 X 射线谱(EDS)等技术对碳基催化剂的结构进行表征。结果表明: 碳基催化剂基本保持着 Cu-BTC 前驱体的八面体形貌,并主要呈现面心立方铜结构。通过碳基催化剂的脱硝性能 研究发现: CuO<sub>x</sub>/C 表现出最佳的催化活性,且其活性随着 Ag 的掺入得到进一步的提高。当 Cu/Ag 摩尔比为 6:1, 活化温度为 600 ℃ 时,碳基催化剂具有最优的催化活性,其脱硝效率达到 100%时温度可降低至 235 ℃。该催化 反应过程中,主要是 Cu<sup>+</sup>起催化作用。

关键词: 有机金属骨架; Cu-BTC 前驱体; 碳基催化剂; 低温脱硝; CO

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988