活化温度对 CuBTC 催化 CO 氧化反应性能的影响

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摘要: 考察了金属有机骨架材料 CuBTC (BTC 为均苯三酸) 催化 CO 氧化的反应性能, 发现 CuBTC 对 CO 氧化反应表现出良好的催化活性, 且 CuBTC 样品的活化温度对其催化活性的影响很大. 原位漫反射红外光谱、粉末 X 射线衍射、扫描电镜、热重分析和差示扫描量热结果表明, CO 在 CuBTC 骨架中不饱和金属位点上的配位是加速 CO 氧化的主要原因, 且这种不饱和金属位点越多, 其催化活性越高.

关键词: 金属有机骨架材料; 铜均苯三酸; 一氧化碳; 活化条件; 气固催化

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Effect of Activation Temperature on Catalytic Performance of CuBTC for CO Oxidation

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Abstract: CuBTC (BTC = benzene-1,3,5-tricarboxylate), an metal-organic framework (MOF), is active for CO oxidation. The activation temperature has a significant effect on its activity. In-situ diffuse reflectance Fourier transform infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) characterization showed that the coordination of CO on the open metal sites occurred during the oxidation reaction, and more open metal sites in the CuBTC framework gave a higher activity.

Key words: metal-organic framework; copper benzene-1,3,5-tricarboxylate; carbon monoxide; activation condition; gas-solid catalysis

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Metal-organic frameworks (MOFs) have received attention as catalytic materials in addition to their applications in gas storage and separation [1–3]. The unique features of

MOFs include their crystallinity, porous structure, huge specific surface area, and the high density of open metal sites in the framework. Catalysis based on MOFs include

cyanosilylation of benzaldehyde and acetone [4], Friedel-Crafts benzylation [5], enantioselective transesterification [6], Suzuki-Miyaura coupling [7,8], Friedland reaction [9], oxidation of alkanes, olefins, alcohols, and amines [10–17], hydroxylation of aromatic compounds [18], hydrolysis of esters [19], esterification of acetic acid with 1-propanol [20], and regioselective ring opening of epoxides [21]. Most of these MOF catalyzed reactions are in a liquid phase. Gas solid catalytic reactions over MOFs are scarce. Xu and co-workers [22–25] reported that CO can be converted to CO₂ over MOFs with active Lewis acid sites on the channel walls and over a gold catalyst supported on ZIF-8 (ZIF = zeolite imidazolate framework) [24]. Ye et al. [26] reported that crystalline and amorphous CuBTC (BTC = benzene-1,3,5-tricarboxylate) have good activity for the oxidation of CO. It has been shown that the catalytic activity of MOFs depends on the amount of unsaturated coordination sites in the framework where the catalytic reactions take place [4,27,28]. In general, these active sites are occupied by solvent molecules. There are few reports on how the activation conditions of MOFs affect their catalytic properties [29–32], and the role of the coordinatively unsaturated sites is not fully understood.

In this work, CuBTC, one of the most studied MOFs and often denoted as HKUST-1 [33], was used as a model catalyst for CO oxidation for its high density of open metal sites in the framework. Significant differences in CO oxidation activity were observed over CuBTC catalysts activated at different temperatures. Results from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), powder X-ray diffraction (XRD), thermogravimetric analysis and differential scanning calorimetry (TGA/DSC), and scanning electron microscopy (SEM) characterization confirmed that CuBTC was a highly active catalyst for CO oxidation and its activity depended on the activation temperature, which controlled the removal of coordinated water molecules and allowed the chemisorption of CO molecules on exposed metal sites.

1 Experimental

1.1 Synthesis and characterization of CuBTC

Cu(NO₃)₂·3H₂O (99%) and 1,3,5-benzenetricarboxylic acid (98%) were, respectively, purchased from Sinopharm Chemical Reagent Co. Ltd. and Alfa Aesar. All CuBTC samples were prepared using the low temperature procedure [4] in order to obtain pure CuBTC samples. The synthesized products were dried in an oven at 378 K for 12 h. The sample was activated in a flow of nitrogen at 443, 473, 503, 523, and 553 K, respectively, to give CuBTC-443, CuBTC-473, CuBTC-503, CuBTC-523, and CuBTC-553. XRD was per-

formed on a Bruker AXS D8 Advance using Cu-K_α radiation ($\lambda = 0.15406$ nm) at room temperature and a scan speed of 8°/min. Nitrogen adsorption measurement was performed at 77 K and 0–1.01325×10⁵ Pa on a Micromeritics ASAP 2020. A sample of approximately 70 mg was outgassed at the desired temperatures, e.g., 393, 443, 503, or 523 K, for 12 h. The nitrogen isotherm at 77 K was measured using a UHP-grade (99.999%) gas. The Brunauer-Emmett-Teller (BET) surface area of CuBTC was calculated based on the nitrogen adsorption isotherm. TGA measurement was performed on a Perkin Elmer STA6000 instrument under a nitrogen atmosphere (20 ml/min). The sample was heated at a constant rate of 10 K/min from 303 to 773 K. SEM images were taken with a Hitachi S 4300 and JEOL-2010 at room temperature.

1.2 DRIFTS measurements

DRIFTS analysis of CO adsorption was performed with a Nicolet 6700 FT-IR spectrometer equipped with a high temperature reaction chamber (Harrick) and a MCT detector working at liquid nitrogen temperature [34]. The spectra were collected at atmospheric pressure and the desired temperature with a resolution of 4 cm⁻¹ using an accumulation of 32 scans. Before CO adsorption, the CuBTC sample (about 100 mg) was pretreated at the desired temperatures by in situ calcination for 3 h in a flow of nitrogen with a flow rate of 30 ml/min. It was then cooled to 313 K for collecting the background spectrum to calibrate the CO adsorption DRIFT spectra. Subsequently, pure CO (99.99%) with a flow rate of 30 ml/min was introduced into the chamber cell for 30 min, and it was then purged with pure nitrogen (30 ml/min). The DRIFT spectra were recorded after the desired CO exposure time. In the following step, the temperature was increased again to the desired temperature under a nitrogen atmosphere and the CO adsorption spectra were repeatedly collected after the temperature had been stable for 0.5 h. In another type of characterization, after introducing a pure CO flow for 30 min at 443 K, the sample was exposed to a flowing mixture (CO:O₂ = 1:1 or CO:N₂ = 1:1) controlled at a total flow rate of 60 ml/min at atmospheric pressure (denoted as mixture condition).

1.3 Catalyst activity test

The CO oxidation activity of the CuBTC catalysts was evaluated with a quartz tube microreactor (i.d. = 4 mm) with a thermocouple located in the middle of the catalyst bed. The temperature range used was 323–573 K. The mass of the catalyst sample was 100 mg and it was well mixed with 1 g quartz sand. Prior to the reaction, the CuBTC samples were activated at the experiment temperatures for 3 h and

then cooled to the room temperature in flowing nitrogen with a flow rate of 30 ml/min. A gas mixture of 1% CO-0.5% O₂-98.5% N₂ was passed through the catalyst bed at a flow rate of 100 ml/min, which gave a space velocity (SV) of 30000 h⁻¹. The effluent gases were analyzed by an online gas chromatograph (GC, Shimadzu GC-2010) equipped with a TCD detector. CO conversion was calculated from the measured CO concentration using the formula $\text{CO conversion} = [(\text{CO}_{\text{in}} - \text{CO}_{\text{out}})/\text{CO}_{\text{in}}]$, where CO_{in} and CO_{out} were the inlet and outlet CO concentrations, respectively.

2 Results and discussion

All CuBTC samples were prepared using the procedure reported in the literature [4]. The SEM images of the CuBTC samples showed that the CuBTC crystals were of octahedral shape (Fig. 1). The crystal sizes of the CuBTC samples were in the range of 10–30 μm. The BET surface area was 1310 m²/g.

CO conversions over CuBTC catalysts activated at different temperatures are shown in Fig. 2. CuBTC-443, CuBTC-473, CuBTC-503, CuBTC-523, and CuBTC-553 exhibited significant differences in CO oxidation catalytic activity, which increased in the order CuBTC-553 < CuBTC-443 ≈ CuBTC-473 < CuBTC-503 < CuBTC-523. CuBTC-443 and CuBTC-473 showed no activity until the temperature reached 473 K. The CO conversion over these two catalysts reached 100% at 513 K. CO complete conversion temperatures for CuBTC-503 and CuBTC-523 were

Fig. 2. CO conversion over the CuBTC catalysts activated at 443, 473, 503, 523, and 553 K, respectively. Reaction conditions: 1% CO, 0.5% O₂, N₂ as balance, GHSV = 30000 h⁻¹.

473 and 443 K, respectively, indicating they had a much higher activity than those previously reported [26]. For the CuBTC-553 sample, an obvious decrease in the catalytic activity was observed: CuBTC-553 did not exhibit any activity for CO oxidation until 523 K. The CO complete conversion temperature over CuBTC-553 was as high as 563 K. The low activity of CuBTC-553 could be due to the partial destruction of the MOF framework, which was seen in the changes in its SEM image and XRD patterns (discussed later). The CO oxidation reaction data showed that the acti-

Fig. 1. SEM images of non-activated CuBTC (a), CuBTC-443 (b), CuBTC-523 (c), and CuBTC-553 (d).

vation temperature of CuBTC had a significant effect on its activity.

In order to follow the changes of the CuBTC samples during the activation and identify the surface species that is responsible for the high activity of MOF in CO oxidation, in situ DRIFTS investigation using CO as a probe molecule was conducted over activated and non-activated CuBTC samples. CO adsorption is an excellent probe to study the catalytic surface sites since the stretching frequency of CO is sensitive to the strength of the metal–CO bonding [35].

Figure 3 presents the DRIFTS spectra at room temperature of CO adsorption over non-activated CuBTC, CuBTC-443, and CuBTC-523. Two broad and intense bands at ca. 2170 and 2120 cm^{-1} were observed, which can be ascribed to CO in the gas phase [23]. In the case of the non-activated CuBTC, the two adsorption bands gradually became weak as the N_2 purging time increased and disappeared after 30 min, indicating that no stable chemisorbed CO existed in the CuBTC (Fig. 3(a)). For the CuBTC-443 and CuBTC-523 samples, the CO adsorption band at 2167 cm^{-1} gradually vanished, but the band at 2120 cm^{-1} was still present although with a decrease in the band intensity as the sample was purged by nitrogen (Fig. 3(b) and (c)). The relatively stable CO adsorption band at 2120 cm^{-1} can be assigned to the stretching vibration of CO interacting with open Lewis acid sites in the MOF framework, and indicated that linear CO adsorption had occurred on the surface of accessible copper sites [36]. A similar phenomenon for CO adsorption on MOFs was previously observed by Xu et al. [23]. The intensity of this CO chemisorption band decreased with an increase in CO adsorption temperature together with a blue shift from 2120 to 2126 cm^{-1} for the band position (Fig. 4).

It has been reported that CO adsorption on Cu^{2+} or Cu^0 is very weak and the CO is easily removed by purging with an inert gas at room temperature [37,38]. From these data from

Fig. 4. Changes in the CO chemisorption band at various temperatures.

the literatures [27,29,35,39], the CO adsorption band at 2120 cm^{-1} can be assigned to the stretching vibration of the Cu(I)–CO bond, which was formed from CO adsorption on open copper sites due to the reducing property of the adsorbate (CO) [40]. It is known that adsorbed CO on Cu(I) sites can be oxidized [41]. Therefore, the Cu(I)–CO species on the MOF framework can be the intermediates for CO oxidation over the CuBTC catalysts. Furthermore, the intensity of the CO adsorption band at 2120 cm^{-1} from CuBTC-523 was higher than that from CuBTC-443, which showed the existence of more Cu(I)–CO species in CuBTC-523. This indicated that the density of open metal sites in the MOF framework increased as the activation temperature was increased. The DRIFTS data of the CuBTC samples are consistent with their corresponding catalytic activity, suggesting that the coordination of CO molecules at the open metal sites was responsible for the enhanced oxidation reaction

Fig. 3. In situ DRIFTS spectra at room temperature of CO adsorbed on non-activated CuBTC (a), CuBTC-443 (b), and CuBTC-523K (c) as a function of N_2 purging time.

rate.

In order to further explore CO oxidation on MOFs, DRIFTS experiments under an atmosphere of CO and O₂ mixture at 443 K were performed (Fig. 5). Both CuBTC-443 and CuBTC-523 showed two bands at 2172 and 2126 cm⁻¹, which was similar to CO adsorption under a CO atmosphere at room temperature except that there was a blue shift of the band from 2120 to 2126 cm⁻¹. In the case of CuBTC-523, two new carbonyl stretching vibration bands appeared at 2360 and 2340 cm⁻¹, suggesting the formation of CO₂ in the system. This result further confirmed that CuBTC-523 was more active than CuBTC-443 due to the higher density of open metal sites in the former. CO molecules are activated on these sites via coordination.

Fig. 5. In situ DRIFTS spectra of CO adsorbed on CuBTC-443 (a) and CuBTC-523 (b) from a CO and O₂ mixture at 443 K.

It is known that copper oxides have high activity for CO oxidation [42–45]. The activation of MOFs at a high temperature can cause the decomposition of the MOF structure, leading to the formation of a trace amount of copper oxides. In order to further explore the contribution of Cu ions bonded in the CuBTC framework and that of the copper oxides to CO oxidation, the thermal stability of CuBTC was studied using TG/DSC, SEM, XRD, and N₂ adsorption techniques. The TG/DSC experiment showed that there was a continuous mass loss that totaled 10.8% from room tem-

perature to 378 K. This was due to the loss of physisorbed H₂O and residual ethanol in the MOF channels (Fig. 6). Between 378 and 473 K, a mass loss of 4.3% was observed, which was followed by an additional mass loss (1.8%) at 473–558 K. These corresponded to the dehydration of coordinated H₂O in CuBTC. Although the mass loss data were not in full agreement with the calculated mass change ($4.1\% \times 2$) for coordinated H₂O, the two desorption steps for coordinated water molecules observed suggested the presence of two nonequivalent coordinated water molecules on the paddlewheel. This result is consistent with a theoretical calculation by Grajciar et al. [30]. In Fig. 6, one can also see a significant mass loss above 573 K, indicating the disintegration of the MOF structure. The TGA/DSC data also confirmed that the activation of the CuBTC sample was related to its catalytic activity.

Fig. 6. TG/DSC curves of CuBTC.

The SEM images of the fresh and activated CuBTC samples (CuBTC-443 and CuBTC-523) revealed that the size and morphology of the MOF crystal particles were almost unchanged after activation (Fig. 1). However, in the case of CuBTC-553, significant breaking up of the crystal particle was observed (Fig. 1(d)), indicating a change in the MOF structure at the elevated temperature. This change was confirmed by the changes of its XRD patterns (Fig. 7), where a new peak at $2\theta = 43.4^\circ$ due to copper powder appeared. Trace copper powder can be generated during the activation procedure of CuBTC under an inert atmosphere [4]. From the XRD patterns of the CuBTC samples activated at various temperatures (Fig. 7), it can be seen that the crystalline CuBTC samples were unchanged until the temperature reached 523 K [4]. The low catalytic activity of CuBTC-553 revealed that the contribution of the trace copper powder to CO oxidation was small. The most likely explanation for the activity decrease of CuBTC-553 was the destruction of the MOF framework. The stability of the MOF framework was also shown by the BET data. The specific surface areas of

Fig. 7. XRD patterns of CuBTC samples activated at various temperatures.

CuBTC-443, CuBTC-503, and CuBTC-523 samples were 1382, 1441, and 1449 m²/g, respectively, indicating that the microporous framework of the CuBTC samples remained intact after activation at their activation temperatures.

3 Conclusions

CuBTC was an effective catalyst for CO oxidation. The catalytic activity of CuBTC samples increased in the order CuBTC-553 < CuBTC-443 ≈ CuBTC-473 < CuBTC-503 < CuBTC-523. The removal of coordinated water molecules at the high temperatures of activation allowed CO molecules to coordinate at the metal sites, which resulted in the activation of the CO molecules. Cu(I)-CO species formed from the chemisorption of CO on open copper sites were the intermediates in CO oxidation. An activation temperature of CuBTC that is too high will decrease its activity due to the destruction of MOF framework. The present investigation demonstrated the importance of the activation condition of MOFs.

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