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Synthesis of octahedral like Cu-BTC derivatives derived from MOF calcined under different atmosphere for application in CO oxidation

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ABSTRACT

A series of octahedral structure Cu-BTC derivatives were successfully achieved through direct calcination of copper based metal organic framework Cu-BTC under different atmosphere (CO reaction gas, oxidizing gas O_2, reducing gas H_2, inert gas Ar). The Cu-BTC derivatives were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), laser Raman spectroscopy (LRS), N_2 adsorption-desorption isotherm, element analysis, H_2-temperature program reduction (H_2-TPR) and X-ray photoelectron spectroscopic (XPS). It is found that Cu-BTC derivative derived from MOF calcined under reaction gas/O_2 (Cu-BTC-CO/Cu-BTC-O) only retain Cu_2O and CuO species. In addition, a weak Cu-BTC structure and Cu particles were observed on Cu-BTC derivative derived from MOF calcined under H_2 (Cu-BTC-H). Obviously differently, Cu-BTC derivative derived from MOF calcined under Ar (Cu-BTC-Ar) still retains good MOF structure. The catalytic performance for CO oxidation over Cu-BTC derivatives was studied. It was found that Cu-BTC-CO showed a smaller specific surface area (8.0 m^2/g), but presented an excellent catalytic performance, long-term stability and cycling stability with a complete CO conversion temperature (T_{100}) of 140 °C, which was ascribed to the higher Cu_2O/CuO ratio, good low temperature reduction behavior and a high quantity of surface active oxygen species.

1. Introduction

Recently, the researchers pay more attention to the dangers of gaseous pollutants [1–15]. Among them, a typical small molecular atmospheric pollutant CO has widely attracted the attention. Moreover, probe molecular CO is used to study the structure and catalytic mechanism of catalysts [16–21]. Therefore, in order to acquire favorable catalytic performance, the improvement of a suitable catalyst is extraordinary significant.

Metal organic frameworks (MOFs), inorganic metal ions bridged by organic ligands in tridimensional arrangements, are relatively new crystalline materials with micropores and mesopores [22,23]. MOFs materials have high pore volumes and specific surface areas, chemical tenability and well defined structures, which have attracted much attention in many fields for photocatalysis [24,25], chemical sensor [26], catalysis [27], gas separation and storage [28,29]. Recently, some MOFs are used as precursors or templates to synthesize metal oxide nanoparticles or supported materials for CO oxidation [30–36]. Chen et al. have reported that porous Ag/Co_3O_4 nanocomposites derived from $Ag_3[Co(CN)_6]$ nanoparticles show high and stable catalytic activity for CO oxidation [30]. Co_3O_4 nanoparticles were prepared using ZIF-8 as host by a simple liquid phase method, and show good catalytic performance, long-term stability, and cycling stability for CO oxidation [31]. Our previous studies reported CeO_2, Mn_2O_3, Fe_2O_3, CuO derives from MOFs were successfully synthesized [32–36]. These MOFs derivates both exhibit super catalytic performance, long-term and cycling stability for CO oxidation.

Among them, copper oxides are of interest as catalysts for CO oxidation owing to their low cost and abundance [37–39]. Chen et al. [40] have reported that $Cu/CuO_x/C$ nanocomposites derives from Cu-BTC calcined 500 °C at under N_2 were prepared. The experiment and density functional theory (DFT) simulation prove that the improvement of catalytic performance for CO oxidation is related to the increase in electron density on Cu/CuO and Cu/Cu_2O interface. Lu et al. [41] have developed a method for prepared CuO/Cu_2O with original Cu-BTC morphologies, including wire, rod, octahedron and

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cube. That is, Cu-BTC were treated at 300–400 °C in N_2 followed by 20 min of oxidation in air. Moreover, these nanocomposites showed good catalytic activities for CO oxidation. At present, although some copper oxides catalysts derived from Cu-BTC were prepared, there is no system to study the effect of calcination atmosphere on structure and catalytic performance of Cu-BTC. Therefore, in this work, a series of octahedral structure Cu-BTC derivatives were successfully achieved through direct calcination of copper based metal organic framework Cu-BTC at 250 °C under different atmosphere. Here, typical oxidizing gas O_2, reducing gas H_2, inert gas Ar and reaction gas were chosen to deal with Cu-BTC. It was found that Cu-BTC derivative derived from MOF calcined under reaction gas showed a smaller specific surface area (8.0 m^2/g), but presented an excellent catalytic performance, long-term stability and cycling stability with a complete CO conversion temperature (T_{100}) of 140 °C, which was ascribed to the higher Cu_2O/CuO ratio, good low temperature reduction behavior and a high quantity of surface active oxygen species. Finally, our works provide a novel sight for synthesizing other MOFs derivatives derived from MOF calcined under reaction atmosphere.

2. Experimental

2.1. Catalyst preparation

The Cu-BTC was prepared by a modified method reported by Wang et al. [42]. In a typical preparation, 1.9664 g of benzene-1, 3, 5-tricarboxylic acid was dissolved in 20 ml of ethanol. The mixture was stirred until the complete dissolution of benzene-1,3,5-tricarboxylic acid. In addition, 4.48 g of $Cu(NO_3)_2\cdot 3H_2O$ was added to 10 ml of deionized water in another flask and mixed thoroughly, until it was completely dissolved. Then the two solutions were mixed and stirred at room temperature for 30 min. The resulting viscous mixture was introduced into Teflon-lined stainless steel autoclave. The autoclave was heated at 140 °C under hydrothermal conditions for 24 h. The reaction vessel was then cooled to room temperature. Blue crystals of Cu-BTC were recovered by filtration, washed thoroughly with deionized water and dried at 100 °C overnight. The resulting powders were calcined at 250 °C for 2 h under reaction gas (1% CO, 20% O_2, 79% He), O_2, H_2 and Ar, which were named as Cu-BTC-CO, Cu-BTC-O, Cu-BTC-H, Cu-BTC-Ar, respectively.

2.2. Catalysts characterization

The textural properties of the samples were determined by nitrogen physisorption at liquid nitrogen temperature (− 196 °C) using a Quantachrome autosorb-iQ-2MP. The samples were degassed at 110 °C for 24 h before the measurements. The pore textural properties including specific BET (Brunauer-Emmett-Teller) surface area, pore size and pore volume were obtained by analyzing N_2 adsorption/desorption isotherm. Pore size distribution calculation was provided by Quantachrome autosorb-iQ-2MP equipped with the software based on Density Functional Theory (DFT). Routine X-ray powder diffraction (XRD) experiments were carried out on a Bruker D8 Advance X-ray diffractometer by a monochromatic detector. High-resolution TEM experiments were performed with FEI Tecnai G2 F20 microscope. SEM images were taken with a TESCAN VEGA3 SBH instrument. The H_2-TPR experiments were performed with a ChemBET TPR/TPD under 10 vol% H_2 flow diluted with Ar gas. 0.05 g catalyst was exposed to a flow of H_2/Ar mixture. The temperature was ramped from room temperature to 700 °C at a heating rate of 10 °C min^{-1}. Laser Raman spectroscopy (LRS) was performed using a LabRam spectrometer (Horiba-Jobin-Yvon) coupled to an Olympus confocal microscope equipped with a CCD detector cooled to about 200 K. The excitation wavelength was 532 nm (Spectra Physics argon-ion laser). The laser power was set at 100 mV. C, H and N contents of the catalysts were measured using an Element Macro elemental analyzer (Vario Micro cube, Germany). X-ray photoelectron spectroscopic (XPS) analysis (THERMO ESCALAB 250XZ) was carried out to examine the composition and surface property of the samples. The binding energies (Eb) were calibrated internally by the carbon deposit C1s binding energy at 284.6 eV.

2.3. Catalytic activity measurements

CO oxidation activity measurements were carried out in a fixed-bed flow reactor (6 mm outer diameter) at the atmospheric pressure and with 0.05 g of catalyst (20–40 mesh). The reactants were fed with a volume ratio of $He/CO/O_2$ = 79/1/20 (a total flow rate of 30 ml/min) controlled by independent thermal mass flow controllers. The CO conversion was analyzed after 30 min of the reaction by using on-line gas chromatograph (GC 2060) with a thermal conductivity detector (TCD) equipped with 5 A molecular sieve column (length: 3 m, inner diameter: 3 mm).

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 shows the XRD patterns of uncalcined Cu-BTC and Cu-BTC derivatives derived from MOF calcined with different atmospheres. Uncalcined Cu-BTC exhibits all the previously diffraction peaks for this typical material [43,44]. Differently, the MOF structure of Cu-BTC-CO and Cu-BTC-O completely disappear, and two new species CuO and Cu_2O form. 2θ angles of 35.5°, 38.7°, 48.7°, 53.5°, 58.3°, 61.5°, 65.8°, 67.9°, 72.4° and 75.0° correspond to the (002), (111), (− 202), (020), (202), (− 113), (022), (113), (311), and (004) reflections of CuO (PDF # 45-0937), respectively. Moreover, the diffraction peaks at 36.5°, 42.4° and 73.7° are attributed to (111), (200) and (311) lattice planes of Cu_2O (PDF # 65-3288), respectively. The height of the characteristic diffraction peaks of Cu_2O (111) and CuO (111) planes are used to calculate the relative amounts of Cu_2O and CuO, respectively [41,45,46]. The relative ratio of CuO equals to $I\mathrm{CuO}(111)/(I\mathrm{Cu_2O}_{(111)} + I\mathrm{CuO}_{(111)})$. Here, $I\mathrm{CuO}_{(111)}$ should be substituted by $I\mathrm{CuO}_{(002)}$. The related results are presented in Table 1. It is obviously observed that Cu_2O/CuO content ratio of Cu-BTC-CO is higher than that of Cu-BTC-O, which may be related to the nature of the atmosphere. The reaction gas containing a few reducing atmosphere CO is favour to the formation of Cu_2O species. When treatment atmosphere changes to H_2, Very weak MOFs structure is observed. Moreover, it is not found any copper oxygen species. Three new peaks at 43.3°, 50.5° and 74.2° appear, corresponding to (111), (200) and (220) reflections of Cu (PDF # 65-9026), respectively, which indicate that framework Cu^{2+} are

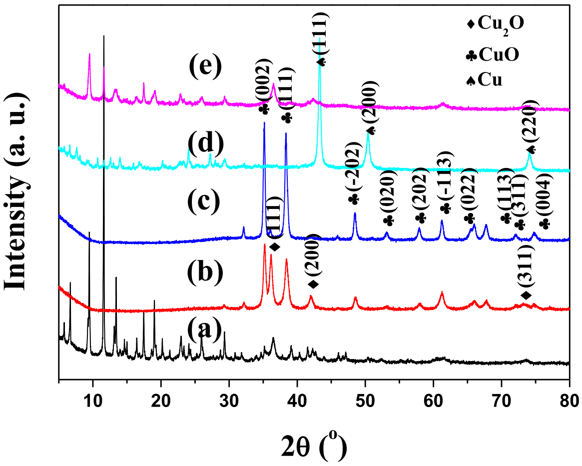

Fig. 1. XRD patterns of uncalcined Cu-BTC (a) and Cu-BTC derivatives derived from MOF calcined with different atmospheres: (b) reaction gas, (c) O_2, (d) H_2, (e) Ar.