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Simple Preparation of Crystal $\text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ and Its Catalytic Activity in CO Oxidation Reaction

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Abstract: Crystalline metal-organic framework cobalt (II) benzenetricarboxylate $\text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ (MOF-Co) has been prepared using solvothermal method. The reaction of cobalt (II) nitrate and 1,3,5-benzenetricarboxylic (BTC) acid in a mixed solution of N,N-dimethylformamide (DMF)/ $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (1:1:1, v/v) at low temperature for short reaction times produced this crystalline compound. Compared with traditional hydrothermal method, a mixed solution method for the synthesis of crystalline metal complex was found to be highly efficient. After water molecules were removed from this metal complex, its exposed nodes served as active sites. When this MOF-Co was employed in the oxidation of CO, it showed good catalytic properties causing 100% conversion of CO to CO_2 at low temperature of 160 °C.

Key words: metal-organic framework; solvothermal synthesis; crystalline compound; cobalt catalyst; CO oxidation reaction

1 Introduction

Nowadays metal-organic frameworks (MOFs) have been extensively studied as catalysts because of their flexible structural building units, the possible functionalization of inner pore surfaces and high dispersion of active metal sites^[1-3]. However, most of the reported applications are for liquid phase reaction^[4,5], probably due to their stability limitation since most MOFs decompose at about 350 °C. In fact most catalytic reactions are not carried out in solution but involving gas phase. CO oxidation is often used as a reaction model for heterogeneous gas phase reactions. Additionally, MOFs have the following excellent characters. Firstly, the porous structures of coordinated metal sites of the MOFs can limit the migration and aggregation of metal nanoparticles, leading to ultra-high dispersion of metal sites. Secondly, unsaturated

coordination metal sites on the MOFs will increase its activity in catalytic reactions^[6-8]. Recently many MOFs have been investigated for use as catalysts for CO oxidation reactions^[9-11]. Ye and Liu^[12] reported that crystalline and amorphous $\text{Cu}_3(\text{BTC})_2$ (MOF-Cu) could be used as catalysts for CO oxidation, with 100% conversion at 220 and 240 °C respectively. But these temperatures are close to the thermal stability limitation of $\text{Cu}_3(\text{BTC})_2$.

The synthesis of $\text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ (MOF-Co) has been reported by Li *et al.*^[13]. The compound could only be obtained after conducting different stages of the reaction at different high temperature for long duration. Such harsh conditions are unfavourable for large-scale catalyst synthesis. In present work a simple route was used for the synthesis of MOF-Co by a solvothermal method. The synthesis was carried out at low temperature (85 °C) and short time (20 h). The simplified process is suitable for the production of large-scale catalysts. Additionally, we also studied MOF-Co catalytic activity for CO oxidation reaction.

2 Experimental

2.1 Synthesis of $\text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$

1, 3, 5-benzenetricarboxylic acid (0.005 mol, 1.05 g) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol, 2.908 g) were

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dissolved in 60 mL solvent (N,N-dimethylformamide (DMF): $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}=1:1:1$, v/v). The resultant solution was stirred for 0.5 h and placed in a stainless steel vessel, which was sealed and placed in a programmable furnace. The mixture was heated to 85 °C at 5 °C/min and held at that temperature for 20 h, then cooled to room temperature. The resultant large mauve crystals were filtered, washed with deionized water (3×10 mL) and ethanol (3×10 mL), and then air-dried to give 1.33 g of $[\text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}]$. The samples were calcined at 300 °C for 4 h.

10% Co/SiO₂ and 10% Co/Al₂O₃ catalysts were prepared by incipient wetness impregnation of SiO₂ and Al₂O₃ respectively by aqueous solution of cobalt nitrate. The samples were dried at 120 °C for 12 h, followed by calcination at 500 °C for 5 h.

2.2 Crystal structure determination

A mauve single crystal with dimensions of 0.12 mm × 0.10 mm × 0.10 mm was chosen for X-ray diffraction analysis. The measurements were performed on a Bruker SMART APEX-CCD diffractometer equipped with a graphite-monochromatic Moka radiation ($\lambda=0.710$ Å) at 25 °C. A total of 4443 reflections were collected in the range of $2.01 < \theta < 26.00^\circ$ by using a ψ - ω scan mode with 2 583 independent scans ($R_{\text{int}}=0.0665$). The data set was corrected by SADABS program^[14]. The structure was solved by direct methods and expanded by different Fourier transform techniques with SHELXS-97^[15]. The nonhydrogen atoms were added according to the theoretical models. The structure was refined by full-matrix least-squares method on F^2 with SHELXL-97^[16]. The final refinement gave $R=0.0376$, $wR=0.0961$, and $w=1/[^2(F^{\circ 2})+(0.0785P)^2+0.3386P]$ ($P=(F^{\circ 2}+2F_c^2)/3$).

2.3 Characterization

Fourier transform infrared (FT-IR) spectra were obtained with a Nicolet 6700 intelligence Fourier transform infrared instrument using KBr pellet in the 4 000-400 cm^{-1} range. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. TG-DSC analysis was performed with a NETZSCH STA449F3 analyzer in a temperature range of 30 to 600 °C in flowing O₂ with a heating rate of 10 °C/min. Prior to analysis the sample was first dried at 100 °C for 4 h. A Bruker advanced D8 powder X-ray diffractometer with monochromatic *Cu* α radiation and nickel filter equipped with VANTEC-1 detector was used for XRD measurements, the large angle scan ranges were 20-80°. X-Ray photoelectron spectroscopy(XPS) analyses were performed on a VG Multilab 2000 spectrometer

with AlK α (1 486.6 eV) radiation. The binding energy was calibrated against the C1s peak (284.6 eV) of surface adventitious carbon, and prior to analysis the sample was first calcined at 240 °C for 4 h.

2.4 Catalysis measurements

The CO catalytic oxidation activity was determined by using a fixed bed plug flow reactor system equipped with an on-line GC. Typically, pure CO and atmosphere were supplied through mass flow controllers and mixed with each other, and then the final reactant gas (800 mL/min) passed through the catalyst bed (1.0 g). Reaction gas was composed of CO (1 vol%) and atmosphere (37.5 vol%) and the gas hourly space velocity (GHSV) was 48 000 mL/(hg). The reaction temperature was programmed and controlled by means of thermocouple extended to the catalyst bed inside the reactor. Heating rate of 2 °C/min was used to reach pre-set reaction temperature and the product gas was analyzed after 20 minutes of reaction at the set temperature. Reaction gas composition was monitored through on-line sampling using computer controlled Agilent 3000 MicroGC. The analysis was done after every 6 minutes of reaction time. CO conversion was calculated as follows:

$$\text{CO conversion (\%)} = ([\text{CO}]_1 - [\text{CO}]_2) / [\text{CO}]_1 \times 100$$

where $[\text{CO}]_1$ and $[\text{CO}]_2$ are inlet and outlet gas concentrations in ppm respectively.

3 Results

3.1 The Crystal structure of the title compound

Single-crystal structure analysis results of $\text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ are shown in Fig.1. Two of the carboxylate units (O4, O5 and O4A, O5A) of BTC are bound in a unidentate fashion to the axial positions of two nearly perfect octahedral and symmetry-equivalent cobalt centers (Co1 and Co1A), while the third carboxylate (O6 and O6A) is bound in a bidentate fashion to the equatorial positions of a symmetry-inequivalent and distorted, octahedral cobalt center (Co2). Water ligands O7 and O9 on Co1 are engaged in hydrogen bonding, respectively, to carboxylate oxygens O2 and O5 of an adjacent BTC within the chain, while O11 and O11A on Co2 are hydrogen-bonded to O7 and O9 of an adjacent chain to form hydrogen-bonded layers. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre with No. CCDC 921721. Additionally, Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_{24}\text{Co}_3 = \text{Co}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$: C,

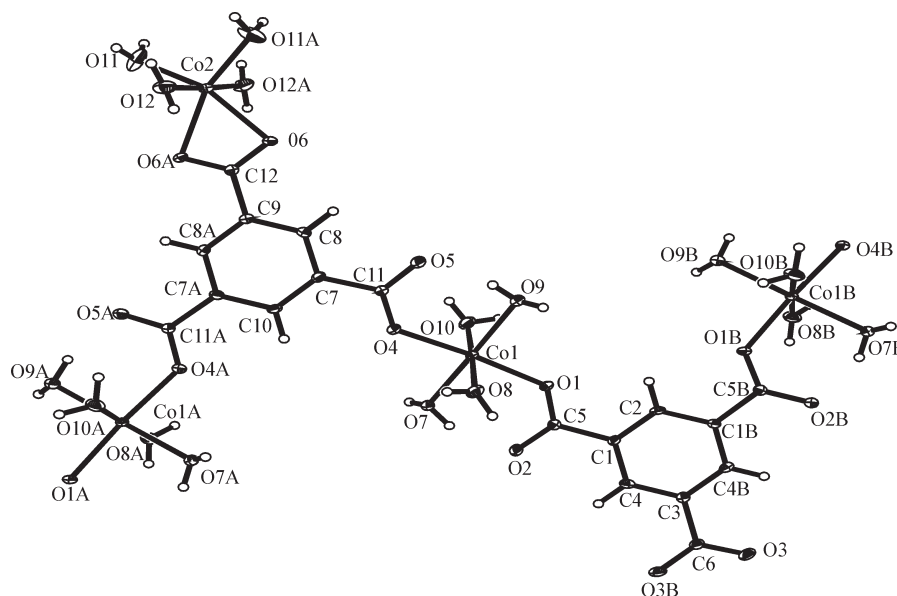


Fig.1 View of the coordination environment of Co (II) atom of the title compound (symmetry codes: $a = -x, y, z, b = 1 - x, y, 1 - z$)

26.75; H, 3.72. Found: C, 26.77; H, 3.47. FT-IR (KBr 4000-500 cm^{-1}): 3 456 (vs, broad), 3 110 (vs, broad), 1 611 (vs), 1 519 (sh), 1 473 (s), 1 433 (vs), 1 372 (vs).

Table 1 Crystallographic data for MOF-Co

Formula	$\text{C}_{18}\text{H}_{30}\text{O}_{24}\text{Co}_3$
M	807.21
Crystal system	Monoclinic
Space group	C2
$a/\text{\AA}$	17.431 4(9)
$b/\text{\AA}$	12.952 0(7)
$c/\text{\AA}$	6.556 6(3)
$\beta/(\text{^\circ})$	111.926 0(10)
Z	2
$V/\text{\AA}^3$	1 373.22(12)
$d_{\text{calc}}/(\text{g}/\text{cm}^3)$	1.952
μ/mm^{-1}	1.899
$R(R_w)$	0.037 6(0.096 1)
Wightingscheme/ w^{-1}	$w = 1/[F_c^2 + (0.078 5P)^2 + 0.338 6P]$ $P = (F_c^2 + 2F_o^2)/3$

Table 2 Selected bond lengths and angles for MOF-Co

Item	Distance / \AA	Bond	Angle/ (^\circ)
Co(1)-O(1)	2.057(3)	O(9)-Co(1)-O(1)-C(5)	164.3(3)
Co(1)-O(8)	2.132(3)	O(8)-Co(1)-O(1)-C(5)	71.1(3)
Co(1)-O(10)	2.128(3)	O(1)-Co(1)-O(4)-C(11)	137.8(11)
Co(2)-O(6)	2.150(3)	O(11)-Co(2)-C(12)-O(6)	164.42(19)
Co(2)-O(11)	1.998(3)	O(12)-Co(2)-C(12)-O(6)	-100.19(18)
Co(2)-O(12)	2.129(3)	O(6)#1-Co(2)-C(12)-O(6)	180.0

The details of the crystal structure and refinements are summarized in Table 1. The selected bond lengths and bond angles are shown in Table 2.

3.2 X-ray powder diffraction (XRPD) results

In order to test the purity of as-synthesized sample, the complex MOF-Co was characterized by X-ray powder diffraction (XRPD) at room temperature

(Fig.2). The experimental patterns of MOF-Co are in good agreement with the corresponding simulated ones, indicating that the bulk synthesized material and as-grown crystals are homogeneous, the subtle differences in peaks for the simulations may be due to the preferred orientation of the powder samples.

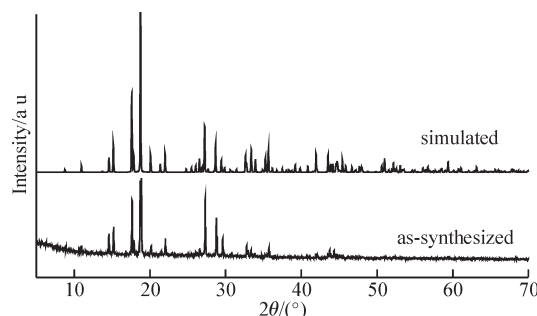


Fig. 2 XRPD patterns of MOF-Co

3.3 TG results

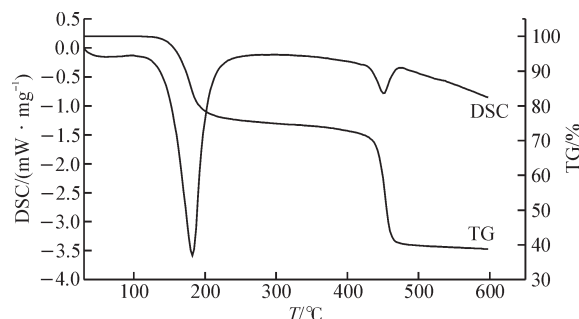


Fig.3 TG-DSC curves for MOF-Co

TG-DSC analysis curves of the catalyst are shown in Fig.3. The result indicates a two-step weight loss. The first weight loss corresponds to the removal of water in the temperature range of 150-200 $^{\circ}\text{C}$ (about 28%). The second weight loss from 450 to 480 $^{\circ}\text{C}$ corresponds to the decomposition of BTC ligand (about

30%). The structure is stable upon water removal but collapses at 450 °C.

3.4 XPS results

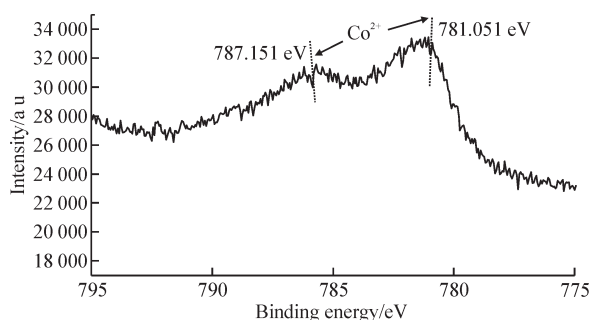


Fig.4 XPS spectrum of MOF-Co catalysts

The XPS spectrum of Co in MOF-Co is shown in Fig.4. The spectrum demonstrates that Co of MOF-Co is divalent cobalt ions because the binding energies at 796.8 eV and 781.3 eV are characteristic peaks for divalent cobalt^[17,18].

3.5 Catalytic activity results

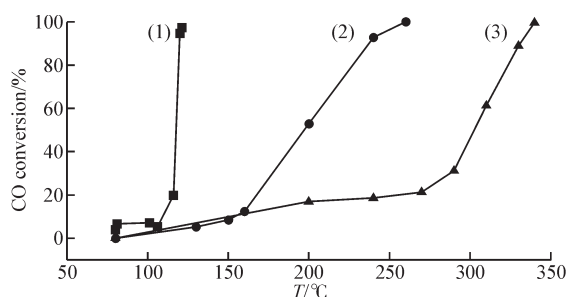


Fig.5 Conversion-temperature curves for CO oxidation over (1) MOF-Co, (2) 10% Co/SiO₂, (3) 10% Co/Al₂O₃

The data of CO conversion for the three prepared catalysts are presented in Fig.5. It is demonstrated that MOF-Co, 10% Co/SiO₂ and 10% Co/Al₂O₃ samples are all catalytically active for CO oxidation. The temperature for 100% conversion is 160, 260 and 340

°C for MOF-Co, 10% Co/SiO₂ and 10% Co/Al₂O₃, respectively. The MOF-Co sample clearly shows the highest activity at low temperature.

4 Discussion

The single crystal XRD and the XPS results indicate that in this metal complex, divalent cobalt ions are situated in a six-fold coordination environment. Each metal centre is linked with BTC through two coordination sites, leaving the other four sites for associated water ligands^[13]. Because metal coordination to BTC is much stronger than to water, it can be expected that water liberation by heating will occur first, as shown in Fig.6(a). The nodes will be exposed after the removal of water molecules and this should be beneficial for CO catalytic oxidation. There are two ways of coordination in this compound, one is the Co atom coordination with two oxygen atoms from the same carboxyl (Fig.1). The other is the Co atom coordination with two oxygen atoms from different BTCs (Fig.1). All water molecules in this complex can be easily removed (Fig.6(a)) and the resultant vacancies can combine with oxygen, which could then facilitate CO catalytic oxidation. The calcination process activates and stabilizes the catalyst. Furthermore, the Co atoms in the complex are anchored by carboxylate ligand leading to the increase of contact space of Co centre with oxygen. Obviously these Co centres are very active and easy to adsorb O₂ molecules to provide O atom for CO oxidation. The possible reaction mechanism is illustrated in Figs.6 (b,c). A great number of coordinative vacancies of Co centres are available for adsorbing O₂ molecules after water

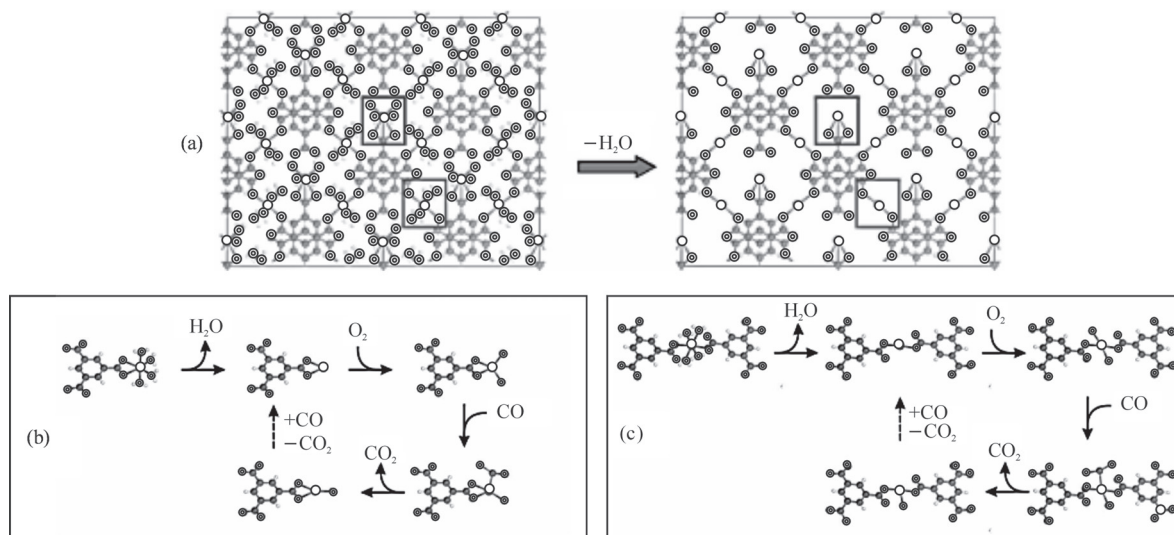


Fig.6 The possible catalytic mechanism of CO oxidation on MOF-Co (o ball is Co, ● ball is O, ● ball is C, ● ball is H)

molecules were removed. Additionally, because Co has the strong coordination capability, the dissociative CO molecules could also be adsorbed on the exposed Co centres and then react rapidly with adsorbed oxygen to produce CO₂. The Co centre would be regenerated upon the desorption of CO₂. The porous structures and the unsaturated coordination sites lead to an ultra-high dispersion of Co-species. Hence it has much higher activity than other catalysts such as Co nanoparticles supported on Al₂O₃ and SiO₂.

5 Conclusions

In Summary, the crystalline metal complex Co₃(BTC)₂·12H₂O has been prepared by using mixed solvent at low temperature and short reaction time. Compared with traditional thermal and solvothermal method, the mixed solvent synthesis of crystalline metal complex has been demonstrated to be highly efficient, especially for the large scale manufacture of those crystalline metal complex. The framework of the title compound is still stable upon removal of water molecules. Using this compound as catalyst for the oxidation reaction of CO has achieved 100% conversion at low temperature of 160 °C. The experimental results suggest that using divalent cobalt based MOFs as catalyst for CO catalytic oxidation reaction is potentially feasible.

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