第15卷 第2,3期　　广东有色金属学报　　Vol.15, No.2,3
2005年9月　　JOURNAL OF GUANGDONG NON-FERROUS METALS　　Sep 2005

Article ID: 1003－7837(2005)02,03－0238－06

Solvothermal synthesis and reaction mechanism of CoO nanoparticles

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Abstract: Pure CoO nanoparticles have been synthesized using solvothermal method at 150℃ with $Co(CH_3COO)_2 \cdot 4H_2O$ and anhydrous ethanol as reactants. SEM, TEM and XRD were employed to characterize the size, morphology and crystalline structure of the as-synthesized CoO nanoparticles. It is revealed that the CoO nanoparticles are of octahedron configuration in face-centered cubic (FCC) structure with a lattice constant of 0.426 nm and have an average particle size of about 50 nm. Typically, when the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in CH_3CH_2OH reduces from 0.24 mol/L to 0.08 mol/L, the size of CoO nanoparticles decreases from 500 nm to 50 nm. Based on the results of IR analysis of the finished reaction liquid and XRD of products, the reaction mechanism of the solvothermal system has been discussed.

Key words: solvothermal synthesis; CoO; octahedron; nanoparticles; esterification

CLC number: TQ138.12　　**Document code**: A

1 Introduction

Cobalt monoxide, as a transition-metal monoxide, has attracted particular attention due to its distinct structure and properties and its potential application in many fields[1]. CoO is not only used in preparation of gas-sensing materials[2], but widely used as anode material of lithium-ion batteries[3,4].

Normal methods of preparing the CoO powders are heating up the metallic cobalt in air or in vapor, or pyrogenation of the hydroxide, carbonate or oxalate of cobalt in isolated air at high temperature[1]. However, the sizes of particles prepared by these methods are at the μm level. Zhang, *et al.*[5] have synthesized CoO nanoparticles in the 10－80 nm range by heating the gel precursor obtained by drying a solution of $Co(NO_3)$ and poly(vinyl alcohol) at 225℃ under a H_2 atmosphere. Moumita Ghosh, *et al.*[6] have recently obtained CoO nanoparticles in the 4.5－18 nm range by the decomposition of Co(II) cupferronate in decalin at 270℃ under solvothermal conditions. However, there are not many reports on the preparation of pure CoO nanoparticles. Because it is difficult to prepare pure CoO, on account of the greater stability of Co_3O_4 and the readily reducibility of CoO to Co metal[6]. Nanocrystals of CoO are even more difficult to prepare, due to the surface oxidation of nanoparticles.

Received date: 2005－06－30

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In this paper, a novel synthesis method of pure CoO nanoparticles by a single step was reported. The CoO nanoparticles of octahedron configuration have been obtained by solvothermal method at 150℃ using $Co(CH_3COO)_2 \cdot 4H_2O$ and anhydrous ethanol as reactants. This simple synthesis method just needs only a single step to obtain pure CoO nanoparticles with good dispersibility and narrow size distribution. Equally importantly, the influences of concentration of reactants and reaction time on the size of synthesized CoO were investigated.

2 Experimental

$Co(CH_3COO)_2 \cdot 4H_2O$ (AR grade) and CH_3CH_2OH (AR grade) were put and sealed in a Teflon lined stainless steel autoclave of 100 mL capacity allowing 50%-60% filling. In a typical reaction, 1.0 g (8 mmol) of $Co(CH_3COO)_2 \cdot 4H_2O$ and 50 mL of CH_3CH_2OH were kept at 150℃ for 24 h under continuous stirring. Then, it was allowed to cool to room temperature. A brownish-black solid insoluble in ethanol was obtained as the product. Then the solid products were collected by centrifugation and washed with ethanol for several times. Finally, the CoO particles were obtained after the products were dried in air at room temperature. The size of the particles are controllable through adjusting the concentration of reactants as well as the reaction time, with the amount of ethanol, the volume of the autoclave and the reaction temperature unchanged. The CoO particles synthesized in ethanol solution could be readily dispersed in ethanol by sonication.

X-ray diffraction (XRD) was performed on X'Pert PRO MPD type X-ray diffractometer using Cu Kα radiation ($\lambda=0.1541$ nm) with the scanning rate of 0.03°/s. The morphology and structure of the samples were characterized by a JSM—6700F cold field emission scanning electron microscope (SEM) and a HITACHI—8100 transmission electron microscope (TEM). The finished reaction liquid was analyzed by Spectrum GX type Fourier transform spectrometer.

3 Results and discussion

Fig. 1 shows the typical XRD patterns of the solid products obtained after 0.24 mol/L $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol was heated at 150℃ under solvothermal conditions for different reaction time. It was showed that the components of products varied with the increase of reaction time. The XRD pattern of product for 8 h shown in Fig. 1(a) reveals that it is pure $Co_3(CH_3COO)_5(OH)$. It is indicated that $Co(CH_3COO)_2 \cdot 4H_2O$ is firstly turned into intermediate product, i. e., cobalt acetate hydroxide ($Co_3(CH_3COO)_5(OH)$) at the early stage of the reaction. When the reaction time was increased to 24 h, the XRD pattern shown in Fig. 1(b) indicates that the products are the mixture of $Co_3(CH_3COO)_5(OH)$ and CoO crystals. As the reaction time increases further, more and more intermediate product $Co_3(CH_3COO)_5(OH)$ is turned into the final product CoO. The pattern of product for 48 h shown in Fig. 1(c) reveals that it is pure CoO. All the peaks are

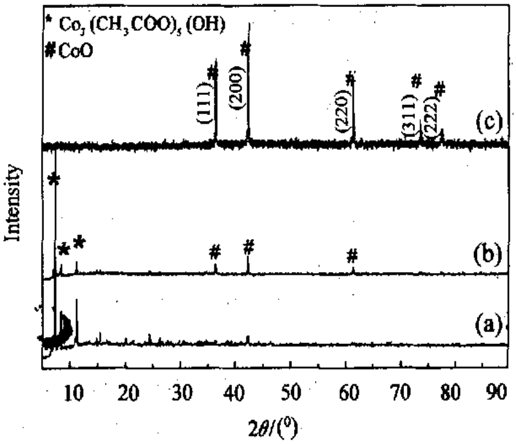

Fig. 1 XRD patterns of the products synthesized at 150℃ for different time
(a)—8 h; (b)—24 h; (c)—48 h

well indexed as cubic crystalline CoO in FCC structure (JCPDS card No. 071—1178) with no impurities detected. Thus, the pure CoO powders can be obtained, when the reaction time is long enough.

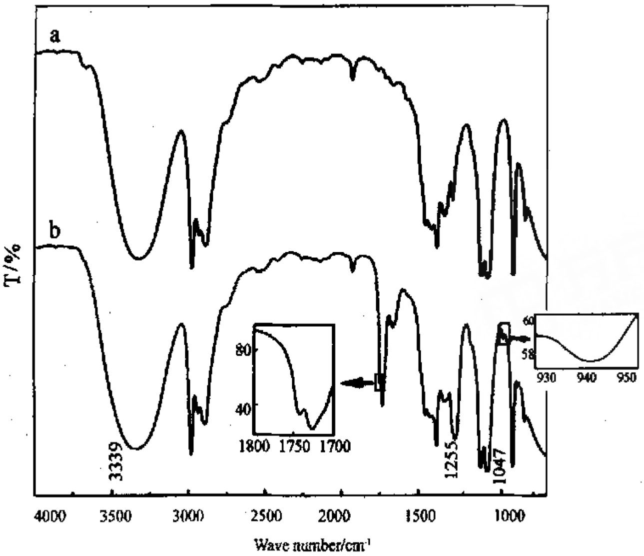

Fig. 2 FT-IR absorption spectra of the unreacted liquid (a) and the finished reaction liquid (b)

Plot (a) and (b) in Fig. 2 are the FT-IR absorption spectra of the unreacted liquid and the finished reaction liquid, respectively. The strong absorption at about 1742 cm^{-1} is attributed to the typical absorption of C=O stretch vibration of saturated ester. The strongest peak at 1047 cm^{-1} can be indexed to the C—O—C symmetric stretch vibration, while the slight broad strong peak at 1255 cm^{-1} is of C—O—C asymmetric stretch vibration. These three absorption peaks are in good accordance with the standard IR spectra of ethyl acetate, which proves the generation of ethyl acetate during the reaction. Additionally, the strong aromatic odor would provide another evidence to support the presence of ethyl acetate. The strong absorption peak at 1727 cm^{-1} is ascribed to C=O strength vibration of saturated fatty acid, while the weak absorption peak at 940 cm^{-1} is of the hydroxyl out of plane bending vibration of dipolymer of carboxylic acid. Due to the existence of CH_3COO^- in reactants, it can be deduced that acetic acid does exist in the finished reaction liquid. The broad peak centered at 3339 cm^{-1} is the typical absorption of —OH, which implies the existence of a great deal of unreacted ethanol.

Based on the FT-IR absorption spectra and XRD patterns above, it was considered that the reaction steps can be expressed as follows:

$$3\,Co(CH_3COO)_2\cdot 4H_2O \longrightarrow Co_3(CH_3COO)_5(OH)\downarrow + CH_3COOH + 11H_2O \tag{1}$$

$$Co_3(CH_3COO)_5(OH) + 5HOCH_2CH_3 \longrightarrow 5CH_3COOCH_2CH_3 + 3CoO\downarrow + 3H_2O \tag{2}$$

$$Co_3(CH_3COO)_5(OH) + 5H_2O \longrightarrow 5CH_3COOH + 3CoO\downarrow + 3H_2O \tag{3}$$

The overall reaction is expressed as follows:

$$Co(CH_3COO)_2 4H_2O + 2HO\text{-}CH_2CH_3 \longrightarrow 2CH_3COOCH_2CH_3 + CoO\downarrow + 5H_2O \tag{4}$$

Eq. 1 is testified by the evidence of the presence of acetic acid in the finished reaction liquid and existence of $Co_3(CH_3COO)_5(OH)$ in the product for 8 h. The presence of ethyl acetate in the finished reaction liquid and the achievement of CoO as the finial product are both supportive to Eq. 2. Except reacting with ethanol, $Co_3(CH_3COO)_5(OH)$ also possibly reacts with the crystal water of $Co(CH_3COO)_2\cdot 4H_2O$ and water product of esterification reaction, which results in formation of CoO particles. However, since the water here is relatively rare, only a small proportion of CoO is obtained in this way. It can be deduced that the product CoO mainly comes from esterification reaction (Eq. 2), because there are much more ethanol than water.

Fig. 3 is the typical SEM image of the CoO particles obtained after 0.24 mol/L $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol heated at 150℃ for 48 h. The morphology of as-synthesized CoO crystals of octahedron configuration with average size of 500 nm is shown in Fig. 3. Fig. 4 and its inset show the TEM image and the selected area electron diffraction (SAED) pattern of the as-synthesized CoO particles. All the particles show tetragonal projected shape with average size of 600 nm. The observed ring pattern can be indexed as the FCC structure, which is in very perfect agreement with the result of XRD analysis.

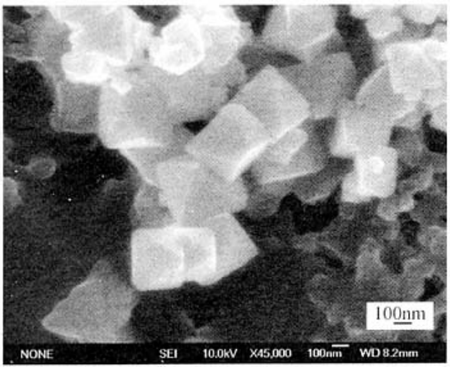

Fig. 3 SEM image of CoO at 150℃ for 48 h

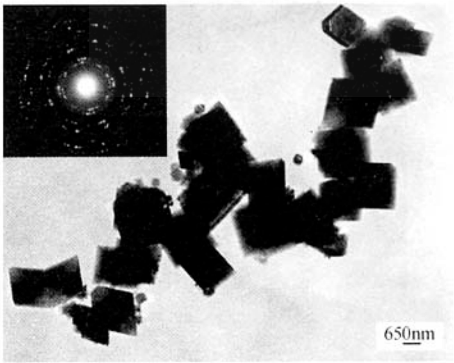

Fig. 4 TEM image of CoO particles at 150℃ for 48 h

Fig. 5 is a typical XRD pattern of as-synthesized CoO nanoparticles. It is shown that pure CoO nanoparticles can be obtained after 0.08 mol/L $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol was heated at 150℃ for 24 h, however, the product obtained after calefaction of 0.24 mol/L $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol at 150℃ for 24 h has the unreacted intermediate product $Co_3(CH_3COO)_5(OH)$ as shown in Fig. 1(b). Consequently, pure CoO nanoparticles can be synthesized with shorter time under a lower concentration of $Co(CH_3COO)_2 \cdot 4H_2O$.

Fig. 6 is a typical SEM image of as-synthesized CoO nanoparticles obtained after 0.08 mol/L $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol was heated at 150℃ for 24 h, and Fig. 7 is its corresponding TEM image. The CoO nanoparticles, which are uniformly dispersed in ethanol solvent, are of octahedron configuration with an average particle size of about 50 nm. The mean size of CoO particles decreased from 500 nm to 50 nm, when the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol reduced from 0.24 mol/L to 0.08 mol/L.

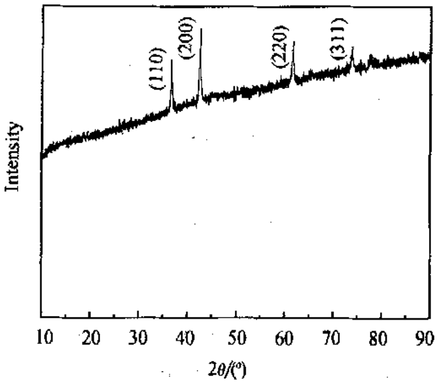

Fig. 5 XRD pattern of as-synthesized CoO nanoparticles at 150℃ for 24 h (the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol: 0.08 mol/L)

According to the coordination polyhedron growth mechanism model[7], the growth unit of the system under discussion is $Co(OH)_6^{4-}$. The dehydration reaction among growth units takes place at the interface during the process of crystal growth[8]. It can be expressed as follows:

$$Co_mO_p(OH)^{(n+2p-2m)-} + Co(OH)_6^{4-} = Co_{m+1}O_{p+1}(OH)_{n+4}^{(n+2p-2m+4)-} + H_2O \tag{5}$$

The mean size of the particles is influenced by the reaction rate calculated according to Eq. 5, determined by the concentration of $Co(OH)_6^{4-}$. And the concentration of $Co(OH)_6^{4-}$ is determined by the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol. Consequently, the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol is the key factor for the mean size of as-synthesized CoO nanoparticles. The higher concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol, the larger the as-synthesized CoO nanoparticles. The size of CoO nanoparticles can be controlled by adjusting the concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol.

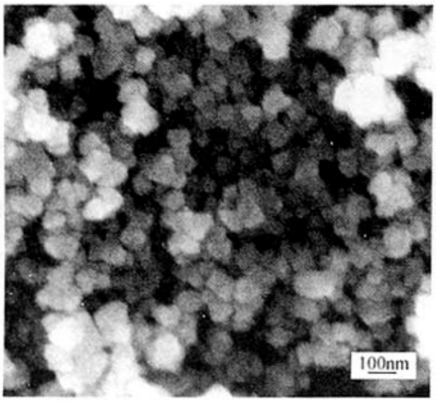

Fig. 6 SEM image of as-synthesized CoO nanoparticles at 150℃ for 24 h

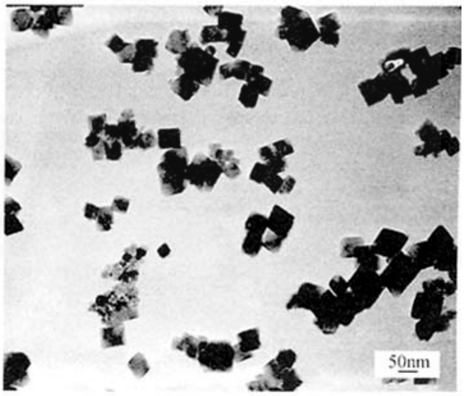

Fig. 7 TEM image of as-synthesized CoO nanoparticles at 150℃ for 24 h

3 Conclusions

Pure CoO nanoparticles have been synthesized by esterification reaction using solvothermal method at 150℃ with $Co(CH_3COO)_2 \cdot 4H_2O$ and anhydrous ethanol as reactants. The as-synthesized CoO nanoparticles with an average particle size of about 50 nm have been obtained after 0.08 mol/L $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol was heated at 150℃ for 24 h. The as-synthesized CoO nanoparticles are of octahedron configuration in FCC structure with good crystallinity.

The concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol is the key factor for the mean size of as-synthesized CoO nanoparticles. The lower concentration of $Co(CH_3COO)_2 \cdot 4H_2O$ in ethanol, the smaller average size of CoO nanoparticles.

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