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Article

Effects of Co_3O_4 nanocatalyst morphology on CO oxidation: Synthesis process map and catalytic activity

Liangpeng Zeng ^{a,b}, Kongzhai Li ^{a,b,*}, Fan Huang ^{a,b}, Xing Zhu ^{a,b}, Hongcheng Li ^{a,b}^a State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, Yunnan, China^b Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China

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ABSTRACT

This study focuses on drawing a hydrothermal synthesis process map for Co_3O_4 nanoparticles with various morphologies and investigating the effects of Co_3O_4 nanocatalyst morphology on CO oxidation. A series of cobalt-hydroxide-carbonate nanoparticles with various morphologies (i.e., nanorods, nanosheets, and nanocubes) were successfully synthesized, and Co_3O_4 nanoparticles were obtained by thermal decomposition of the cobalt-hydroxide-carbonate precursors. The results suggest that the cobalt source is a key factor for controlling the morphology of cobalt-hydroxide-carbonate at relatively low hydrothermal temperatures ($\leq 140^\circ\text{C}$). Nanorods can be synthesized in CoCl_2 solution, while $\text{Co}(\text{NO}_3)_2$ solution promotes the formation of nanosheets. Further increasing the synthesis temperature (higher than 140°C) results in the formation of nanocubes in either $\text{Co}(\text{NO}_3)_2$ or CoCl_2 solution. The reaction time only affects the size of the obtained nanoparticles. The presence of CTAB could improve the uniformity and dispersion of particles. Co_3O_4 nanosheets showed much higher catalytic activity for CO oxidation than nanorods and nanocubes because it has more abundant Co^{3+} on the surface, much higher reducibility, and better oxygen desorption capacity.

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1. Introduction

CO emitted from industrial activities and transportation is a toxic gas for humans and animals [1,2]. Among all the possible solutions for reducing CO emissions, catalytic conversion of CO into non-toxic gases has been a hot topic [2–6]. Generally, supported noble metals have excellent activity for low-temperature CO oxidation, but the high cost because of their limited global resources inhibits their practically permanent application [1,7]. The design of alternative and cheaper

catalysts for CO catalytic oxidation has therefore received much attention [8–10].

With the rapid progress in the preparation technology for nanomaterials, nanocatalysts have received wide interest because of the specificity of their nanostructures (e.g., morphologies and size effects) [11]. Nanoscale effects can cause some non-noble catalysts to have activity in CO oxidation comparable with that of noble metal catalysts. Many studies indicate that Co_3O_4 has remarkable activity for low-temperature CO oxidation [12–20]. It is also clear that the morphology dependence of

* Corresponding author. Tel/Fax: +86-871-65153405; E-mail: kongzhai.li@aliyun.com, kongzhai.li@foxmail.com

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Co₃O₄ nanocatalysts is a greater influence than its size dependence [21–23]. Rational design and skillful synthesis of Co₃O₄ catalysts with various morphologies has become one important path to improve its catalytic activity.

Generally, the synthesis of Co₃O₄ nanostructures can be achieved through the thermal decomposition of precursors at elevated temperatures. With such a procedure, the shape of the Co₃O₄ materials is largely dependent on the structure of the precursors (e.g., cobalt-hydroxide-carbonate) [24]. Several methods, such as sol-gel processing, microemulsion, forced hydrolysis, hydrothermal synthesis, and chemical precipitation have been developed for the fabrication of cobalt-hydroxide-carbonate nanoparticles [25–30]. Among these methods, the hydrothermal method offers functional control over the size and morphology of the particles with relatively simple steps and short reaction time, providing well-crystallized reaction products with high homogeneity [27,28].

Many cobalt-hydroxide-carbonate nanostructures with varied morphologies have been synthesized by a hydrothermal approach, including nanorods, nanotubes, nanobelts, nanospheres, nanosheets, and hollow core/shell hierarchical nanostructures [4,22,29,30]. In particular, Hu et al. [4] prepared nanocube and nanobelt cobalt-hydroxide-carbonate precursors via a hydrothermal process by varying the annexing agent (octadecenylamine and glycerol, respectively) in the mixture and controlling the reaction temperature. Xu et al. [22] reported an investigation of the formation of cobalt-basic-carbonate compounds $[\text{Co}(\text{OH})_x(\text{CO}_3)_{0.5(2-x)} \cdot n\text{H}_2\text{O}]$ with dimensional and morphological control using different cobalt sources (CoCl₂ and Co(NO₃)₂). They found that samples synthesized by urea hydrolysis consisted of large well-crystallized nanorods, and the counteranion effect was significant in the experiment. Samples obtained in Co(NO₃)₂ solution have uniform diameters of approximately 50 nm and lengths of 1–2 μm, whereas samples from CoCl₂ solution show needle-like crystallites with a much larger size (100–200 nm in diameter, and 1–5 μm in length). Similarly, Wang et al. [29] synthesized Co(CO₃)_{0.5}(OH)·0.11H₂O precursor nanowires by a facile hydrothermal method and showed how the additive (urea) concentration controlled the uniformity and the overall structure. The carbonate ions produced via the hydrolysis of urea not only participate in the formation of the intermediate compound and facilitate the anisotropic growth of the nanowires, but also behave like coordinating agents that help to organize and give rise to a more complex hierarchical structure at high concentrations. Sarawade et al. [30] also demonstrated that the type of surfactant template and the reaction temperature played crucial roles in controlling the size, shape, and morphology of the products. It is also clear that Co₃O₄ nanorods with preferentially exposed {110} planes are extremely active and stable for low-temperature CO oxidation [3,31,32]. The Co³⁺ sites on {110} planes over Co₃O₄ nanobelts have much higher turnover frequency (TOF) than those on {100} planes over Co₃O₄ nanocubes [4]. These results demonstrate that structure-dependent effects play a very important role in determining the catalytic activity of Co₃O₄ for CO oxidation.

Almost all of these studies use various methods to acquire different products. For a hydrogen thermal process, researchers studied only the effect of limited factors (e.g., one or two experimental parameters) on the formation of cobalt-hydroxide-carbonate with different morphologies. Because the relationship between the control parameters and product morphology is multifactorial in a hydrothermal process, there is still a lack of knowledge on the growth mechanism of cobalt-hydroxide-carbonate particles under various conditions. In the present work, however, considering the influence of multiple factors and their interactions, a comprehensive hydrothermal process map involving the roles of cobalt source, temperature, time, and surfactant in the growth of cobalt-hydroxide-carbonate particles is presented. It will provide insight into the nature of the formation of cobalt hydroxide carbonate nanoparticles with various morphologies (i.e., nanorods, nanosheets, and nanocubes). The corresponding Co₃O₄ particles were obtained by thermal decomposition of the resultant cobalt-hydroxide-carbonate precursor. Meanwhile, the physicochemical properties of these materials were characterized, and their catalytic performance for CO oxidation was also investigated.

2. Experimental

2.1. Synthesis of cobalt-hydroxide-carbonate nanoparticles

Cobalt-hydroxide-carbonate particles with various morphologies were synthesized by a hydrothermal method [4,27,33]. All of the chemical reagents used in the experiment were of analytical grade and used without further purification. In a typical procedure, 0.006 mol of CoCl₂·6H₂O or Co(NO₃)₂·6H₂O, 0.024 mol of urea, and 1.5 g of CTAB were dissolved in deionized water (150 mL) at room temperature with magnetic stirring. The mixture was stirred vigorously for at least 30 min to form a transparent pink solution, which was then transferred into a Teflon®-lined autoclave. The autoclave was sealed and inserted into a temperature-controlled furnace at the set reaction temperature. The controlling parameters reaction temperature (95–200 °C), time (4–24 h), and surfactant amount (0 or 1.5 g of CTAB) were varied in a systematic fashion, as summarized in Table 1. The obtained precipitates were collected and washed with distilled water and anhydrous alcohol for several times until no Cl[−] could be detected by silver nitrate titration. After that, they were dried at 100 °C for 24 h.

2.2. Synthesis of Co₃O₄ nanoparticles

The Co₃O₄ was readily obtained by thermal decomposition of the resultant cobalt-hydroxide-carbonate precursor. The products obtained in Section 2.1 were calcined in air at 400 °C for 4 h (heating rate was 2 °C/min) to produce Co₃O₄ nanoparticles.

2.3. Catalyst characterization

The X-ray powder diffraction (XRD) data for the prepared

Table 1

A summary of the reaction conditions during the hydrothermal processes and the final morphologies of the obtained cobalt-hydroxide-carbonate.

CoCl ₂ /Co(NO ₃) ₂	Temperature (°C)	Process time (min)	Amount of surfactant (CTAB, g)	Morphology
S(Cl)1/S(N)1	95	16	0	rod/sheet
S(Cl)2/S(N)2	100	16	0	rod/sheet
S(Cl)3/S(N)3	120	16	0	rod/sheet
S(Cl)4/S(N)4	140	16	0	rod/sheet
S(Cl)5/S(N)5	160	16	0	rod/sheet
S(Cl)6/S(N)6	180	16	0	rod/sheet
S(Cl)7/S(N)7	200	16	0	cube/cube
S(Cl)8/S(N)81/S(N)82	120/160/200	16	1.5	rod/sheet/cube
S(Cl)9/S(N)91/S(N)92	120/160/200	4	1.5	rod/sheet/cube
S(Cl)10/S(N)101/S(N)102	120/160/200	8	1.5	rod/sheet/cube
S(Cl)11/S(N)111/S(N)112	120/160/200	12	1.5	rod/sheet/cube
S(Cl)12/S(N)121/S(N)122	120/160/200	24	1.5	rod/sheet/cube

samples were collected on a Rigaku D/max-III λ X-ray diffractometer at a scanning rate of 2°/min with 2 θ ranging from 10° to 90° (Cu K α radiation λ = 0.15406 nm).

The thermogravimetric analysis (TGA-DTA) measurements were performed with the aid of an STA-449-F3 instrument (produced by Netzsch Co.) using a linear heating rate of 10 °C/min and a sample mass of 9.5 mg in air flow.

The morphology of the samples was observed using a scanning electron microscopy (SEM, Hitachi S4800) instrument with an accelerating voltage of 3 kV. Samples for SEM were dusted on an adhesive conductive carbon belt attached to a copper disk and were coated with 10 nm of Au prior to measurement. Transmission electron microscopy (TEM) images of the nanoparticles were taken on a JEOL2010 transmission electron microscope.

The specific surface area of as-synthesized Co₃O₄ samples was calculated according to the Brunauer-Emmett-Teller (BET) method by the N₂ adsorption isotherm at -196 °C, using a Quantachrome Autosorb-iQ instrument.

X-ray photoelectron spectroscopy (XPS) studies were carried out on a PHI-5500 system equipped with a monochromatic Mg K α (1253.6 eV) X-ray source. Spectra were registered at ambient temperature in a vacuum (residual pressure < 10⁻⁷ Pa). Sample charging during the measurement was compensated by an electron flood gun. The standard deviation in the binding energy values of the XPS line is 0.10 eV. Binding energy (BE) was determined by computer fitting of the measured spectra and calibrated using the C 1s peak (284.8 eV) as a reference. The surface composition and chemical state were evaluated based on the areas and binding energies of the Co 2p and O 1s photoelectron peaks.

Temperature-programmed reduction (TPR) experiments were performed on TPR Winv1.50 (produced by Quantachrome Instruments Co.) under a flow of a 10% H₂/He mixture (25 mL/min) using 30 mg of catalyst at a heating rate of 10 °C/min.

Temperature-programmed desorption (TPD) experiments were performed on the same instrument as the TPR experiments. Each sample was first pretreated in He (99.99% purity) at 400 °C for 1 h. After the O₂ adsorption in pure O₂ at 80 °C for 50 min and subsequent cooling to room temperature, pure He

was flowed through the reactor for 1 h. Then, desorption profiles of O₂ were obtained by ramping the reactor to 900 °C at a heating rate of 10 °C/min in a He stream (30 mL/min).

2.4. Catalytic activity evaluation for CO oxidation

The evaluation of the activity for CO oxidation was performed in a fixed-bed quartz tubular reactor at atmospheric pressure under steady-state conditions. Prior to testing, the samples (200 mg, 40–60 mesh) were treated in argon (200 mL/min) at ambient temperature for 20 min. The reactant gases (1% CO, 10% O₂, and the balance Ar) were passed continuously through the sample bed at flow rates of 200, 300, or 400 mL/min (giving a gas hourly space velocity (GHSV) of 33000, 50000, or 66000 h⁻¹, respectively). The reactor was heated through a temperature-programmed route at a heating rate of 5 °C/min. The amounts of CO, CO₂, and O₂ in the outlet streams were measured on-line by a gas chromatograph.

The kinetic experiment was conducted to investigate the intrinsic activity of the catalysts, which was defined as a reasonable correlation with the active site density of catalysts. The reaction rate of CO oxidation was determined by an isothermal reaction at 65 °C in the kinetic regime, in which the influences of internal and external mass and heat transfer were all excluded. The reaction gas composition and total flow rate were the same as for the aforesaid CO oxidation reaction.

The conversion of CO (X) was calculated from the change in CO concentration between the inlet gases and outlet gases (Eq. (1)). For comparison of catalytic activity, the parameters reaction rate (r , mol g⁻¹ s⁻¹) and TOF (s⁻¹) were calculated at a specified temperature of 65 °C. Here, C_{CO} is the concentration of CO; C_0 (mol/s) is the initial CO concentration per second; m is the mass of catalyst; and n is the molar mass of catalyst.

$$X = \frac{C_{CO,in} - C_{CO,out}}{C_{CO,in}} \times 100\% \quad (1)$$

$$r = \frac{X \times C_0}{m} \quad (2)$$

$$TOF = \frac{X \times C_0}{n} \quad (3)$$

The stability of the catalysts was tested under dry conditions and in the presence of moisture. In the case of water va-

por introduction, 0.5 vol% H₂O was introduced by passing the feed stream through a water saturator at a certain temperature.

3. Results and discussion

3.1. Growth mechanism of cobalt-hydroxide-carbonate

Cobalt-hydroxide-carbonate nanoparticles with various morphologies and sizes were prepared by altering experimental conditions and parameters. To investigate the growth mechanism of the Co₃O₄ nanocatalysts, a series of contrasting experiments were conducted. SEM and TEM techniques were used to monitor the achievement of the particular shape and to enable a comparison with the controlled morphology of cobalt-hydroxide-carbonate precursor.

Fig. 1 shows the morphology of as-prepared cobalt-hydroxide-carbonate nanoparticles using two kinds of cobalt source (Co(NO₃)₂ and CoCl₂) in the presence of surfactant (CTAB). Two different morphologies (nanorods and nanosheets) can be observed. The sample synthesized using CoCl₂ as the cobalt source was composed of a large amount of rods, with average diameters of 40 to 80 nm and lengths of up to several micrometers (Fig. 1(a) and (b)). Fig. 1(c) and (d) display the SEM and TEM images of the sample prepared from Co(NO₃)₂. The obtained cobalt-hydroxide-carbonate is in the form of well-defined rectangular nanosheets, 6–8 μm long and 2–3 μm wide. This indicates that the morphologies of the samples were completely discrepant when different cobalt sources were introduced into the hydrothermal reaction at low temperature.

This result is similar to the observation by Xu et al. [22]. They also found that the crystallinity of cobalt precipitates was affected by the type of counteranion. When Co(NO₃)₂ was dissolved into water with urea (NH₂CO), cobalt carbonate hydroxide hydrate was formed initially by slow hydrolysis of the urea precipitant. With increasing temperature, the NH₄⁺ formation reaction consumes the proton, which makes the pH of the overall solution system over 7.0. The cobalt ions were easily precipitated as cobalt hydroxide in the aqueous solution. Subsequently, a brucite-type cobalt double hydroxide with a lay-

ered structure can be formed, suggested by the appearance of divalent metal cation hydroxides [34–36]. Moreover, anions such as NO₃[−] could be intercalated into the interlamellar spaces, causing the interlayer distance to increase [35,37,38]. This is beneficial for the formation of cobalt-hydroxide-carbonate with a nanosheet morphology.

The NO₃[−] and Cl[−] ions can also affect the morphology by controlling the growth orientation of the particles. In a typical cobalt-hydroxide-carbonate synthesis process, more carbonate anions and hydroxide anions are released from urea as the hydrothermal reaction proceeds. As the concentration of building blocks (carbonate anions and hydroxide anions) becomes sufficiently high, they tend to aggregate into nuclei through homogeneous nucleation. With a continuous supply of the building blocks, these nuclei can serve as seeds for further growth to form larger structures. It should be stressed that the growth of Co(NO₃)₂ seeds is different from the growth of CoCl₂ seeds. In the growth of CoCl₂ seeds, the carbonate anions may act as an inhibitor that selectively decreases the rates of crystal growth along both the {001} and {100} directions, resulting in {010}-elongated nanorods [3,19,29,32]. However, in the growth of Co(NO₃)₂ seeds, the existence of nitrate anions may affect the location of carbonate anions and discount the effect of the inhibitor because of steric hindrance [37]. This would result in inhibition of growth along the {012} direction and the acceleration of the growth along the {110} direction, leading to the formation of nanosheets.

Temperature-resolved study of cobalt-hydroxide-carbonate intermediates was performed with respect to the individual reaction parameters. The TEM images in Fig. 2 illustrate the morphologies of the materials grown in the absence of CTAB at temperatures ranging from 95 to 200 °C (Samples S(Cl)1/S(N)1, S(Cl)2/S(N)2, S(Cl)3/S(N)4, S(Cl)5/S(N)5, S(Cl)7/S(N)7) with a reaction time of 16 h. As shown in Fig. 2(a)–(c), the as-synthesized materials presented rod-like structures with average diameters of 20 to 120 nm and lengths of up to 3 μm. In addition, the top of the nanorod turned from pointed to round as the hydrothermal temperature increased from 95 to 120 °C. The nanosheet particles revealed a similar evolution with increasing reaction temperature. The anoma-

Fig. 1. SEM images (a, b, d, and e) and TEM images (c, f) of obtained cobalt-hydroxide-carbonate, which are hydrothermal products synthesized at 120 or 140 °C, for a reaction time of 16 h, from two kinds of cobalt source in the absence of CTAB. 120 °C for CoCl₂ (a–c) and 140 °C for Co(NO₃)₂ (d–f), respectively.

Fig. 2. TEM images of the hydrothermal products synthesized in the absence of a surfactant for a reaction time of 16 h. (a) 95 °C, (b) 100 °C, and (c) 120 °C for CoCl_2 ; (d) 95 °C, (e) 100 °C, and (f) 140 °C for $\text{Co}(\text{NO}_3)_2$; (g) 160 °C for CoCl_2 , (h) 160 °C for $\text{Co}(\text{NO}_3)_2$, and (i) 200 °C for both $\text{Co}(\text{NO}_3)_2$ (1) and CoCl_2 (2).

lous sheets generally grew up and trended to become rectangular (Fig. 2(d)–(f)). However, when the temperature increased to 160 °C, using either $\text{Co}(\text{NO}_3)_2$ or CoCl_2 as the cobalt source, nanocube-like morphology was observed, as shown in Fig. 2(g) and (h). With a further increase in the temperature, the former morphologies (rod or sheet) vanished, the nanocubes gradually became larger, and the morphology tended to mature. All of the samples became nanocubes when the temperature increased to 200 °C. These results indicate that the reaction temperature only affects the size of the samples when it is lower than 140 °C. With increasing hydrothermal temperature, the cobalt-hydroxide-carbonate rod or sheet slightly grows from primary to mature. However, when the hydrothermal temperature is high enough (160–200 °C), the temperature is a determining factor in the control of the formation of nanocube particles.

Generally, in the homogeneous precipitation of the hydrothermal reaction, the urea hydrolysis provides both carbonate and hydroxyl anions to react with cobalt cations. The formation of orthorhombic cobalt hydroxide carbonate can be formulated as follows [39]: $\text{Co}^{2+} + x\text{OH}^- + 0.5\text{CO}_3^{2-} + 0.11\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OH})_x(\text{CO}_3)_{0.5} \cdot 0.11\text{H}_2\text{O}$. As the temperature rises, the reaction can be expressed as follows: $2\text{Co}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-} \rightleftharpoons \text{Co}_2(\text{OH})_2\text{CO}_3$. The control of the kinetics by the temperature and the concentration of reagents, which control the hydrolysis rate and ratio in the reaction, thus modulate the nucleation and growth processes. At higher temperatures, the crystal shape

anisotropy and the growth orientation of cobalt-hydroxide-carbonate began to dominate.

Wang et al. [40] changed the reaction temperature in a certain range (95–120 °C) to observe the changes in the morphology of synthesized cobalt-hydroxide-carbonate nanorods using CoCl_2 and urea as original materials. The results indicate that the temperature only affects the size and length. As revealed by Li et al. [41], only using cobalt salts and urea, needle-like single-crystalline nanorods with the growth direction along the {010} direction were synthesized at a reaction temperature of 100 °C. As the reaction temperature increased from 140 to 180 °C, cobalt-hydroxide-carbonate nanorod grew epitaxially to a 3D architecture, which was quite different from the samples obtained at 100 and 140 °C.

The TEM images suggest that layer-by-layer growth from small primary nanoparticles to the final cubic structure occurred as the temperature increased. It is generally accepted that, at high temperature, a sudden burst occurs to the nuclei and the nuclei subsequently grow into larger crystallites by an aggregation mechanism [42]. The decomposition rate of the urea in the solution increased with increasing temperature, resulting in the combination of ions and rapid growth. Consequently, the synthesis temperature dramatically affects the crystallite morphology. The results also suggest that the optimal temperature of the products can be determined by the specific shapes.

Fig. 3 shows the variation in the morphology and size of

Fig. 3. TEM images of the hydrothermal products synthesized in the absence of a surfactant at a reaction time of 4 or 24 h. 120 °C for nanorods, 4 h (a) and 24 h (b); 140 °C for nanosheets, 4 h (c) and 24 h (d); 200 °C for nanocubes, 4 h (e) and 24 h (f).

as-synthesized samples as the reaction time increased from 4 to 24 h. In this process, the morphologies of the samples remain the same, while the size of all nanoparticles tends to increase. The diameters of rod-like nanoparticles increase to approximately 180 nm as the reaction time increases to 24 h. Also, the sizes of the sheet crystals grow to several micrometers and the thickness of plates begins to grow (Fig. 4(c) and (d)) during the hydrothermal process after 24 h. The growth of nanocubes is similar to that of sheet crystals. There is no obvious effect on the morphology of the sample series with further increasing reaction time.

To determine the effect of the surfactant on the shape and size of the products, contrasting experiments were conducted in both the absence and presence of surfactant (CTAB). The TEM images in Fig. 4 show three typical morphologies of as-prepared cobalt-hydroxide-carbonate obtained with and without the surfactant with 16 h of reaction time at 120, 140, and 200 °C. Well-dispersed nanoparticles were observed in the presence of CTAB surfactant. Moreover, the products were relatively uniform and well-developed. This finding suggests that nanoparticles with relatively uniform, well-developed morphology and high dispersion can be obtained in the presence of CTAB.

CTAB is an ordinary cationic surfactant and is extensively used as a “shape-inducing” agent to synthesize metal nanopar-

ticles. CTAB can remarkably influence the dispersibility of the produced nanoparticles because of its fine surface activation performance. For metal catalysts, CTAB could enhance the dispersion of the catalyst particles because of the strong binding of CTAB molecules to the metal surface [43]. Sun et al. [44] found that the CTAB surfactant could be selectively absorbed on the crystal face of Co_3O_4 , which finally induces the formation of nanoplates. In this synthesis process, because of the attraction between the cationic CTAB micelles and the negative ions in solution, CTAB micelles were easily absorbed on metal ions. This could enhance the distribution of the ions in the solution. In the present work, it was observed that there were no obvious changes in the morphologies of the precursor particles obtained in the absence and presence of CTAB. The presence of CTAB results in relatively uniform sizes and high dispersion of particles. In this case, the primary role of surfactant CTAB is to make particles grow in multiple directions and reduce agglomeration (dispersing agent).

Fig. 5 provides a generalized summary of the hydrothermal products as a function of cobalt source, temperature, time, and surfactant (CTAB). A comprehensive hydrothermal synthesis process map is provided for the formation of three morphologies of cobalt-hydroxide-carbonate nanoparticles from two kinds of cobaltic solution. Furthermore, the different growth mechanisms of cobalt-hydroxide-carbonate nanoparticles from

Fig. 4. TEM images of the hydrothermal products synthesized with and without the addition of CTAB surfactant at a reaction time of 16 h at 120 °C (a–with vs. b–without for rod formation), 140 °C (c–with vs. d–without for sheet formation) and 200 °C (a–with vs. b–without for cube formation).

Fig. 5. Process map illustrating the development of the shape from two kinds of cobalt sources by hydrothermal method and the effect of cobalt source, temperature, time, and surfactant (CTAB) on the morphology of cobalt-hydroxide-carbonate.

the two cobalt source are also set out. Preparation along with the growth mechanism using different cobalt sources and controlling the experimental parameters (reaction temperature, reaction time, and surfactant) means that the various morphologies (nanorods, nanosheets, and nanocubes) of cobalt-hydroxide-carbonate can be accurately produced. The definite function of the experimental parameters has been stated clearly as well. CTAB additions were found to improve the dispersibility and make the products more uniform. Suitable temperature can promote the morphologies (nanosheets and nanorods) to mature, but further increasing the temperature leads to the formation of nanocubes, for both CoCl_2 and $\text{Co}(\text{NO}_3)_2$ as cobalt sources. The reaction time only affects the size of the obtained nanoparticles.

3.2. Morphologies of Co_3O_4 catalysts

By controlling the optimum synthesis conditions, cobalt-hydroxide-carbonate precursors with typical morphologies (nanosheets, nanorods, and nanocubes) were successfully

synthesized. Co_3O_4 nanoparticles were prepared via a thermal decomposition process on the cobalt-hydroxide-carbonate precursor. The TG-DTA measurements of dried cobalt-hydroxide-carbonate precursors were performed to determine the appropriate calcination temperature. The obtained TGA-DTG curves are shown in Fig. 6. Only one weight loss step can be observed on heating the three precursors to 800 °C, which takes place in the temperature range of 265–370 °C. Therefore, cobalt-hydroxide-carbonate precursors were calcined at 400 °C in air for 4 h to obtain Co_3O_4 nanoparticles.

Fig. 7 shows the TEM and SAED images of various Co_3O_4 samples. All the samples inherit the morphology of the precursors. The lattice spacing of rod-shaped Co_3O_4 nanoparticles is 0.28 nm, which corresponds to the {110} crystal [3,45,46]. From Fig. 7(c), (f), and (i), the {110} planes, which are rich in Co^{3+} active sites, were exposed in all Co_3O_4 samples.

3.3. Physicochemical properties of Co_3O_4 catalysts

The obtained Co_3O_4 samples with three optimal morpholo-

Fig. 6. TGA-DTG curves obtained for the dried precursor: nanosheets (a), nanorods (b), and nanocubes (c).

Fig. 7. TEM, HRTEM, and SAED images of Co_3O_4 samples. (a–c) Co_3O_4 nanorods; (d–f) Co_3O_4 nanosheets; (g–i) Co_3O_4 nanocubes.

gies were further examined by XRD (Fig. 8). The XRD pattern of each sample exhibits characteristics of the Co_3O_4 phase, which is perfectly in agreement with the cubic Co_3O_4 spinel phase (space group $Fd3m$; JCPDS PDF# 42–1467). No other diffraction peaks were detected, confirming the complete decomposition of the cobalt precursors after 400 °C calcination. For all three Co_3O_4 catalysts, the diffraction peaks were sharp, with high intensity, suggesting good crystallinity.

The specific surface area and pore-size distributions of as-synthesized Co_3O_4 samples were calculated according to the Brunauer-Emmett-Teller (BET) method by the N_2 adsorption isotherm at -196 °C, using a Quantachrome Autosorb-iQ instrument. Fig. 9 shows the representative N_2 adsorption-desorption isotherms and pore-size distributions of the three samples, and their textural properties are given in Table 3. Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) formula. The isotherms for the nanosheet and nanorod samples belong to type-II of BET's classification, with a type H3 hysteresis loop in the relative

pressure (p/p_0) range of 0.8–1.0, characteristic of particulate materials. These pores may originate from the interstices among the self-assembling nanoparticles, which usually present a broad pore distribution because of interparticle voids.

Fig. 8. XRD patterns of Co_3O_4 samples with different morphologies.

Fig. 9. N_2 adsorption-desorption isotherms (a) and BJH pore-size distributions (b) of as-prepared Co_3O_4 samples.

For the nanocube sample, a small hysteresis loop in the p/p_0 range of 0.6–0.8 was observed, which is related to the capillary condensation taking place in mesopores. This suggests the presence of mesopores in the nanocube sample, although the content is very limited. The specific surface area of the Co_3O_4 nanosheets (32.5 m^2/g) is noticeably higher than those of nanorods and nanocubes (15.5 and 7.7 m^2/g , respectively). The textural properties may be caused by the irregular stacking of the particles in the calcination process.

XPS analysis is a powerful means for characterizing the surface properties of catalysts. Fig. 10 presents the XPS spectra of the Co 2p and O 1s electronic levels of Co_3O_4 nanocubes, nanorods, and nanosheets. As shown in Fig. 10(A), two sharp peaks at 780.1 and 795.0 eV were observed in all three Co_3O_4 samples, which correspond to the Co 2p_{3/2} and Co 2p_{1/2} spin-orbit peaks of Co_3O_4 spinel [5]. This result indicates that the surface

of the three Co_3O_4 nanocatalysts comprise both Co^{2+} and Co^{3+} [47,48]. The spectra of Co 2p_{3/2} can be fitted to five peaks, which can be attributed to Co^{3+} , Co^{2+} , Co–OH phase, and shake-up satellites of Co^{2+} and Co^{3+} , respectively (as the values of binding energy peak increase from low to high) [47–53]. Table 2 shows the binding energy position of each peak and the content of the different Co species. The nanosheet sample showed the largest relative strength of the Co^{3+} peak among the three samples, indicating a relatively higher concentration of Co^{3+} . For the nanocube sample, the peak attributed to the Co–OH phase disappeared.

The XPS spectra of the O 1s electronic levels of the three Co_3O_4 samples are shown in Fig. 10(B). Three component peaks in various positions are observed, which indicates the presence of three types of oxygen species on the surface of the Co_3O_4 samples. The peak with low binding energy (denoted OI) can be

Fig. 10. Co 2p (A) and O 1s (B) XPS spectra of Co_3O_4 nanorods (a), nanocubes (b), and nanosheets (c).

Table 2

Binding energy positions and relative contents of various Co and O species over the three Co_3O_4 samples.

Species	Co_3O_4 nanorods		Co_3O_4 nanocubes		Co_3O_4 nanosheets	
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
Co^{3+}	779.4	22.62	779.6	25.29	779.6	25.86
Co^{2+}	780.3	29.80	780.8	42.69	780.7	26.33
Co–OH	781.7	26.63	—	—	782.0	27.79
Satellite peak of Co^{2+}	785.0	16.24	783.5	25.65	785.8	16.03
Satellite peak of Co^{3+}	789.6	4.69	789.5	6.35	789.8	3.97
Adsorbed oxygen	529.7	38.20	529.8	57.22	529.9	31.50
Lattice oxygen of Co_3O_4	530.5	28.83	531.1	26.48	530.8	40.27
Hydroxyl (OH) species	531.6	32.96	532.5	16.28	532.6	28.28

Fig. 11. H₂-TPR (a) and CO-TPR (b) profiles of Co₃O₄ nanocrystals.

assigned to the atomically adsorbed oxygen on the surface of samples [54]. The signal at 530.5 eV (denoted OII) indicates the presence of lattice oxygen [55]. The third peak (denoted OIII) with low intensity can be attributed to the presence of surface hydroxyl (OH) species, which probably lead to the generation of Co–OH [53,56]. The quantification of each surface cobalt and oxygen species was performed, as shown in Table 2. The results demonstrate that, among the three samples, Co₃O₄ nanocubes contain the highest concentration of surface adsorbed oxygen, while the nanosheet sample reveals the highest concentration

of lattice oxygen.

Fig. 11 compares the H₂-TPR and CO-TPR profiles of the three Co₃O₄ samples. In Fig. 11(a), all three samples exhibit two consecutive hydrogen consumption peaks, which correspond to the sequential conversion of Co³⁺ to Co²⁺ and Co²⁺ to Co⁰, respectively. For the Co₃O₄ nanocube and nanorod samples, similar reduction peaks of Co²⁺ to Co⁰ at 542 °C are observed. Nevertheless, for the nanosheet sample, the reduction temperature of Co³⁺ to Co²⁺ and Co²⁺ to Co⁰ decreases to 389 and 468 °C, respectively. As shown in Fig. 11(b), a similar trend to the one presented in the H₂-TPR was also found in the CO-TPR profiles. Two peaks can be observed for all three samples, suggesting the two-step reduction of Co³⁺. The changes in the reduction temperatures also confirm that the reducibility of Co₃O₄ nanocubes and nanosheets is superior to that of their nanorod counterparts.

By quantitatively analyzing the reduction peaks of the H₂-TPR profiles, the H₂ consumption for each peak can be obtained, as summarized in Table 3. Obviously, the H₂ consumption of the first reduction peak increased in the order of Co₃O₄ nanosheets > nanocubes > nanorods. This result suggests the highest concentration of surface Co³⁺ sites on the Co₃O₄ nanosheets among the three samples, which is consistent with the results of XPS analysis. The reduction degree of Co³⁺ and Co²⁺ in the different samples was obtained by calculating the ratio of the actual H₂ consumption to the theoretical values, as shown in Table 4. Apparently, 22.53% of the cobalt ions in the Co₃O₄ nanosheets were reduced by H₂ during the H₂-TPR process, and the reduction degree of Co³⁺ to Co²⁺ reached 24.80%, suggesting that Co₃O₄ nanosheets exhibit the best reduction performance. For the nanocubes, the reduction degree of cobalt ions reached 17.92%, which is slightly lower than that for the Co₃O₄ nanorods (23.66%). However, the nanocubes (17.20%) show higher reducibility of Co³⁺ than the nanorod samples (17.20% vs. 12.75%). This result suggests that the Co³⁺ in the nanocube sample is more reducible than that in the nanorod sample, which can be used to explain the relatively higher catalytic activity for CO oxidation over the nanocube sample (Fig. 13).

To gain further insight into the mobility of oxygen in the

Table 3

BET surface area, average pore size, reaction rate, E_a , and TOF values for CO oxidation over the Co₃O₄ samples with different morphologies.

Sample	BET surface area (m ² /g)	Average pore size (nm)	Reaction rate ($\times 10^{-7}$ mol·g ⁻¹ ·s ⁻¹)	E_a (kJ/mol)	TOF values ^a ($\times 10^{-4}$ s ⁻¹)
Nanosheets	32.5	6.2	6.05	46.6	1.79
Nanorods	15.5	3.3	—	—	—
Nanocubes	7.7	2.3	4.83	47.5	1.34

^a The values were calculated based on surface area.

Table 4

Surface element compositions, H₂ consumption, and reduction degree of H₂-TPR over the Co₃O₄ samples.

Sample	H ₂ consumption ^a (mmol/g)		Reduction degree ^b (%)		Total reduction degree (%)	Co ³⁺ /Co ²⁺ molar ratio
	Co ³⁺ –Co ²⁺	Co ²⁺ –Co ⁰	Co ³⁺ –Co ²⁺	Co ²⁺ –Co ⁰		
Nanosheets	2.45	6.75	24.80	21.95	22.53	0.98
Nanocubes	1.70	5.62	17.20	18.27	17.92	0.59
Nanorods	1.26	8.41	12.75	27.34	23.66	0.75

^a The data were estimated by quantitatively analyzing the H₂-TPR profiles. ^b The values were the ratio of the actual H₂ consumption during H₂-TPR to the theoretical values.

Fig. 12. O₂-TPD profiles of the three Co₃O₄ nanocatalysts.

Co₃O₄ catalysts, O₂-TPD tests were carried out (Fig. 12). The TPD profile for each catalyst showed two oxygen stripping peaks in the temperature range below 500 °C and higher than 850 °C, respectively. The former peak can be attributed to desorption of surface oxygen species (e.g., adsorbed oxygen and surface lattice oxygen) of catalysts, and the latter corresponds to bulk oxygen consumption by catalysts [57]. A comparison of the tripping peaks of surface oxygen species (first peak) for all three samples indicates that Co₃O₄ nanosheets have more abundant surface oxygen species and higher oxygen mobility.

3.4. Catalytic activity

Fig. 13 shows the catalytic activity of the three Co₃O₄ samples for CO oxidation at various GHSVs. For a GHSV of 33000 h⁻¹, the CO oxidation over the nanosheet sample took place at 47 °C. As the temperature increased, the CO conversion rapidly increased and eventually reached 100% at 106 °C. The CO oxidation over the Co₃O₄ nanocube sample began at a similar temperature, but its complete conversion temperature was delayed to 114 °C. For the Co₃O₄ nanorod sample, the starting temperature for CO oxidation was as low as 130 °C. The values of *T*₁₀ (the temperature when the CO conversion equals 10%) for Co₃O₄ nanosheets, nanocubes, and nanorods are 65, 69, and 146 °C, respectively. These results indicate that Co₃O₄ nanosheet and nanocube samples are markedly more active than the nanorod sample.

As shown in Fig. 13(b) and (c) (GHSV = 50000 and 66000 h⁻¹, respectively), the activity of the catalysts follows the same sequence: nanosheets > nanocubes > nanorods. With an increase in GHSV, the initial reaction temperature for each sample slightly decreased. The relationships between GHSV and *T*₅₀ and *T*₉₀ (corresponding to CO conversion = 50% and 90%, respectively) for all the samples are summarized in Fig. 13(d). The catalytic activity of Co₃O₄ nanosheets is not sensitive to the changes in GHSV, and almost no change in the *T*₅₀ and *T*₉₀ values was observed when the GHSV increased from 33000 to

Fig. 13. Catalytic activity for CO oxidation over the three Co₃O₄ nanocatalysts at GHSV = 33000 h⁻¹ (a), 50000 h⁻¹ (b), and 66000 h⁻¹ (c); and (d) *T*₅₀ and *T*₉₀ over the three catalysts at various GHSVs.

50000 h⁻¹. In contrast, an obvious decrease in the T_{50} and T_{90} values was detected over the Co₃O₄ nanocube and nanorod samples with an increase in GHSV. This indicates that CO oxidation over the Co₃O₄ nanosheet catalyst may not be primarily controlled by the diffusion of the reactants, which may be related to the relatively larger surface area and thinner thickness of the nanosheets. For the nanocube and nanorod catalysts, the catalytic activity decreased with increasing GHSV because of the diffusion effect. From the perspective of T_{50} and T_{90} values, the Co₃O₄ nanosheet catalyst showed comparable or higher activity than the related Co₃O₄ catalysts (without additional pretreatments) at temperatures above room temperature under similar conditions [1,4,10,14].

CO conversion over Co₃O₄ is achieved via Co³⁺ exposed active sites, which can absorb CO sufficiently [3,58]. When the surface lattice oxygen is transferred from Co³⁺ to Co²⁺, the resulting oxygen vacancies are subsequently supplemented with reactant O₂ [58]. Therefore, the formation of oxygen vacancies and the active Co³⁺ sites on Co₃O₄ nanoparticles are the rate-limiting step for determining the catalytic CO oxidation [1]. As observed by XPS, TPR, and TPD techniques, the Co₃O₄ nanosheets exposed many more Co³⁺ sites and a higher concentration of surface oxygen species. These features allow the nanosheet sample to have relatively high catalytic activity for CO oxidation. To further investigate the catalytic performance of the as-prepared catalysts, a kinetic experiment was conducted on Co₃O₄ nanosheets and nanocubes at 65 °C under the condition of a CO conversion of no more than 10%. Moreover, the oxidation of CO in the presence of excessive oxygen (CO/O₂ volume ratio = 1/10) was generally considered to obey a first-order reaction mechanism with respect to CO concentration (C_{CO}): $r = -kC_{CO} = -A \exp(-E_a/RT)C_{CO}$, where r , k , A , and E_a are the reaction rate (mol/s), rate constant (s⁻¹), pre-exponential factor, and apparent activation energy (kJ/mol), respectively [6]. The reaction rates and their E_a over the two samples are presented in Table 3. The CO reaction rate over Co₃O₄ nanosheets at 65 °C is higher than that over nanocubes, which is in accordance with the Co³⁺/Co²⁺ molar ratio (Table 4). Moreover, the value of Co₃O₄ nanosheets is comparable to that of Co₃O₄ nanocubes with predominantly exposed {001} planes reported by Hu *et al.* (6.20 vs. 6.05×10^{-7} mol/g⁻¹s⁻¹) [4]. This indicates that more active Co³⁺ species on the Co₃O₄ nanosheets is beneficial to catalytic oxidation. The E_a values demonstrate that oxidation of CO took place more easily over Co₃O₄ nanosheets than over nanocubes. For the Co₃O₄ nanorods, CO oxidation cannot occur at 65 °C. As shown in Table 3, the TOF value for the nanosheet sample is 1.79×10^{-4} s⁻¹, which is much higher than that for the nanocube sample (1.34×10^{-4} s⁻¹), indicating more abundant active sites on the nanosheets.

Because the Co₃O₄ nanosheets showed the best activity for CO oxidation among the three samples, the stability of the Co₃O₄ nanosheet catalyst in the absence or presence of a stream (0.5 vol% water vapor) was investigated at 88 °C. The results are shown in Fig. 14. Approximately 80% CO conversion to CO₂ was observed during the initial 50 h in the absence of the stream, and no obvious decrease in the catalytic activity

Fig. 14. On/off-stream CO oxidation at 88 °C over Co₃O₄ nanosheets at GHSV = 33000 h⁻¹.

was observed. On the one hand, this suggests that the Co₃O₄ nanosheets have excellent stability for CO oxidation under dry conditions. On the other hand, the CO conversion tended to decrease when water vapor was co-introduced to the reaction system. After the water vapor flow continued for 5 h, the CO conversion decreased to 12%. However, a sharp rise in CO conversion was observed when the water vapor flow was stopped. This result indicates that Co₃O₄ is very sensitive to the presence of moisture, which has been reported by recent studies [3,59,60]. The water molecules were easily adsorbed to the surface of Co₃O₄ when water vapor was co-introduced to the reaction system. Subsequently, the water molecules may have reacted with CO₂ to form carbonate species. With an increase in test duration, the active sites on the surface of Co₃O₄ were gradually covered by the formed carbonate species [61], resulting in a decrease in the catalytic performance for CO oxidation. However, there was apparent improvement in activity during the subsequent operation under dry conditions. This result suggests that the carbonate species can be gradually removed from the active sites in the absence of moisture.

4. Conclusions

Cobalt-hydroxide-carbonate with various morphologies (nanorods, nanosheets, and nanocubes) were successfully synthesized via a facile hydrothermal method. The Co₃O₄ nanoparticles were obtained by thermal decomposition of the cobalt-hydroxide-carbonate precursors. The samples after calcination perfectly inherited the morphology of the precursors. A “process map” for the hydrothermal synthesis of co-

balt-hydroxide-carbonate with various morphologies from $\text{Co}(\text{NO}_3)_2$ or CoCl_2 solution was presented via varying the experimental conditions (such as cobalt source, temperature, time, and surfactant). The formation of rod or sheet morphology was strongly affected by the cobalt source, while the cobalt-hydroxide-carbonate cubes were primarily determined by the hydrothermal temperature. CTAB addition was found to improve the dispersibility and make the products more uniform. The reaction time only affected the size of the obtained nanoparticles. The Co_3O_4 nanosheets contain high concentrations of Co^{3+} , abundant adsorbed oxygen species, high reducibility, and superior oxygen desorption capacity, revealing high catalytic activity for CO oxidation.

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Graphical Abstract

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Effects of Co_3O_4 nanocatalyst morphology on CO oxidation: Synthesis process map and catalytic activity

Liangpeng Zeng, Kongzhai Li*, Fan Huang, Xing Zhu, Hongcheng Li
Kunming University of Science and Technology

We successfully draw a hydrothermal synthesis process map of Co_3O_4 nanoparticles with various morphologies and investigate the effects of Co_3O_4 nanocatalyst morphology on CO oxidation. Co_3O_4 nanosheets shows much higher catalytic activity for CO oxidation than nanorods and nanocubes, due to more abundant Co^{3+} in the surface, much higher reducibility and better oxygen desorption capacity.

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Co₃O₄纳米催化剂催化CO的形貌效应：合成过程和催化活性

曾良鹏^{a,b}, 李孔斋^{a,b,*}, 黄 樊^{a,b}, 祝 星^{a,b}, 李宏程^{a,b}

^a昆明理工大学省部共建复杂有色金属资源清洁利用国家重点实验室, 云南昆明650093

^b昆明理工大学冶金与能源工程学院, 云南昆明650093

摘要: 通过催化剂将CO转化为无毒气体仍然是目前减少CO污染的主要手段。随着纳米技术的快速发展, 纳米催化剂因其在催化反应中呈现出的独特结构效应(如形貌效应、尺寸效应等)而受到人们的广泛关注。已有大量研究表明, 纳米Co₃O₄作为一种非贵金属氧化物催化剂具有强烈的催化形貌效应, 展现出优异的CO低温催化活性。因此, 通过合理的设计来调控催化剂粒子的形貌, 从而进一步改善催化剂的性能已成为近年来催化剂领域的重要研究方向。对于Co₃O₄纳米催化剂的可控制备, 水热法具有反应温和、操作简便和产品形貌易控等特点。早期的研究主要围绕于Co₃O₄形貌的可控合成以及不同形貌Co₃O₄催化剂对其催化活性产生的影响, 较少有对其形貌形成机制的报道。特别是在水热反应中, 系统研究各反应参数对催化剂各异形貌的形成影响鲜有报道。

本文在前人的研究基础上, 重点研究了水热反应过程中各主要反应参数对产品形貌控制的影响, 绘制了一副不同形貌Co₃O₄材料的合成过程图, 并研究了Co₃O₄纳米催化剂催化CO氧化的形貌效应。通过水热法先成功合成了三种不同形貌(纳米棒、纳米片和纳米立方)的碱式碳酸钴纳米粒子, 然后将其焙烧得到了Co₃O₄纳米粒子。采用扫描电子显微镜(SEM), 透射电子显微镜(TEM), X射线粉末衍射仪(XRD), 程序升温还原(H₂-TPR和CO-TPR), 氮气吸附-脱附比表面积测试(BET), 氧气程序升温脱附(O₂-TPD), X射线光电子能谱(XPS)等表征手段研究了不同反应参数对纳米碱式碳酸钴前驱体形貌形成的作用和各异形貌Co₃O₄纳米粒子在催化CO氧化反应中催化性能的差异及原因。

结果表明, Co₃O₄较好地继承了碱式碳酸钴的形貌, 在较低温度条件下(≤ 140 °C), 钴源(CoCl₂或Co(NO₃)₂)是影响前驱体形貌的关键因素, 反应时间只对粒子的尺寸产生较大影响。低温下, CoCl₂作为钴源易诱导生产纳米棒状碱式碳酸钴, 而Co(NO₃)₂则有利于纳米片状生成。当温度高于140 °C后, 无论何种钴源, 最终均制得纳米立方体。表面活性剂CTAB对前驱体的均一性和粒子的分散性产生重要影响, 加入CTAB后得到的产品尺寸更均一, 形貌更加规整。对比于其他两种形貌的

样品, Co_3O_4 纳米片显示出更好的CO催化氧化活性.

XPS结果表明, 各形貌 Co_3O_4 纳米材料的表面组成存在明显差异, 活性物种 Co^{3+} 含量的不同是影响催化活性差异的重要原因. Co_3O_4 纳米片具有更多的 Co^{3+} 活性位, 立方纳米 Co_3O_4 表面吸附氧含量较高, Co_3O_4 纳米棒则暴露出相对更多的 Co^{2+} . 因此, 在三种形貌催化剂上CO氧化反应中, Co_3O_4 纳米片表现出最优的催化活性, 纳米立方次之, 而纳米棒最差. H_2 -TPR, CO-TPR和 O_2 -TPD等结果也表明, Co_3O_4 纳米片拥有更强的还原性能和脱附氧能力, 其次是纳米立方 Co_3O_4 . 这与XPS结果一致, 证实了不同形貌 Co_3O_4 纳米催化剂上暴露活性位的数量和表面氧物种的不同是造成彼此间催化CO氧化活性差异的重要原因. 此外, 通过稳定性测试发现 Co_3O_4 纳米片具有较高的催化稳定性, 在水蒸气存在的情况下 Co_3O_4 纳米片逐渐失活, 但随后在干燥条件下其催化活性又逐渐得到恢复.

关键词: 四氧化三钴纳米催化剂; 合成过程地图; 形貌效应; 催化活性; 一氧化碳氧化

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*通讯联系人. 电话/传真: (0871)65153405; 电子信箱: kongzhai.li@aliyun.com, kongzhai.li@foxmail.com

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