Catalysis Communications 42 (2013) 116–120

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Synthesis of Co_3O_4 nanotubes and their catalytic applications in CO oxidation

Yongge Lv, Yong Li, Wenjie Shen *

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

ARTICLE INFO

Article history:
Received 3 July 2013
Received in revised form 20 August 2013
Accepted 21 August 2013
Available online 27 August 2013

Keywords:
Co_3O_4
Nanotubes
Kirkendall effect
CO oxidation
Morphology-dependence

ABSTRACT

Co_3O_4 nanotubes with the inner of about 8 nm and the length of 200–500 nm were synthesized by oxidizing Co nanowires. Analyses on the structural evolution of the intermediates at different intervals identified that the formation of Co_3O_4 nanotubes followed a nanoscale Kirkendall effect. The outward diffusion of cobalt species was faster than the inward diffusion of oxygen species, resulting in the formation of nanovoids at the initial stage and subsequently the tubular structure. The Co_3O_4 nanotubes showed a higher activity and stability than the spherical nanoparticles in CO oxidation, primarily due of the facile redox feature.

1. Introduction

Tricobalt tetraoxide (Co_3O_4) shows morphology-dependent catalysis in chemical reactions such as CO oxidation [1–6], CH_4 combustion [7], hydrodesulfurization of fuels [8] and selective reduction of NO with NH_3 [9]. In these applications, the reaction rate was intimately associated with the morphology of the oxide particles. For example, Co_3O_4 nanorods containing substantial amounts of exposed {110} planes exhibited superior catalytic activity for low-temperature CO oxidation to the spherical particles mainly enclosed by the {111} facets [1].Similarly, Co_3O_4 nanobelts [2], nanosheets [3], nanowires [4] and nanocubes [5] also showed distinct shape effect in CO oxidation. The activity of Co_3O_4 for catalyzing CH_4 combustion follows the order: nanosheets > nanobelts > nanocubes [7]. These results clearly confirm that controlling the morphology of nanostructured cobalt oxides is beneficial to expose more catalytically active sites.

In recent years, great efforts have been paid to tune the shape of Co_3O_4 nanomaterials [10–15]. Among them, Co_3O_4 nanotubes have received particular attention because of the hollow interior and the high aspect ratio [15]. To date, Co_3O_4 nanotubes with the outer diameter in 30–300 nm range have typically been fabricated by topotactic transformation [11], hydrothermal synthesis [12], microemulsion [13] and template-directed synthesis [14]. The Kirkendall effect was also applied to prepare Co_3O_4 nanotubes. For example, necklace-like Co nanowires were oxidized into Co_3O_4 nanotubes with an outer diameter of about 40 nm [16]. Calcination of $CoC_2O_4 \cdot 2H_2O$ nanorods produced Co_3O_4 nanotubes with an outer diameter of about 200 nm [17]. It was proposed that the hollow nanostructure was created inside the solid nanoparticles because of the difference in the diffusion rates of the metal and oxygen ions [18–22]. However, little is known on the oxidation process of one-dimensional Co nanostructures to Co_3O_4 nanotubes. In this work, we synthesized Co_3O_4 nanotubes with the inner of only about 8 nm by oxidizing Co nanowires through the Kirkendall effect. The influence of the synthetic parameters on the morphology of the resulting oxides was investigated. The as-synthesized Co_3O_4 nanotubes exhibited superior catalytic activity and durability in CO oxidation at room temperature.

2. Experimental

2.1. Catalyst preparation

Co nanowires were prepared by liquid-phase reduction of cobalt acetate in 1,2-propanediol under solvothermal conditions using Ru as the heterogeneous agent and stearic acid as the surfactant, as we previously reported [23]. Co_3O_4 nanotubes were typically prepared by oxidizing the Co nanowires in a U-type quartz tubular reactor. 100 mg of Co nanowires were heated from room temperature to 300 °C at a rate of 1 °C/min under a flow of 1.0 vol.% O_2/N_2 (50 ml/min), and maintained at that temperature for 48 h, yielding Co_3O_4 nanotubes.

Spherical Co_3O_4 nanoparticles were prepared by aqueous-phase precipitation of $Co(OAc)_2 \cdot 4H_2O$ with sodium carbonate; the precipitate was dried at 120 °C overnight and calcined at 450 °C in air [1]. The reference Ru/Co_3O_4 sample with a Ru/Co mole ratio of 0.5% was prepared by impregnating certain amount of aqueous $RuCl_3$ solution on the spherical Co_3O_4 nanoparticles, followed by drying at 100 °C for 4 h and calcination at 300 °C in air for 4 h.

---

* Corresponding author. Tel.: +86 411 84379085; fax: +86 411 84694447.
E-mail address: shen98@dicp.ac.cn (W. Shen).

1566-7367/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2013.08.017

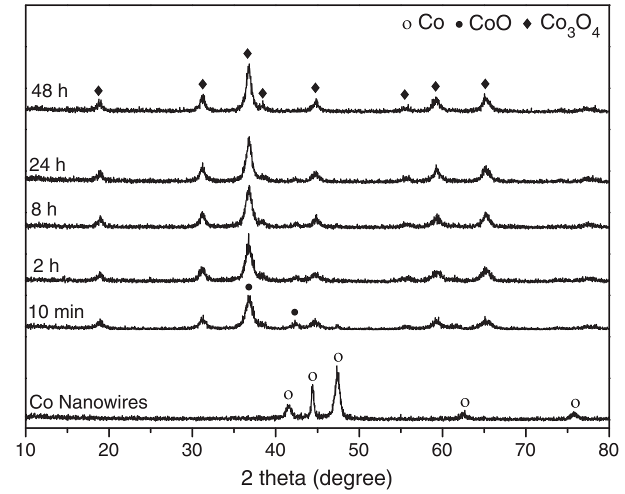

Fig. 1. XRD patterns of the Co nanowires and the samples obtained at different intervals during the oxidation process at 300 °C.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a D/MAX-2500/PC diffractometer (Rigaku) operated at 40 kV and 200 mA, using a Cu Kα radiation.

Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G^2 Spirit microscope operated at 120 kV. High-resolution TEM (HRTEM) images were recorded on a FEI Tecnai G^2 F30S-Twin microscope operated at 300 kV.

N_2 sorption isotherms were recorded at −196 °C using an ASAP 2000 instrument (Micromeritics). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation from the nitrogen adsorption isotherm.

Temperature-programmed reduction of hydrogen (H_2-TPR) measurement was performed with an AutoChem II 2920 instrument (Micromeritics). 20 mg samples were heated to 300 °C (10 °C/min) under a N_2 flow (30 ml/min), and kept at that temperature for 0.5 h. After cooling down to room temperature and introducing the reduction agent of a 10 vol.% H_2/N_2 (30 ml/min) mixture, the temperature was raised to 700 °C at a rate of 10 °C/min. The amount of hydrogen consumed was monitored with a thermal conductor detector.

2.3. Catalytic test

CO oxidation was performed in a fixed-bed U-type quartz tubular reactor under atmospheric pressure. 200 mg samples (40–60 mesh) were loaded and pre-treated with a 1.0 vol.% O_2/N_2 (50 ml/min) gas mixture at 300 °C for 0.5 h. After cooling down to room temperature, the reaction gas of 1.0 vol.% CO/2.5 vol.% O_2/He (50 ml/min) was introduced. The amounts of CO, CO_2 and O_2 in the inlet and outlet streams were measured by an online gas chromatograph.

3. Results and discussion

3.1. Co_3O_4 nanotubes

The oxidation process of Co nanowires to Co_3O_4 nanotubes was examined by TEM and XRD techniques (Figs. 1 and 2). Co nanowires exhibited characteristic diffraction lines of hexagonal close-packed (*hcp*) Co (JCPDS

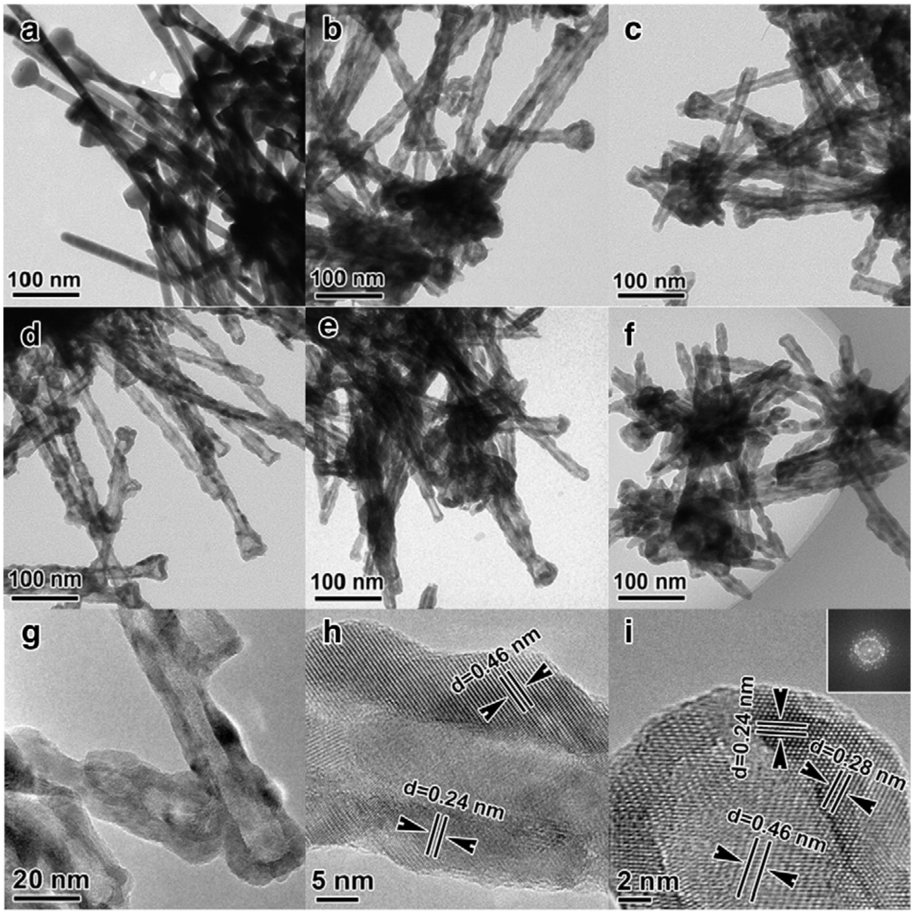

Fig. 2. TEM images of the Co nanowires (a) and the samples obtained at 10 min (b), 2 h (c), 8 h (d), 24 h (e) and 48 h (f) during the oxidation process at 300 °C. (g–i) HRTEM images of the Co_3O_4 nanotubes.