Applied Catalysis B: Environmental 84 (2008) 790–796

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Enhanced carbon monoxide oxidation activity over gold–ceria nanocomposites

Zhi Chen, Qiuming Gao *

State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

ARTICLE INFO

Article history:
Received 1 April 2008
Received in revised form 13 June 2008
Accepted 13 June 2008
Available online 22 June 2008

Keywords:
Gold–ceria nanocomposites
Enhanced catalytic activity
Low content of Au
CO oxidation

ABSTRACT

The composites with nanosized gold loaded in nanoporous ceria were prepared on a large scale by a facial and environment-benign sol–gel process. These materials were characterized by XRD, ICP, BET, UV–vis absorption, XPS, HRTEM and EDX. The main factors such as size and surface state of the Au and defect in the ceria could be adjusted by acid treatment of the composites in ascorbic acid solution to improve the activity and decrease the content of noble metal Au in the materials. Enhanced catalytic activities were obtained for the CO oxidation reaction over the catalysts due to the small crystal sizes with narrow size distributions of gold nanoparticles, a large amount of defects in the nanoporous ceria support, as well as a high ratio of Au^{3+}/Au^0 in the nanocomposites.

1. Introduction

Catalysts with high performance and low cost for environmental clean-up are a topic of increasingly world-wide interests from logical design based on the relationship between structure at the molecular level and catalytic property. Gold was traditionally thought as catalytically inert in chemical processes, while highly dispersed Au nanoparticles supported on metal oxides showed exceptionally high activities for several kinds of reactions, including CO oxidation at low temperature. These phenomena are attributed to the quantum size confinement effect [1–3]. As to the CO oxidation over the Au catalyst, the impacting factors influencing the activity depend on the preparation method, surface defect site and changed electronic structure of the small particles, interaction between the metal and support, and so forth [4–6]. The effective supports were usually the oxides of group VIII and 3d transitional metals such as Fe_2O_3, ZrO_2, ZnO, TiO_2, Co_3O_4 and CeO_2 [7–9].

As one kind of the effective support, CeO_2 samples possessed many attractive properties which make them highly promising in applications such as solid-oxide fuel-cell, automotive three-way catalyst, ultraviolet absorber, oxygen sensor, etc. Particularly, the high oxygen storage abilities of CeO_2 samples associated with their rich oxygen vacancies and low redox potentials between the Ce^{3+} and Ce^{4+} have been hence used in the exhaust gas treatments. Nanocrystalline CeO_2 samples are being expected to pose superior physical properties. Some related results have been obtained for them, such as blue-shift in the UV absorption spectra, lattice expansion, Raman-allowed modes shifting and broadening, four orders of magnitude increase in the electronic conductivity and pressure-induced phase transformation, which are partially attributed to the quantum size effect and surface effect [10–12].

The activity of CO oxidation could be enhanced two orders of magnitude when depositing gold nanoparticles on mesoporous CeO_2 nanocrystals comparing with those supported regular ceria sample or prepared by coprecipitation [13]. Although high catalytic activity at low temperature of this composite was observed, the catalytic resistance at high temperature is also very important which is specially emphasized for the waste gas disposal of automobile. However, there were few reports on the fast catalysis of CO oxidation at a high content of CO with high temperature resistance although high catalytic activity at low temperature was observed, favoring elimination of waste gas for automobile and other applications. The fabrication of catalyst in low Au loading with high on-stream activity and high speed of gas flow may be important for the application. Besides, the methods can be industrially applied if the catalyst shows good activity, productivity and durability. Recently, the preparation and characterization of the nanosized CeO_2 samples attracted great interests for their improved properties. Optical and catalytic performances of CeO_2 nanocrystals with the sizes of about 4–5 nm were studied [10]. Nanowires and nanotubes of CeO_2 were formed and their large-scale syntheses were also realized [14–16]. In this paper, we reported the preparation of uniform-sized CeO_2 nanocrystals with porous structures. Using them as supports, the $Au–CeO_2$ nanocomposite catalysts showed high, durable and

---

* Corresponding author. Tel.: +86 21 52412513; fax: +86 21 52413122.
E-mail address: qmgao@mail.sic.ac.cn (Q. Gao).

0926-3373/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2008.06.012

high temperature resistance catalytic activity in the reaction of CO oxidation.

2. Experimental

2.1. Preparation

The nanoporous CeO_2 samples were prepared via a modified precipitant process. In a typical experiment, 0.91 g of $Ce(NO_3)_3 \cdot 6H_2O$ was first added into 10 mL of deionized water. The solution was heated to 100 °C and kept for 5 min with constant stirring under reflux condition. Then, 7.0 mL of $NH_3 \cdot H_2O$ (5 mol.%) was added with vigorous stirring. And then, the reaction was terminated after 3 min by cooling down the solution to 0 °C. At last, the precipitation powders were recovered by centrifugation, washed with deionized water for three times to remove the additional ions, and dried at 50 °C overnight. The yield was about 90%.

For preparation of the gold-loaded ceria composite, 0.33 g of the as-synthesized ceria samples were put into 20 mL of $HAuCl_4$ solution including 0.1 mmol of Au. Before mixing, the pH value of the solution was adjusted to 7 by using 0.2 M NaOH solution. The mixture was constantly stirred for 2 d at room temperature. The solid powders (denoted as Au–CeO_2-N, where N means neutral) were recovered by centrifugation after washed with deionized water for three times.

Acid treatment was chosen to adjust the composition and structure of the composite. 0.33 g of the as-synthesized ceria samples were put into 20 mL of $HAuCl_4$ solution including 0.1 mmol of Au with pH 7, then the mixture was constantly stirred at room temperature for 2 d, and then the solid powders were separated by centrifugation and washed with deionized water. After that, the obtained solid powders were put into 30 mL of 8.0 mM ascorbic acid solution and stirred constantly for 2 h. The acid-treated powders (denoted as Au–CeO_2-A, where A means acidic) were separated by centrifugation and washed with deionized water for three times.

Both Au–CeO_2-N and Au–CeO_2-A were preserved at room temperature. Large-scale (20 times) preparation of the samples was also carried out by the facial and environment-benign process, where no hazard sources were chosen.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2200 PC with Cu Kα radiation. Inductively coupled plasma (ICP) analyses were operated on a Vista Axial CCD Simultaneous ICP-AES spectrometer. Nitrogen-sorption isotherms were measured at 77 K on a Micromeritics ASAP-2020M instrument under continuous adsorption conditions. Before measurements, the samples were outgassed at 383 K for 5 h under vacuum. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The mesopore and micropore sizes are defined as the positions of the maximum in the pore-size distribution and calculated by the Barrett-Joyner-Halenda (BJH) and Horvath–Kawazoe (HK) methods, respectively, based on the adsorbed branches of the isotherms. Ultraviolet–visible (UV–vis) reflectance spectra of the samples were conducted on a Shimadzu UV-3101 instrument equipped with an integrating sphere using $BaSO_4$ as the reference. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Microlab 310-F Scanning Auger Microprobe equipped with a 150 W (15 kV by 10 mA) aluminum Kα (1486.6 eV) anode as the X-ray source, using a pass energy of 50 eV with a step size of 0.1 eV. The samples were analyzed in the XPS chamber under an ultrahigh vacuum (10^{-7} Pa base pressure). The samples were dried at 40 °C under vacuum for 8 h before the XPS measurement. The XPS spectra of Ce 3d were calibrated by using C 1s spectrum as the standard. High-resolution transmission electron microscopy (HRTEM) images were taken by using a field emission JEM 2010 electron microscope at 200 kV. Energy dispersive X-ray (EDX) fluorescence spectroscopy was performed on an OXFORD Links ISIS EDX attached to the HRTEM.

2.3. Catalytic reactions

The catalysts were monitored in a fixed-bed quartz tubular reactor with diameter of 12 mm. About 100 mg of the catalysts were placed in the reactor. The reactant gases (2.8% CO, 7.2% O_2 and 90% N_2) went through the reactor with space velocity of 86 mL min^{-1} (ambient temperature and pressure), corresponding to a space velocity of 51 600 mL h^{-1} $g_{cat}{}^{-1}$. The concentrations of the outlet CO after stepwise changes in the reaction temperatures were analyzed with an on-line gas chromatograph (SP-6890, molecular sieves 13X column) equipped with a thermal conductivity detector (TCD). Multiple concentrations of the outlet gas were taken and averaged to ensure that the catalytic system had reached steady state. The conversion of CO was calculated using the integrated peak area differences between the CO fed initially and the effluent CO from the reactor with an accuracy of about ±5%.

3. Results and discussion

3.1. XRD analyses

XRD patterns of the as-prepared CeO_2 and the related composites Au–CeO_2-N and Au–CeO_2-A are shown in Fig. 1. The two-theta peaks at 28.68°, 33.10°, 47.44°, 56.44°, 59.02°, 69.40°, 76.71° and 79.00° could be indexed to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) planes of fluorite cubic CeO_2 structure (JCPDS# 81-0792), respectively. No change was found after loading Au, indicating that the structures of CeO_2 were well preserved in the composites. The sizes of the CeO_2 particles were about 14.6 nm, calculated based on the Scherrer formula using the (1 1 1) diffraction peaks. The two-theta peaks at 38.30° in correspondence with (1 1 1) plane of fcc Au structure (JCPDS# 89-3697) could be observed for both composite samples Au–CeO_2-N and Au–CeO_2-A, indicating that the well-crystallized gold particles existed in the composites.

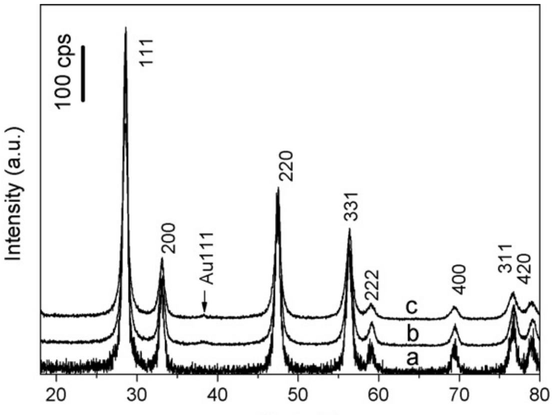

Fig. 1. XRD patterns of the as-synthesized CeO_2 (a) and the nanocomposite samples Au–CeO_2-N (b) and Au–CeO_2-A (c).