Chemical Engineering Journal 228 (2013) 965–975

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Au/3DOM $LaCoO_3$: High-performance catalysts for the oxidation of carbon monoxide and toluene

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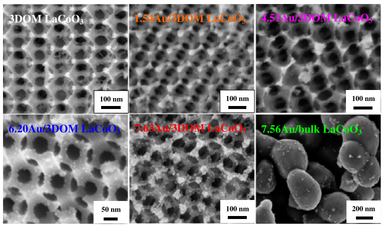
HIGHLIGHTS

- 3DOM $LaCoO_3$ is prepared by the polymethyl methacrylate-templating method.
- xAu/3DOM $LaCoO_3$ are prepared by the polyvinyl alcohol-protected reduction method.
- xAu/3DOM $LaCoO_3$ show high surface area and O_{ads} concentration and good reducibility.
- xAu/3DOM $LaCoO_3$ perform excellently in the oxidation of CO and toluene.
- Activity is governed by O_{ads} content, reducibility, and strong Au–$LaCoO_3$ interaction.

GRAPHICAL ABSTRACT

xAu/3DOM $LaCoO_3$ (x = 1.54–7.63 wt%) are prepared using the PMMA-templating and PVA-protected reduction methods. The high O_{ads} concentration, good low-temperature reducibility, and strong interaction between Au and 3DOM $LaCoO_3$ are responsible for the excellent catalytic performance of 7.63Au/3DOM $LaCoO_3$.



ARTICLE INFO

Article history:
Received 10 March 2013
Received in revised form 16 May 2013
Accepted 20 May 2013
Available online 29 May 2013

Keywords:
Three-dimensionally ordered macroporous perovskite-type oxide
Lanthanum cobaltite-supported Au catalyst
Metal–support interaction
Toluene oxidation
Carbon monoxide oxidation

ABSTRACT

Rhombohedrally crystallized three-dimensionally ordered macroporous (3DOM) $LaCoO_3$ and its supported Au (xAu/3DOM $LaCoO_3$, x = 0–7.63 wt%) catalysts were prepared using the polymethyl methacrylate-templating and polyvinyl alcohol-protected reduction methods, respectively. Physicochemical properties of the materials were characterized by means of numerous analytical techniques, and their catalytic activities were evaluated for the oxidation of toluene and CO. It is shown that the xAu/3DOM $LaCoO_3$ samples displayed a 3DOM architecture and a high surface area of 24–29 m^2/g. The 7.63Au/3DOM $LaCoO_3$ sample exhibited the highest adsorbed oxygen species concentration and the best low-temperature reducibility, and hence the best catalytic performance. Over 7.63Au/3DOM $LaCoO_3$, the $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ (corresponding to the temperatures required for achieving a reactant conversion of 10%, 50%, and 90%) were 136, 188, and 202 °C for toluene oxidation at space velocity (SV) = 20,000 mL/(g h), and −61, −6, and 42 °C for CO oxidation at SV = 10,000 mL/(g h), respectively. Over xAu/3DOM $LaCoO_3$, the apparent activation energies were 31.4–37.4 kJ/mol for toluene oxidation and 16.6–19.4 kJ/mol for CO oxidation. We believe that the high oxygen adspecies concentration, good low-temperature reducibility, and strong interaction between Au and 3DOM $LaCoO_3$ might account for the excellent catalytic performance of 7.63Au/3DOM $LaCoO_3$.

1. Introduction

Au has been considered as inert catalytic activity in its bulk state for a long time. However, Haruta et al. [1] demonstrated that

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http://dx.doi.org/10.1016/j.cej.2013.05.070

the highly dispersed Au exhibited an extraordinary activity for the oxidation of CO at low temperatures. The efforts of exploring different methods to prepare highly active gold catalysts have been made during the last 20 years. Although the nanosized gold supported on some metal oxide supports displays high performance for CO oxidation at low temperatures (even below 0 °C) [2], only few reports focus the oxidation of toluene over the supported gold catalysts [3–6].

The catalytic performance of supported gold is associated with several factors, such as the size of gold particles, the property of the support, and the preparation approach. Generally speaking, a narrow size (lower than 5 nm) distribution of gold [7,8] exhibits high catalytic activity. The key issue is how to prepare such size-distributed Au nanoparticles (NPs).

It has been reported that gold was supported on some supports, such as TiO_2 [9,10], $Ce_{1-x}Zr_xO_2$ [11], CeO_2 [12], Fe_3O_4 [13], MgO [14], and CeO_2-modified SBA-15 [15], which showed a narrow gold size distribution and high catalytic activity but some of them exhibited insufficient stability. Therefore, the attainment of stable gold NPs and reproducible catalytic activity during successive catalytic runs is still a challenge [16]. Three-dimensionally ordered macroporous (3DOM) perovskite-type oxides (ABO_3) possess relatively large surface areas, high thermal stability, and good catalytic performance [17,18]. The unique ordered macroporous structure can provide easy mass transfer to the reactant molecules, facile accessibility to the active sites, and convenient loading of active components [12]. Therefore, 3DOM-structured ABO_3 is considered to be one of the most promising catalytic materials [19]. It is envisioned that the loading of Au on the 3DOM ABO_3 support can generate a catalyst that would show high catalytic performance and good thermal stability. For example, Jia et al. [20] adopted the deposition–precipitation technique to obtain the Au/$LaCoO_3$ catalysts, which exhibited a good performance and stability in the oxidation of CO. They also employed the same approach to prepare the Au/$LaMnO_3$ catalysts, and found that these materials were highly stable in CO oxidation [21]. There are two ways to prepare gold supported on the 3DOM-structured supports. One is the gas bubble-assisted membrane reduction (GBMR) method [11], whereas the other is the gas bubble-assisted deposition–precipitation, which was successfully used to obtain the highly active Au/3DOM CeO_2 catalysts for CO oxidation [12]. The key issue for the gas bubble-assisted deposition–precipitation route is to control an appropriate pH value of the Au precursor solution, so that a higher actual Au loading and narrow size distribution of Au NPs could be achieved in the supported Au samples. With the protection of polyvinyl alcohol (PVA), however, the gas bubble-assisted PVA-protected reduction strategy is a good one that can generate narrow size-distributed Au NPs and a higher actual Au loading.

To the best of our knowledge, rare reports on the fabrication and catalytic applications of 3DOM ABO_3-supported nanosized gold catalysts have been seen in the literature. Recently, our group has generated a number of 3DOM ABO_3-supported precious metal catalysts using the gas bubble-assisted PVA-protected reduction method. In this work, we report the preparation, characterization, and catalytic activities of xAu/3DOM $LaCoO_3$ (x = 0–7.63 wt%) for the oxidation of toluene and CO via a combined polymethyl methacrylate (PMMA)-templating and gas bubble-assisted PVA-protected reduction strategy.

2. Experimental

2.1. Catalyst preparation

The 3DOM $LaCoO_3$ catalysts were prepared using the well-arrayed PMMA microspheres (with an average diameter of ca. 300 nm) as hard template [22]. In a typical procedure, 8.66 g of $La(NO_3)_3·6H_2O$ and 5.821 g of $Co(NO_3)_2·6H_2O$ were dissolved in 7.0 mL of methanol and 3.0 mL of ethylene glycol (EG) at room temperature (RT) under stirring for 2 h, obtaining a transparent solution. 0.7 g of L-lysine was dissolved in 2.0 mL of deionized water and the pH value of the solution was adjusted to around 5 with a certain amount of citric acid. Then, the L-lysine-containing solution and the metal nitrate-containing transparent solution were mixed together under stirring for 1 h, obtaining the precursor solution. 2.0 g of the PMMA hard template was thoroughly soaked in the precursor solution for 4 h. After filtration and drying, the solid was transferred to a ceramic boat and thermally treated in a tubular furnace first in a N_2 flow of 50 mL/min at a ramp of 1 °C/min from RT to 300 °C for 3 h, then cooled in the same atmosphere to RT, and finally in an air flow of 50 mL/min at a ramp of 1 °C/min from RT to 650 °C and kept at this temperature for 3 h.

The xAu/3DOM $LaCoO_3$ (the theoretical x values = 2, 5, 8, and 10 wt%) catalysts were prepared using the gas bubble-assisted PVA-protected reduction method. In a typical preparation, 100 mL of the $HAuCl_4$ aqueous solution and PVA (Au/PVA mass ratio = 1.5: 1 mg/mg) were mixed in an ice-water bath for 1 h at RT under vigorous stirring. After that, an appropriate amount (Au/$NaBH_4$ molar ratio = 1:5 mol/mol) of 0.1 mol/L $NaBH_4$ aqueous solution (prepared in an ice-water bath) was injected rapidly. The transparent solution instantly changed to a dark orange-brown solution, indicating the formation of a gold sol. Then, the 3DOM $LaCoO_3$ powders were added to the gold sol and treated supersonically for 0.5–1 min for the generation of Au NPs highly dispersed on the 3DOM $LaCoO_3$ support. Since the magnetic stirring might destroy the 3DOM structure of $LaCoO_3$, the gas bubble-assisted stirring operation with four bubbling outlets was adopted to achieve a homogenous deposition of Au NPs on the 3DOM $LaCoO_3$ support. After bubbling the 3DOM $LaCoO_3$-containing gold sol with N_2 for 6 h, the solid was filtered and washed with deionized water until no chloride ions were detected using a 0.1 mol/L $AgNO_3$ aqueous solution. After being dried in an oven at 60 °C for 24 h and calcined in an O_2 flow of 30 mL/min at 500 °C for 1 h, the obtained 3DOM $LaCoO_3$-supported gold samples were denoted as xAu/3DOM $LaCoO_3$. According to the results of inductively coupled plasma atomic emission spectroscopic (ICP-AES) investigations, the actual Au contents (x) were 1.54, 4.51, 6.20, and 7.63 wt% for the theoretical Au contents of 2, 5, 8, and 10 wt%, respectively, as described in Table 1.

For comparison purposes, a bulk $LaCoO_3$ catalyst was prepared by the citric acid-complexing method described elsewhere [23]. The obtained solid precursor was first calcined in air at a ramp of 1 °C/min in a muffle furnace from RT to 300 °C and maintained at this temperature for 3 h, and then from 300 to 850 °C at the ramp of 5 °C/min and kept at 850 °C for 3 h. The 7.56Au/bulk $LaCoO_3$ catalyst was prepared using the above gas bubble-assisted PVA-protected reduction method and after calcination in an O_2 flow of 30 mL/min at 500 °C for 1 h.

All of the chemicals (A.R. in purity) were purchased from Beijing Chemical Reagent Company and used without further purification.

2.2. Catalyst characterization

The ICP-AES technique was employed to determine the actual Au contents in the as-prepared samples. The powder X-ray diffraction (XRD, Bruker/AXS D8 Advance) with Cu Kα radiation and nickel filter (λ = 0.15406 nm) (the operating voltage and current was 40 kV and 35 mA, respectively) was used to measure the crystal structures of the samples. The crystal phases were identified by referring to the JCPDS Database. The scanning electron microscopic (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus operating at 10 kV. The transmission electron