



# Au–Pd/3DOM Co<sub>3</sub>O<sub>4</sub>: Highly active and stable nanocatalysts for toluene oxidation



Shaohua Xie<sup>a</sup>, Jiguang Deng<sup>a,\*</sup>, Simiao Zang<sup>a</sup>, Huanggen Yang<sup>a</sup>, Guangsheng Guo<sup>a</sup>, Hamid Arandiyan<sup>b</sup>, Hongxing Dai<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Beijing on Regional Air Pollution Control, Beijing Key Laboratory for Green Catalysis and Separation, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, People's Republic of China

<sup>b</sup> Particles and Catalysis Research Group, School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia

## ARTICLE INFO

### Article history:

Received 28 July 2014

Revised 27 September 2014

Accepted 29 September 2014

Available online 9 December 2014

### Keywords:

Three-dimensionally ordered macroporous cobalt oxide

Supported Au–Pd alloy nanocatalyst

Toluene oxidation

Water vapor effect

Oxygen activation

## ABSTRACT

The polymethyl methacrylate-templating and polyvinyl alcohol-protected reduction routes were adopted to prepared three-dimensionally ordered macroporous (3DOM) Co<sub>3</sub>O<sub>4</sub> and its supported gold–palladium alloy (*x*AuPd/3DOM Co<sub>3</sub>O<sub>4</sub>, *x* = 0.50–1.99 wt% and Au/Pd mass ratio = 1:1) nanocatalysts. The 3DOM Co<sub>3</sub>O<sub>4</sub> supported Au–Pd samples performed much better than supported single Au or Pd samples, with the 1.99AuPd/3DOM Co<sub>3</sub>O<sub>4</sub> sample showing the best performance: the *T*<sub>10%</sub>, *T*<sub>50%</sub>, and *T*<sub>90%</sub> (temperatures required for achieving toluene conversions of 10%, 50%, and 90%) were 145, 164, and 168 °C at a space velocity of 40,000 mL/(g h), respectively. The 3DOM Co<sub>3</sub>O<sub>4</sub> supported Au–Pd nanocatalysts also exhibited better catalytic stability and more moisture-tolerant ability than the supported Au or Pd samples for toluene oxidation. The apparent activation energies (33–41 kJ/mol) over *x*AuPd/3DOM Co<sub>3</sub>O<sub>4</sub> were much lower than those (52–112 kJ/mol) over 3DOM Co<sub>3</sub>O<sub>4</sub> and supported single Au or Pd samples, with the 1.99AuPd/3DOM Co<sub>3</sub>O<sub>4</sub> sample exhibiting the lowest apparent activation energy (33 kJ/mol). It is concluded that better oxygen activation ability and stronger noble metal–3DOM Co<sub>3</sub>O<sub>4</sub> interaction were responsible for the excellent catalytic performance of 1.99AuPd/3DOM Co<sub>3</sub>O<sub>4</sub>.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Most of the volatile organic compounds (VOCs) emitted from industrial activities are harmful to the environment and human health. In the last several decades, many technologies for VOCs abatement have been developed, of which catalytic oxidation is regarded as one of the most promising approaches owing to its high efficiency and low operating temperatures [1,2]. The key issue of this technology is the availability of a highly active catalyst. Although various transition-metal oxides and mixed metal oxides exhibit good catalytic performance for VOC combustion [3–5], supported noble metals are the most desirable catalysts due to their excellent low-temperature activity [6–12].

Since Hutchings and co-workers' recent finding that supported gold was an efficient catalyst for acetylene hydrochlorination [7,8], catalytic oxidation of VOCs over supported gold materials has attracted much attention [9–13]. For example, Ma et al. reported that mesoporous Co<sub>3</sub>O<sub>4</sub> and its supported Au nanoparticles (NPs)

showed high activity for the oxidation of ethylene at 0 °C [10]. Liu et al. found that three-dimensionally ordered macroporous (3DOM) La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>-supported gold [12] and mesoporous Co<sub>3</sub>O<sub>4</sub>-supported gold [13] gave *T*<sub>90%</sub> (temperature at 90% toluene conversion) values of 170 and 138 °C for toluene combustion at a space velocity (SV) of 20,000 mL/(g h), respectively. Although these gold-based catalysts were effective for toluene oxidation [11–13], they were not catalytically durable in the presence of water vapor in the feedstock.

It has recently been reported that Pd alloyed with Au showed extremely high catalytic performance for H<sub>2</sub>O<sub>2</sub> synthesis, N<sub>2</sub>O decomposition, and alcohol and toluene oxidation [14–20]. For instance, Hutchings and co-workers investigated the oxidation of primary alcohols [18] and toluene [20] over Au–Pd/TiO<sub>2</sub> catalysts and found that the Au acted as an electronic promoter for Pd and the active catalyst had a surface significantly enriched in Pd for alcohol oxidation, and surface-bound oxygen-centered radicals played a positive role in activating toluene over supported Au–Pd alloy catalysts for toluene oxidation. In the model studies, Li et al. [19] and Goodman et al. [21] pointed out that Au could isolate the Pd sites within the bimetallic systems. As we know, the nature

\* Corresponding authors. Fax: +86 10 6739 1983.

E-mail addresses: [jgdeng@bjut.edu.cn](mailto:jgdeng@bjut.edu.cn) (J. Deng), [hxdai@bjut.edu.cn](mailto:hxdai@bjut.edu.cn) (H. Dai).

of the support exerts an important impact on the activity of a supported noble metal catalyst [22]. Due to its excellent low-temperature reducibility and large number of oxygen vacancies, cobalt oxide is a versatile transition-metal oxide that performs better than  $\text{TiO}_2$  and  $\text{CeO}_2$  in the low-temperature oxidation of VOCs, especially for the oxidation of toluene [23,24]. Although many studies have been carried out on supported Au–Pd alloy catalysts, there have been no reports on the preparation and catalytic applications of porous cobalt oxide-supported Au–Pd alloy catalysts for VOC combustion.

In the past decade, 3DOM-structured materials have been applied to catalyze the combustion of soot and VOCs [25,26] because of their easy transportation and diffusion properties. Previously, our group adopted the polymethyl methacrylate (PMMA)-templating and polyvinyl alcohol (PVA)-protected reduction strategies to successfully generate a number of 3DOM (mixed) metal oxide-supported gold NPs, such as Au/3DOM  $\text{Co}_3\text{O}_4$  [11], Au/3DOM  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  [12], Au/3DOM  $\text{LaCoO}_3$  [27], and Au/ $\text{LaMnO}_3$  [28]. We observed that compared to bulk supported gold materials, the 3DOM-structured counterparts showed much better catalytic performance in the oxidation of CO and/or VOCs. One drawback of these porous samples, however, is poor hydrothermal stability. To improve their hydrothermal stability, we herein report for the first time the preparation, characterization, and catalytic properties of 3DOM  $\text{Co}_3\text{O}_4$ -supported Au–Pd alloy NPs for toluene oxidation. It is observed that the 1.99 wt% AuPd/3DOM  $\text{Co}_3\text{O}_4$  (Au/Pd mass ratio = 1:1) sample showed excellent catalytic performance and hydrothermal stability.

## 2. Experimental

### 2.1. Catalyst preparation

Well-arrayed PMMA microspheres with an average diameter of ca. 300 nm were synthesized according to procedures described elsewhere [27]. 3DOM  $\text{Co}_3\text{O}_4$  was fabricated via the PMMA-templating route. In a typical fabrication, 20 mmol  $\text{Co}(\text{NO}_3)_2$  was dissolved in 10 mL of polyethylene glycol (PEG) and methanol (MeOH) solution (PEG/MeOH volumetric ratio = 1:9) at room temperature (RT), obtaining a transparent mixed solution after 1 h of stirring. Then 2.0 g of the PMMA template was soaked in the above mixed solution for 4 h, so that the voids of the template microspheres were completely filled with the transparent solution. After being filtered, the obtained wet powders were dried at RT for 48 h. The calcination

procedures for the samples were as follows: (i) The dried powders were first calcined in a  $\text{N}_2$  flow of 200 mL/min from RT to 300 °C at a ramp of 1 °C/min and kept at 300 °C for 3 h, and then cooled to RT; (ii) the pretreated samples were calcined in an air flow of 200 mL/min from RT to 450 °C at a ramp of 1 °C/min and maintained at this temperature for 4 h, thus generating the 3DOM  $\text{Co}_3\text{O}_4$  support (Scheme S1 of the Supplementary Material). From the TG/DTG result (Fig. S1 of the Supplementary Material), one can realize that the template was completely removed above 400 °C. In other word, heating the sample precursors in air at 450 °C for 4 h could guarantee the complete removal of the organics.

The 3DOM  $\text{Co}_3\text{O}_4$ -supported gold–palladium ( $x\text{AuPd}/3\text{DOM } \text{Co}_3\text{O}_4$ ) samples were prepared via a gas-bubble-assisted PVA-protected reduction route with PVA (MW = 10,000 g/mol) as the protecting agent and  $\text{NaBH}_4$  as the reducing agent. The typical preparation procedure was as follows: A desired amount of PVA (noble metal/PVA mass ratio = 1:1.2) was added to a  $\text{HAuCl}_4$  and  $\text{PdCl}_2$  mixed aqueous solution (Au/Pd molar ratio = 1:1.85) in an ice bath under vigorous stirring. A desired amount of 3DOM  $\text{Co}_3\text{O}_4$  was then added to the mixed solution, with the theoretical Au–Pd loading being 0.5, 1.0, of 2.0 wt%. Then the stirring operation was replaced by bubbling  $\text{N}_2$  to make the reaction homogenous in the solution. After the suspension was bubbled with  $\text{N}_2$  (200 mL/min) for 20 min, a 0.1 mol/L  $\text{NaBH}_4$  aqueous solution (noble metal/ $\text{NaBH}_4$  molar ratio = 1:5) was rapidly injected to form a dark brown suspension (i.e., the formation of Au–Pd NPs on the surface of 3DOM  $\text{Co}_3\text{O}_4$ ), and the reaction system was further vigorously bubbled with  $\text{N}_2$  (200 mL/min) for 4 h. The wet solid was filtered and washed with deionized water. After being dried at 80 °C for 12 h and calcined in air at 450 °C for 4 h, the  $x\text{AuPd}/3\text{DOM } \text{Co}_3\text{O}_4$  samples were obtained (Scheme S1). For comparison, Au/3DOM  $\text{Co}_3\text{O}_4$  and Pd/3DOM  $\text{Co}_3\text{O}_4$  samples with appropriate Au or Pd loading were also prepared via the gas-bubble-assisted PVA-protected reduction route. The results (Table 1) of inductively coupled plasma atomic emission spectroscopic (ICP–AES) investigations reveal that the real noble metal loading ( $x$ ) was 0.50, 1.00, or 1.99 wt% in  $x\text{AuPd}/3\text{DOM } \text{Co}_3\text{O}_4$  and 0.99 wt% in Au/3DOM  $\text{Co}_3\text{O}_4$  and Pd/3DOM  $\text{Co}_3\text{O}_4$ , and the Au/Pd mass ratio was rather close to 1:1. Due to the strong interaction between the 3DOM support and the precious metal precursor, a small amount of precious metal was removed during the filtration process, giving rise to the result that the actual loadings were close to the theoretical loadings. Therefore, the PVA-protected reduction route was suitable for the preparation of supported noble metal catalysts.

**Table 1**

BET surface areas, pore volumes, average crystallite sizes ( $D_{\text{Co}_3\text{O}_4}$ ), average Au particle sizes, and real Au contents of the  $x\text{AuPd}/\text{Co}_3\text{O}_4$  samples.

Sample	BET surface area (m <sup>2</sup> /g)	Macropore diameter <sup>a</sup> (nm)	Mesopore diameter <sup>b</sup> (nm)	Pore volume (cm <sup>3</sup> /g)	$D_{\text{Co}_3\text{O}_4}$ <sup>c</sup> (nm)	Noble metal particle size <sup>d</sup> (nm)	Au content <sup>e</sup> (wt%)	Pd content <sup>e</sup> (wt%)
3DOM $\text{Co}_3\text{O}_4$	34.6	225–235	12–14	0.043	32	–	–	–
0.99Au/3DOM $\text{Co}_3\text{O}_4$	36.2	220–230	14–16	0.029	34	3.3	0.99	–
0.99Pd/3DOM $\text{Co}_3\text{O}_4$	33.2	230–240	13–15	0.027	33	3.7	–	0.99
0.50AuPd/3DOM $\text{Co}_3\text{O}_4$	35.4	225–235	14–16	0.039	34	2.6	0.25	0.25
1.00AuPd/3DOM $\text{Co}_3\text{O}_4$	33.8	230–240	15–17	0.028	33	2.7	0.50	0.50
1.99AuPd/3DOM $\text{Co}_3\text{O}_4$	33.1	230–240	12–14	0.024	33	2.7	0.99	1.00

<sup>a</sup> Estimated according to the SEM images.

<sup>b</sup> Estimated according to the BJH pore size distributions.

<sup>c</sup> Determined according to the Scherrer equation using the FWHM of the (311) line of  $\text{Co}_3\text{O}_4$ .

<sup>d</sup> Estimated according to the TEM images.

<sup>e</sup> Determined by the ICP–AES technique.

Download English Version:

<https://daneshyari.com/en/article/60870>

Download Persian Version:

<https://daneshyari.com/article/60870>

[Daneshyari.com](https://daneshyari.com)