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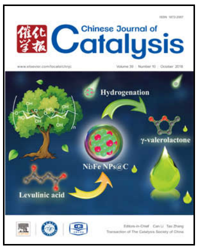

Article

Enhancement of the activity and durability in CO oxidation over silica-supported Au nanoparticle catalyst *via* CeO_x modification

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ABSTRACT

The supported Au nanoparticles have been regarded as promising catalysts for CO oxidation but still suffer from unsatisfactory catalytic activity and durability. Herein, we show a simple and efficient strategy to simultaneously enhance the catalytic activity and durability for CO oxidation. Key to the success is modification of the supported Au nanoparticle catalyst with nanosized CeO_x to construct abundant Au-CeO_x interface. Owing to the maximized interfacial effect on the CeO_x-modified Au nanoparticles, the concentration of positively-charged Au species ($Au^{\delta+}$) was remarkably improved, leading to enhanced catalytic activities in the oxidation of CO. Importantly, the stability of Au nanoparticles is remarkably increased by CeO_x modification, exhibiting good durability in a continuous test of CO oxidation at higher temperatures.

1. Introduction

Catalytic oxidation of CO is a classical and crucial reaction, concerning the practical applications such as the gas sensors of trace amount of CO, automobile exhaust purification, and safety masks, which attracted enormous research interests. The supported Au nanoparticles (NPs), which play an important role in many catalytic reactions for the unusual catalytic performances [1], show unexpected performances in CO oxidation [2,3]. Currently, the supported Au nanoparticles have been regarded to be promising for potential wide applications, but these catalysts still suffer from the challenges of stability and deactivation, where the sintering of NPs at high reaction temperature usually occurs [4].

To overcome the aforementioned issues, various strategies have been developed, including isolating the Au NPs on the surfaces [5,6] or in the mesopores of supports [7], covering the Au NPs with metal oxide/silica/carbon overlayers [8,9], encapsulating them in the rigid solids [10–14]. Particularly, construction of the strong metal-support interaction (SMSI) [15] to cover or encapsulate metal NPs by metal oxides, has been shown as an efficient route to stabilize the NPs. Several reducible oxides have been chosen to prepare these supported Au NP catalysts, including TiO_2 [16–18], Nb_2O_5 [19], ZnO [20], and CeO_2 [21,22]. These strategies have effectively improved the stability of supported Au catalysts, but relatively complicated procedures for these strategies has a challenge for the industrial applications.

Herein, we developed a simple and efficient route to improve the catalytic activity and durability of Au NPs on an inert support of SiO_2 modified with CeO_x. Key to this success is to anchore a slight amount of CeO_x NPs onto the surface of Au NPs in the presence of ethylenediaminetetraacetic acid (EDTA), which was denoted as CeO_x@Au/SiO_2. Owing to the modifica-

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tion by CeO_x, abundant Au-CeO_x interfaces were reasonably achieved, leading to increase of positively-charged Au ($Au^{\delta+}$) concentration. Catalytic tests in CO oxidation show that the CeO_x@Au/SiO_2 exhibits much better activity and stability than conventional Au nanoparticles supported on silica support (Au/SiO_2).

2. Experimental

2.1. Catalyst preparation

Synthesis of Au NPs. As a typical run, 1.0 g of polyvinyl pyrrolidone (PVP, K-30) was added to 100 mL of $HAuCl_4$ aqueous solution (0.05 mmol of $HAuCl_4$). After stirring the mixture in an ice bath for 0.5 h, 10 mL of $NaBH_4$ aqueous (0.01 mmol of $NaBH_4$) was added quickly with vigorous stirring. After stirring for another 2 h, the Au NPs colloid were finally obtained.

Synthesis of CeO_x@Au/SiO_2. In a typical run, 0.4 mmol of $Ce(NO_3)_3$ was added to the 100 mL of Au NPs colloid with stirring, followed by addition of 0.8 mL of $NH_3\cdot H_2O$ and 5 mL of EDTA aqueous solution (0.4 mmol of EDTA). After stirring for 0.5 h, 1.0 g of amorphous SiO_2 was impregnated with the colloid. The liquid mixture was continuously stirred for another 3 h at room temperature. After distilling under vacuum condition to remove the water, drying at 105 °C overnight, and calcining at 400 °C for 4 h, the CeO_x@Au/SiO_2 was finally obtained.

Synthesis of CeO_x-Au/SiO_2. 0.04 mmol CeO_2 was added to the 100 mL of Au NPs colloid directly. After stirring for 0.5 h, 1.0 g of amorphous SiO_2 was impregnated with the colloid. The liquid mixture was continuously stirred for another 3 h at room temperature. After distilling under vacuum condition to remove the water, drying at 105 °C overnight, and calcining at 400 °C for 4 h, the CeO_x-Au/SiO_2 was obtained.

Synthesis of Au/SiO_2. The Au/SiO_2 was prepared *via* the similar impregnation without the addition of Ce species.

Synthesis of CeO_2/SiO_2. The CeO_2/SiO_2 was synthesized by physically mixing 0.08 mmol of CeO_2 and 1.0 g of amorphous SiO_2.

2.2. Catalytic tests

The CO oxidation was carried out in a continuous fixed-bed glass vertical reactor (length at 450 mm and inner diameter at 6 mm). As a typical run, quartz sands were placed into both ends of the catalyst to maintain the bed height and reduce the dead volume. 0.15 g of catalyst (40–60 mesh) was diluted with 0.3 g of quartz sands (40–60 mesh) in the catalyst bed. Before the reaction, the catalyst was pretreated by O_2 (20% in He) at 300 °C for 1 h. CO/O_2/He (2%/16%/82%) was introduced to the upper inlet of the reactor with a rate of 40 mL/min. The reactor temperature was programmed by a temperature-controlled instrument. The composition of effluent gas was analyzed with a Fu Li-9790 gas phase chromatography (GC) equipped with a thermal conductivity detector (TCD).

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX 2550 diffract meter with Cu K_α radiation (λ = 1.5406 Å). The composition of catalysts was measured with an inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Transmission electron microscopy (TEM) images were obtained on a JEM-2100F electron microscopy with an acceleration voltage of 200 kV and a FEI Tecnai G^2 F20 S-TWIN electron microscopy with an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) of the samples were recorded using a Kratos AXIS SUPRA with Al K_α X-ray radiation as the X-ray source. The binding energies were calibrated on the basis of the C 1*s* (284.8 eV) peak. H_2-temperature programmed reduction (H_2-TPR) was performed on a Finesorb-3010. Infrared (IR) spectra were recorded using a Bruker Vestor 22 FT-IR spectrometer equipped with a MCT/A detector and ZeSe windows and a high temperature reaction chamber. As a typical run, 50 mg of solid sample was localized in the chamber and pretreated at 200 °C for 30 min in flowing pure Ar (20 mL/min). Then, the chamber was adjusted to desired temperature (200 °C), and CO (10% CO in Ar) was flowed to the sample for 30 min. After removing the physically adsorbed CO by pure Ar gas, the FTIR spectra of CO adsorbed on the samples were recorded. Then O_2 (10% O_2 in Ar) was introduced, the spectra were collected when gas was flowed through the chamber.

3. Results and discussion

Liang Wang *(Zhejiang University) received the* ***Rising Star Award of Catalysis in China in 2017****, which was presented by The Catalysis Society of China. Dr. Liang Wang was born in Shandong, China in 1986. He received his B.S. (2008) in Chemistry from Jilin University, China. Since 2008, he started a continuous academic project involving master and doctor study under the guidance of Prof. Feng-Shou Xiao in the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University and got his Ph.D. degree in 2013. Then he joined the Institute of Catalysis in Zhejiang University for a postdoctoral work under the guidance of Prof. Feng-Shou Xiao. Currently he is an associate research professor of Chemistry in Zhejiang University. His research is focused on the development of nanoporous materials and supported nano/subnano catalysts for energy conversion and fine chemical synthesis. For his research in heterogeneous catalysis, Dr. Wang was recognized with the Young Scientist Award of 16th International Congress on Catalysis (2016), and Outstanding Award of Young Scientists in Science Foundation of Zhejiang Province in China (2017).*