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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^{δ+}) 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.

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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 TiO₂ [16–18], Nb₂O₅ [19], ZnO [20], and CeO₂ [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 SiO₂ modified with CeO_x. Key to this success is to anchor 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/SiO₂. 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 ($\text{Au}^{\delta+}$) concentration. Catalytic tests in CO oxidation show that the $\text{CeO}_x/\text{Au}/\text{SiO}_2$ 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 $\text{CeO}_x/\text{Au}/\text{SiO}_2$. In a typical run, 0.4 mmol of $\text{Ce}(\text{NO}_3)_3$ was added to the 100 mL of Au NPs colloid with stirring, followed by addition of 0.8 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ 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 $\text{CeO}_x/\text{Au}/\text{SiO}_2$ was finally obtained.

Synthesis of $\text{CeO}_x\text{-Au}/\text{SiO}_2$. 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 $\text{CeO}_x\text{-Au}/\text{SiO}_2$ 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 $\text{CeO}_2/\text{SiO}_2$. The $\text{CeO}_2/\text{SiO}_2$ 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. $\text{CO}/\text{O}_2/\text{He}$ (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 $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). 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 G² 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 $\text{K}\alpha$ X-ray radiation as the X-ray source. The binding energies were calibrated on the basis of the C 1s (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 Vektor 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).

Fig. 1. XRD patterns of Au/SiO₂, CeO_x@Au/SiO₂ and CeO_x-Au/SiO₂.

3.1. Synthesis and characterization

By ICP-AES analysis, the Au and Ce loading on the CeO_x@Au/SiO₂ were measured to be 0.9 and 5.0 wt%, respectively. For comparison, the CeO_x-Au/SiO₂ was synthesized with similar method in the absence of EDTA, and the CeO₂/SiO₂ was prepared from a physical mixture of CeO₂ and SiO₂.

Fig. 1 shows XRD patterns of Au/SiO₂, CeO_x@Au/SiO₂ and CeO_x-Au/SiO₂, giving peaks at 38.2°, 44.3°, 64.6° and 77.5°, which are characteristics of (111), (200), (220) and (311) planes of metallic Au, respectively. In addition, CeO_x@Au/SiO₂ and CeO_x-Au/SiO₂ samples also show diffraction peaks at 28.5°, 33.0°, 47.5° and 56.3° associated with of CeO₂, indicating the successful loading of CeO_x species on the Au/SiO₂ catalyst. The CeO₂ signals of CeO_x-Au/SiO₂ are stronger than those of CeO_x@Au/SiO₂, suggesting the relatively larger CeO_x particles on CeO_x-Au/SiO₂ (Fig. S1).

TEM images give direct observation of the Au and CeO_x distribution on silica support. As shown in Fig. 2(a), the Au NPs are uniformly distributed on the SiO₂ support, displaying narrow diameter distribution at 6.0–15.0 nm and mean size at 10.6 nm. Very interestingly, small CeO_x crystals (lattice distance at 0.31 nm, corresponding to the (111) plane) with diameters at ~2 nm were observed on the surface of Au nanoparticle (Fig. 2(b)).

Furthermore, XPS characterization was employed to analyze the surface composition of the catalysts. As shown in Fig. 3, Au 4f_{7/2} XPS spectra give binding energy signals at 83.6, 84.5 and 85.7 eV [23]. These signals can be assigned to the metallic Au NPs and surface positive Au species of Au⁺ and Au³⁺, respectively. Notably, the positively charged Au concentration of CeO_x@Au/SiO₂ catalyst is much higher than those of Au/SiO₂ and CeO_x-Au/SiO₂ catalysts, which could reasonably be attributed to the modification of Au/SiO₂ by CeO_x species, where the electronic interaction occurred between Au species and CeO_x nanocrystals (Fig. S2). This interaction should be favorable for the catalytic oxidations since the positively charged Au species have been considered as an active site for the activation of oxygen [24,25].

3.2. Catalytic activity

Fig. 4 shows CO oxidation light-off curves over CeO_x@Au/SiO₂, CeO_x-Au/SiO₂, CeO₂/SiO₂, and Au/SiO₂ catalysts, exhibiting quite different catalytic performances. The Au/SiO₂ catalyst shows low CO conversion (4.0%) at 160 °C and complete conversion of CO at 340 °C. In contrast, the CeO_x@Au/SiO₂ catalyst exhibits CO conversion of 98.8% at 160 °C and the complete conversion is achieved at 180 °C. When the CeO_x-Au/SiO₂ is employed, the complete CO conversion is at 300 °C, which is slightly better than the Au/SiO₂ catalyst. In addition, the CeO₂/SiO₂ catalyst without Au is also active for CO

Fig. 2. TEM (a) and HRTEM (b) images of CeO_x@Au/SiO₂.

Fig. 3. Au 4f XPS spectra of Au/SiO₂ (a), CeO_x@Au/SiO₂ (b) and CeO_x-Au/SiO₂ (c).

oxidation, but the CO conversion is much lower (half CO conversion at 460 °C). Considering the CeO_x@Au/SiO₂, CeO_x-Au/SiO₂, and Au/SiO₂ have similar Au nanoparticles and loading as well as the same silica support, a significant enhancement of catalytic activity should be directly assigned to the CeO_x modification rather than other factors. In addition, the CeO_x-Au/SiO₂ is much less active than the CeO_x@Au/SiO₂, therefore it is suggested that the EDTA might be also important. One possibility is that the EDTA serves as a ligand to maximize the interaction between CeO_x nanocrystals and Au nanoparticles.

3.3. In situ DRIFT

In attempt to understand the promotion of CeO_x, we have performed *in situ* DRIFT experiments over the CeO_x@Au/SiO₂ and Au/SiO₂ catalysts. For CO adsorption (Fig. 5(a)), the Au/SiO₂ catalyst gives IR bands at 2156 and 2117 cm⁻¹ [26,27] associated with the CO adsorbed on positive and metallic Au species, but the CeO_x@Au/SiO₂ catalyst shows additional IR bands at 2230, 1599, 1493 and 1449 cm⁻¹. The band at 2230 cm⁻¹ is correspondent to [Au(CO)₂]^{δ+} species [28], which formed by two CO species adsorbed on the same positive Au nanoparticle. The bands at 1599, 1493 and 1449 cm⁻¹ are as-

signed to the bidentate, polydentate, and monodentate carbonate (CO₃²⁻) species. These species might mean that the CO indeed interacts with the active oxygen species on the catalyst surface. The invisibility of these bands over the Au/SiO₂ suggests the lack of active oxygen species. In addition, it is also observed a strong band at 2173 cm⁻¹ on the CeO_x@Au/SiO₂, which is attributed to the adsorption of CO on Ce⁴⁺ species. In a word, the existence of Au-CeO_x interface strengthens the CO adsorption on the CeO_x@Au/SiO₂, which benefits for the CO conversion.

When oxygen was introduced to the CO-adsorbed catalysts, as shown in Fig. 5(b), new bands at 2232, 1492, and 1447 cm⁻¹ are observed on the Au/SiO₂, which are correspondent to

Fig. 4. CO oxidation light-off curves on the various catalysts.

Fig. 5. Operando DRIFT of CO adsorption (a) and CO oxidation (b) of CeO_x@Au/SiO₂ and Au/SiO₂ at 200 °C.

Fig. 6. Durability tests of the CeO_x@Au/SiO₂ and Au/SiO₂.

[Au(CO)₂]^{δ+} species, polydentate, and monodentate CO₃²⁻ species, respectively. These signals indicate the generation of CO₂. Besides, bands at 2156 and 2117 cm⁻¹ on the CO-adsorbed Au/SiO₂ shift to 2162 and 2120 cm⁻¹, meaning that the CO adsorption become weak. For the CeO_x@Au/SiO₂ catalyst, bands at 2361 and 2334 cm⁻¹ assigned to gas phase CO₂ are observed, demonstrating higher CO oxidation activity of CeO_x@Au/SiO₂ than that of Au/SiO₂. Part of [Au(CO)₂]^{δ+} species (2241 and 2231 cm⁻¹) and CO species adsorbed on the Au NPs (2175, 2137 and 2120 cm⁻¹) still exist, but their intensities are significantly reduced. In contrast, the bands at 1602, 1492 and 1447 cm⁻¹ are obviously strengthened, suggesting that the CO₃²⁻ species are mainly derived from CO adsorbed on the CeO_x@Au/SiO₂. Moreover, it is observed a weak band at 2343 cm⁻¹ assigned to CO₂ adsorbed on Ce⁴⁺, confirming strong oxidation activity from CO to CO₂ over the CeO_x@Au/SiO₂ catalyst,

in good agreement with those shown in the catalytic results.

3.4. Catalytic durability

Fig. 6 shows the durability of the CeO_x@Au/SiO₂ and Au/SiO₂ catalysts. In the beginning of reaction at 180 °C over the CeO_x@Au/SiO₂, the CO is completely converted. Changing the temperature to 140 °C, it is given the CO conversion at 78%. To evaluate the stability of the Au NPs, we employed a high temperature of 260 °C. After reaction at 260 °C for 18 h, we cannot observe any decrease for the CO conversion. After cooling to 180 °C for another 12 h, full CO conversion is also achieved, confirming very high durability of the CeO_x@Au/SiO₂ catalyst. In contrast, the CO conversion of the Au/SiO₂ is remarkably reduced after reaction at 260 °C for 10 h, which is reasonably attributed to the aggregation of Au NPs [4]. In addition, we also performed the calcination treatment of the catalysts at 600 °C for 3 h (Fig. 7), which is harsh for the survival of normal Au NPs. Interestingly, it is almost unchangeable for the Au NPs of CeO_x@Au/SiO₂ (10.8 nm) before and after the calcination, but it is obviously observed the aggregation of the Au NPs on the calcined Au/SiO₂.

4. Conclusions

In summary, we report a significant enhancement of the catalytic activity and durability over silica supported Au NP catalyst by CeO_x modification in the presence of EDTA. The existence of CeO_x nanocrystals on the Au NPs surface increases positively charged Au^{δ+} concentration, improving the CO oxidation activity. More importantly, the CeO_x@Au/SiO₂ catalyst shows excellent durability. *In situ* IR spectra reveal that CeO_x modification greatly promotes the CO adsorption on the cata-

Fig. 7. TEM images and Au NPs size distributions of Au/SiO₂ (a) and CeO_x@Au/SiO₂ (b) after calcination at 600 °C for 3 h.

Graphical Abstract

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

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It has been successfully synthesized a CeO_x@Au/SiO₂ catalyst with both high activity and excellent durability in CO oxidation. Key to the success is to construct abundant Au-CeO_x interfaces by modification of Au nanoparticles with CeO_x nanocrystals.

lyst, leading to the efficient conversion of CO to CO₂ in the oxidative atmosphere. The strategy in this work might open an alternative way to develop more active and stable catalysts for the catalytic oxidations in the future.

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通过CeO_x修饰提高金纳米颗粒在CO氧化反应中的催化活性和耐久性

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摘要: CO催化氧化是一个重要的经典反应, 与许多应用息息相关, 包括痕量CO气体检测、汽车尾气净化和安全防护等, 吸引了人们广泛的研究兴趣. 负载型Au纳米颗粒在CO氧化等许多反应中有着与众不同的催化活性, 具有广泛的应用前景, 但依然存在着稳定性差、易团聚失活的问题. 人们通过应用多孔载体隔离Au纳米颗粒, 在Au纳米颗粒表面覆盖金属氧化物、二氧化硅或碳, 以及对Au纳米粒子进行封装等方法解决这些问题. 尤其是利用金属氧化物与Au纳米粒子间的强相互作用对其进行覆盖或封装, 有效地提高了Au催化材料的稳定性. 但以上策略操作流程复杂, 不利于应用. 本文发展了一种简单有效的方法, 通过EDTA的络合作用引入CeO_x对Au纳米粒子进行修饰, 得到的CeO_x@Au/SiO₂催化剂活性和耐久性明显提升.

采用X射线衍射(XRD)和高分辨透射电子显微镜(HRTEM)证明了CeO_x成功地修饰在Au纳米颗粒上. 且通过EDTA引入CeO_x所制备的CeO_x@Au/SiO₂催化剂结构明显不同于直接加入纳米CeO₂所得到的CeO_x-Au/SiO₂的结构. EDTA的络合作用能有效地连结Ce与Au物种, 经焙烧消除EDTA后, 加强了CeO_x与Au间相互作用, 最终在Au纳米粒子表面形成丰富的CeO_x颗粒与原子级厚度的CeO_x层. 进一步应用X射线光电子能谱(XPS)和氢气程序升温还原(H₂-TPR)等手段研究了CeO_x修饰对Au纳米粒子的影响. XPS结果表明, CeO_x@Au/SiO₂催化剂带正电的Au⁺和Au³⁺的浓度明显高于一般的Au/SiO₂和直接加入CeO₂制备得到的CeO_x-Au/SiO₂催化剂. H₂-TPR同样表明, CeO_x修饰调变了Au纳米粒子的氧化还原性. 这些均对其在CO催化氧化反应中的催化活性具有重要影响.

将CeO_x@Au/SiO₂催化剂用于CO催化氧化反应中, 160 °C时, CO转化率达98.8%, 至180 °C后实现了CO的完全转化. 而一般的Au/SiO₂催化剂在160 °C时CO转化率仅为4.0%, CO的完全转化则需340 °C. 直接加入纳米CeO₂所得到的CeO_x-Au/SiO₂催化剂, 其催化活性略有提升, CO完全转化所需的温度为300 °C. 这充分证明了通过CeO_x修饰Au纳米粒子, 能有效提升其催化活性.

原位漫反射红外光谱(DRIFT)结果表明, CeO_x修饰促进了CO在Au表面的吸附, 并能形成[Au(CO)₂]^{δ+}物种; 同时还观察到大量的单齿CO₃²⁻物种信号, 反映了CeO_x@Au/SiO₂催化剂表面存在丰富的活性氧物种. 通入O₂后, 观察到了大量CO₃²⁻物种信号和气相CO₂, 印证了催化剂表面发生的CO催化氧化过程, 也表明其具有非常高的催化活性.

考察了CeO_x@Au/SiO₂催化剂的耐久性, 发现经50 h CO氧化反应, 催化剂依然能有效保持活性. 相比之下, Au/SiO₂催化剂经10 h反应后, 开始明显失活. 由此可见, CeO_x@Au/SiO₂催化剂具有相当高的耐久性. 在600 °C将催化剂焙烧3 h, 发现Au/SiO₂催化剂中Au纳米粒子存在明显团聚现象, 而CeO_x@Au/SiO₂催化剂的Au纳米粒子依然均匀分布在载体表面, 且粒径未发生明显变化.

关键词: 一氧化碳氧化; 金; 二氧化铈; 界面; 抗烧结

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