



## Short Communication

Influence of pretreatment atmospheres on the activity of Au/CeO<sub>2</sub> catalyst for low-temperature CO oxidation

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## ABSTRACT

Au/CeO<sub>2</sub> catalyst was prepared via a deposition–precipitation method and further pretreated in different atmospheres prior to CO oxidation. A reductive atmosphere pretreatment slightly improved the low-temperature activity of Au/CeO<sub>2</sub>. The greatest activity was achieved when Au/CeO<sub>2</sub> catalyst was subjected to an oxidative atmosphere followed by a reductive atmosphere pretreatment. Analysis using XRD, TEM and nitrogen sorption measurement showed that pretreatment retains the crystal phase, morphology and pore structure of CeO<sub>2</sub>. However, there was a change in the interaction between gold species and CeO<sub>2</sub> support, as revealed by H<sub>2</sub>-TPR measurement.

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## 1. Introduction

Gold nanoparticles finely dispersed on the surface of oxide exhibit an extraordinary catalytic activity in CO oxidation [1–5]. Numerous investigations have been performed regarding the influence of the size of gold nanoparticles, support structure, preparation methods [6] and pretreatment conditions [7] on the activities of supported gold catalysts, with the aim of fully understanding the reaction mechanism of gold catalysis.

It was demonstrated that the pretreatment of a catalyst can determine the interaction between the gold species and the support, and thus change its catalytic activity [7–13]. For example, Cao et al. found [12] that Au/ $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> catalyst pretreated in helium exhibited higher activity for CO oxidation than when pretreated in O<sub>2</sub> or H<sub>2</sub>. Zou et al. [13] reported that Au/Al<sub>2</sub>O<sub>3</sub> catalysts pretreated in H<sub>2</sub> had smaller gold particles, and thus higher activity than those directly treated in air. Clearly, pretreatment can significantly change the physicochemical property of a catalyst and in turn affect its catalytic activity.

Ceria is an active support for gold catalysis because of its unique redox property and high oxygen storage capability [14]. It has been shown that the morphology [15], surface oxygen [16] and preparation method [17] of ceria can all affect the activity of the supported catalysts. Our previous works [18,19] also confirmed that the morphology and particle sizes of ceria significantly influence the catalytic activity of Au/CeO<sub>2</sub> in CO oxidation. However, detailed studies on its pretreatment in different atmospheres have not been undertaken. In this work, we

focus on the influence of pretreatment atmospheres on CO oxidation activity of Au/CeO<sub>2</sub> catalyst.

## 2. Experiments

2.1. Preparation of Au/CeO<sub>2</sub> catalyst

Ceria was prepared by nanocasting pathway using hierarchical monolith silica (HMS) as template, which was synthesized as described elsewhere [20]. In a typical synthesis of ceria, HMS was first impregnated with 9.785 M aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, which was then dried overnight at 50 °C and calcined at 300 °C for 2 h in order to decompose cerium nitrate. The obtained CeO<sub>2</sub>/HMS composite was leached with 4 M NaOH aqueous solution to remove the silica. The final ceria was obtained after centrifugation, washing and drying.

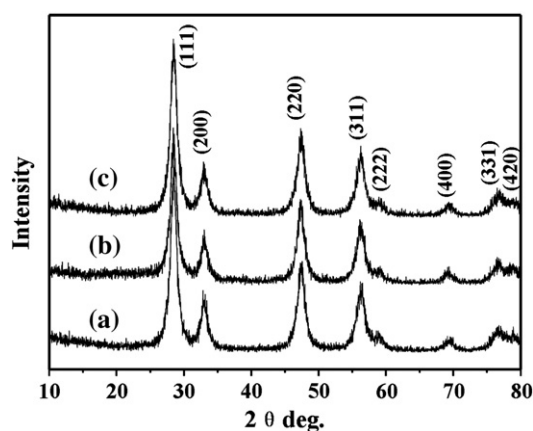
Gold catalyst was prepared by a deposition–precipitation (DP) method. 0.10 g of ceria was firstly dispersed in 5.08 mL water to form suspension. 127  $\mu$ L HAuCl<sub>4</sub> solution (7.888 g L<sup>-1</sup>) was added dropwise into the ceria suspension under vigorous stirring. The pH value of the mixed solution was adjusted to 9–10 by the addition of 0.5 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution. The mixture was heated to 60 °C and maintained for 2 h under stirring. The obtained precipitate was washed with deionized water until free of Cl<sup>-</sup> and OH<sup>-</sup>, and subsequently dried in a desiccator under vacuum for 3 h with P<sub>2</sub>O<sub>5</sub> as desiccant. Finally, Au/CeO<sub>2</sub> catalyst was obtained.

## 2.2. Pretreatment and activity test for CO oxidation

The catalytic activity of Au/CeO<sub>2</sub> in CO oxidation was tested in a fixed bed quartz reactor using 75 mg of catalyst. The total flow rate of the

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**Fig. 1.** XRD pattern of (a) CeO<sub>2</sub>, (b) Au/CeO<sub>2</sub> pretreated in O<sub>2</sub>, (c) Au/CeO<sub>2</sub> pretreated in O<sub>2</sub>-H<sub>2</sub>.

reaction gas was 67 mL min<sup>-1</sup> with a composition of 1 vol.% CO, 20 vol.% O<sub>2</sub> and 79 vol.% N<sub>2</sub>, corresponding to a space velocity of 60,000 mL h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup>. The products were analyzed on-line using a GC-7890 gas chromatograph equipped with a thermal conductivity detector (TCD). Prior to the reaction, the catalyst was pretreated at 250 °C for 90 min respectively in six different atmospheres including air, O<sub>2</sub>, N<sub>2</sub>, 14% H<sub>2</sub> (balanced with N<sub>2</sub>), first O<sub>2</sub> and then switched to 14% H<sub>2</sub> (balanced with N<sub>2</sub>), and first 14% H<sub>2</sub> (balanced with N<sub>2</sub>) and then switched to O<sub>2</sub>. Hereafter, the last two pretreatments are designed as O<sub>2</sub>-H<sub>2</sub> and H<sub>2</sub>-O<sub>2</sub>, respectively.

### 2.3. Catalyst characterization

The samples were analyzed with X-ray diffraction (XRD) using a Philips X'pert PRO X-ray diffractometer (Cu K<sub>α</sub> radiation, λ = 0.154 178 nm). Transmission electron microscopy (TEM) analyses were recorded on a Tecnai G<sup>2</sup>20S-Twin instrument operated at 200 kV. N<sub>2</sub> sorption measurements were carried out at -196 °C using a Micromeritics Tri star 3000 device. Element analysis was performed by inductively coupled plasma (ICP) atomic emission spectroscopy using optima 2000DV. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were performed in the 30–900 °C range on a self-designed instrument. The product was pretreated in an Ar flow of 30 mL/min at 200 °C for 1 h. The product was finally reduced in a 8%H<sub>2</sub>-92%Ar mixed gas flow of 20 mL/min at a ramp of 10 °C/min.

## 3. Results and discussion

### 3.1. Catalyst characterization

**Fig. 1** shows the XRD patterns of CeO<sub>2</sub> and Au/CeO<sub>2</sub> pretreated in different atmospheres. Both the loading of gold and the pretreatment

**Table 1**  
Texture parameters of HMS, CeO<sub>2</sub> and Au/CeO<sub>2</sub>.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	D <sub>peak</sub> (nm)	Gold content (%)
HMS	775	0.87	3.0	–
CeO <sub>2</sub>	129	0.45	7.5	–
Au/CeO <sub>2</sub> <sup>a</sup>	148	0.44	5.5	0.34

<sup>a</sup> Au/CeO<sub>2</sub> was first pretreated in O<sub>2</sub> followed by H<sub>2</sub>.

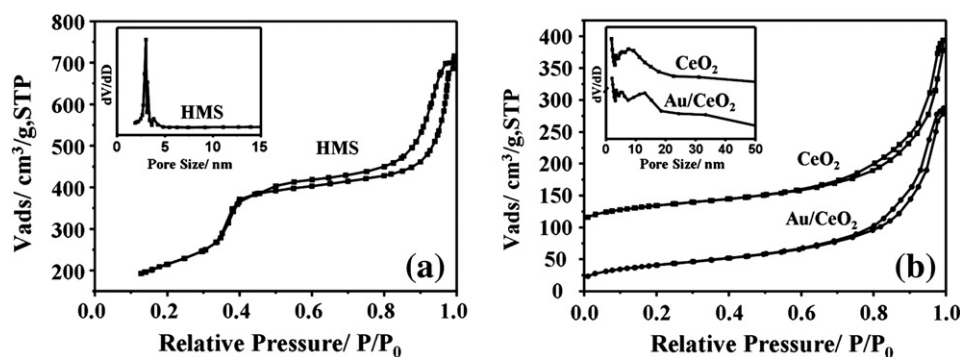
had no effect on the crystal phase of the ceria. The well-resolved XRD reflections can be assigned to the cubic fluorite structure (space group: Fm3m, JCPDS 34-0394) of CeO<sub>2</sub>. The diffraction peaks of metallic gold (2θ = 38.2°, 44.4° and 64.5°) or gold oxides (2θ = 25.5°, 30.2° and 32.5°) were not detected. This is due to the fine dispersion of gold particles on ceria support and fewer amounts of gold species that is out of the detected limitation of XRD [21].

**Fig. 2** shows nitrogen sorption isotherms and pore size distributions of the silica template (HMS), CeO<sub>2</sub> and Au/CeO<sub>2</sub> pretreated in O<sub>2</sub>-H<sub>2</sub>. As shown in **Fig. 2a**, the isotherm of HMS is of type IV, with a characteristic hysteresis loop, indicating the presence of mesopores. The pore size distribution of HMS exhibited a trimodal pore structure. In **Fig. 2b**, the templated ceria still displayed a type IV isotherm, however, the hysteresis loop moved to a higher relative pressure, indicating the formation of the larger mesopores due to the agglomeration of ceria particles. Loading with gold didn't change the isotherm shape of the Au/CeO<sub>2</sub> catalyst. The texture parameters of these three samples are compiled in **Table 1**. The gold loading had the little effect on surface area and pore volume due to the small amount of gold (0.34 wt.%, detected by ICP technique).

**Fig. 3** shows the TEM images of Au/CeO<sub>2</sub> catalysts pretreated with O<sub>2</sub>-H<sub>2</sub> and N<sub>2</sub>. It can be seen that both catalysts show an almost identical morphology and particle sizes of ceria (in the approximate range of 8–9 nm) with highly dispersed gold nanoparticles (approximately 2–3 nm in size). Hence, pretreatment with either O<sub>2</sub>-H<sub>2</sub> or N<sub>2</sub> causes no visible changes to the morphology or the particle sizes of the Au/CeO<sub>2</sub> catalysts.

### 3.2. Catalytic activity

After pretreatment in different atmospheres, Au/CeO<sub>2</sub> catalysts were tested in CO oxidation and the catalytic activities are shown in **Fig. 4a**. Surprisingly, the activity of Au/CeO<sub>2</sub> is highly sensitive to the pretreatment atmospheres. The determined initial reaction rate, T<sub>50%</sub> (temperature for 50% CO conversion) and T<sub>100%</sub> (temperature for 100% CO conversion) are listed in **Table 2**. For the fresh Au/CeO<sub>2</sub> catalyst, although 100% CO conversion can be achieved at 80 °C, it shows almost no activity until 50 °C. N<sub>2</sub>-pretreatment of Au/CeO<sub>2</sub> significantly enhances the low-temperature activity with a T<sub>50%</sub> of 54 °C. However, complete conversion of CO was not possible below 120 °C. A pretreatment in oxidative atmospheres such as in air and especially in oxygen, can remarkably improve the catalytic activity of Au/CeO<sub>2</sub>



**Fig. 2.** Nitrogen sorption isotherms and pore size distributions of (a) HMS, (b) CeO<sub>2</sub> and Au/CeO<sub>2</sub> pretreated in O<sub>2</sub>-H<sub>2</sub>. The isotherm of CeO<sub>2</sub> was offset vertically by 100 cm<sup>3</sup>g<sup>-1</sup>.

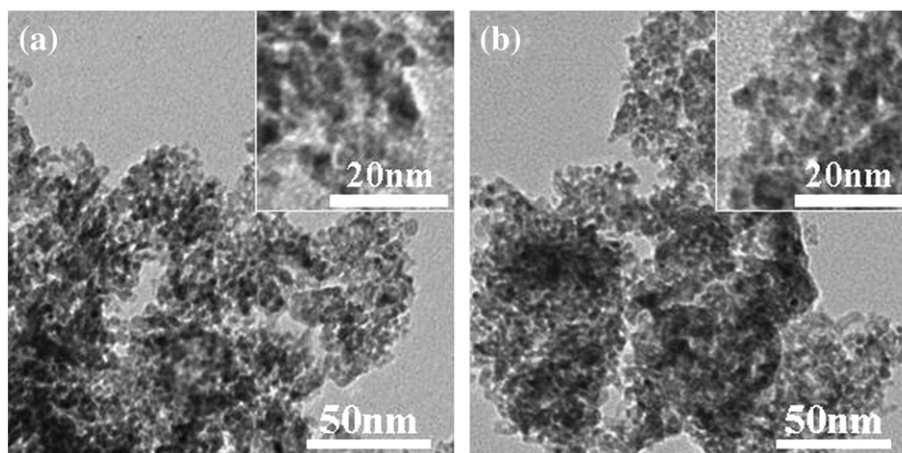


Fig. 3. TEM images of (a) Au/CeO<sub>2</sub> pretreated in O<sub>2</sub>-H<sub>2</sub>; (b) Au/CeO<sub>2</sub> pretreated in N<sub>2</sub>.

catalysts, and the T<sub>50%</sub> is reduced to 26 °C. H<sub>2</sub>-pretreatment results in the Au/CeO<sub>2</sub> with the same T<sub>100%</sub> as the unpretreated sample, but with a significantly improved low-temperature activity. The calculated initial reaction rate of the Au/CeO<sub>2</sub> pretreated in hydrogen is the highest among all samples.

Furthermore, we pretreated one sample first in oxygen and then hydrogen in order to integrate both advantages of the oxygen and hydrogen pretreatments. As expected, the sample Au/CeO<sub>2</sub> pretreated in oxygen followed by hydrogen shows the highest initial reaction rate and the lowest temperature of T<sub>50%</sub>. When the Au/CeO<sub>2</sub> catalyst was pretreated in hydrogen followed by oxygen, the initial reaction rate was similar to the Au/CeO<sub>2</sub> pretreated in H<sub>2</sub> and the complete CO conversion temperature shifted to 60 °C, better than that of Au/CeO<sub>2</sub> pretreated in hydrogen.

The catalyst stability was tested (Fig. 4b). In this case, less amount of catalyst (50 mg) was used to ensure that the conversion did not reach 100% at the test temperature so that any deactivation can be observed. As shown, Au/CeO<sub>2</sub> pretreated in oxygen only lost approximately 4% of its initial conversion in the 50 h span, and hydrogen pretreatment even led to a slightly improved activity in the same period, indicating a good stability of the catalyst.

Furthermore, H<sub>2</sub>-TPR experiments of Au/CeO<sub>2</sub> catalysts pretreated in different atmospheres were conducted, and the results are shown in Fig. 5. According to the literature [22], the high temperature peak (at ca. 800 °C) corresponds to the reduction of bulk oxygen and the formation of lower oxides of cerium, the low-temperature peak can be assigned to the co-reduction of Au<sup>3+</sup> and surface oxygen of CeO<sub>2</sub>. The

presence of gold can help to improve the reducibility of the surface oxygen on CeO<sub>2</sub>, which facilitates the oxygen transfer across the solid-gas interface during reaction.

As seen in Fig. 5, pretreatments almost do not change the position of the high temperature peak, and the low-temperature peak of Au/CeO<sub>2</sub> catalysts shifts to lower temperature in the sequence: O<sub>2</sub>-H<sub>2</sub> ≈ O<sub>2</sub> < air < H<sub>2</sub>-O<sub>2</sub> < H<sub>2</sub> < unpretreated ≈ N<sub>2</sub>. As suggested [22], Au<sup>0</sup> is usually responsible for the activation of O<sub>2</sub> molecule and the hydroxyl containing Au<sup>x+</sup> provides the pathway for the conversion of CO to CO<sub>2</sub>. However, a high amount of Au<sup>x+</sup> or Au<sup>0</sup> will cause a decrease in the activity. The appropriate ratio of Au<sup>x+</sup> and Au<sup>0</sup> is crucial to achieve the best catalytic activity for CO oxidation [7,23]. In our case, unpretreated Au/CeO<sub>2</sub> catalyst only has Au<sup>3+</sup> and do not possess Au<sup>0</sup>. N<sub>2</sub>-pretreatment can only remove the surface impurities of Au/CeO<sub>2</sub> catalyst. Au/CeO<sub>2</sub> pretreated in oxygen followed by hydrogen should present the appropriate ratio of Au<sup>x+</sup> and Au<sup>0</sup>, thus a higher activity. Au/CeO<sub>2</sub> catalyst pretreated in air or oxygen has a certain amount of Au<sup>x+</sup> on the surface of ceria, while H<sub>2</sub>-, N<sub>2</sub>- and H<sub>2</sub>-O<sub>2</sub> pretreated Au/CeO<sub>2</sub> catalysts possess less Au<sup>x+</sup> on the surface of ceria. This could be the reason that the pretreatments in the different atmospheres lead Au/CeO<sub>2</sub> catalysts showing different activities.

#### 4. Conclusion

We have demonstrated that Au/CeO<sub>2</sub> catalysts pretreated in different atmospheres can significantly affect their activity for CO oxidation. The

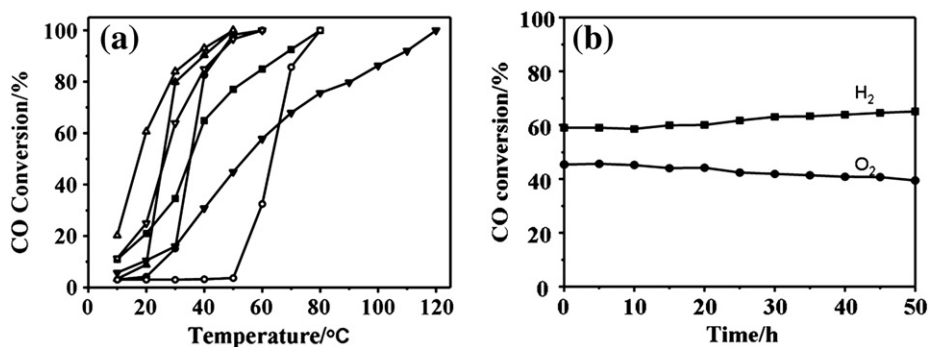
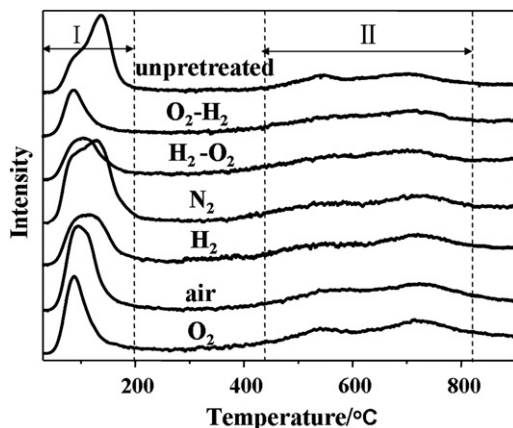


Fig. 4. a) Catalytic activity of Au/CeO<sub>2</sub> pretreated in different atmospheres (■:H<sub>2</sub>; ●:air; ▲:O<sub>2</sub>; ▼:N<sub>2</sub>; △:O<sub>2</sub>-H<sub>2</sub>; ▽:H<sub>2</sub>-O<sub>2</sub>; ○:unpretreated); b) Stability test of Au/CeO<sub>2</sub> pretreated in H<sub>2</sub> and O<sub>2</sub>.

**Table 2**

Initial conversion and reaction rate,  $T_{50\%}$  and  $T_{100\%}$  for Au/CeO<sub>2</sub> catalysts pretreated in different atmospheres.

Pretreatment atmospheres	Initial conversion (%)	Initial reaction rate (mol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup> )	$T_{50\%}$ (°C)	$T_{100\%}$ (°C)
H <sub>2</sub>	10.94	0.244	35	80
Air	3.00	0.067	35	60
O <sub>2</sub>	3.33	0.074	26	50
N <sub>2</sub>	5.71	0.127	54	120
O <sub>2</sub> -H <sub>2</sub>	20.23	0.451	17	50
H <sub>2</sub> -O <sub>2</sub>	11.34	0.253	26	60
Unpretreated	2.99	0.067	63	80



**Fig. 5.** H<sub>2</sub>-TPR of Au/CeO<sub>2</sub> pretreated in different atmospheres (I: low-temperature peak. II: high-temperature peak).

greatest catalytic activity was achieved when Au/CeO<sub>2</sub> catalyst was subjected to a pretreatment under an oxidative atmosphere. It was found that pretreatment does not change the morphology and structure of the

catalysts, but does change the activity. As demonstrated by H<sub>2</sub>-TPR, the surface interaction between gold and ceria is changed depending on a pretreatment.

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