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The preparation of Au/CeO_2 catalysts and their activities for low-temperature CO oxidation

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Au/CeO_2 catalysts prepared by co-precipitation (CP) and deposition-precipitation (DP) methods were tested for low temperature CO oxidation reaction. The structural characters and redox features of the catalysts were investigated by XRD, XPS and H_2-TPR. Their catalytic performances for low temperature CO oxidation were studied by means of a microreactor -GC system. It showed that the catalytic activities of Au/CeO_2 catalysts greatly depended on the preparation method. The catalysts prepared by DP method exhibited a surprisingly higher activity towards CO oxidation than that prepared by CP method. This may arise from the differences in the particle sizes of Au and redox properties of the catalysts. The low Au loading and the resistance to high temperature of DP-prepared catalyst made it more applicable.

KEY WORDS: Au/CeO_2 catalysts; co-precipitation method; deposition-precipitation method; low temperature CO oxidation.

1. Introduction

Since Haruta *et al.* [1] found that nano-dimension gold deposited on metal oxides had high catalytic activity towards CO oxidation at low temperature, a great deal of attention has been given to the gold-supported catalysts. Various supports were applied to this reaction, such as Fe_2O_3 [1–4], Co_3O_4 [2, 5], TiO_2 [2, 5–9], MnO_2 [1, 10, 11], ZrO_2 [5], SiO_2 [2], Al_2O_3 [2, 5, 12], and it has been suggested that reducible transition metal oxides (Fe_2O_3, MnO_2, TiO_2) showed a better catalytic performance than those irreducible ones (Al_2O_3, SiO_2) due to their capability to adsorb oxygen [2]. CeO_2 was widely reported to be a good reducible metal oxide, which has a high oxygen storage capability, furthermore, it is a structure promoting component which enhances noble metal dispersion and participates in the stabilization against thermal sintering of other used supports [13–15]. Now it is commonly used as a key component in automobile three-way catalysts.

Gold-ceria was a kind of preferential catalyst first reported by Gardner *et al.* used for CO oxidation [10]. In recent decade it has arisen more people's interesting for its application to a series of reactions, such as water gas shift reaction (WGS) [13, 14, 16–19], the catalytic combustion of VOC [20], selective oxidation of CO in H_2-rich gas [21]. For low temperature CO oxidation, Liu and Stephanopoulos investigated La doped Au/CeO_2 catalysts [22], Carrettin and Guzman *et al.* [23–25] evidenced nanocrystalline CeO_2 increased the activity of Au by two orders magnitude and identified reactive oxygen species in this process. Most recently, several articles were reported to study the influence factors including method, aging time and surface area of ceria [26–28].

In our study, we focus on low-content (≤1wt%) Au/CeO_2 catalysts considering the high cost of gold. Co-precipitation and deposition-precipitation were used to compare the influence of preparation methods on the catalytic properties. The effects of the support, calcination temperature and gold content upon the catalytic activity have been studied.

2. Experimental section

2.1. Catalyst preparation

Gold supported on ceria catalysts were prepared via two methods: co-precipitation (CP) method and deposition-precipitation (DP) method, using $HAuCl_4\cdot 4H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$ as precursors.

For the CP method, calculated amount of $HAuCl_4 \cdot 4H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$ were dissolved in distilled water, then the aqueous mixture was added into the solution of $(NH_4)_2CO_3$(0.5 mol/L) at 70 °C under vigorous stirring, the pH was maintained at a constant value of 9.0. The slurry was stirred for an hour and then washed several times with distilled water until no Cl^- could be detected ($AgNO_3$ test).

In the case of DP method, cerium oxide was prepared from $Ce(NO_3)_3\cdot 6H_2O$ by the similar procedure as

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co-precipitation described above, the dried product was calcined at 400 °C for 4 h, then a yellow CeO_2 powder was obtained. Appropriate volume of $HAuCl_4$ solution (0.01 g/mL) was added into the suspension of CeO_2 under vigorous stirring, using $(NH_4)_2CO_3$(0.5 mol/L) to adjust pH till it reached 9.0, stirred the slurry at 60 °C for 2 h, then washed the precipitate with distilled water to eliminate Cl^- completely.

Both the CP and DP prepared samples were dried at 80 °C. In order to commence the ceria–gold interaction, the as-prepared samples should be heated in air to 200 °C or higher [18]. Therefore, the catalysts were calcined at different temperatures after drying.

The samples prepared by co-precipitation method were donated as AuCeCP, and prepared by deposition-precipitation method were donated as AuCeDP.

2.2. Catalysts characterization

X-ray power diffraction (XRD) analysis of the samples were performed on a D/MAX-2500 diffractometer using CuKα radiation(40 kV 100 mA) and scanning in the region $2\theta = 20°–80°$. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File. The average crystal sizes of ceria and gold were calculated from the peak broadening using the Scherrer's equation.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Perkin-Elmer PHI 1600 spectrophotometer with the MgKα radiation. The operating conditions were kept constant at 29.35 eV and 250.0 W. In order to subtract the surface charging effect, the C1s peak has been fixed, in agreement with the literature, at a binding energy of 285 eV [18].

Temperature-programmed reduction (TPR) experiment was performed under the mixture of 5% H_2 in N_2 flowing (20 ml/min) over 0.05 g catalysts, and the catalyst bed was heated to 1000 °C at a rate of 10 °C min^{-1}. Prior to TPR, the samples were treated in air at room temperature for 30 min. The H_2 uptake amount during the reduction was measured by using a thermal conductivity detector (TCD).

All characterizations were performed on 1 wt% Au loading samples.

2.3. Measurement of catalytic activity

Catalytic tests of the catalysts for CO oxidation were carried out in a fixed-bed flow microreactor (12 mm i.d.) under atmospheric pressure using 100 mg catalyst powder. Reaction gas mixture consisting of 1% CO balanced with air is passed through the catalyst bed at a total flow rate of 33.6 ml/min. The reactant and product composition is analyzed on-line with a GC-508A gas chromatograph equipped with a thermal conductivity detector (TCD). The activity was expressed by the degree of conversion of CO.

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the XRD patterns of pure CeO_2, AuCeDP and AuCeCP (calcined at 300 °C for 3 h). All samples exhibited a typical fluorite structure of CeO_2 and the diffraction peaks could be indexed to (111), (200), (220), (311), (222), (400), (331) and (420) phases. In the case of AuCeCP sample, a small broad peak at about 38° was observed, which was assigned to metallic gold. However, no obvious peak related to the gold was discernible in the catalyst of AuCeDP, it is probably due to the very small size of gold particles and fine dispersion on the surface of support. Our work further confirms that the preparation method plays an important role in determining the size of gold particle, which may arise different catalytic activity in CO oxidation [29]. The calculated average sizes of ceria and gold particles are listed in Table 1.

Figure 2 gives the XRD patterns of Au/CeO_2 catalysts prepared by DP method calcined at different temperatures. It showed that no peak attributed to metallic gold crystal phase was detected for the samples calcined at 200–500 °C, which indicated that gold particles were finely dispersed on CeO_2 support. However, when calcined at 600 °C, a small gold peak appeared. We can conclude that high temperature may lead to agglomeration of gold particles. Table 1 also gives the variation of CeO_2 particle size with the temperature. It can be seen that the CeO_2 crystalline sizes grew slightly when the temperature increased. For all prepared catalysts, gold addition seems to have a significant effect in suppressing the crystal growth of ceria [18].

XPS is used to give the surface information about the catalysts. Figure 3 Shows the XPS spectra of Au 4f region. In this region gold species showed two main peaks due to the Au $4f_{7/2}$ and the Au $4f_{5/2}$. AuCeCP sample gave peaks centered at 84.0 and 87.0 eV, typical

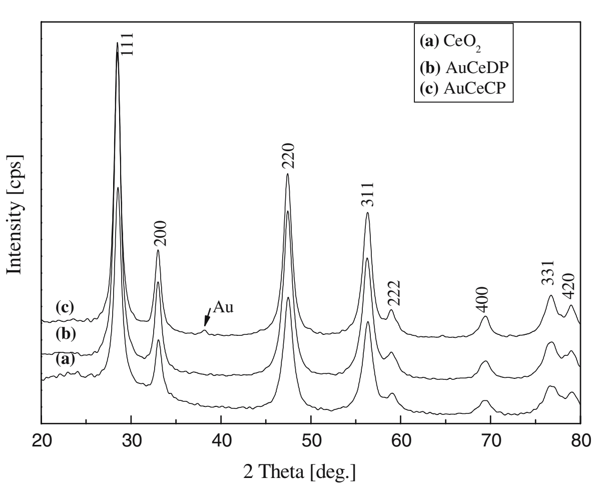

Figure 1. XRD spectra of AuCeDP, AuCeCP (calcined at 300 °C for 3 h) and pure CeO_2.

Table 1
Average sizes of ceria and gold particles prepared by CP and DP calcined at different temperatures

Catalysts	T(°C)	$d_{CeO}2$(nm)	d_{Au}(nm)
CeO2	400	7.51	–
AuCeCP	200	8.56	12.3
AuCeCP	300	8.94	14.4
AuCeCP	400	9.28	19.3
AuCeDP	200	9.05	n.d.
AuCeDP	300	7.25	n.d.
AuCeDP	400	8.05	n.d.
AuCeDP	500	8.39	n.d.
AuCeDP	600	9.87	18.2

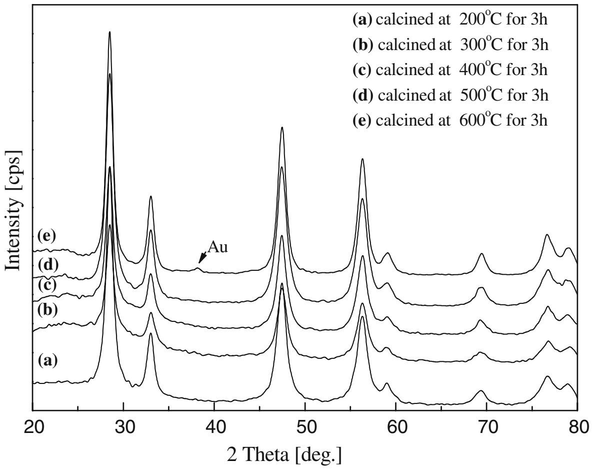

Figure 2. XRD patterns of 1 wt% Au/CeO_2 (DP) catalysts calcined at different temperatures.

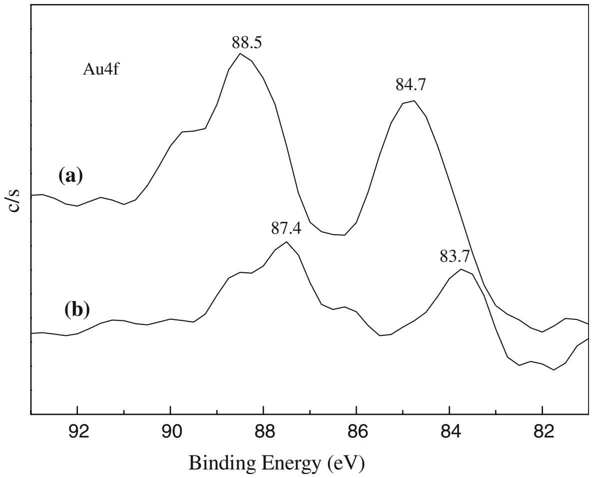

Figure 3. XPS patterns of Au 4f (a) AuCeDP (b) AuCeCP (calcined at 300 °C for 3 h).

binding energy of gold in metallic state [14, 18, 19], but the intensity was rather weak, this may due to the fact that most gold was buried inside the support at the preparation process. For AuCeDP sample, the Au 4f peak showed a doublet at 84.7 and 88.5 eV, which had a positive shift compared to typical metallic gold binding energy, similar finding was reported by Tabakova [30], they assigned it to the highly dispersed gold clusters on the surface of AuCeDP sample. The results were in accordance with XRD patterns, obviously, DP-prepared sample could give higher gold dispersion on the surface, where Au may perform its function more easily.

The XPS spectra for O1s peak of Au/ceria catalysts prepared by DP and CP method (figure 4) showed identical pattern with a main peak centered at 529.3 eV and a broad shoulder at 531.5 eV, which indicated the existence of two different oxygen species. The larger peak was assigned to lattice oxygen of CeO_2, and the peak at higher binding energy was attributed to chemisorbed water and hydroxyl [31]. By comparing the results, AuCeDP sample showed an obvious higher amount of hydroxyl groups on the surface than AuCeCP. It is expected that the near-surface region containing a significant quantity of hydroxyl groups may play a crucial role in the catalytic reaction, and Schryer *et al.* has proposed a mechanism on how hydroxyl groups improved CO oxidation for Pt/CeO_2 catalysts [32]. A combination influence of Au^+-OH^- and metallic gold was suggested by Costello to evidence the effect of hydroxyl on CO conversion [33].

From the figure 5, we can find six Ce 3d XPS peaks at B.E. about 882, 888, 898, 900, 907 and 916 eV for both samples, which were consistent with the previous report of Ce^{4+} [34], indicating the main valence of Ce was +4. A small fraction of Ce^{3+} can also be detected with a BE at 885.3 eV.

The TPR profiles of DP and CP samples calcined at 300 °C are shown in figure 6. As reported in literature, pure CeO_2 showed two reduction peak at about 500 °C and 800 °C, and interpreted as the reduction of surface-capping oxygen and bulk phase lattice oxygen, respectively [35]. For both method prepared Au/CeO_2

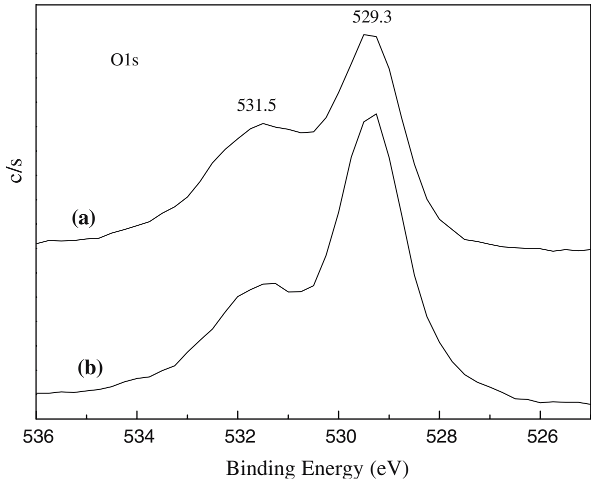

Figure 4. XPS patterns of O 1s (a) AuCeDP (b) AuCeCP (calcined at 300 °C for 3 h).

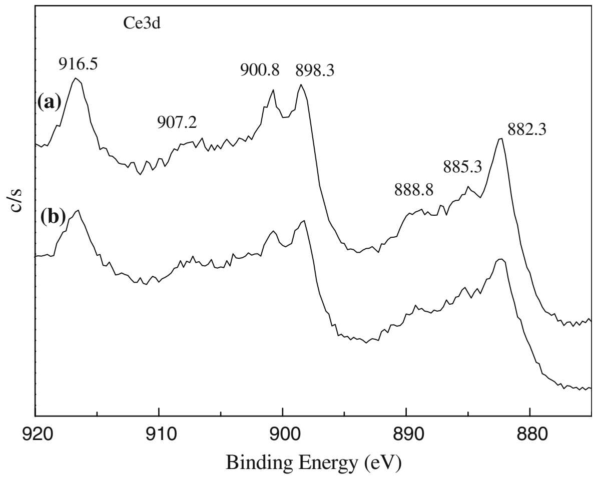

Figure 5. XPS patterns of Ce 3d (a) AuCeDP (b) AuCeCP (calcined at 300 °C for 3 h).

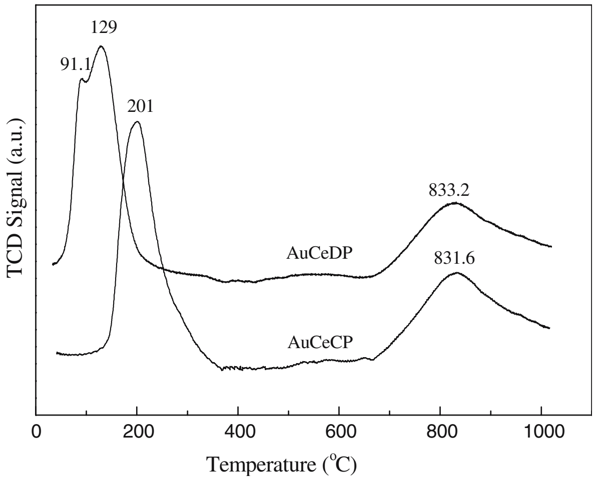

Figure 6. H_2-TPR profiles of AuCeDP and AuCeCP catalysts (calcined at 300 °C for 3 h).

catalysts, the peaks corresponding to the reduction of surface capping oxygen of ceria became sharper and significantly shifted to lower temperatures, while the high temperature peak unchanged, which is in agreement with previous findings [16, 28]. This indicates that the presence of gold facilitates the reducibility of surface oxygen, and the effect is more pronounced on DP-prepared sample. As can be seen from the spectra, AuCeDP sample gave a small peak at 91.1 °C and a maximum peak at 129 °C. We may attribute the former peak to the reduction of oxygen species on the fine gold species and the latter to the reduction of surface ceria [14]. In contrast, AuCeCP sample only showed a single low temperature peak at around 201 °C.

3.2. *Catalytic activity evaluation*

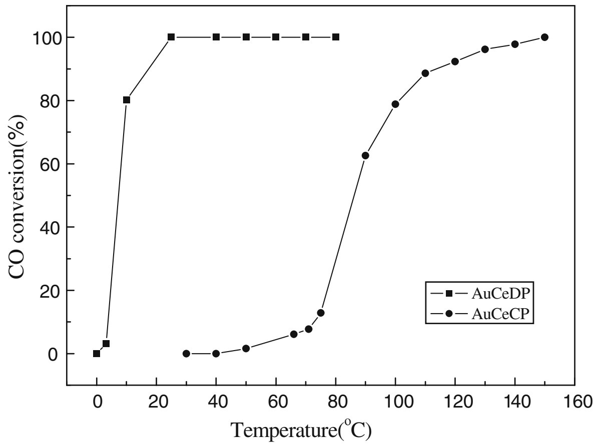

Figure 7. Catalytic activity for CO oxidation of Au/CeO_2 catalysts prepared by CP and DP (calcined at 300 °C for 3 h).

Figure 7 shows the conversion of CO oxidation of Au/CeO_2 catalysts prepared by CP and DP. We found that with the same gold content (as low as 1wt%), AuCeDP samples gave a surprisingly higher activity than the AuCeCP ones. The DP samples started the conversion as soon as the gas mixture passed through the catalyst bed at about 3 °C, a complete CO conversion was obtained when the temperature reached around 20 °C. While for the CP sample, no activity was observed below 40 °C, with the temperature increasing, the CO conversion increased and a 100% conversion was gotten at 150 °C. As can be inferred from characterizations, the highly dispersed gold particle and increased oxygen mobility may contribute to the superior activity of AuCeDP sample.

The catalytic activities for CO conversion of 1 wt% AuCeDP catalysts calcined on different temperatures were also studied (figure 8). It seemed that the calcination temperatures had little effect on the catalytic activities of the samples calcined below 500 °C, they all showed room temperature light-off for CO oxidation. The results were just opposite to the report by Pillai that the activity were significantly lost on heating them beyond 200 °C [27], this may due to the different preparation procedure we have chosen. But for the sample

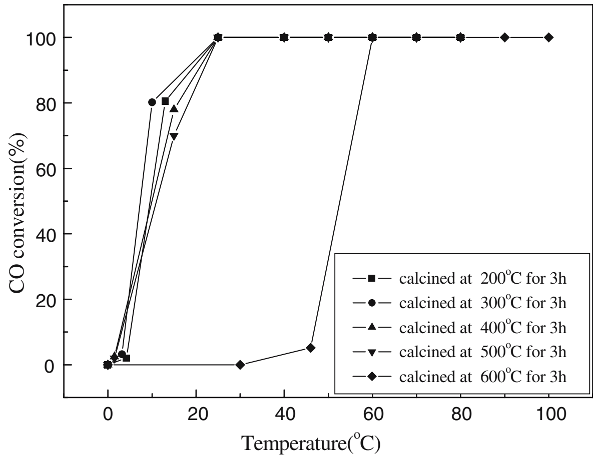

Figure 8. Catalytic activity for CO oxidation of AuCeDP catalysts calcined at different temperatures.

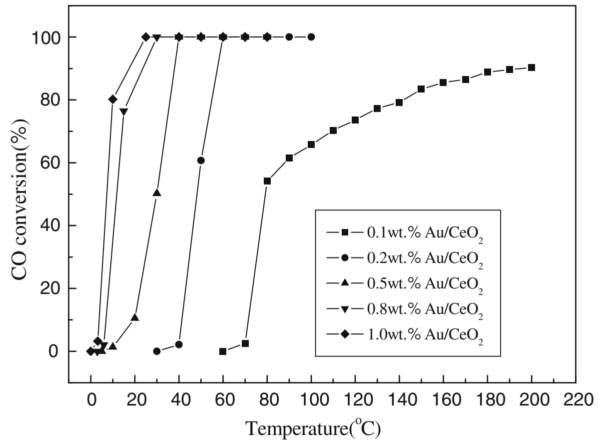

Figure 9. Catalytic activity for CO oxidation of AuCeDP catalysts with different gold contents.

calcined at 600 °C, the light-off temperature of CO oxidation increased to 50 °C, which showed a significantly decrease in redox properties. These results were just in good agreement with XRD patterns. This confirms that Au particle size can play an important role in the redox process.

For comparison, different gold-loading (≤1wt%) DP-prepared catalysts have been examined (figure 9), Au-free cerium oxide was also tested. Pure CeO_2 showed no activity blow 200 °C. Obviously, the presence of gold greatly improved the performance of ceria. This may attributed to the synergetic effect between the support and Au particles at the interface [23]. Apparently, the conversion of CO rose with the increase of gold content, whereas 0.5 wt% Au/CeO_2 was good enough to give a room temperature light-off under our condition, which may allow Au catalysts more applicable. Moreover, we did not observe any decline of the catalytic activity during a 14 h on stream measurement.

4. Conclusions

The catalytic performance of Au/CeO_2 catalysts greatly depended on the preparation method, for our prepared samples, deposition-precipitation method exhibited a surprisingly higher activity towards CO oxidation than co-precipitation method. The structure and surface characterization evidenced the existence of nanosized ceria and gold species, an intimate contact between them may lead to a higher surface oxygen mobility and improved the reducibility of CeO_2. The low loading, high activity and the resistance to high temperature of DP-prepared catalyst make it very useful in commerce.

Acknowledgments

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