

Article

Cerium phosphate-supported Au catalysts for CO oxidation☆

Yulin Wang, Huan Liu, Zhen Ma *

Shanghai Key Laboratory of Atmospheric Particle Pollution & Prevention (LAP³), Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

ARTICLE INFO

Article history:

Received 22 June 2017

Received in revised form 6 August 2017

Accepted 10 August 2017

Available online 19 August 2017

Keywords:

Gold

Catalysis

Catalyst support

CePO₄

Carbon monoxide

Oxidation

ABSTRACT

LaPO₄ and hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) are typical metal phosphates recently found to be useful for making supported metal or metal oxide catalysts, but CePO₄ (also belonging to the metal phosphate family) has been rarely used to make supported catalysts. It would be interesting to develop CePO₄-supported catalysts and explore their catalytic applications. Herein, hexagonal CePO₄ nanorods (denoted as CePO₄-H), hexagonal CePO₄ nanowires (CePO₄-HNW), monoclinic CePO₄ nanoparticles (CePO₄-M), and monoclinic CePO₄ nanowires (CePO₄-MNW) prepared by different methods were used to support gold via deposition-precipitation with urea (DPU). The gold contents of these catalysts were all around 1 wt%. The catalytic activities of these Au/CePO₄ catalysts in CO oxidation were found to follow the sequence of Au/CePO₄-MNW > Au/CePO₄-HNW > Au/CePO₄-M > Au/CePO₄-H. These catalysts were characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), N₂ adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), oxygen temperature-programmed desorption (O₂-TPD), and CO₂ temperature-programmed desorption (CO₂-TPD) to find possible correlations between the physicochemical properties and catalytic activities of these catalysts.

© 2017 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

Gold was rarely used as a catalyst component several decades ago, not only because gold is expensive, but also because heterogeneous gold catalysts were found to be barely active in catalysis at that time. However, since Haruta and co-workers discovered that gold loaded on a suitable metal oxide support (such as TiO₂) could be active for CO oxidation below room temperature [1], research on the synthesis, characterization, and application of supported gold catalysts has been booming. Supported gold catalysts are useful for catalyzing a number of reactions related to environmental remediation and the synthesis of chemicals [2–6].

Supports typically used for the preparation of heterogeneous gold catalysts include TiO₂, Fe₂O₃, Al₂O₃, and SiO₂ [2,3]. Supports can influence the physicochemical properties and catalytic performance of supported gold catalysts in profound ways. For instance, it was found that reducible supports are more suitable for making active gold catalysts than non-reducible supports [7,8]. Different solid supports (with different isoelectric points) can not only influence the amount of gold to be deposited onto these supports, but also influence the size and thermal stability of the supported gold nanoparticles. As a result, the activities of different supported gold catalysts in a catalytic reaction

can differ widely. Oxide supports have often been modified by other metal oxides to tune the physicochemical properties and the catalytic performance of the resulting supported gold catalysts [9]. In addition, supported gold catalysts based on metal oxides with different crystal phases or morphologies were found to show different catalytic performance [10–13]. However, metal salts have been seldom used as supports for making supported gold catalysts.

LaPO₄ and hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) are non-reducible metal phosphates. They have different acid-base properties and good thermal stability, and thus have been used as supports for making supported catalysts such as Au/LaPO₄ [14–18], Pt/LaPO₄ [19,20], Pd/LaPO₄ [21], Rh/LaPO₄ [22–24], Au/hydroxyapatite [15,25–28], Pt/hydroxyapatite [19], Rh/hydroxyapatite [22,29,30], and Ru/hydroxyapatite [31–33] useful for CO oxidation [14–19,24,26,27], N₂O decomposition [22,24,29,30,33], NO decomposition [21], three-way catalysis [23], photocatalytic reduction of CO₂ [20], the water-gas shift reaction [31], direct tandem synthesis of imines and oximes [25], aerobic oxidation of cyclohexane [28], and aerobic oxidation of benzyl alcohols [32].

Similar to LaPO₄, CePO₄ also belongs to the metal phosphate family. CePO₄ has been used as a catalyst for the dehydration of isopropanol [34], the oxidative dehydrogenation of isobutene [35], the removal of mercury elements [36], and the selective catalytic reduction of NO with NH₃ [37]. CePO₄ can also be used as a support to make supported catalysts such as Au/CePO₄ for CO oxidation [38] and electrochemical oxygen reduction reaction [39], Pt/CePO₄ for the electrochemical methanol oxidation [40], Ru/CePO₄ for the aerobic oxidation of alcohols

☆ Supported by the National Natural Science Foundation of China (21177028 and 21477022).

* Corresponding author. Fax: +86 21 65643597.

E-mail address: zhenma@fudan.edu.cn (Z. Ma).

[41], and Rh/CePO₄ for N₂O decomposition [42,43]. Nevertheless, examples on the synthesis and application of CePO₄-supported catalysts are still limited in number. It would be interesting to develop CePO₄-supported catalysts and explore their catalytic applications.

The physicochemical properties of CePO₄ supports may influence the catalytic performance of CePO₄-supported catalysts. CePO₄ materials prepared by different methods and with specific preparation parameters may have different morphologies and crystal phases. For instance, hexagonal CePO₄ nanorods can be prepared by precipitation [44], whereas hexagonal CePO₄ nanowires can be prepared by a hydrothermal method [45,46]. Monoclinic CePO₄ materials can be prepared by heating hexagonal CePO₄ at high temperatures (>600 °C) [47,48]. These preparation methods may provide new opportunities for us to investigate the influence of different CePO₄ supports on the catalytic performance of supported gold catalysts.

One issue in the preparation of supported gold catalysts *via* a deposition–precipitation (DP) method is that the gold complex in the synthesis mixture cannot be effectively deposited onto supports and the amount of gold deposited varies greatly when using different supports [15,49]. A DPU (deposition–precipitation with urea) method [50,51] could circumvent this problem so that the gold precursor can be used economically and the catalytic activities of different supported gold catalysts can be compared at the same gold content level.

In this work, CePO₄ materials with different crystal phases and morphologies were used as supports to load gold *via* a DPU method. The catalytic activities of these catalysts in CO oxidation were investigated. CO oxidation is not only a reaction of environmental relevance, but also a sensitive probe reaction that can be used to compare the activities of different catalysts [52]. Interestingly, the catalytic activities of different Au/CePO₄ catalysts prepared using different CePO₄ supports were found to differ obviously. Relevant characterization was conducted to find the reason for this observation.

2. Experimental

2.1. Catalyst preparation

To 80 ml deionized water, 6.95 g Ce(NO₃)₃·6H₂O (Aladdin, 99.9%) and 1.84 g NH₄H₂PO₄ (Sinopharm, AR) were added. The mixture was magnetically stirred for 20 min to allow for the complete dissolution of these salts.

Hexagonal CePO₄ nanorods (CePO₄-H) and monoclinic CePO₄ nanoparticles (CePO₄-M) were prepared according to the literature [47,53]. The pH value of the above solution was adjusted to 7 by adding aqueous ammonia (27 wt%) dropwise, and the mixture was then stirred at room temperature for 6 h. The product (CePO₄-H) was filtered, washed with ethanol, and dried in an oven at 80 °C for 4 h. CePO₄-M was prepared by calcining CePO₄-H at 900 °C for 4 h.

Hexagonal CePO₄ nanowires (CePO₄-HNW) and monoclinic CePO₄ nanowires (CePO₄-MNW) were prepared according to the literature [45,54]. The pH value of the above solution was adjusted to 1 by adding aqueous ammonia (27 wt%) dropwise. The suspension was transferred to a Teflon-lined stainless steel autoclave and He was bubbled through the suspension for 1 h to remove the air from the autoclave in order to prevent the oxidation of Ce³⁺ to Ce⁴⁺. Then the autoclave was sealed, heated at 150 °C for 12 h, and naturally cooled to room temperature. The product (CePO₄-HNW) was filtered, washed with ethanol, and dried in an oven at 80 °C for 4 h. CePO₄-MNW was obtained by calcining CePO₄-HNW at 900 °C for 4 h.

Supported gold catalysts were prepared *via* deposition–precipitation with urea (DPU) [18]. Urea (1.89 g) was dissolved in 75 ml HAuCl₄ solution (2.03×10^{-3} mol·L⁻¹), and 3 g CePO₄ was added, and the mixture was stirred at 80 °C for 4 h. The suspension was centrifuged, washed with deionized water, and dried at 80 °C for 12 h. The collected

powders were calcined in a muffle furnace in static air at 350 °C (or 500 °C) for 3 h.

2.2. Catalytic activity tests

The catalytic tests were performed using a FINESORB-3010 instrument (fixed-bed continuous flow microreactor, FINETEC) at atmospheric pressure. Before each test, a catalyst (0.15 g) was packed within the U-shaped glass tube and then pretreated with flowing He (30 ml·min⁻¹) at 200 °C for 2 h. The catalyst was completely cooled to room temperature or 0 °C and subjected to CO oxidation testing. The reaction gas, containing 1 vol% CO/air at a flow rate of 50 ml·min⁻¹, was introduced into the reactor. The reaction temperature at 0 °C was achieved by using an ice-water bath in a Dewar. The reaction temperature between 0 °C and room temperature was actualized by removing portions of ice water or cold water and adding almost the same amount of water maintained at room temperature. The actual temperature was measured by a thermal couple inserted in the reactor. The reaction temperature above room temperature was increased to 200 °C at a heating rate of 0.5 °C·min⁻¹ using a furnace. The reaction products were analyzed by using gas chromatograph (Agilent 7890A) with a thermal conductivity detector. The CO conversion was calculated as $([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}} \times 100\%$, where $[\text{CO}]_{\text{in}}$ refers to the concentration of CO without any catalyst in the U-shaped glass tube, and $[\text{CO}]_{\text{out}}$ refers to the concentration of CO exiting the catalyst bed.

2.3. Catalyst characterization

The Au contents of catalysts were determined by ICP-OES (Perkin–Elmer OPTIMA 2100 DV optical emission spectrometer). Gold of precisely weighed samples was dissolved in *aqua regia*, and the obtained solutions were diluted and analyzed.

The specific Brunauer–Emmett–Teller (BET) surface areas of samples were determined by using a Micromeritics Tristar 3000 instrument at the liquid nitrogen temperature (–196 °C).

X-ray diffraction (XRD) data were obtained with a MSAL XD2 instrument using a graphite monochromator and Cu K α radiation. The scanning angles (2 θ) were 10°–80°, and the scanning rate was 8(°)·min⁻¹.

Transmission electron microscopic (TEM) experiments were conducted using a JEM-2011F transmission electron microscope operated at 200 kV. The sample was dispersed in ethanol, loaded on Cu grid-supported carbon film, and dried under an infrared lamp before analysis.

X-ray photoelectron spectroscopic (XPS) experiments were conducted using a Perkin–Elmer PHI 5000 C spectrometer with Mg K α X-ray as the emission source. The binding energies were calibrated by using the C1s peak at 284.8 eV.

Temperature-programmed desorption of O₂ or CO₂ (O₂-TPD or CO₂-TPD) were conducted on a FINESORB-3010 instrument with a TCD. A sample (0.1 g) was loaded into a U-shaped quartz tube, and then pretreated with He (30 ml·min⁻¹) at 200 °C for 2 h. The sample was cooled down to room temperature, and the sample was then heated from room temperature to 50 °C at a rate of 5 °C·min⁻¹. At the same time, pure O₂ or 5 vol% CO₂/air was fed at a flow rate of 50 ml·min⁻¹ for 1 h. The system was then purged with He (30 ml·min⁻¹) for 3 h. Finally, the sample was heated to 550 °C at a ramping rate of 10 °C·min⁻¹.

3. Results and Discussion

3.1. Catalytic activity of Au/CePO₄ in CO oxidation

Fig. 1 compares the catalytic activities of different Au/CePO₄ catalysts (calcined at 350 °C) in CO oxidation. The catalytic activities were tested as a function of reaction temperature. As shown in the figure, Au/CePO₄-MNW calcined at 350 °C is the most active, achieving 71% CO conversion

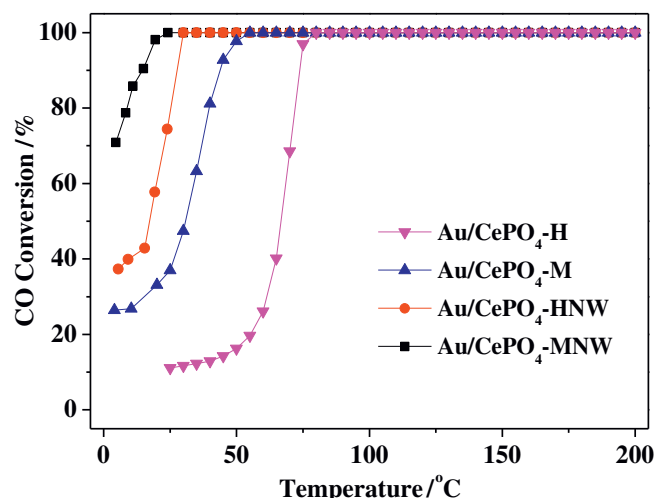


Fig. 1. CO conversions on Au/CePO₄ catalysts calcined at 350 °C.

at 5 °C and complete CO conversion at 20 °C. Au/CePO₄-HNW is the second most active, achieving complete CO conversion at 30 °C. Au/CePO₄-M is the third most active, achieving complete CO conversion at 55 °C. Au/CePO₄-H shows the lowest activity among these catalysts. It achieves 11% CO conversion at 25 °C and 100% CO conversion at 80 °C. Overall, the activities of these catalysts clearly follow the sequence of: Au/CePO₄-MNW > Au/CePO₄-HNW > Au/CePO₄-M > Au/CePO₄-H, *i.e.*, Au/CePO₄-MNW and Au/CePO₄-HNW prepared by using CePO₄ nanowires (either monoclinic or hexagonal) are more active than Au/CePO₄-M and Au/CePO₄-H prepared by using monoclinic CePO₄ nanoparticles or hexagonal CePO₄ nanorods. The most active Au/CePO₄-MNW in this study is slightly less active than Au/LaPO₄-NW (with 1 wt% Au, achieving *ca.* 90% CO conversion at 0 °C and 100% CO conversion at 15 °C) reported previously [18]. Note that in both sets of experiments (the current experiments and those in our previous work [18]), the reaction conditions (*i.e.*, catalyst amount, CO concentration, gas flow rate) are the same except that the catalysts are different.

To see whether these catalysts can withstand high-temperature calcination and whether the activity trend observed above is general, Au/CePO₄ catalysts calcined at 500 °C were also tested in CO oxidation. Such a high-temperature calcination step is usually used to test the thermal stability of supported gold catalysts as the agglomeration of gold nanoparticles upon high-temperature treatment may be a problem for practical applications [55,56].

As shown in Fig. 2, the activities of the catalysts calcined at 500 °C still follow the sequence of Au/CePO₄-MNW > Au/CePO₄-HNW > Au/CePO₄-M > Au/CePO₄-H, but the activities of the former three catalysts decrease obviously compared with those of the corresponding Au/CePO₄ catalysts calcined at 350 °C. This observation may be due to the sintering of gold nanoparticles to some extent, as will be proved by TEM data later. However, the activity of the least active Au/CePO₄-H calcined at 500 °C is almost the same as that of the same catalyst calcined at 350 °C. This point will be discussed further using TEM data presented later.

As seen from Figs. 1 and 2, the difference of catalytic activity of different Au/CePO₄ catalysts is more obvious for the catalysts calcined at 350 °C, and Au/CePO₄ catalysts calcined at 350 °C are in general more active than the corresponding catalysts calcined at 500 °C. Thus, subsequent characterization was mainly focused on Au/CePO₄ calcined at 350 °C.

3.2. Characterization of Au/CePO₄

To understand why the activities of Au/CePO₄ catalysts are so different, we first resort to XRD characterization. As shown in Fig. 3,

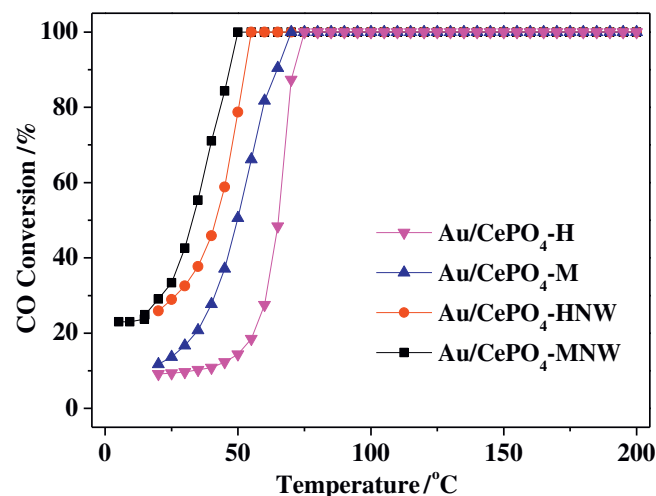


Fig. 2. CO conversions on Au/CePO₄ catalysts calcined at 500 °C.

CePO₄-H and CePO₄-HNW both exhibit the hexagonal phase of CePO₄ (in reference to a standard card: PDF#04-0632), whereas CePO₄-M and CePO₄-MNW (prepared by calcining CePO₄-H and CePO₄-HNW, respectively, at 900 °C) show the monoclinic phase (PDF#32-0199). Their respective crystal phases are kept after loading gold, but no gold peaks can be observed, probably due to the low gold loading (theoretical value 1 wt%) and high dispersion of gold nanoparticles. Indeed, the gold contents of Au/CePO₄-H, Au/CePO₄-M, Au/CePO₄-HNW, and Au/CePO₄-MNW were determined by ICP-OES as 1.07 wt%, 0.97 wt%, 0.97 wt%, and 0.99 wt% (Table 1), all close to 1 wt%, and gold nanoparticles were found to be dispersed on CePO₄ supports (as presented by TEM data in Fig. 4).

TEM data can provide direct information about the morphologies of CePO₄ supports as well as the dispersion and sizes of gold nanoparticles. Fig. 4 shows the TEM images of Au/CePO₄ catalysts calcined at 350 °C. Au/CePO₄-H mainly exhibits CePO₄ nanorods (packed together) with lengths on the order of 100 nm, and some relatively big gold nanoparticles are dispersed on the support. Au/CePO₄-M is composed of large CePO₄ nanoparticles with sizes on the order of 50–100 nm. However, the morphologies of the CePO₄ supports change obviously after calcination at 900 °C. Both Au/CePO₄-HNW and Au/CePO₄-MNW exhibit uniform CePO₄ nanowires with lengths of several hundred nanometers.

The BET surface areas of Au/CePO₄-H, Au/CePO₄-M, Au/CePO₄-HNW, and Au/CePO₄-MNW are 114.0, 10.1, 31.3, and 18.1 m²·g^{−1}, respectively (Table 1). Since the gold loading of each catalyst is close to 1 wt%, the surface areas of the supported gold catalysts should be mainly determined by those of the CePO₄ supports. The surface area data thus show that CePO₄-H prepared by precipitation has a higher surface area than CePO₄-HNW prepared by hydrothermal synthesis at 150 °C for 12 h, whereas CePO₄-M and CePO₄-MNW prepared by calcining CePO₄-H and CePO₄-HNW, respectively, at 900 °C both have low surface areas. The surface area data seem to be consistent with the morphologies and sizes of the CePO₄ supports imaged by TEM, in the sense that supports with larger sizes usually have low surface areas.

From the TEM images in Fig. 4, we can also see the presence of gold nanoparticles on CePO₄ supports. It should be mentioned that these are representative TEM images, meaning that other TEM photos were taken and used in the statistics of gold particle sizes. Fig. 5 summarizes the gold particle size distribution based on the statistics of 100 gold particles for each sample. The average sizes of gold nanoparticles were obtained using the DigitalMicrograph software. The average gold particle sizes of Au/CePO₄-H, Au/CePO₄-M, Au/CePO₄-HNW, and Au/CePO₄-MNW are 8.4, 7.2, 6.8, and 5.6 nm, respectively, correlating with the activities of these catalysts, *i.e.*, Au/CePO₄-MNW with the smallest average gold particle size shows the highest activity in CO oxidation, whereas Au/

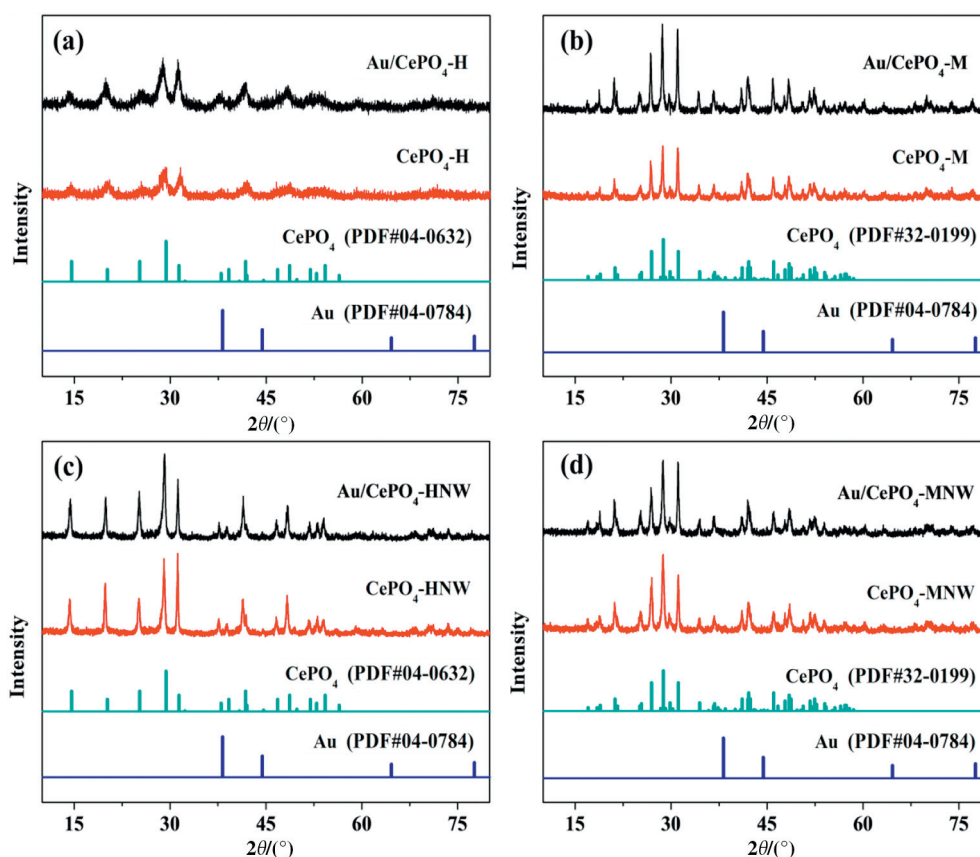


Fig. 3. XRD patterns of Au/CePO₄ catalysts and corresponding supports.

Table 1

ICP, BET surface areas, T_{50} values, and average gold particle size of Au/CePO₄ catalysts

Sample	Au content /wt.%	BET surface areas /m ² ·g ⁻¹	T_{50} ^① /°C	T_{50} ^② /°C	Average ^③ gold particle size /nm	Average ^④ gold particle size /nm
Au/CePO ₄ -H	1.07	114.0	67	66	8.4	8.4
Au/CePO ₄ -M	0.97	10.0	31	50	7.2	7.5
Au/CePO ₄ -HNW	0.97	31.3	17	44	6.8	7.2
Au/CePO ₄ -MNW	0.99	18.1	<0	34	5.6	6.3

① T_{50} (temperature required for 50% CO conversion) values of Au/CePO₄ calcined at 350 °C.

② T_{50} values of Au/CePO₄ calcined at 500 °C.

③ Average gold particle size of Au/CePO₄ calcined at 350 °C.

④ Average gold particle size of Au/CePO₄ calcined at 500 °C.

CePO₄-H with the biggest average gold particle size shows the lowest activity.

To know why the activities of Au/CePO₄-MNW, Au/CePO₄-HNW, and Au/CePO₄-M decrease after calcination at 500 °C whereas that of Au/CePO₄-H calcined at 500 °C is similar to that of Au/CePO₄-H calcined at 350 °C (Figs. 1 and 2, Table 1), TEM experiments involving Au/CePO₄ catalysts calcined at 500 °C were also conducted. As shown in Fig. S1, the morphologies of these CePO₄ supports are the same as those of the corresponding supports of Au/CePO₄ calcined at 350 °C. Fig. 6 summarizes the gold particle size distribution based on the statistics of 100 gold particles for each sample. The average gold particle sizes of Au/CePO₄-MNW, Au/CePO₄-HNW, and Au/CePO₄-M increase to 6.3 nm (c.f. 5.6 nm for the sample calcined at 350 °C), 7.2 nm (c.f. 6.8 nm), 7.5 nm (c.f. 7.2 nm), respectively, whereas the average gold particle size of Au/CePO₄-H is 8.4 nm (c.f. 8.4 nm). The data thus show that the sizes of gold nanoparticles on CePO₄ support correlate to the activities of these Au/CePO₄ catalysts. In addition, the seemingly small increase of average particle size (e.g., from 5.6 to 6.3 nm for Au/CePO₄-MNW) when increasing the calcination temperature from 350 to 500 °C can make the catalytic activity decrease obviously (Figs. 1

and 2), indicating that catalytic activity is sensitively influenced by the gold particle size. It was found previously that the size of gold nanoparticles on supports matters for achieving high activity in CO oxidation, and the reason for a supported gold catalyst to keep its high activity after high-temperature treatment is the stabilization of gold nanoparticles by a suitable support [55,56]. Of course, high-temperature calcination may also change the contents of Au⁺, Au⁰, and surface hydroxyls as well as the microscopic details and other physicochemical properties of the support. These factors may also exert subtle influences on the catalytic performance.

As mentioned before, the BET surface areas of Au/CePO₄-H, Au/CePO₄-M, Au/CePO₄-HNW, and Au/CePO₄-MNW are 114.0, 10.1, 31.3, and 18.1 m²·g⁻¹, respectively (Table 1). It seems that CePO₄-H with the highest surface area cannot lead to the formation of very small gold nanoparticles, probably due to the intrinsic nature of the support, but at least it can mitigate the sintering of gold nanoparticles at 500 °C since the hexagonal CePO₄ nanorods are packed together (Fig. 4), creating rough surfaces and relatively high surface areas.

Above, we have shown that the size of gold nanoparticles matters for catalytic CO oxidation. However, gold species may exist on the support

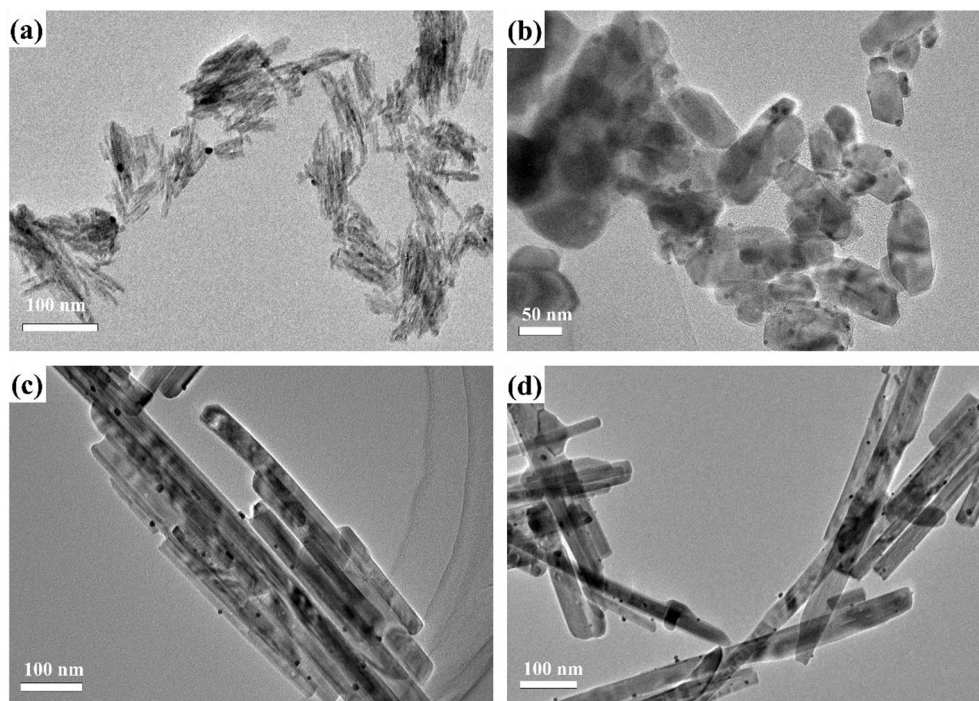


Fig. 4. TEM images of (a) Au/CePO₄-H, (b) Au/CePO₄-M, (c) Au/CePO₄-HNW, and (d) Au/CePO₄-MNW catalysts calcined at 350 °C.

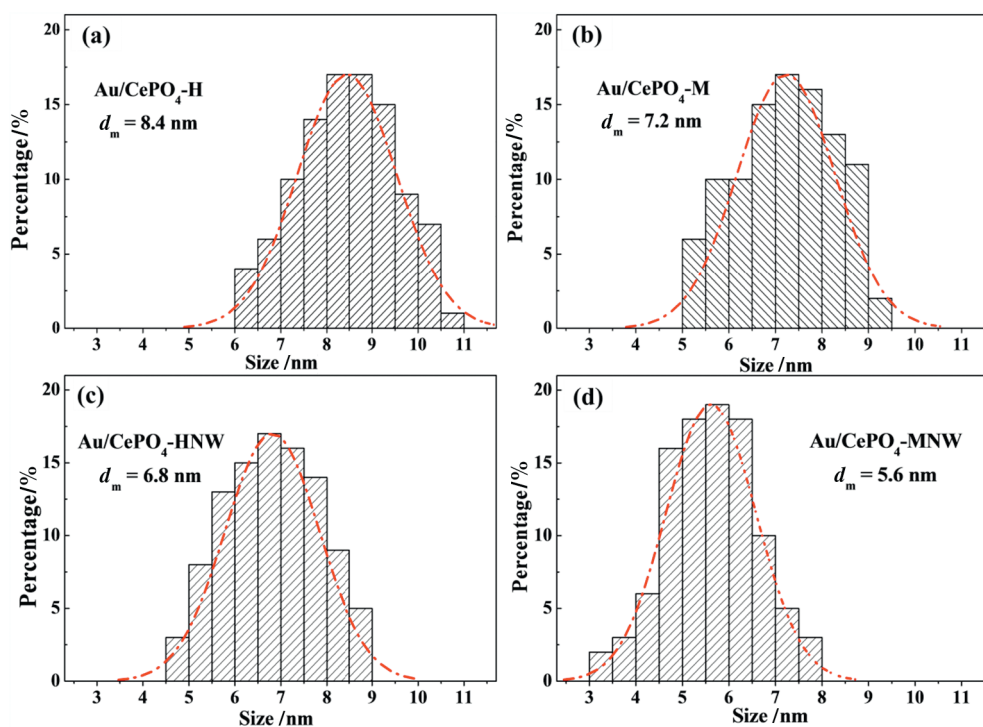


Fig. 5. The size distributions of gold nanoparticles of Au/CePO₄ catalysts calcined at 350 °C.

in different forms, *i.e.*, cationic or metallic. Fig. 7 shows the Au 4f XPS spectra of Au/CePO₄ catalysts calcined at 350 °C (without undergoing reaction testing). The peak at about 84.3 eV corresponds to Au⁰ of supported gold catalysts [57,58], whereas the peak located at 84.8 eV [58] or 85.6 eV [59] corresponds to Au⁺. Detailed data are summarized in Table 2. In any case, Au⁰ is the main gold species, and Au⁺ is a minority

gold species. Au/CePO₄-MNW with the highest activity has a relatively low Au⁺ content, whereas for Au/CePO₄-H with the lowest catalytic activity, the Au⁺ content is not the highest. For Au/CePO₄ catalysts collected after reaction, the Au⁺ content of each catalyst is similar to that of the corresponding fresh catalyst (Fig. S2 and Table 2). These data indicate that probably Au⁺ does not play a major role in

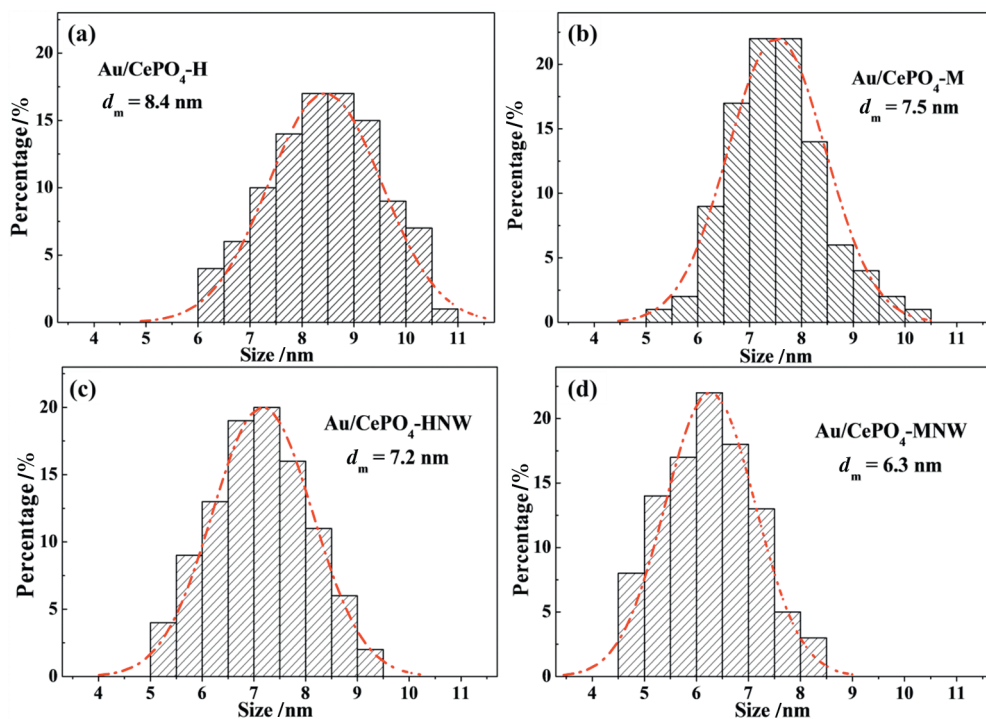


Fig. 6. The size distributions of gold nanoparticles of Au/CePO₄ catalysts calcined at 500 °C.

determining the catalytic activity, and that metallic Au nanoparticles are more important for catalytic CO oxidation [2,3].

Above, we have showed that the catalytic activities of catalysts follow the sequence of Au/CePO₄-MNW > Au/CePO₄-HNW > Au/CePO₄-M > Au/CePO₄-H, and ascribed the difference in activity to the size of gold nanoparticles. However, other factors (physicochemical

properties) should be considered and discussed. Surface hydroxyls were claimed to be able to be involved in CO oxidation over certain gold catalysts [60]. Thus, Fig. 8 summarizes the O 1s XPS spectra of Au/CePO₄ catalysts before reaction. The O 1s peak can be divided into two main characteristic peaks. The peak at about 531.1 eV corresponds to lattice oxygen, whereas the peak centered at about 532.5 eV is due to

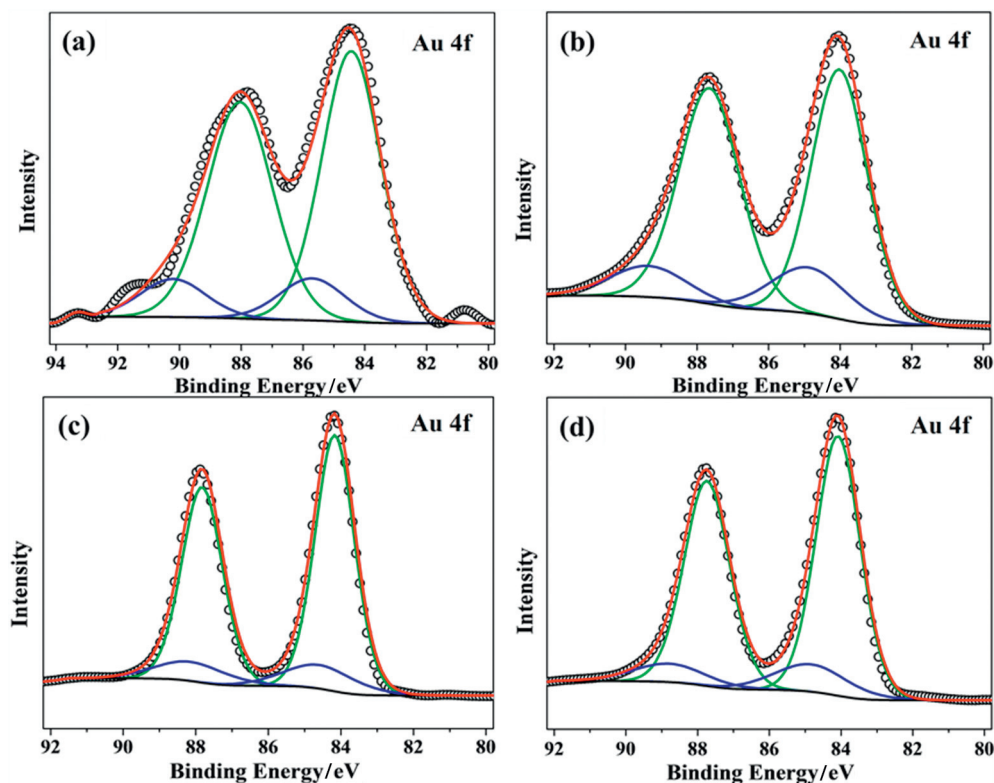


Fig. 7. Au 4f XPS spectra of (a) Au/CePO₄-H, (b) Au/CePO₄-M, (c) Au/CePO₄-HNW, and (d) Au/CePO₄-MNW before reaction.

Table 2The binding energy of Au 4f and the corresponding proportions of Au⁺

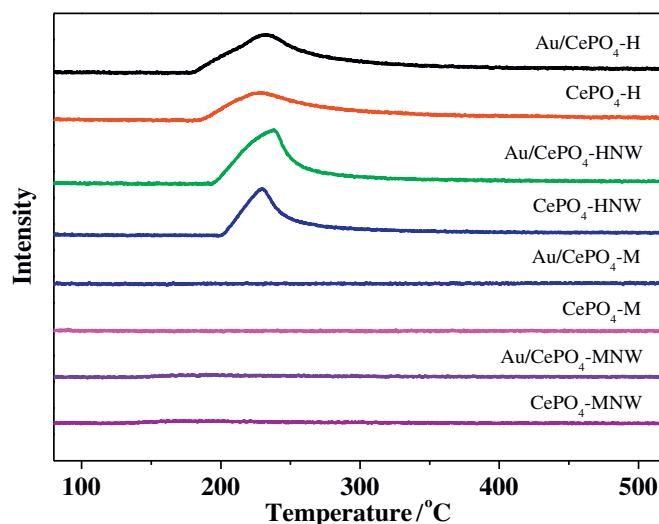
Sample	Au ⁰ 4f _{7/2} /eV	Au ⁺ 4f _{7/2} /eV	Au ⁺ /(Au ⁰ + Au ⁺) ^① /%	Au ⁺ /(Au ⁰ + Au ⁺) ^② /%
Au/CePO ₄ -H	84.4	85.7	14.8	15.2
Au/CePO ₄ -M	84.0	84.8	17.7	18.0
Au/CePO ₄ -HNW	84.1	84.6	14.4	14.0
Au/CePO ₄ -MNW	84.0	84.8	13.8	13.5

① Before reaction.

② After reaction.

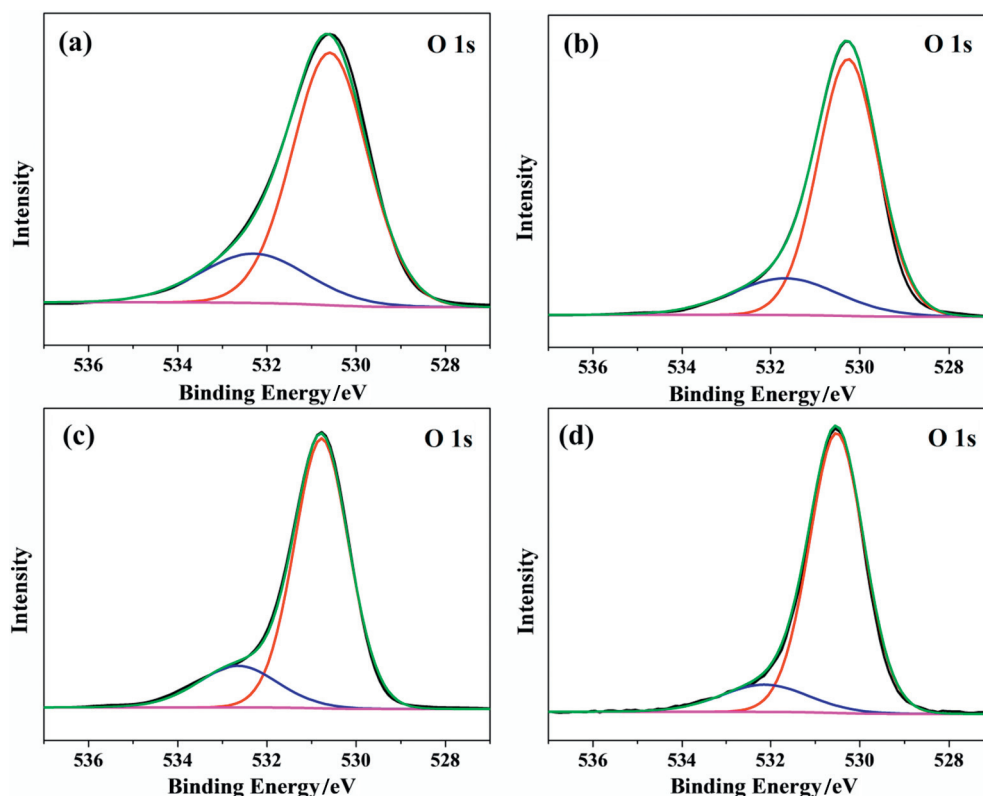
surface hydroxyls [10,47]. The relative percentages of the surface hydroxyls in oxygen species of Au/CePO₄-H, Au/CePO₄-M, Au/CePO₄-HNW, and Au/CePO₄-MNW calcined at 350 °C (without catalyzing CO oxidation) are 21.6%, 20.0%, 19.2%, and 13.4%, respectively. The corresponding values of these catalysts collected after reaction testing are 22.0%, 20.7%, 20.6%, and 14.4%, respectively (Fig. S3). The data show that the surface hydroxyl concentration increases a little after the reaction, but there is no simple correlation between the surface hydroxyl concentration and catalytic activity.

The abilities for CePO₄ supports or Au/CePO₄ in adsorbing and releasing oxygen should also be considered. Fig. 9 shows the O₂-TPD data of Au/CePO₄ catalysts and the corresponding supports. For Au/CePO₄-H and Au/CePO₄-HNW prepared with hexagonal CePO₄ supports, there is an O₂ desorption peak at 180–300 °C, indicating that oxygen can be adsorbed on these catalysts and released upon heating towards 300 °C. On the other hand, there is no O₂ desorption peak for Au/CePO₄-M and Au/CePO₄-MNW prepared with monoclinic CePO₄ supports, indicating that there is virtually no O₂ adsorption on these catalysts or the adsorption of O₂ on these catalysts is reversible, *i.e.*, there is no strong adsorption of O₂. In addition, it is clear from the figure that the O₂-TPD profiles of these Au/CePO₄ catalysts are quite similar to those of their corresponding supports, meaning that the O₂ adsorption–desorption behavior of Au/CePO₄ catalysts is largely determined

**Fig. 9.** O₂-TPD profiles of Au/CePO₄ catalysts.

by their corresponding CePO₄ supports. There is a marked difference between hexagonal CePO₄ supports and monoclinic supports. However, such a difference in terms of oxygen adsorption–desorption behavior cannot account for the observed activity difference (Au/CePO₄-MNW > Au/CePO₄-HNW > Au/CePO₄-M > Au/CePO₄-H). Rather, the difference is merely intrinsic for different CePO₄ supports.

A similar argument can be made for the lack of correlation between the basicity of Au/CePO₄ catalysts and their catalytic activity. CO₂ can be adsorbed on basic sites, and its desorption upon heating can indicate the basicity of the solid sample. If the CO₂ desorption peak is big, then that means that the solid sample contains a lot of basic sites. On the other hand, if CO₂ molecules desorb at high temperatures, that means that

**Fig. 8.** O 1s XPS spectra of (a) Au/CePO₄-H, (b) Au/CePO₄-M, (c) Au/CePO₄-HNW, and (d) Au/CePO₄-MNW before reaction.

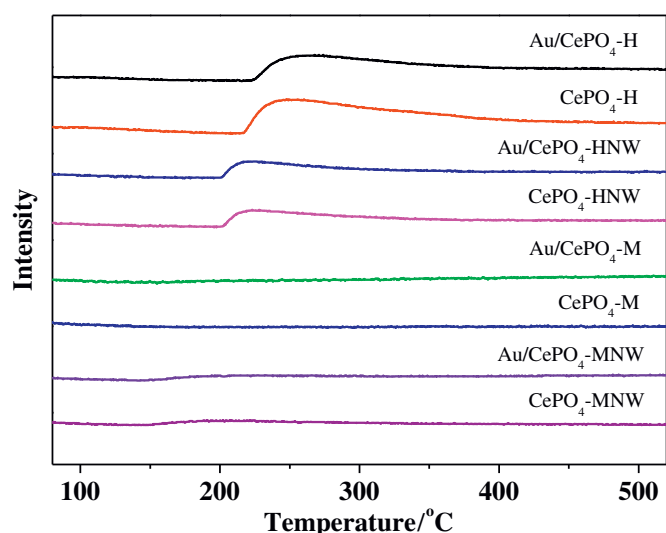


Fig. 10. CO₂-TPD profiles of Au/CePO₄ catalysts.

the solid sample has strong basicity. Fig. 10 shows the CO₂-TPD profiles of Au/CePO₄ catalysts and their corresponding supports. It is found that while Au/CePO₄-H and Au/CePO₄-HNW show an obvious CO₂ desorption peak above 200 °C, there is virtually no CO₂ desorption from Au/CePO₄-M and Au/CePO₄-MNW. The CO₂ desorption behaviors of Au/CePO₄ catalysts are similar to those of their corresponding CePO₄ supports, *i.e.*, hexagonal CePO₄ supports have an obvious CO₂ desorption peak whereas monoclinic CePO₄ supports virtually do not have CO₂ desorption peak. The data indicate that the basicity is an intrinsic property of the CePO₄ supports, and there is no clear correlation between the basicity of Au/CePO₄ catalysts and their catalytic activities in CO oxidation.

The overall conclusion of the work is that metallic gold nanoparticles with small sizes seem to play a major role in determining the catalytic activity of Au/CePO₄ in CO oxidation, whereas the size of gold nanoparticles is determined by the nature (*i.e.*, physicochemical properties such as sizes, morphologies, surface areas) of CePO₄ supports and by the calcination temperature. To put the work in perspective, it should be mentioned that our group also found that Au/LaPO₄ based on hexagonal LaPO₄ nanowires is more active in CO oxidation than Au/LaPO₄ based on commercial (hexagonal) LaPO₄ composed of many short nanorods packed together, due to the smaller average gold particle (3.7 nm) for the former catalyst than that (5.9 nm) of the latter [18]. Further theoretical input is needed for revealing the fundamental reasons of the stabilization of gold nanoparticles on supports with different crystal phases and morphologies.

4. Conclusions

Hexagonal CePO₄ nanorods (CePO₄-H) were prepared by precipitation, and hexagonal CePO₄ nanowires (CePO₄-HNW) were prepared by hydrothermal synthesis. Monoclinic CePO₄ nanoparticles (CePO₄-M) and monoclinic CePO₄ nanowires (CePO₄-MNW) were prepared by calcining CePO₄-H and CePO₄-HNW, respectively, at 900 °C for 4 h. Gold was loaded onto these supports *via* DPU (deposition-precipitation with urea). The activities of catalysts (calcined at 350 or 500 °C) in CO oxidation consistently follow the sequence of Au/CePO₄-MNW > Au/CePO₄-HNW > Au/CePO₄-M > Au/CePO₄-H. XRD and TEM results show the gold particles on supports are highly dispersed. The average size of Au nanoparticles correlates to the catalytic activity. The smaller the gold nanoparticles are, the higher the activity. XPS data indicate that Au⁰ is a majority gold species, whereas Au⁺ is a minority gold species. The O₂ adsorption–desorption behaviors and basicity of Au/CePO₄ catalysts are largely determined by those of their corresponding CePO₄

supports, *i.e.*, these properties are intrinsic to CePO₄ supports. There is no clear correlation between the O₂ adsorption–desorption behaviors (or basicity) of Au/CePO₄ catalysts and the catalytic activities in CO oxidation. Rather, metallic gold nanoparticles with small sizes seem to play a major role. This work provides a catalyst system for further theoretical work and fundamental application in catalytic CO oxidation and other reactions.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2017.08.008>.

References

- [1] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0 °C, *Chem. Lett.* 6 (1987) 405–408.
- [2] M. Haruta, M. Date, Advances in the catalysis of Au nanoparticles, *Appl. Catal. A Gen.* 222 (2001) 427–437.
- [3] A.S.K. Hashmi, G.J. Hutchings, Gold catalysis, *Angew. Chem. Int. Ed.* 45 (2006) 7896–7936.
- [4] A. Corma, H. Garcia, Supported gold nanoparticles as catalysts for organic reactions, *Chem. Soc. Rev.* 37 (2008) 2096–2126.
- [5] Y. Zhang, X. Cui, F. Shi, Y. Deng, Nano-gold catalysis in fine chemical synthesis, *Chem. Rev.* 112 (2012) 2467–2505.
- [6] M. Stratakis, H. Garcia, Catalysis by supported gold nanoparticles: beyond aerobic oxidative processes, *Chem. Rev.* 112 (2012) 4469–4506.
- [7] M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, CO oxidation over supported gold catalysts—“inert” and “active” support materials and their role for the oxygen supply during reaction, *J. Catal.* 197 (2001) 113–122.
- [8] S.H. Overbury, L. Ortiz-Soto, H.G. Zhu, B. Lee, M.D. Amiridis, S. Dai, Comparison of Au catalysts supported on mesoporous titania and silica: investigation of Au particle size effects and metal-support interactions, *Catal. Lett.* 95 (2004) 99–106.
- [9] Z. Ma, S. Dai, Development of novel supported gold catalysts: a materials perspective, *Nano Res.* 4 (2011) 3–32.
- [10] L.C. Wang, Y.M. Liu, M. Chen, Y. Cao, H.Y. He, K.N. Fan, MnO₂ nanorod supported gold nanoparticles with enhanced activity for solvent-free aerobic alcohol oxidation, *J. Phys. Chem. C* 112 (2008) 6981–6987.
- [11] R. Si, M. Flytzani-Stephanopoulos, Shape and crystal-plane effects of nanoscale ceria on the activity of Au–CeO₂ catalysts for the water–gas shift reaction, *Angew. Chem. Int. Ed.* 47 (2008) 2884–2887.
- [12] X.-S. Huang, H. Sun, L.-C. Wang, Y.-M. Liu, K.-N. Fan, Y. Cao, Morphology effects of nanoscale ceria on the activity of Au/CeO₂ catalysts for low-temperature CO oxidation, *Appl. Catal. B Environ.* 90 (2009) 224–232.
- [13] G.Q. Yi, H.W. Yang, B.D. Li, H.Q. Lin, K. Tanaka, Y.Z. Yuan, Preferential CO oxidation in a H₂-rich gas by Au/CeO₂ catalysts nanoscale CeO₂ shape effect and mechanism aspect, *Catal. Today* 157 (2010) 83–88.
- [14] W.F. Yan, S. Brown, Z.W. Pan, S.M. Mahurin, S.H. Overbury, S. Dai, Ultrastable gold nanocatalyst supported by nanosized non-oxide substrate, *Angew. Chem. Int. Ed.* 45 (2006) 3614–3618.
- [15] Z. Ma, H.F. Yin, S.H. Overbury, S. Dai, Metal phosphates as a new class of supports for gold nanocatalysts, *Catal. Lett.* 126 (2008) 20–30.
- [16] Z. Ma, H.F. Yin, S. Dai, Influence of preparation methods on the performance of metal phosphate-supported gold catalysts in CO oxidation, *Catal. Lett.* 138 (2010) 40–45.
- [17] M. Li, Z. Wu, S.H. Overbury, CO oxidation on phosphate-supported Au catalysts: effect of support reducibility on surface reactions, *J. Catal.* 278 (2011) 133–142.
- [18] H. Liu, Y. Lin, Z. Ma, Au/LaPO₄ nanowires: synthesis, characterization, and catalytic CO oxidation, *J. Taiwan Inst. Chem. Eng.* 62 (2016) 275–282.
- [19] X.S. Qian, H.M. Qin, T. Meng, Y. Lin, Z. Ma, Metal phosphate-supported Pt catalysts for CO oxidation, *Materials* 7 (2014) 8105–8130.
- [20] B. Pan, S.J. Luo, W.Y. Su, X.X. Wang, Photocatalytic CO₂ reduction with H₂O over LaPO₄ nanorods deposited with Pt cocatalyst, *Appl. Catal. B Environ.* 168 (2015) 458–464.
- [21] H. Tamai, T. Ikeya, F. Nishiyama, H. Yasuda, K. Iida, S. Nojima, NO decomposition by ultrafine noble metals dispersed on the rare earth phosphate hollow particles, *J. Mater. Sci.* 35 (2000) 4945–4953.
- [22] Y. Lin, T. Meng, Z. Ma, Catalytic decomposition of N₂O over RhO_x supported on metal phosphates, *J. Ind. Eng. Chem.* 28 (2015) 138–146.
- [23] M. Machida, T. Eidome, S. Minami, H.P. Buwono, S. Hinokuma, Y. Nagao, Y. Nakahara, Tuning the electron density of Rh supported on metal phosphates for three-way catalysis, *J. Phys. Chem. C* 119 (2015) 11653–11661.
- [24] H. Liu, Z. Ma, Effect of different LaPO₄ supports on the catalytic performance of Rh₂O₃/LaPO₄ in N₂O decomposition and CO oxidation, *J. Taiwan Inst. Chem. Eng.* 71 (2017) 373–380.
- [25] H. Sun, F.Z. Su, J. Ni, Y. Cao, H.Y. He, K.N. Fan, Gold supported on hydroxyapatite as a versatile multifunctional catalyst for the direct tandem synthesis of imines and oximes, *Angew. Chem. Int. Ed.* 48 (2009) 4390–4393.
- [26] M.I. Dominguez, F. Romero-Sarria, M.A. Centeno, J.A. Odriozola, Gold/hydroxyapatite catalysts synthesis, characterization and catalytic activity to CO oxidation, *Appl. Catal. B Environ.* 87 (2009) 245–251.

- [27] J. Huang, L.-C. Wang, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, Gold nanoparticles supported on hydroxylapatite as high performance catalysts for low temperature CO oxidation, *Appl. Catal. B Environ.* 101 (2011) 560–569.
- [28] Y.M. Liu, H. Tsunoyama, T. Akita, S.H. Xie, T. Tsukuda, Aerobic oxidation of cyclohexane catalyzed by size-controlled Au clusters on hydroxylapatite: size effect in the sub-2 nm regime, *ACS Catal.* 1 (2011) 2–6.
- [29] C.Y. Huang, Z. Ma, P.F. Xie, Y.H. Yue, W.M. Hua, Z. Gao, Hydroxylapatite-supported rhodium catalysts for N₂O decomposition, *J. Mol. Catal. A Chem.* 400 (2015) 90–94.
- [30] C.Y. Huang, Y.X. Jiang, Z. Ma, P.F. Xie, Y. Lin, T. Meng, C.X. Miao, Y.H. Yue, W.M. Hua, Z. Gao, Correlation among preparation methods/conditions, physicochemical properties, and catalytic performance of Rh/hydroxylapatite catalysts in N₂O decomposition, *J. Mol. Catal. A Chem.* 420 (2016) 73–81.
- [31] A. Venugopal, M.S. Scurrall, Hydroxylapatite as a novel support for gold and ruthenium catalysts: behaviour in the water gas shift reaction, *Appl. Catal. A Gen.* 245 (2003) 137–147.
- [32] C. Mondelli, D. Ferri, A. Baiker, Ruthenium at work in Ru-hydroxylapatite during the aerobic oxidation of benzyl alcohol: an *in situ* ATR-IR spectroscopy study, *J. Catal.* 258 (2008) 170–176.
- [33] Y.W. Cui, H. Liu, Y. Lin, Z. Ma, Metal phosphate-supported RuO_x catalysts for N₂O decomposition, *J. Taiwan Inst. Chem. Eng.* 67 (2016) 254–262.
- [34] H. Onoda, H. Nariiai, A. Moriawaki, H. Maki, I. Motooka, Formation and catalytic characterization of various rare earth phosphates, *J. Mater. Chem.* 12 (2002) 1754–1760.
- [35] Y. Takita, X. Qing, A. Takami, H. Nishiguchi, K. Nagaoka, Oxidative dehydrogenation of isobutane to isobutene III: reaction mechanism over CePO₄ catalyst, *Appl. Catal. A Gen.* 296 (2005) 63–69.
- [36] X.L. Weng, R.J. Mei, M.P. Shi, Q.Y. Kong, Y. Liu, Z.B. Wu, CePO₄ catalyst for elemental mercury removal in simulated coal-fired flue gas, *Energy Fuel* 29 (2015) 3359–3365.
- [37] W.Y. Yao, Y. Liu, X.Q. Wang, X.L. Weng, H.Q. Wang, Z.B. Wu, The superior performance of sol-gel made Ce-O-P catalyst for selective catalytic reduction of NO with NH₃, *J. Phys. Chem. C* 120 (2016) 221–229.
- [38] F. Romero-Sarria, M.I. Dominguez, M.A. Centeno, J.A. Odriozola, CO oxidation at low temperature on Au/CePO₄: mechanistic aspects, *Appl. Catal. B Environ.* 107 (2011) 268–273.
- [39] J. Kang, S. Byun, S. Nam, S. Kang, T. Moon, B. Park, Synergistic improvement of oxygen reduction reaction on gold/cerium-phosphate catalysts, *Int. J. Hydrog. Energy* 39 (2014) 10921–10926.
- [40] J. Park, Y. Oh, Y. Park, S. Nam, J. Moon, J. Kang, D.-R. Jung, S. Byun, B. Park, Methanol oxidation in nanostructured platinum/cerium-phosphate thin films, *Curr. Appl. Phys.* 11 (2011) S2–S5.
- [41] Y.J. Zhang, J.H. Wang, T. Zhang, Novel Ca-doped CePO₄ supported ruthenium catalyst with superior catalytic performance for aerobic oxidation of alcohols, *Chem. Commun.* 47 (2011) 5307–5309.
- [42] H. Liu, Z. Ma, Rh₂O₃/monoclinic CePO₄ composite catalysts for N₂O decomposition and CO oxidation, *Chin. J. Chem. Eng.* (2017) <https://doi.org/10.1016/j.cjche.2017.02.007> (in press).
- [43] H. Liu, Z. Ma, Rh₂O₃/hexagonal CePO₄ nanocatalysts for N₂O decomposition, *Front. Chem. Sci. Eng.* (2017) <https://doi.org/10.1017/s11705-017-1659-6> (in press).
- [44] S. Lucas, E. Champion, D. Bregiroux, D. Bernache-Assollant, F. Audubert, Rare earth phosphate powders RePO₄·nH₂O (Re = La, Ce or Y) - part I. Synthesis and characterization, *J. Solid State Chem.* 177 (2004) 1302–1311.
- [45] Y.P. Fang, A.W. Xu, R.Q. Song, H.X. Zhang, L.P. You, J.C. Yu, H.Q. Liu, Systematic synthesis and characterization of single-crystal lanthanide orthophosphate nanowires, *J. Am. Chem. Soc.* 125 (2003) 16025–16034.
- [46] M.H. Cao, C.W. Hu, Q.Y. Wu, C.X. Guo, Y.J. Qi, E.B. Wang, Controlled synthesis of LaPO₄ and CePO₄ nanorods/nanowires, *Nanotechnology* 16 (2005) 282–286.
- [47] Q.J. Zheng, X. Wang, J.T. Tian, R. Kang, Y.S. Yin, Synthesis and characterization of LaPO₄ powder heat treated at various temperatures, *Mater. Chem. Phys.* 122 (2010) 49–52.
- [48] D. Palma-Ramirez, M.A. Dominguez-Crespo, A.M. Torres-Huerta, H. Dorantes-Rosales, E. Ramirez-Meneses, E. Rodriguez, Microwave-assisted hydrothermal synthesis of CePO₄ nanostructures: correlation between the structural and optical properties, *J. Alloys Compd.* 643 (2015) S209–S218.
- [49] M. Haruta, When gold is not noble: catalysis by nanoparticles, *Chem. Rec.* 3 (2003) 75–87.
- [50] R. Zanella, L. Delannoy, C. Louis, Mechanism of deposition of gold precursors onto TiO₂ during the preparation by cation adsorption and deposition-precipitation with NaOH and urea, *Appl. Catal. A Gen.* 291 (2005) 62–72.
- [51] M. Khoudiakov, M.C. Gupta, S. Deevi, Au/Fe₂O₃ nanocatalysts for CO oxidation: a comparative study of deposition-precipitation and coprecipitation techniques, *Appl. Catal. A Gen.* 291 (2005) 151–161.
- [52] S. Royer, D. Duprez, Catalytic oxidation of carbon monoxide over transition metal oxides, *ChemCatChem* 3 (2011) 24–65.
- [53] F.Y. Lu, Y.Q. Shen, X. Sun, Z.L. Dong, R.C. Ewing, J. Lian, Size dependence of radiation-induced amorphization and recrystallization of synthetic nanostructured CePO₄ monazite, *Acta Mater.* 61 (2013) 2984–2992.
- [54] Y.J. Zhang, H.M. Guan, Hydrothermal synthesis and characterization of hexagonal and monoclinic CePO₄ single-crystal nanowires, *J. Cryst. Growth* 256 (2003) 156–161.
- [55] W.F. Yan, S.M. Mahurin, Z.W. Pan, S.H. Overbury, S. Dai, Ultrastable Au nanocatalyst supported on surface-modified TiO₂ nanocrystals, *J. Am. Chem. Soc.* 127 (2005) 10480–10481.
- [56] Z. Ma, S.H. Overbury, S. Dai, Au/M_xO_y/TiO₂ catalysts for CO oxidation: promotional effect of main-group, transition, and rare-earth metal oxide additives, *J. Mol. Catal. A Chem.* 273 (2007) 186–197.
- [57] E.A. Willneff, S. Braun, D. Rosenthal, H. Bluhm, M. Havecker, E. Kleimenov, A. Knop-Gericke, R. Schlögl, S.L.M. Schroeder, Dynamic electronic structure of a Au/TiO₂ catalyst under reaction conditions, *J. Am. Chem. Soc.* 128 (2006) 12052–12053.
- [58] H.Y. Xu, W. Chu, J.J. Luo, M. Liu, New Au/FeO_x/SiO₂ catalysts using deposition-precipitation for low-temperature carbon monoxide oxidation, *Catal. Commun.* 11 (2010) 812–815.
- [59] J.M.C. Soares, P. Morrall, A. Crossley, P. Harris, M. Bowker, Catalytic and noncatalytic CO oxidation on Au/TiO₂ catalysts, *J. Catal.* 219 (2003) 17–24.
- [60] M.C. Kung, R.J. Davis, H.H. Kung, Understanding Au-catalyzed low-temperature CO oxidation, *J. Phys. Chem. C* 111 (2007) 11767–11775.