Active Gold-Ceria and Gold-Ceria/Titania Catalysts for CO Oxidation: From Single-Crystal Model Catalysts to Powder Catalysts

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Abstract

CO oxidation was studied on model and powder catalysts of Au-CeO₂ and Au-CeO_x/TiO₂. Phenomena observed in Au-CeO₂(111) and Au-CeO₂/TiO₂(110) provided useful concepts for designing and preparing highly active and stable Au-CeO_x/TiO₂ powder catalysts for CO oxidation. Small particles of Au dispersed on CeO₂(111) displayed high catalytic activity, making Au-CeO₂(111) a better CO oxidation catalyst than Au-TiO₂(110) or Au-MgO(100). An excellent support for gold was found after depositing nanoparticles of ceria on TiO₂(110). The CeO_x nanoparticles act as nucleation centers for gold, improving dispersion of the supported metal and helping in the creation of reaction sites efficient for the adsorption of CO and the dissociation of the O₂ molecule. High-surface area catalysts were prepared by depositing gold on ceria nanorods and CeO_x/TiO₂ powders. The samples were tested for the low-temperature (10 – 70 °C) oxygen-rich (1%CO/4%O₂/He) CO oxidation reaction after pre-oxidation (20%O₂/He, 300 °C) and pre-reduction (5%H₂/He, 300 °C) treatments. Synchrotron-based *operando* X-ray diffraction (XRD) and X-ray absorption (XAS) spectroscopy were used to study the Au-CeO₂ and Au-CeO_x/TiO₂ catalysts under reaction conditions. Our *operando* findings indicate that the most active phase of these catalysts for low-temperature CO oxidation consist of small particles of metallic Au dispersed on CeO₂ or CeO_x/TiO₂.

Keywords: Gold; Ceria; Titania; CO oxidation; X-ray diffraction; X-ray absorption; Active site

1. Introduction

Although bulk gold materials have normally shown poor activity as catalysts, Au nanoparticles strongly interacting with the oxide supports were first described by Haruta et al. to be extremely active CO oxidation catalyst in 1989 [1]. Numerous studies since then have been reported to confirm the activity of well dispersed gold species for the CO oxidation reaction [2-21], and to explore the role of the oxide support using various reducible oxides including titania (TiO_2) [2-5], iron oxide (FeO_x) [6-9] and ceria (CeO_2) [7, 9-21], and non-reducible oxides such as silica (SiO_2) [5, 22] and alumina (Al_2O_3) [5]. While a full mechanism of this catalytic process still needs to be established, the nature of the support is commonly considered to be one of the key factors for dispersion and stabilization of ultra-fine gold structures and the activation of CO oxidation catalysts.

Ceria, as one of the most important rare earth oxides, has been extensively applied in catalysis and electrocatalysis due to its unique physical and chemical properties. The ability of cerium to switch between Ce^{4+} and Ce^{3+} oxidation states, releasing or storing oxygen, makes ceria an active oxide component of various oxidation catalysts used in diverse redox catalytic reactions. CeO_2 retains its fluorite-type crystal structure during the oxygen storage and release processes. To further improve the performance of Au- CeO_2 catalysts for the CO oxidation reaction, different preparation methods, including deposition-precipitation (DP) [7, 12-17], coprecipitation [9, 17], and urea-gelation coprecipitation [7], have been used to control and optimize the interaction of the Au-O-Ce structure, as well as the size and shape of ceria. The oxide support, especially if it is reducible, is included in the mechanism, as a source of active oxygen for the redox reactions. Thus, the basic questions regarding the structure–activity relationship and the interaction of gold and ceria in the low-temperature CO oxidation reaction have been addressed, but often with divergent conclusions. In our opinion, a careful investigation of the reported strong metal–support interaction through structural studies may provide further mechanistic insights as well as rationalize the design of practical catalysts.

Considering the oxidation state of gold in the active catalysts, different gold species have been proposed for various redox reactions. For instance, gold cations or positively charged nanoclusters (< 1 nm), comprising a few gold atoms are the active sites for the water-gas shift (WGS) reaction [23-25], while for CO oxidation reaction, there are still arguments whether ~ 3 nm Au particles on TiO_2 [2] or $\text{Ce}(\text{La})\text{O}_x$ [7] are most active or bi-layer gold clusters (0.5 nm in size) on Fe_2O_3 [8] effectively catalyze the CO oxidation reaction. Furthermore, due to the difficulties in controlling the catalyst structure, there is no direct evidence showing the location of the active sites yet. The Au surface, the support surface (especially Ce^{3+} or oxygen vacancies [10,21,26]), or the gold/support interface all have been suggested as important for the catalytic activity. Therefore, *operando* characterizations [27], such as X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and diffuse reflectance Infra-red Fourier transform (DRIFTS), are required to monitor the catalytic process; probe the active phase for the gold-ceria catalyst and unravel the reaction mechanism for the CO oxidation reaction.

In this paper, we use model single-crystal and powder catalyst to study the effect of the Au-ceria interactions on the activity of gold towards CO oxidation. To maximize Au-ceria interactions, we co-deposit nanoparticles of Au and ceria on titania or use ceria nanorods as a support. Previously, catalysts involving gold and ceria nanorods have been proved to be highly active for the water-gas shift (WGS) process [28], methanol steam reforming [29], and CO oxidation [16, 30]. In our study with the powder catalysts, we will focus on *operando* XAS & XRD characterizations, monitoring the structural changes of gold species and the oxide support under realistic reaction conditions, and determining the active phase for the low-temperature oxygen-rich CO oxidation. Our study shows that $\text{Au/CeO}_x/\text{TiO}_2$ powders are highly active and stable catalysts for this process.

2. Experimental Section

2.1 Studies with Au/CeO₂(111) and Au/CeO_x/TiO₂(110): The studies with model catalysts were performed in a system which combines an ultrahigh-vacuum (UHV) chamber (base pressure $\sim 5 \times 10^{-10}$ Torr) and a batch reactor [10,20]. The sample could be transferred between the reactor and UHV chamber without exposure to air. The UHV chamber (base pressure $\sim 5 \times 10^{-10}$ Torr) was equipped with instrumentation for X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), low-energy electron diffraction (LEED), ion scattering spectroscopy (ISS), and temperature-programmed desorption (TPD) [20]. The Au/CeO₂(111) and Au/CeO_x/TiO₂(110) catalysts were prepared following a methodology described in previous studies [10,20]. Au was evaporated on CeO₂(111) and CeO_x/TiO₂(110) at 25 °C. In the kinetic measurements the sample was transferred to the batch reactor at ~ 25 °C, then the reactant gases were introduced (4 Torr of CO and 2 Torr of O₂) and the sample was held at a reaction temperature of 27 °C. The amount of molecules produced was normalized by the geometric area exposed of the CeO₂(111) and TiO₂(110) samples [10,20].

2.1 Studies with Au-CeO₂ nanorods and Au-CeO_x/TiO₂

A. Synthesis of Au-CeO₂ nanorods: For the hydrothermal preparation of ceria nanorods [28], Ce(NO₃)₃·6H₂O (99.5%, Alfa; 4.5 mmol) was dissolved in 90 mL of an aqueous NaOH (98%, Alfa) solution of 6 mol/L. This stock solution was stirred at room temperature for 10 min in a Teflon bottle and then sealed tightly in a stainless-steel autoclave. Hydrothermal treatment was carried out at 100 °C for 24 h. After cooling, the white precipitates obtained were collected, washed with deionized (DI) water, and dried in vacuo at 70–80 °C overnight. The dried yellow powders were calcined in air at 400 °C for 4 h. For the gold deposition-precipitation (DP), 3 g of CeO₂ powder were slurried in DI water (150 mL) whilst stirring and an aqueous (NH₄)₂CO₃ solution (75 mL; 1M) was

then added. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99%, Alfa; 0.174 mmol) was dissolved in DI water (75 mL) and added to the above solution dropwise. The pH value was kept at 8–9 during the whole process. The resulting precipitate was aged at room temperature for 1 h, then filtered and washed three times with DI water at 60–70 °C. The product was dried in vacuo at 70–80 °C overnight and then calcined in air at 400 °C for 4 hours (fresh catalyst).

B. Synthesis of the CeO_2 -modified TiO_2 support and the $\text{Au/CeO}_x/\text{TiO}_2$ catalyst: The TiO_2 support (titanium (IV) oxide, Alfa Aesar) was pretreated in still air at 500 °C for 4 h. The CeO_2 -modified TiO_2 support, $\text{Ti}(\text{xCe})\text{O}_2$ (x is the weight percentage of CeO_2 ; $x = 0, 6$ or 15 in this work), was prepared by wet impregnation of pretreated TiO_2 powders with aqueous solution of cerium nitrate (Alfa Aesar, 99.5%) [27]. After cerium impregnation the solid was calcined under air at 500 °C for 4 h.

For the gold deposition-precipitation (DP) [27], 1–1.5 grams of $\text{CeO}_x/\text{TiO}_2$ powder were slurried in DI water (100 mL) whilst stirring and an aqueous $(\text{NH}_4)_2\text{CO}_3$ solution (25 mL; 1 mol/L) was then added. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.99%, Alfa) was dissolved in DI water (25 mL) and added to the above solution dropwise. The gold loading amount was designed to be 1 at.% with respect to $\text{CeO}_x/\text{TiO}_2$. The pH value was kept at 8–9 during the whole process. The resulting precipitates were aged at room temperature for 1 h, then filtered and washed three times with DI water. The product was dried in vacuo at room temperature for 2–3 days thoroughly and tested without any pretreatment (fresh catalyst). We found that appropriate drying in vacuum and storage in cold and dark conditions were very important to maintain the ultra-fine gold species on ceria-modified TiO_2 . The powder samples used in this study will be denoted as $\text{Au-Ti}(15\text{Ce})\text{O}_2$ {1 at.% Au on 15wt%- $\text{CeO}_x/\text{TiO}_2$ }.

C. Transmission electron microscopy (TEM): TEM and high-resolution TEM (HRTEM) images were obtained using a JEOL2100F microscopy equipped with a $2k \times 2k$ CCD camera at the Center of Functional Nanomaterials (CFN) at Brookhaven National Laboratory.

D. X-ray diffraction: The time-resolved X-ray diffraction experiments were carried out on beamline X7B ($\lambda = 0.3196 \text{ \AA}$) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The powder sample ($\sim 20 \text{ mg}$) was loaded into a Kapton tube (O.D. = 0.125 inch) which was attached to a flow system. Two small resistance heating wires were installed right above and below the in-situ cell, and the temperature was monitored with a 0.5-mm chromel-alumel thermocouple that was placed inside the tube near the sample. In-situ diffraction patterns were collected during CO oxidation reaction ($1\% \text{CO}/4\% \text{O}_2/\text{He}$, 20 mL/min , $\sim 100,000 \text{ h}^{-1}$) under a “steady-state” mode between -65 and $70 \text{ }^\circ\text{C}$ ($15 \text{ }^\circ\text{C/step}$, 30 min each). The fresh Au-CeO₂ catalysts were pre-oxidized ($20\% \text{O}_2/\text{He}$, $300 \text{ }^\circ\text{C}$, 1 h) or pre-reduced ($5\% \text{H}_2/\text{He}$, $200 \text{ }^\circ\text{C}$, 1 h) before the reaction. For the temperatures below room-temperature, the powder sample was cooled by a nitrogen liquid/flow gun. Two-dimensional powder patterns were collected with an image-plate detector (Perkin-Elmer), and the powder rings were integrated using the FIT2D code [31]. The lattice constants of ceria were calculated through Rietveld refinement [32]. The catalyst sample was mounted on a micro-reactor suited for *operando* studies as a function of temperature ($-100 \text{ }^\circ\text{C}$ to $800 \text{ }^\circ\text{C}$) and pressures ($1\text{-}5 \text{ atm}$) [27]. For the activity measurement, CO ($m/e = 28$) and CO₂ ($m/e = 44$) concentrations in the outlet of the micro-reactor were continuously determined by a residual gas analyzer (RGA).

E. X-ray absorption spectroscopy: Au L-III absorption edge ($E_0 = 11919$ eV) XAFS spectra were collected *in-situ* at beamline X19A of the NSLS at BNL during the CO oxidation reaction under similar conditions as the XRD experiments with the exception of the testing temperature was always kept at 25 °C. The X-ray absorption spectra were taken repeatedly in the “fluorescence-yield mode” using a Vortex detector. The energy was calibrated for each scan with the first inflection point of the Au L-III-edge in Au metal foil. The EXAFS data have been analyzed using the Athena and Artemis programs [33].

3. Results

3.1 CO oxidation on Au/CeO₂(111) and Au/CeO_x/Ti(110)catalysts

Studies of scanning-tunneling microscopy (STM) indicate that Au grows on CeO₂(111) forming three-dimensional (3D) particles that bind to the steps and defects in the terraces of the surface [11]. The bonding of the Au particles to the oxide substrate is relatively weak and the interaction of the particles with a gas mixture of CO and O₂ induced segregation [11]. Figure 1 displays the CO oxidation activity of Au/CeO₂(111) as a function of Au coverage. A maximum in the production of CO₂ is seen at Au coverages of 0.3-0.4 ML. Previous studies have shown that there is a marked size effect on the catalytic activity of gold [1,2,6]. Comparing our CO oxidation results with the particle size seen in STM for Au/CeO₂(111) [11], one can conclude that Au particles in the range of 1-3 nm exhibit the highest activity, with a drop in catalytic activity for Au particles with sizes above 4 nm. The maximum catalytic activities found for the Au/CeO₂(111) systems are close to those measured in our laboratory for Au/TiO₂(110) surfaces [10] and much better than those found for Au/MgO(100), see Figure 2. Thus, the

data obtained with the model catalysts indicate that the nature of the oxide support affects catalytic activity, in agreement with results obtained with powder catalysts [1,2,28].

Studies of STM indicate that, as in the case of Au/CeO₂(111) [11], gold grows on TiO₂(110) forming 3D particles anchored on steps and defect sites of the surface [2]. A drastic increase in the population of gold on the surface terraces can be obtained by depositing ceria nanoparticles on the TiO₂(110) substrate [10,27]. The ceria nanoparticles act as nucleation centers for small clusters and particles of gold [10,27]. We investigated the activity for CO oxidation of Au/CeO_x/TiO₂(110) surfaces, see Figure 1. In these studies the titania surface was pre-covered by ~ 8 % or 27% of ceria before depositing the Au. Figure 1 shows the production of CO₂ over Au/CeO_x/TiO₂(110) catalysts as a function of gold coverage. Maxima of activity are found at gold coverages of 0.4-0.5 ML. The Au/CeO_x/TiO₂(110) systems are 4-5 times more active than Au/CeO₂(111) or Au/TiO₂(110). This, in part, can be a consequence of a better dispersion of Au on the terraces of the oxide support [10,27]. In addition, the ceria nanoparticles are more chemically active than bulk ceria [10,27] and can help with the dissociation of O₂ [10,26]. The drop in the catalytic activity seen when going from a titania surface pre-covered by 8% of ceria to a surface pre-covered by 27% of ceria probably reflects a decrease in the dispersion of gold [10] and a reduction in the reactivity of the supported ceria [10,26]. The best catalysts in Figure 1 contain small amounts of Au and ceria.

Post-reaction characterization with XPS indicated that the active phase of the Au/CeO₂(111) and Au/CeO_x/TiO₂(110) catalysts contained metallic Au, as seen in previous studies with model single-crystal catalysts [2], and some carbonate species probably associated with the oxide support.

3.2 CO oxidation on Au/CeO₂ nanorods

From the results in Figure 1, it is clear that one must maximize gold-ceria interactions to obtain a good performance during the oxidation of CO. On the basis of this, we decided

to investigate the behavior of catalysts generated by depositing gold on ceria nanorods [28]. Figure 3a is the TEM image of a fresh 1 at.%Au-CeO₂ catalyst after air-calcination at 400 °C. Rod-like nanocrystals with the widths of ca. 10 nm and lengths of around 50 nm were observed. It agrees with previous reports on the nanoshapes of ceria [34, 35] and gold-ceria nanorods [28], which are enclosed by {110} and {100} facets of the oxide. In the gold-ceria system displayed in Figure 3a, the gold species are very well dispersed over the ceria substrate and no big gold particles are observed. No obvious morphology changes were detected by TEM or HRTEM when the Au/ceria catalysts were pre-treated in O₂ (Fig 3b) or pre-reduced in H₂ (Fig. 3c and 3d). Furthermore, we investigated hundreds of nanorods in HRTEM with the aids of fast Fourier transform (FFT) and found only evidence for a high dispersion of small gold particles.

The steady-state “light-off” profiles of the Au-CeO₂ nanorods with different pretreatments were measured at temperatures between 10 and 70 °C. XANES spectra indicated that the fresh or as-prepared catalysts contained AuO_x dispersed on ceria (see below). Pre-reduction of the Au-CeO₂ nanorods with H₂ led to a AuO_x → Au transformation and the generation of very active catalysts. Figure 4 shows the CO conversion for a pre-reduced Au-CeO₂ catalyst as a function of temperature. At 50 °C and temperatures above, the conversion of CO is essentially 100%. This high conversion was maintained after several cycles of cooling and heating.

Figure 5 displays *operando* XRD patterns collected for pre-reduced Au-CeO₂ at different temperatures (T= 10 – 70 °C) under CO oxidation conditions. Fluorite cubic CeO₂ (*F*_{m-3m}, JCPDS card #: 34-394) is the major phase in the Au-CeO₂ catalyst seen throughout the whole *operando* studies. In addition, a very weak XRD peak assigned to the Au(111) diffraction is seen (close to 8° in 2θ). We used the General Structure Analysis System (GSAS) software to run a sequential Rietveld refinement [32] on the XRD profiles of the Au-CeO₂ ceria nanorod catalyst. This analysis indicated that the averaged

cell dimensions for the CeO₂ support during the *operando* XRD measurements remained constant around a value of 5.40 Å.

Operando XAFS measurements at the Au L-III edge for the pretreated Au-CeO₂ catalysts were carried out under the same testing conditions as the XRD studies, except that the reaction temperature was maintained at 25 °C. The line shapes of the two spectra (fresh and used) in Figure 6 for a pre-oxidized sample show a clear feature at 2.5 eV above the edge, which is characteristic of ionic gold in Au₂O₃ [36,37,38]. Compared with the fresh catalyst, the used pre-oxidized Au-CeO₂ nanorods display a lower intensity of the white-line, indicating the partial reduction of Au³⁺ species during the CO oxidation reaction at room-temperature. On the other hand, both fresh and used profiles for the pre-reduced sample have the typical characteristics of metallic gold (Au⁰) [36,37,38] in the *operando* XANES experiments.

Using the *operando* XANES data, linear combination calculations [39] were done to determine the variation of the cationic and metallic Au species in the pre-oxidized and pre-reduced Au-CeO₂ catalysts under reaction conditions. The fresh pre-oxidized and pre-reduced Au-CeO₂ catalysts were used as the reference components and labelled as “OX” (oxidized) and “RE” (reduced), respectively. The results of the linear combination calculations are displayed in Figure 7. It can be clearly seen that gold was kept in a metallic form (“RE”) during the whole CO oxidation reaction for the pre-reduced sample (red points); while the oxidation states of Au changed from pure “OX” to a mixture of roughly 70%“OX” + 30%“RE” after 10 h reaction at room-temperature for the pre-oxidized sample (blue points).

Considering the data in Figure 7 together with the catalytic activity measured for pre-oxidized and pre-reduced Au-CeO₂ catalysts, we can draw the following conclusions on the relationship between the gold oxidation state and the CO oxidation reactivity. (1)

Both ionic and metallic gold are catalytically active, since the pre-oxidized (Au-O) and pre-reduced (Au-Au) catalysts showed good CO oxidation activities. (2) Metallic gold is more active than ionic Au. The activation of the pre-oxidized Au-CeO₂ nanorods was accompanied by the gradual reduction of gold species in the catalyst. Figure 8 illustrates two possible routes to enhance the activity of gold-ceria nanostructures under different reaction conditions. A pre-oxidized sample with a main phase of Au cations or positive-charged clusters (structure 1) is less active for the low-temperature CO oxidation reaction. The pre-reduced catalyst with dominant metallic gold species (structure 2) or the pre-oxidized and used Au-CeO₂ nanorods with an increased Au⁰ fraction (structure 3) are more active. In any case, the ceria nanorod support is predominantly kept in an oxidized Ce⁴⁺ form.

3.3 CO oxidation on Au/CeO_x/TiO₂ powders

The results of XANES indicated that the as-prepared Au/CeO_x/TiO₂ samples contained AuO_x dispersed on top of the ceria-titania support. Following the study with the Au-ceria nanorods, the Au/CeO_x/TiO₂ samples were pre-reduced with H₂ to induce a AuO_x → Au transformation and generate a highly active catalyst for CO oxidation. Figure 9 displays TEM images for a pre-reduced Au/CeO_x/TiO₂ system. Large irregular nonuniform (10-100 nm) TiO₂ (anatase + rutile) particles are the main textural phase in the catalytic material. The HRTEM image in Figure 9B clearly confirms the presence of ultrafine gold nanoparticles on all the ceria-modified titania support. The average Au size was calculated to be around 1 nm in the catalyst. With the aid of EDX, we were able to identify the morphology of CeO_x supported on titania. The related ceria particle size was 5-7 nm, much smaller than that of the titania support. Previous studies have shown that ceria grows on titania forming very small clusters, plates and 3D nanoparticles [40]. At the ceria-titania interface, there is an intermixing of the two oxides that favors the

formation of Ce^{3+} cations [40,41]. We found that a large fraction of the Au and CeO_x nanoparticles in $\text{Au/CeO}_x/\text{TiO}_2$ were in contact with each other.

The steady-state “light-off” profile for a pre-reduced $\text{Au/CeO}_x/\text{TiO}_2$ catalyst is shown in Figure 4. The $\text{Au/CeO}_x/\text{TiO}_2$ is highly active for CO oxidation reaching a conversion close to 100% at 30 °C. In general, we found that the $\text{Au/CeO}_x/\text{TiO}_2$ powders were more active for CO oxidation than Au/ceria nanorods, in good agreement with trend seen in Figure 1 for the model $\text{Au/CeO}_2(111)$ and $\text{Au/CeO}_x/\text{TiO}_2(110)$ catalysts. In stability tests, see Figure 10, we found no sign for deactivation of a $\text{Au/CeO}_x/\text{TiO}_2$ catalyst after 20 hours of operation. This probably reflects the strong interaction that exists between the gold and ceria nanoparticles which prevents sintering and deactivation of the catalyst [27].

Operando studies with XANES showed that the gold in pre-reduced $\text{Au/CeO}_x/\text{TiO}_2$ remained in a metallic state during the oxidation of CO. On the other hand, the cerium was fully oxidized in a +4 state. The complete oxidation of cerium is expected due to the large ratio of 4/1 used for O_2/CO in our experiments. In a set of experiments pulsing O_2 and CO in a sequential manner over a $\text{Au/CeO}_x/\text{TiO}_2$ catalyst, we found a fast $\text{Ce}^{4+} \text{Ce}^{3+}$ switching, which is consistent with the idea that ceria nanoparticles dissociate O_2 fast and do not hold O atoms strongly [26], making them ideal components in catalysts for CO oxidation.

4. Conclusions

In this work, we have studied the oxidation of CO on model and powder catalysts of Au- CeO_2 and $\text{Au-CeO}_x/\text{TiO}_2$. The phenomena observed in $\text{Au-CeO}_2(111)$ and $\text{Au-CeO}_2/\text{TiO}_2(110)$ did provide useful concepts for the design and preparation of highly active and stable $\text{Au-CeO}_x/\text{TiO}_2$ powder catalysts for CO oxidation. Small particles of Au dispersed on $\text{CeO}_2(111)$ displayed high catalytic activity, making the $\text{Au/CeO}_2(111)$ system a better CO oxidation catalyst than $\text{Au/TiO}_2(110)$ or $\text{Au/MgO}(100)$. An excellent

support for gold was found after depositing nanoparticles of ceria on $\text{TiO}_2(110)$. The CeO_x nanoparticles act as nucleation centers for gold, improving the dispersion of the supported metal and helping in the creation of reaction sites which are efficient for the adsorption of CO and the dissociation of the O_2 molecule.

High-surface area catalysts were prepared by depositing gold on ceria nanorods and $\text{CeO}_x/\text{TiO}_2$ powders. The samples were tested for the low-temperature (10 – 70 °C) oxygen-rich (1%CO/4% O_2 /He) CO oxidation reaction after pre-oxidation (20% O_2 /He, 300 °C) and pre-reduction (5% H_2 /He, 300 °C) treatments aimed at generating different concentrations of ionic (AuO_x) and metallic (Au) gold species. The activity tests and the related *operando* XANES characterizations indicated that both oxidized and reduced gold nanostructures were able to catalyze the oxygen-rich low-temperature CO oxidation reaction, but the ones in metallic form were more active. Furthermore, even under oxygen-rich conditions, the cationic gold was not stable and a $\text{AuO}_x \rightarrow \text{Au}$ transformation took place. In selecting the proper methods of preparation and pretreatment, the findings of this work rationalize the design of a catalyst with ~ 1 at% Au on $\text{CeO}_x/\text{TiO}_2$ with hydrogen pre-reduction in order to maximize the concentration of metallic gold active sites.

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Figure Captions:

Figure 1. CO oxidation activity of Au/CeO₂(111) and Au/CeO_x/TiO₂(110) as a function of Au coverage. The area covered by ceria on the titania substrate was measured by ion-scattering spectroscopy [10], before depositing gold, and was found to be ~ 8 and 27% of the clean titania. The reported values for the production of CO₂ were obtained after exposing the catalysts to 4 Torr of CO and 2 Torr of O₂ at 27 °C for 5 min.

Figure 2. Maximum production of CO₂ during the oxidation of CO on Au/MgO(100), Au/TiO₂(110) [10] and Au/CeO₂(111). The amount of gold deposited on the oxide supports was 0.3-0.4 ML. The reported values for the production of CO₂ were obtained after exposing the catalysts to 4 Torr of CO and 2 Torr of O₂ at 27 °C for 5 min.

Figure 3. TEM (a, c) and HRTEM (b, d) images of 1 at.%Au-CeO₂ samples: (a) Fresh; (b) Pre-oxidized with O₂ and used in CO oxidation; (c, d) Pre-reduced with H₂ and used in CO oxidation.

Figure 4. CO conversion as a function of temperature for pre-reduced Au-CeO₂ nanorod and Au-CeO_x/TiO₂ catalysts (Pre-reduction conditions: 5%H₂/He, 200 °C, 1 h. Testing conditions: 1% CO / 4% O₂ / 95% He, 20 mL/min, 25 mg catalyst).

Figure 5. *Operando* XRD ($\lambda = 0.3196 \text{ \AA}$) patterns of a pre-reduced Au-CeO₂ nanorod catalyst collected at different temperatures (Temperature range = 10 – 70 °C. Testing conditions: 1%CO/4%O₂/He, 20 mL/min, 25 mg catalyst)

Figure 6. *Operando* XANES (Au L-III edge) spectra for the Au-CeO₂ nanorod catalysts. (Testing conditions: 1%CO/4%O₂/He, 20 mL/min, 25 mg catalyst, 25 °C.)

Figure 7. Linear combination results for the oxidation states of gold species as a function of reaction time when performing the low-temperature oxidation of CO on pre-oxidized and pre-reduced Au-CeO₂ nanorod catalysts (Testing conditions: 1%CO/4%O₂/He, 20 mL/min, 25 mg catalyst, 25 °C). “OX” denotes a fully oxidized sample, and “RE” a fully reduced one.

Figure 8. Possible routes for the activation of Au-CeO₂ nanorod catalysts under different reaction conditions.

Figure 9. TEM (A) and HRTEM (B) images for a pre-reduced Au-CeO_x/TiO₂ catalyst.

Figure 10. CO conversion as a function of time for a pre-reduced Au-CeO_x/TiO₂ catalyst (Testing conditions: 1% CO / 4% O₂ / 95% He, 20 mL/min, 25 mg catalyst).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Graphical abstract