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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-CeO_2 and Au-CeO_x/TiO_2. Phenomena observed in Au-CeO_2(1 1 1) and Au-CeO_2/TiO_2(1 1 0) provided useful concepts for designing and preparing highly active and stable Au-CeO_x/TiO_2 powder catalysts for CO oxidation. Small particles of Au dispersed on CeO_2(1 1 1) displayed high catalytic activity, making Au-CeO_2(1 1 1) a better CO oxidation catalyst than Au-TiO_2(1 1 0) or Au-MgO(1 0 0). An excellent support for gold was found after depositing nanoparticles of ceria on TiO_2(1 1 0). 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 O_2 molecule. High-surface area catalysts were prepared by depositing gold on ceria nanorods and CeO_x/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. Synchrotron-based *operando* X-ray diffraction (XRD) and X-ray absorption (XAS) spectroscopy were used to study the Au-CeO_2 and Au-CeO_x/TiO_2 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 CeO_2 or CeO_x/TiO_2.

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.

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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 $Ce(La)O_x$ [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 and 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 $Au/CeO_x/TiO_2$ powders are highly active and stable catalysts for this process.

2. Experimental

2.1. Studies with $Au/CeO_2(1\,1\,1)$ and $Au/CeO_x/TiO_2(1\,1\,0)$

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 $Au/CeO_2(1\,1\,1)$ and $Au/CeO_x/TiO_2(1\,1\,0)$ catalysts were prepared following a methodology described in previous studies [10,20]. Au was evaporated on $CeO_2(1\,1\,1)$ and $CeO_x/TiO_2(1\,1\,0)$ 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 O_2) and the sample was hold at a reaction temperature of 27 °C. The amount of molecules produced was normalized by the geometric area exposed of the $CeO_2(1\,1\,1)$ and $TiO_2(1\,1\,0)$ samples [10,20].

2.2. Studies with Au-CeO_2 nanorods and Au-CeO_x/TiO_2

2.2.1. Synthesis of Au-CeO_2 nanorods

For the hydrothermal preparation of ceria nanorods [28], $Ce(NO_3)_3{\cdot}6H_2O$ (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 CeO_2 powder were slurried in DI water (150 mL) whilst stirring and an aqueous $(NH_4)_2CO_3$ solution (75 mL; 1 m) was then added. $HAuCl_4{\cdot}3H_2O$ (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 h (fresh catalyst).

2.2.2. Synthesis of the CeO_2-modified TiO_2 support and the $Au/CeO_x/TiO_2$ 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, $Ti(xCe)O_2$ (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 g of CeO_x/TiO_2 powder were slurried in DI water (100 mL) whilst stirring and an aqueous $(NH_4)_2CO_3$ solution (25 mL; 1 mol/L) was then added. $HAuCl_4{\cdot}3H_2O$ (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 CeO_x/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 Au-$Ti(15Ce)O_2$ {1 at.% Au on 15 wt%-CeO_x/TiO_2}.

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

2.2.2.2. X-ray diffraction. The time-resolved X-ray diffraction experiments were carried out on beamline X7B ($\lambda = 0.3196$ Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The powder sample (~20 mg) was loaded into a Kapton tube (O.D. = 0.125 in.) 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%CO/4%O_2/He, 20 mL/min, ~100,000 h^{-1}) under a “steady-state” mode between −65 and 70 °C (15 °C/step, 30 min each). The fresh Au-CeO_2 catalysts were pre-oxidized (20%O_2/He, 300 °C, 1 h) or pre-reduced (5%H_2/He, 200 °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 (PerkinElmer), 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