Effect of Ceria on Gold–Titania Catalysts for the Water–Gas Shift Reaction: Fundamental Studies for Au/CeOₓ/TiO₂(110) and Au/CeOₓ/TiO₂ Powders

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ABSTRACT: We have carried out a fundamental study of the WGS reaction on model Au/CeOₓ/TiO₂(110) and powder Au/CeOₓ/TiO₂ catalysts paying particular attention to the effect of ceria on the activity of the gold–titania systems. CeOₓ nanoparticles deposited on TiO₂(110) act as anchoring sites for gold improving the dispersion of the admetal on the oxide support. When compared to a typical benchmark system like Cu(111), Au/CeOₓ/TiO₂(110) catalysts exhibit TOFs, which are 10–30 times larger, and a substantial reduction in the apparent activation energy for the WGS, which decreases from 18 kcal/mol on Cu(111) to 7 kcal/mol on Au/CeOₓ/TiO₂(110). Low concentrations of ceria (6 and 15 wt %) were deposited onto a titania powder support via a wetness impregnation process. 1 atom % gold was then deposited on the CeOₓ/TiO₂ mixed-oxide supports via a deposition–precipitation (DP) method. The Au/CeOₓ/TiO₂ powder catalysts were characterized with HRTEM and a combination of in situ time-resolved XRD and XAFS. The XRD measurements indicated that a main effect of ceria was to enhance the concentration of oxygen vacancies in the catalysts and, thus, help with the dissociation of water during the reaction. Results of in situ XAFS showed that the gold oxidation state in the Au/CeOₓ/TiO₂ powder catalysts changed from ionic (Au⁶⁺) to metallic (Au⁰) with the start of the WGS. The active phase for these powder catalysts contained gold particles with average sizes of ~2 nm. This study shows that the phenomena observed in model Au/CeOₓ/TiO₂(110) catalysts do provide useful concepts for the design and preparation of highly active and stable powder catalysts for the WGS reaction.

INTRODUCTION

The water–gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂) plays an important role in hydrogen purification process. The active phase of the conventional low-temperature (175–250 °C) WGS catalysts is copper dispersed on a zinc oxide substrate (Cu–ZnO). However, this material has important drawbacks; it is pyrophoric and deactivates rapidly when exposed to air and/or water condensation. Therefore, novel catalysts are currently in great demand and developed to enhance reactivity and improve stability, particularly for the employment of H₂ in the polymer electrolyte membrane (PEM) fuel cells, which require stability to start/stop cycles and high-low-temperature performance.¹ ²

Because metal oxide-supported Au nanoparticles or clusters were discovered by Haruta et al. to be extremely active CO oxidation catalysts,³ many research groups have investigated the activity of gold nanostructures for various catalytic reactions. Previously, gold on reducible supports such as iron oxide (Fe₂O₃),⁴ ⁵ titania (TiO₂),⁶ ⁷ and cerium oxide (CeO₂)⁸ were reported to be highly active WGS catalysts and very promising for fuel-cell applications. For instance, Sakurai et al. confirmed that gold on titania, which was prepared by a deposition–precipitation (DP) method, exhibits very high activity for the low-temperature WGS reaction, comparable with the conventional Cu/ZnO/Al₂O₃ catalyst.⁹

The unique catalytic properties of gold are strongly dependent on the metal particle size.³ ¹¹ Valden et al. reported a structure sensitivity of CO oxidation reaction on gold clusters supported on TiO₂(110) single crystal, which is related to a quantum size effect with respect to the thickness of the gold islands.¹¹ Recently, Williams et al. found a strong size effect for the Au–TiO₂ powder catalyst; that is, the WGS reaction rate per mol % Au significantly increases with the decrease of average gold particle size, more importantly for those less than 1 nm.¹² However, gold–titania catalysts usually have relatively poor thermal stability against the sintering under the reaction conditions. Once gold metal particles are obtained, their size can evolve even in the presence of light or in ambient air at room temperature.¹³ To resolve the stability problem on Au–TiO₂ catalyst, the optimization of synthesis procedures has
been investigated. Hugon et al. reported that a deposition–precipitation with urea results in higher gold loading amounts, lower Au crystal sizes, and less residual chloride impurities than either an impregnation or an anion adsorption method.14

To stabilize ultrafine (<2 nm) gold particles/clusters on titania, one must have a large amount of oxygen vacancies on the oxide support or disperse a secondary phase of a reducible metal oxide (e.g., CeO₂ or Fe₂O₃) on the titania.15,16 The deposition of ceria nanoparticles on TiO₂ produces an oxide–oxide interface that has unique structural and catalytic properties.15,17–20 The CeO₂ nanoparticles have an unusual coordination mode, which stabilizes Ce³⁺ ions.16,18 The increase in the stability of the Ce(III) oxidation state leads to an enhancement in the chemistry and catalytic activity of the ceria nanostructures.15,17,18 The CeO₂/TiO₂ mixed-metal oxide appears as an excellent substrate to enhance metal–oxide interactions and the participation of the oxide support in the WGS reaction.17,21 Previously, it has been determined that a small coverage of ceria on rutile TiO₂(110) helps in the dispersion of Au producing highly active catalysts for the WGS reaction.15,16 Can the phenomena and interactions seen in Au/CeO₂/TiO₂(110) be transferred to more realistic Au–CeO₂/TiO₂ powder catalysts?

In this Article, we present a fundamental study of model Au/CeO₂/TiO₂(110) and powder Au/CeO₂/TiO₂ catalysts, paying particular attention to the effect of ceria on the activity of the gold–titania system. A combination of synchrotron-based time-resolved X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) is used to characterize the powder Au/CeO₂/TiO₂ catalysts under reaction conditions. The in situ measurements indicate that gold atoms/clusters are reduced under reaction conditions at ~150 °C, and Au nanoparticles with an average size of ~2 nm appear as the WGS reaction happens. In Au/CeO₂/TiO₂(110) and the Au/CeO₂/TiO₂ powders, the introduction of ceria significantly increases the presence of O vacancies on the catalysts and stabilizes the Au particles. Au/CeO₂/TiO₂ powder catalysts showed very good long-term stability for the WGS reaction at 250 °C.

## EXPERIMENTAL SECTION

### A. Studies for Model Au/CeO₂/TiO₂(110) Catalysts

The Au/CeO₂/TiO₂(110) were studied in a system, which combines an ultrahigh-vacuum (UHV) chamber (base pressure ~5 × 10⁻¹⁰ Torr) and a batch reactor.15,16,22 The sample could be transferred between the reactor and UHV chamber without exposure to air. The UHV chamber (base pressure ~5 × 10⁻¹⁰ Torr) was equipped with instrumentation for X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), low-energy electron diffraction (LEED), ion scattering spectroscopy (ISS), and temperature-programmed desorption (TPD). The microscopy studies were carried out in an Omicron variable-temperature scanning tunneling microscopy (STM) system that is directly attached to a main UHV chamber equipped with optics for low-energy electron diffraction, instrumented for Auger electron spectroscopy, and surface cleaning facilities. The kinetic tests were done using a TiO₂(110) single crystal cleaned following standard procedures.15–17 An Oxford evaporator was also used to deposit CeO₂ on TiO₂(110).15,17 Au was evaporated on TiO₂(110) and CeO₂/TiO₂(110) at 25 °C. In the kinetic measurements, the sample was transferred to the batch reactor at ~25 °C, and then the reactant gases were introduced (20 Torr of CO and 10 Torr of H₂O) and the sample was rapidly heated to reaction temperatures in the range of 275–360 °C. The amount of molecules produced was normalized by the active area exposed by the sample.15,17,22 In our reactor, a steady-state regime for the production of H₂ and CO₂ was reached after 2–3 min of reaction time.22

### B. Studies for Au/CeO₂/TiO₂ Powder Catalysts

#### 1. Synthesis of the CeO₂-Modified TiO₂ Support

The TiO₂ support (titanium(IV) oxide, Alfa Aesar) was pretreated in dry air at 500 °C for 4 h. The CeO₂-modified TiO₂ support, Ti(xCeO₂) (x is the weight percentage of CeO₂; y = 0, 6, or 15 in this work), was prepared by wet impregnation of pretreated TiO₂ powders with aqueous solution of cerium nitrate (Alfa Aesar, 99.5%).14 After cerium impregnation, the solid was calcined under air at 500 °C for 4 h.

#### Synthesis of Au/CeO₂/TiO₂ Catalysts

For the gold deposition—precipitation (DP)15,16,22 1–1.5 g of CeO₂/TiO₂ powder was slurried in DI water (100 mL) with stirring, and an aqueous (NH₄)₂CO₃ solution (25 mL; 1 mol/L) was then added. HAuCl₄·3H₂O (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 CeO₂/TiO₂. The pH value was kept at 8–9 during the whole process. The resulting precipitates were aged at room temperature for 1 h, and then filtered and washed three times with DI water. The product was dried in vacuum at room temperature for 2–3 days thoroughly and tested without any pretreatment (fresh catalyst). All of the DP procedures were carried out in darkness to avoid light.13 We also found that the appropriate drying in vacuum and storage in cold and dark conditions was very important to maintain the ultrafine gold species on TiO₂ or ceria-modified TiO₂. The powder samples used in this study will be denoted as Au–TiO₂ {1 at. % Au on clean TiO₂}, Au–Ti(6Ce)O₂ {1 at. % Au on 6 wt % CeO₂/TiO₂}, and Au–Ti(15Ce)O₂ {1 at. % Au on 15 wt % CeO₂/TiO₂}.

#### 2. Transmission Electron Microscopy (TEM)

High-resolution TEM (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) results were obtained using a JEOL2100F equipped with a 2k × 2k CCD camera and a EDX detector at the Center of Functional Nanomaterials (CFN) at Brookhaven National Laboratory.

#### 3. X-ray Diffraction

The time-resolved X-ray diffraction experiments were carried out on beamline X7B (λ = 0.3196 Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The powder sample (~3 mg) was loaded into a glass tube (I.D. = 0.8 mm), which was attached to an in situ flow cell. One small resistance heating wire was installed right below the tube, and the temperature was monitored with a 0.5 mm chromel–alumel thermocouple that was placed inside the tube near the sample. The in situ WGS reaction (1% CO/3% H₂O/He, 10 mL/min, ~100 000 h⁻¹) was carried out under a “steady-state” mode between 100 and 350 °C (50 °C/step, 1 h each). H₂O was introduced into the flow system via a water bubbler at room temperature. Two-dimensional XRD patterns were collected with an image-plate detector (Perkin-Elmer), and the powder rings were integrated using the FIT2D code.24 The instrument parameters (Thompson–Cox–Hastings profile coefficients) were derived from the fit of a LaB₆ reference pattern. The lattice constants of TiO₂ and CeO₂ were calculated through Rietveld refinement.25 The average grain size (D) of TiO₂ was estimated according to the Scherrer equation26 D = 0.90λ/β cos θ, where θ is the diffraction angle of the (101) peak of anatase phase, and β is the full width at half-maximum (fwhm) of the (101) peak (in
4. X-ray Absorption Fine Structure. Au L-III absorption edge ($E_0 = 11919$ eV) XAFS spectra were collected in situ at beamline X19A of the NSLS at BNL. The powder sample (~30 mg) was loaded into a Kapton tube (O.D. = 0.125 in.), which was the same in situ cell as the XRD measurement. An electrical heating gun was installed right below the tube. The in situ WGS reaction (1% CO/3% H$_2$O/He, 30 mL/min, ~30 000 h$^{-1}$) was measured at 25, 150, and 250 °C for 1 h each. The X-ray absorption spectra were taken at room temperature after the catalyst was cooled from elevated temperatures, in a “fluorescence-yield mode” using a 4 element 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 X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) data have been analyzed using the Athena and Artemis programs.$^{27}$

## RESULTS AND DISCUSSION

A. Behavior and Catalytic Properties of Au/CeO$_2$/TiO$_2$(110). Studies have been published examining in detail the deposition of small amounts of Au on TiO$_2$(110) with scanning tunneling microscopy.$^{11,28,29}$ These studies indicate that Au grows on this oxide substrate, forming three-dimensional (3D) nanoparticles with a diameter of 5–6 nm and a height of 1–2 nm were seen, but smaller metal particles were also present on individual “a” and “b” sites of the CeO$_2$/TiO$_2$(110) substrate. In general, when STM images for the Au/CeO$_2$/TiO$_2$(110) system are compared to those collected for plain Au/TiO$_2$(110),$^{11,28,29}$ it is clear that the presence of ceria favors the dispersion of the gold on the titania terraces and the metal particles are not located mainly at steps of the surface as happens in the case of Au/TiO$_2$(110). As we will see below, the close contact between Au and CeO$_2$ leads to a very high catalytic activity.

Figure 2 shows the production of H$_2$ and CO$_2$ over Au/TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) catalysts as a function of time at ~350 °C with CO and H$_2$O pressures of 20 and 10 Torr, respectively. The amount of Au present in these catalysts was ~0.4 ML. The area of TiO$_2$(110) covered by CeO$_2$ was measured with ISS, before depositing gold, and was found to be ~12% of the clean substrate. The data in Figure 2 indicate that steady-state rates are reached very fast on the Au/TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) catalysts. In our test experiments, we found no signs for the deactivation of the catalysts after 2 h of reaction time. From the slopes in the lines in Figure 2, one can estimate that the WGS rate on the Au/CeO$_2$/TiO$_2$(110) catalyst is ~3.1 times larger than that on the Au/TiO$_2$(110) catalyst.

Using plots for H$_2$ production versus time, similar to those in Figure 2, we calculated the corresponding reaction rates and turnover frequencies (TOFs) for the WGS on Au/TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) catalysts as a function of gold coverage. Assuming that all of the metal atoms deposited on TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) participate in the reaction, a common assumption in this type of studies,$^{11}$ we estimated the TOFs shown in Figure 3. These TOFs are much larger than the values found in previous studies for the WGS reaction. 

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**Figure 1**

**Figure 1A** shows an STM image acquired after depositing Ce on TiO$_2$(110) under an atmosphere of O$_2$.$^{5,16}$ Most of the spots (~70%, labeled “a”) have a height of 1.3 ± 0.2 Å and correspond to small wires of CeO$_2$.$^{15}$ A minority of the spots (~30%, labeled “b”) have a height of 1.9 ± 0.3 Å and probably correspond to (1 × 2) reconstructions of TiO$_2$(110) induced by O$_2$ chemisorption.$^{15,31,32}$ Figure 1B displays an STM image taken after ~0.25 ML of Au was deposited on the CeO$_2$/TiO$_2$(110) surface of Figure 1A. The deposition of Au was done at 25 °C, and the Au/CeO$_2$/TiO$_2$(110) system was subsequently heated to ~325 °C. One can see large particles of Au that were simultaneously located on “a” and “b” sites. Au nanoparticles with a diameter of 5–6 nm and a height of 1–2 nm were seen, but smaller metal particles were also present on individual “a” and “b” sites of the CeO$_2$/TiO$_2$(110) substrate. In general, when STM images for the Au/CeO$_2$/TiO$_2$(110) system are compared to those collected for plain Au/TiO$_2$(110), it is clear that the presence of ceria favors the dispersion of the gold on the titania terraces and the metal particles are not located mainly at steps of the surface as happens in the case of Au/TiO$_2$(110). As we will see below, the close contact between Au and CeO$_2$ leads to a very high catalytic activity.

**Figure 2**

Number of H$_2$ and CO$_2$ molecules produced though the WGS as a function of time on Au/TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) catalysts that contain 0.4 ML of Au. Each surface was exposed to a mixture of 20 Torr of CO and 10 Torr of H$_2$O at 352 °C.
Figure 3. Calculated TOFs for Au/TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) catalysts as a function of Au coverage. Each surface was exposed to a mixture of 20 Torr of CO and 10 Torr of H$_2$O at 352 °C.

reaction on benchmark surfaces such as Cu(111) or Pt(111), where TOFs are always smaller than 1 molecule/metal site sec. In Figure 3, the large TOFs found on the Au/CeO$_2$/TiO$_2$(110) catalysts are quite remarkable and illustrate the major benefits obtained by coadsorbing gold and ceria nanoparticles. An analysis of the shape of the curves in Figure 3 suggests that there is a set of metal particle sizes that has optimal activity for the water–gas shift reaction, in agreement with studies for Au–TiO$_2$ powder catalysts. Comparing the results in Figure 3 to STM data for Au/CeO$_2$/TiO$_2$(110), one finds that a Au coverage of 0.05 ML with a large concentration of particles with sizes below 1 nm does not produce the most active WGS catalyst. On the other hand, Au coverages above 0.4 ML produce a large concentration of particles with sizes above 4 nm, and the catalytic activity decreases significantly.

Experiments like the ones shown in Figure 2 were also carried out at temperatures of 302, 327, and 377 °C for the WGS on Au/TiO$_2$(110) and Au/CeO$_2$/TiO$_2$(110) at an admetal coverage of 0.4 ML. Using the ln of the reaction rates, we constructed Arrhenius plots for the two catalysts. Figure 4 summarizes the results together with reported data for Cu(100) and Cu(111). Note that Au(111) or polycrystalline Au does not have any catalytic activity for the WGS. Copper is a common component in WGS catalysts. In Figure 4, Au/CeO$_2$/TiO$_2$(110) is the best WGS catalyst at all temperatures. The Au nanoparticles supported on CeO$_2$/TiO$_2$(110) produce a catalyst, which is 12 (at 377 °C) to 33 times (at 302 °C) more active than Cu(111), a typical benchmark for WGS studies. In general, Au/TiO$_2$(110) is not as good a catalyst as Au/CeO$_2$/TiO$_2$(110), but its performance is still quite remarkable because, as mentioned above, neither Au(111) nor polycrystalline Au are able to catalyze the WGS. Figure 4 includes the apparent activation energies for a series of Au and Cu catalysts. On Cu(111) and Cu(100), the apparent activation energies are 18 and 15 kcal/mol, respectively. The apparent activation energy decreases to 10 kcal/mol on Au/TiO$_2$(110) and 7 kcal/mol on Au/CeO$_2$/TiO$_2$(110). The catalyst that has the highest activity in Figure 4 has also the lowest apparent activation energy. These data corroborate the benefits of codepositing Au and ceria nanoparticles on the titania support.

In principle, the high catalytic activity of Au/CeO$_2$/TiO$_2$(110) can be attributed to a better dispersion of the Au particles on the oxide substrate (see Figure 1). However, one must not neglect the fact that CeO$_2$/TiO$_2$(110) is extremely efficient for the dissociation of water (the molecule dissociates almost spontaneously on this mixed-metal oxide surface), and metal–oxide interactions also could enhance the chemical reactivity of the Au admetal as it has been seen for Pt in Pt/CeO$_2$/TiO$_2$(110). In the second half of this Article, we will focus our attention on the behavior of Au/CeO$_2$/TiO$_2$ powder catalysts, paying particular attention to the in situ characterization of gold and ceria under WGS reaction conditions.

B. Behavior and Catalytic Properties of Au/CeO$_2$/TiO$_2$ Powders. To prepare the active Au/CeO$_2$/TiO$_2$ powder catalysts, a two-step approach, including an impregnation of ceria onto the surface of pretreated (air, 500 °C) titania and a general deposition–precipitation of gold onto the above mixed-oxide support, was carried out (see Experimental Section). Measurements with XANES and XRD indicate that our synthetic approach led to the formation of AuO/CeO$_2$/TiO$_2$ materials. Figure 5 shows XRD patterns for the fresh or as-prepared Au/CeO$_2$/TiO$_2$ powder catalysts. The powder samples used in this study are denoted as Au–TiO$_2$ {1 at. % Au on clean TiO$_2$}, Au–Ti(6Ce)O$_2$ {1 at. % Au on 6 wt % CeO$_2$/TiO$_2$}, and Au–Ti(15Ce)O$_2$ {1 at. % Au on 15 wt % CeO$_2$/TiO$_2$}. Anatase (tетragonal, JCPDS card no. 4-477) is the main phase for TiO$_2$ in the fresh samples, with some weak diffraction peaks for rutile (tетragonal, JCPDS card no. 4-515). The XRD patterns obtained for the fresh and as-prepared Au/CeO$_2$/TiO$_2$ powder catalysts.
data in Figure 5 point to the existence of a fluorite CeO$_2$ (cubic, JCPDS card no. 34-394) phase in the sample Au−Ti(15Ce)O$_2$. For Au−Ti(6Ce)O$_2$, no distinct peaks belonging to ceria were determined, probably because of the low Ce concentration in this sample. For the same reason, no diffraction features were found for gold species. The presence of AuO$_x$ species was clearly detected with XANES measurements at the Au L-III edge, as seen in Figure 6. The big jump near the Au L-III edge of the fresh samples (25 °C data) is due to ionic gold species.$^{37}$ As we will see below, a AuO$_x$→Au transformation occurred when the powder catalysts were exposed to the reactants of the WGS. In general, the AuO$_x$ species were not stable in the presence of CO/H$_2$O, CO, or H$_2$. Figure 6 also displays that the jump near the edge of the fresh or as-prepared (25 °C data) Au−Ti(15Ce)O$_2$ is higher than that of Au−TiO$_2$, pointing to a more ionic gold species on the ceria-doped titania support. This probably contains a AuO$_x$/CeO$_x$ mixture.

The steady-state “light-off” profiles of the powder Au/CeO$_x$/TiO$_2$ catalysts are shown in Figure 8. Obviously, gold on 15 wt % CeO$_2$ modified TiO$_2$ has the highest reactivity for the WGS reaction, followed by Au−Ti(6Ce)O$_2$, which shows slightly lower CO conversions at elevated reaction temperatures (300 °C and above) perhaps as a consequence of some sintering of the gold particles. Both ceria-containing samples exhibit much higher activities than the undoped Au−TiO$_2$ catalyst. Furthermore, in test of stability, we found that the Au−Ti(15Ce)O$_2$ catalyst showed only minor signs of deactivation with a drop of ~15% in the conversion after 20 h under reaction conditions. This is a very remarkable result because the major drawback of gold based catalysts is their stability problems due to the ease of particle sintering.$^{14}$ The strong interaction between gold and ceria−titania support seems to prevent the massive agglomeration of gold particles.

Calculated reaction rates and apparent activation energies ($E_a$) for the WGS on the Au/CeO$_x$/TiO$_2$ powder catalysts are shown in the Arrhenius plots of Figure 9. The data correspond to a temperature range of 450 to 550 K. The obtained rates at 500 K follow the sequence of Au−Ti(15Ce)O$_2$ (3.1 μmol CO$_2$/g/s) ≈ Au−Ti(6Ce)O$_2$ (3.0 μmol CO$_2$/g/s) > Au−TiO$_2$ (1.4 μmol CO$_2$/g/s), in good agreement with the “light-off”
The calculated $E_a$ values are 7−9 kcal/mol, which are consistent with values reported in the literature (7−11 kcal/mol) for Au−TiO$_2$ powder catalysts prepared by a similar DP method$^6$ and with the values seen in Figure 4 (7−10 kcal/mol) for the model Au/TiO$_2$(110) and Au/CeO$_x$/TiO$_2$(110) catalysts.

In situ measurements of XAFS and XRD were used to study the structural transformations in the Au/TiO$_2$ and Au/CeO$_x$/TiO$_2$ catalysts during the WGS reaction. Here, we will focus on comparisons between the Au−Ti(15Ce)O$_2$ and Au−TiO$_2$ catalysts, the best and worst catalysts in Figure 8. The XANES results in Figure 6 show the disappearance of the features for AuO$^x$ when the Au−Ti(15Ce)O$_2$ catalysts is exposed to a mixture of the reactants at temperatures around 150 °C. The corresponding EXAFS data in R-space after Fourier transform (FT) are shown in Figure 10. Only one strong shell at ∼2.0 Å (phase shift: + 0.5 Å) can be identified for the fresh catalysts (Figure 10a and b). This peak comes from the Au−O bonding and is consistent with the XANES results in Figure 6. The Au−O shell was simulated by using first shell fit in Artemis, and the fitted parameters are listed in Table 1. The coordination number of Au−O (CN$_{Au-O}$) in Au−Ti(15Ce)O$_2$ is 2.7, which is higher than that in Au−TiO$_2$ (CN$_{Au-O}$ = 2.0). This means that gold initially was more oxidized on ceria-modified titania than on the pure TiO$_2$ support. No other shells in R-space were found in Figure 10a and b. In agreement with the XANES data in Figure 6, the EXAFS results in Figure 10c and d point to a change of Au$^δ$+ to Au$^0$ as soon as the reaction temperature is raised to 150 or 250 °C. In Figure 10c and d, there are two strong peaks located at ∼2.7 and 3.5 Å, which can be assigned to a single Au−Au path contribution.$^{38}$ This splitting is due to a Ramsauer−Townsend resonance at a single energy in the backscattering amplitude of Au.$^{38}$ The FEFF6 theory$^{39}$ was used to fit the Au−Au shell by a model of bulk gold metal. Table 1 shows that the obtained CN$_{Au-Au}$ values are 8.1 and 8.9 for the 150 and 250 °C samples, respectively, and correspond to an average Au particle size of ∼2.0 and 2.5 nm.$^{40}$ For the other two gold catalysts, Au−TiO$_2$ and Au−Ti(6Ce)O$_2$, similar XAS results were obtained (please see Table 1). Therefore, in the studied gold catalysts, metallic Au particles with average sizes of ∼2 nm are the main structures during the WGS reaction at elevated temperatures (150 °C and above).

Time-resolved XRD patterns collected in situ during the WGS reaction on Au−TiO$_2$ and Au−Ti(15Ce)O$_2$ catalysts are shown in Figure 11. The XRD patterns are dominated by the peaks for pure titania. For Au−Ti(15Ce)O$_2$, fluorite cubic ceria was identified (Figure 11b). In both catalysts, Au signals were absent during the WGS reaction up to 350 °C, indicating no
severe sintering, which can cause the formation of large gold particles (>2−3 nm).

We also used the General Structure Analysis System (GSAS) software to run the sequential Rietveld refinement on the profiles of the two samples in Figure 11. No structural changes (lattice constants, grain size, and microstrain) for the titania phases other than the thermal effect were identified. However, Figure 12 displays a clear step in the ceria cell dimension at ~100 °C for the Au−Ti(15Ce)O2 catalyst. The lattice constants of CeO₂ jumped from 5.406 to 5.424 Å. This increase in ceria cell dimension is related to the partial reduction of surface ceria species (Ce⁴⁺ → Ce³⁺), which has a larger ionic radius) that are strongly interacting with gold clusters. This Au−O−Ce interaction significantly enhances the reducibility of ceria because the surface reduction of pure CeO₂ nanocrystals begins above 300 °C.10

The presence of Ce³⁺ sites in the Au−Ti(15Ce)O₂ catalyst favors the mechanism for the WGS reaction. Previous results of DF calculations pointed to a very high barrier for the dissociation of H₂O on Au(111) or Au(100) surface,41 which leads to negligible activity of bulk gold for the WGS reaction. It has also been confirmed that even gold nanoparticles cannot dissociate water and catalyze the WGS.41 Thus, the dissociation of H₂O must happen at the surface of the oxide support or the oxide−gold interface.41 Recently, DF calculations determined that a barrier as small as 0.04 eV is estimated for the dissociation of water on the CeO₂/TiO₂ surface, which is 8 times smaller than that computed for a TiO₂ oxygen vacancy.36

On the basis of this, one would expect a higher activity for Au−Ti(15Ce)O₂ than for Au−TiO₂, as seen in Figure 8. Thus, from the in situ XAFS and XRD results, one could expect an active phase for the Au/CeO₂/TiO₂ catalysts where the ceria helps to stabilize small (2−2.5 nm) gold particles and with the dissociation of water. The gold−ceria interface also could participate in the subsequent steps of the WGS that come after the deposition of OH groups on the surface.

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<td>0.002 ± 0.003</td>
<td>7.9 ± 0.5</td>
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<tr>
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<td>Au−Ti(15Ce)O₂</td>
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<tr>
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<td>8.1 ± 0.6</td>
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<td>8.9 ± 0.3</td>
<td>2.82 ± 0.00</td>
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*Tested in 1% CO/3% H₂O/He, 30 mL/min, 30 mg of catalyst, ~30 000 h⁻¹.*

![Figure 11](image-url1). In situ XRD (λ = 0.3196 Å) patterns for (a) Au−TiO₂ and (b) Au−Ti(15Ce)O₂ (testing conditions: 1% CO/3% H₂O/He, 10 mL/min, 3 mg of catalyst).

![Figure 12](image-url2). CO₂ concentration (blue line) and cell dimension of ceria (red line) as a function of reaction time for the Au−Ti(15Ce)O₂ sample (testing conditions: 1% CO/3% H₂O/He, 10 mL/min, 3 mg of catalyst).
CONCLUSIONS

In this Article, we have presented a fundamental study of the WGS reaction on model Au/CeO$_2$/TiO$_2$(110) and powder Au/CeO$_2$/TiO$_2$ catalysts, paying particular attention to the effect of ceria on the activity of the gold–titania system. CeO$_2$ nanoparticles deposited on TiO$_2$(110) act as anchoring sites for gold, improving the dispersion of the admetal on the oxide support. When compared to a typical benchmark system like Cu(111), Au/CeO$_2$/TiO$_2$(110) catalysts exhibit TOFs that are 10–30 times larger. The large dispersion of Au and the special chemical properties of CeO$_2$/TiO$_2$(110) lead to a substantial reduction in the apparent activation energy for the WGS, which decreases from 18 kcal/mol on Cu(111) to 7 kcal/mol on Au/CeO$_2$/TiO$_2$(110).

Au/CeO$_2$/TiO$_2$ powder catalysts were prepared by impregnating small amounts (6 and 15 wt %) of ceria on titania and then depositing 1 atom % gold onto these CeO$_2$/TiO$_2$ mixed-oxide supports. Catalytic tests indicate that these powder catalysts have a high activity and very good stability for the WGS. As in the case of Au/CeO$_2$/TiO$_2$(110), the ceria in the surface of the titania powders probably helps with the dispersion of the gold, improving the performance of the catalysts. Experiments of in situ time-resolved XRD determined that a second effect of ceria is to enhance the concentration of oxygen vacancies in the catalysts and, thus, facilitate the dissociation of water during the reaction. Results of in situ XAFS indicated that the gold oxidation state in the Au/CeO$_2$/TiO$_2$ powder catalysts changed from ionic (Au$^{4+}$) to metallic (Au$^{0}$) with the start of the WGS. Our in situ characterization results showed that the active phase for these powder catalysts contains gold particles with average sizes of $\sim$2 nm, which are preferentially stabilized by the oxygen vacancies in the CeO$_2$/TiO$_2$ surfaces.

This study shows that the phenomena observed in model Au/CeO$_2$/TiO$_2$(110) catalysts do provide useful concepts for the design and preparation of highly active and stable powder catalysts for the WGS reaction.

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Notes
The authors declare no competing financial interest.

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