

The Activation of Gold and the Water–Gas Shift Reaction: Insights from Studies with Model Catalysts

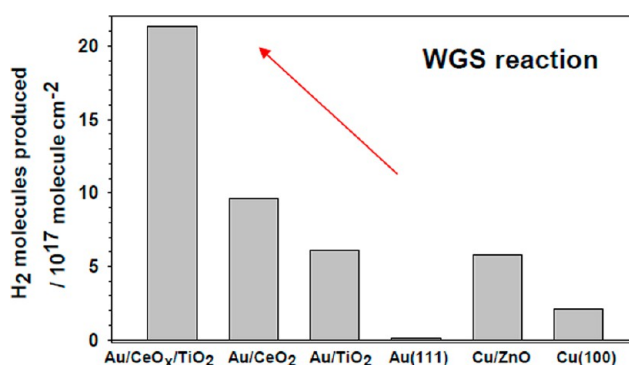
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CONSPECTUS

The activation of gold in catalytic reactions has been the subject of intensive research that has led to the transformation of one of the least chemically reactive elements to a catalyst with excellent activity and selectivity. Scientists have performed numerous systematic experimental and theoretical studies using model systems, which have explained the role of Au in chemical reactions with progressively increasing degrees of structural and chemical complexity. We present an overview of recent studies of model Au(111), CeO_x/Au(111), and Au/CeO_x/TiO₂(110) surfaces that use Au in different structural configurations specifically for the water–gas shift reaction (WGS, CO + H₂O → CO₂ + H₂), an important industrial process for the purification of CO. We demonstrate the significance of key structural components of the Au-based supported catalysts such as the metal–oxide interface (Au–O_x) toward the WGS catalytic activity, a “structure–activity” relationship.

In the WGS reaction, Au(111) or Au nanoparticles have poor catalytic performance due to their inability to activate one of the most important steps of the reaction, the breaking of O–H bonds in the dissociation of water (H₂O → OH + H). The relatively large energetic barrier can be overcome by using O on Au(111) to facilitate the formation of OH at low temperatures, with eventual CO₂ and H₂ production upon reaction between CO and the adsorbed OH. However, the inability to replace the reacted O prevents a sustainable catalytic process from occurring on Au(111). The addition of a small concentration of CeO_x nanoparticles on top of the Au(111) surface facilitates this rate-determining step and easily continues the catalytic cycle in the production of H₂. We have discovered that CeO_x nanoparticles in contact with Au(111) are rich in Ce³⁺. They also have a distinct metal–oxide interface, which sustains excellent activity for the WGS reaction via the formation of a unique carboxylate intermediate, making CeO_x/Au(111) more active than Cu/ZnO(0001), Cu(100), and Cu(111) which are the typical catalysts for this reaction. Taking this knowledge one step further, bringing these components (oxide and metal nanoparticles) together over a second oxide in Au/CeO_x/TiO₂ produces a system with unique morphological and electronic properties. The result is a superior catalyst for the WGS reaction, both as a model system (Au/CeO_x/TiO₂(110)) and as powder material (Au/CeO_x/TiO₂(anatase)) optimized directly in a series of systematic investigations.



1. Introduction

The understanding of the mechanisms for the chemical activation of gold has received considerable attention in recent years.^{1,2} Among the transition metals, gold, often referred to as a “coinage metal”, is by far the least reactive and considered the most noble metal. In valence photoemission spectra for metallic gold,³ states with Au 6s,p character appear from 0 to 2 eV below E_F , while the Au 5d states extend from 2 to 8 eV. The low reactivity of metallic

Au is a consequence of combining a deep-lying valence 5d band and very diffuse valence 6s,p orbitals.^{3–5} While bulk metallic gold is a very poor catalyst for the activation of simple molecules (H₂, O₂, CO, C₂H₄, etc.),^{5,6} atomic or molecular species bonded to low-index single crystal gold surfaces are chemically active.^{1,7–11} Gold nanoparticles exhibit unusual catalytic properties when dispersed on some oxide and carbide supports.^{12–21} For example, extended surfaces of gold and free gold nanoparticles bind

water poorly and are not able to dissociate the O–H bonds in the molecule.²² In contrast, small gold particles dispersed on ceria or titania are excellent catalysts for the water–gas shift reaction (WGS, $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$).^{14,23,24}

Many experimental and theoretical studies have been focused on understanding the high catalytic activity of supported gold nanoparticles.^{4,13,15–17,19,21} Quantum effects related to the small size of the particles or the existence of corner and edge atoms in the particle surface could be responsible for the enhancement in catalytic activity with respect to bulk gold,²⁵ but it is becoming more and more clear that interactions between the gold nanoparticles and the oxide or carbide support do play a very important role.^{26–28} Ideally, one wants to take advantage of these phenomena when designing highly efficient catalysts.

In this Account, we review a series of studies aimed at enhancing the reactivity of gold for the water–gas shift (WGS) reaction following different approaches. In the next section, we describe recent studies examining in detail the interaction of water with a clean Au(111) surface. The combined results from experimental and theoretical studies for water adsorption show that the gold surface is hydrophobic.²⁹ Then, we discuss the effects of chemisorbed O and ceria nanoparticles on the reactivity of Au(111) toward water.³⁰ By building a bifunctional system, in which the metal and oxide nanoparticles catalyze different steps of the reaction, one obtains an excellent catalyst for the WGS.⁸ In the last section, we describe the behavior of Au/CeO_x/TiO₂ systems designed to optimize the simultaneous participation of gold and the oxide support in the catalytic process.^{31,32} Concepts and ideas derived from fundamental studies with well-defined model catalysts can lead to a rational design of powder “technical” catalysts.

2. Interaction of Water with Au(111)

Thermodynamically, the wettability of a surface is determined by the relative energies of the various interfaces (solid–vapor, solid–liquid, and liquid–vapor) formed when water is condensed on the surface. Recent research has largely focused on the molecular structure of water during the initial stages of condensation.^{29,33} The results have demonstrated that the molecular structure of the first water layer adsorbed on a surface governs its wetting properties.³³ A unique property of water molecules is their ability to form strong directional hydrogen bonds, which are responsible for molecular aggregation and formation of amorphous solid water or crystalline solid ice on substrates, depending on the conditions used during the growth of water films.³³

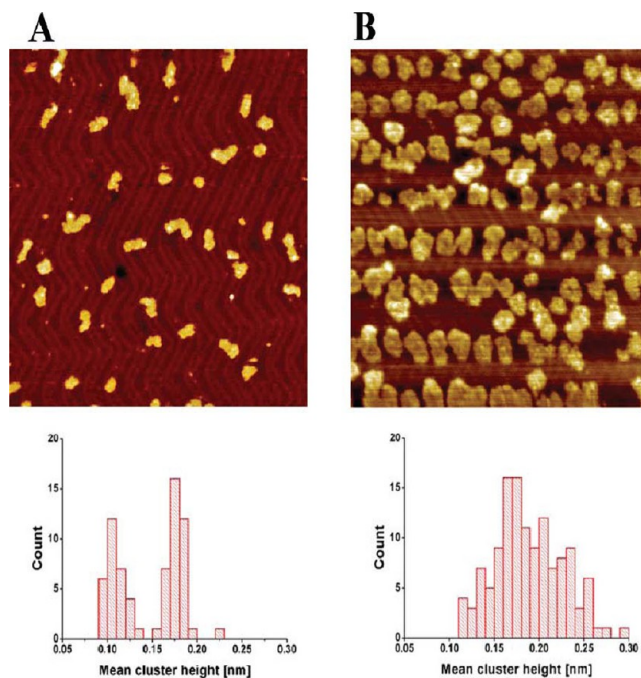


FIGURE 1. STM images ($100 \times 100 \text{ nm}^2$, -6 V , 4 pA) and corresponding histograms of adsorption of water on Au(111) at 20 K (A) after exposure to 0.04 L of H_2O (area fraction covered, 0.07) and (B) after exposure to 0.5 L of H_2O (area fraction covered, 0.38). Taken from ref 29. Copyright 2009 American Chemical Society.

Results of scanning tunneling microscopy (STM) indicate that water does not wet Au(111).^{29,34} The STM images in Figure 1 show that water nucleates in small clusters, predominantly at the elbows of the herringbone reconstruction. At very small coverages of water, we found small clusters with apparent heights ($\sim 0.1 \text{ nm}$) consistent with those reported for single water bilayers adsorbed on metals surfaces.³³ As the water exposure increased, Figure 1A, the clusters also adopted structures with an apparent height twice ($\sim 0.2 \text{ nm}$) that of single bilayers, suggesting the formation of double bilayer structures.²⁹ When the temperature of the sample was increased the water molecules desorbed ($\sim 140\text{--}160 \text{ K}$) without leaving any OH on the surface. The STM images²⁹ and results of temperature-programmed desorption (TPD), infrared spectroscopy (IR),²⁹ and X-ray photoelectron spectroscopy (XPS)³⁰ point to very weak bonding interactions between water and Au(111) in agreement with the results of theoretical calculations.²²

Density-functional (DF) calculations were employed to investigate different stages of water adsorption on Au(111).²⁹ The adsorptions of one bilayer (BL), two BLs, and three BLs of water were each explored in the calculations. The water adsorption energy and the corresponding geometries are plotted in Figures 2 and 3. For one BL water adsorption on

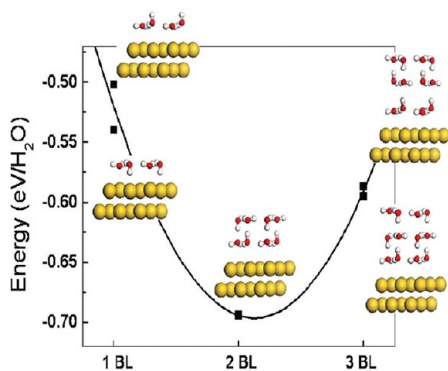


FIGURE 2. DF-calculated adsorption energies for water multilayers adsorbed on Au(111). The figures show the corresponding optimized geometries (yellow, Au; red, O; white, H). Taken from ref 29. Copyright 2009 American Chemical Society.

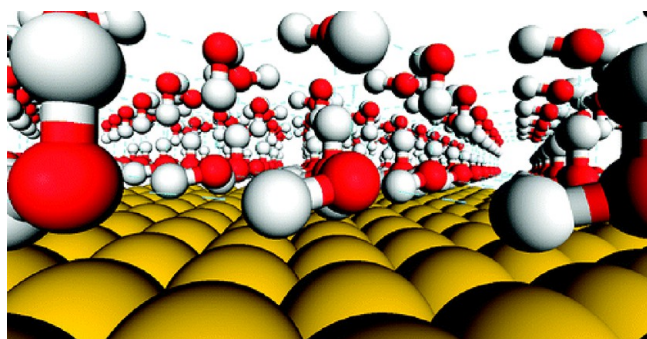


FIGURE 3. Calculated structure for a water bilayer on Au(111). Taken from ref 29. Copyright 2009 American Chemical Society.

Au(111), there are two possibilities, having hydrogen atoms pointing up (H-up) or down (H-down). Theoretical calculations show that the two structures are very close in energy, with the H-down configuration slightly more stable than the H-up configuration by 0.04 eV/H₂O.²⁹ For the two BL system, a structure with all hydrogens locked in the two water layers is the most stable, enhancing the stability per water molecule by ~0.15 eV with respect to the one BL structure. This two BL structure described is similar to a bilayer ice phase confined in pores that was proposed theoretically.³⁵ The growth of the third water BL on Au(111) always results in some of the oxygen atoms coordinated to three hydrogen atoms (Figure 2). As a result, the three BL structures are not energetically preferred and are less stable than the two BL clusters by ~0.1 eV/H₂O, although they remain marginally more stable than one BL clusters (Figure 2). Overall, the DF calculations demonstrate that when the water coverage increased from one BL to three BLs, the two BL structure (H-up or H-down) is energetically favored on Au(111), in agreement with the STM observations.²⁹ The results in Figure 2 must be taken only in qualitative terms since the DF calculations did not include dispersion terms.²⁹

The double bilayer water structures seen in Figures 1–3 are possible by the extremely weak water–Au(111) interactions. In the next section, we will discuss two different approaches to enhance the reactivity of water on the gold substrate.

3. Interaction of Water with O/Au(111) and CeO_x/Au(111): The Assembly of an Efficient Water–Gas Shift Catalyst

The addition of O to Au(111) enhances the chemical reactivity of the system¹ and makes it more reactive for the dissociation of water.³⁶ Figure 4 shows the O 1s XPS data for the interaction of H₂O with clean gold (panel A) and with a gold surface partially covered by oxygen (panel B).³⁶ In Figure 4A, a dose of H₂O onto clean Au(111) at 90 K results in a single peak, at 533.2 eV, in the O 1s region, which corresponds to layers of ice. Annealing to 150 K induces a gradual decrease in the intensity of this peak and a binding-energy shift to 532.7 eV. By 174 K, all of the H₂O has desorbed leaving the Au(111) surface clean. Figure 4B shows a similar experiment on the O/Au(111) surface. The dotted line indicates the clean surface with a single peak at 529.7 eV for chemisorbed O. Exposure to H₂O at 90 K produces a large peak at 533.2 eV corresponding to an ice layer similar to that observed on the Au(111) surface. However, in the H₂O on O/Au(111) system, annealing to 150 K shifts the peak to 530.7 eV, as a result of the formation of OH groups on the surface.³⁶ Further annealing to 200 K shows the disappearance of the OH groups leaving only the chemisorbed O species at 200 K. Our spectroscopic measurements are consistent with previous studies in which TPD and isotopic labeling of water with ¹⁸O and D were used to investigate the H₂O_{gas} + O_{ads} → 2OH_{ads} reaction and its reverse.^{7,9} Here, the O 1s signal for adsorbed OH is detected from 150 to 180 K.

The OH groups generated by the reaction of water with O/Au(111) can react with CO to eventually yield CO₂ and H₂,^{7,29} the final products of the WGS reaction. Thus, the activation of Au(111) has been achieved, but one cannot use O/Au(111) to build a catalytic cycle for the WGS because CO eventually will remove all the O from the gold substrate, and it will not be replaced by the oxidation with water. One can obtain a stable catalyst for the WGS by adding CeO_x nanoparticles to Au(111).^{8,30} Figure 5 shows STM images obtained after depositing ceria on Au(111).³⁷ The oxide nanoparticles were synthesized by exposing a Ce/Au(111) alloy to O₂ gas at 450 K. There is a random distribution of the ceria nanoparticles on the terraces of the gold substrate,

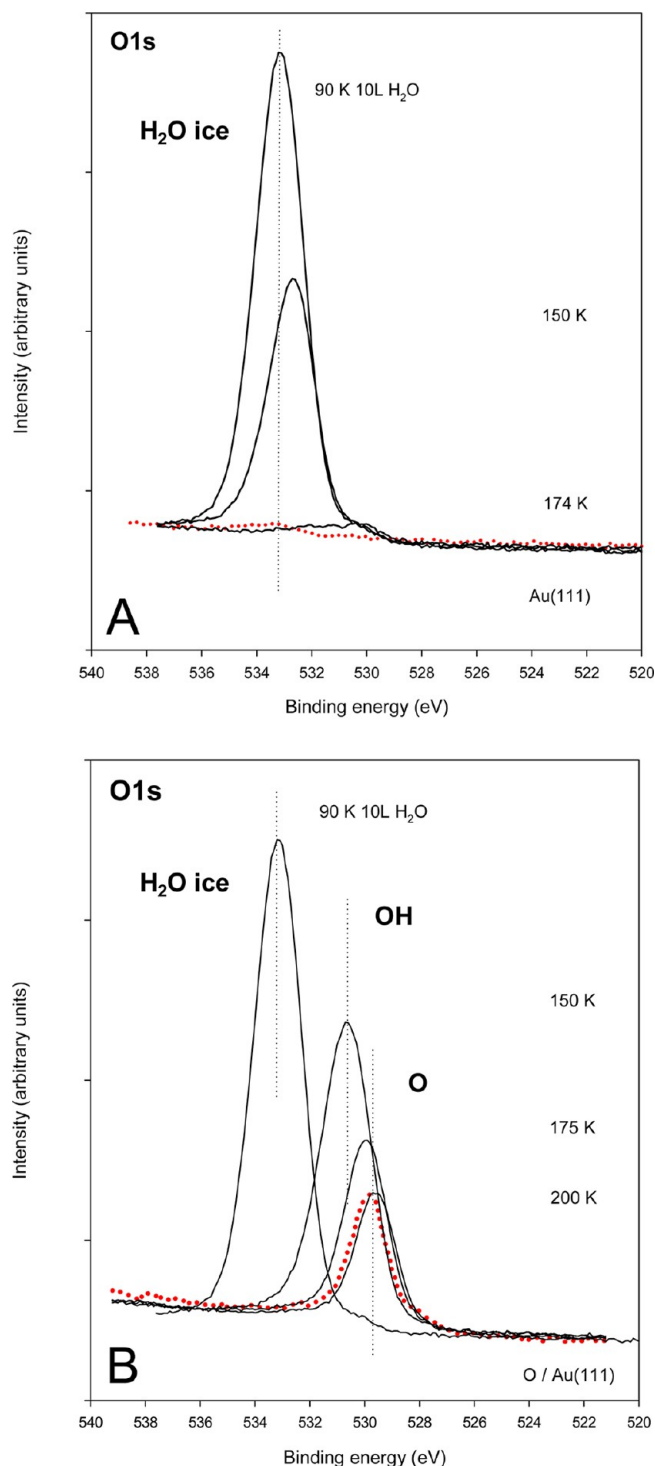


FIGURE 4. XPS spectra for H₂O adsorption at 86 K on (A) Au(111) and (B) O/Au(111) surfaces followed by annealing from 86 to 200 K. The corresponding spectra for clean Au(111) and O/Au(111) are shown as dotted traces. Taken from ref 30. Copyright 2010 Elsevier.

which maintains its characteristic herringbone reconstruction.³⁷ For these CeO_x/Au(111) systems, one can generate ceria nanoparticles fully oxidized as Ce⁴⁺ or partially reduced as Ce³⁺ (Figure 6a).^{8,30,37,38}

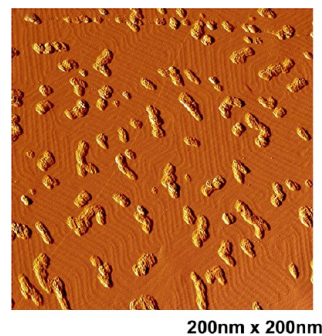


FIGURE 5. STM image obtained after a Ce–Au(111) surface alloy was annealed at 450 K in 1×10^{-8} Torr of O₂ for 30 min and flashed to 650 K. Taken from ref 37. Copyright 2008 Elsevier.

The bottom panel in Figure 6 displays XPS spectra obtained after adsorption of water at 300 K on a ceria/gold system that contained fully oxidized ceria nanoparticles (Ce⁴⁺) and on a system that contained a substantial amount of Ce³⁺.⁴¹ The CeO₂/Au(111) surface was not able to dissociate water to produce adsorbed OH groups. In this respect, it behaved like a flat CeO₂(111) surface.²³ But the CeO₂/Au(111) system was easily reduced with CO gas,^{8,30} and in the presence of Ce³⁺ cations, there is fast dissociation of water at 300 K.^{8,30,38} DF calculations predict a very high barrier (>1 eV) for water dissociation on Au(111).^{8,22} Once the OH groups are formed, subsequent steps for the WGS process occur readily on the gold substrate.^{8,22}

Figure 7 shows an Arrhenius plot for the WGS activity of a CeO_x/Au(111) surface in which 20% of the gold substrate was covered by ceria.³⁰ For comparison we also include results obtained for the WGS on Cu(100), Cu(111), and Cu/ZnO(000 $\bar{1}$) surfaces.²³ The results in Figure 7 indicate that the CeO_x/Au(111) catalyst exhibits a larger WGS activity than those of copper surfaces or even Cu nanoparticles dispersed on a ZnO(000 $\bar{1}$) substrate.³⁰ On Cu(111) and Cu(100), the apparent activation energies for the WGS are 18.1 and 15.2 kcal/mol, respectively.²³ The apparent activation energy decreases to 12.4 kcal/mol on Cu/ZnO(000 $\bar{1}$)²³ and 10.3 kcal/mol on CeO_x/Au(111).³⁰ In the CeO_x/Au(111) catalyst, the reactants can interact with defect sites of ceria nanoparticles, metal sites of the support, or the metal–oxide interface. One can gain activity due to the active participation of the oxide in the catalytic reaction.^{8,30,39}

Postreaction characterization of the model CeO_x/Au(111) catalyst with XPS pointed to a Ce⁴⁺ → Ce³⁺ transformation and identified a C 1s feature at 289–290 eV corresponding to either HCOO or CO_x species on the CeO_x/Au(111) surface.^{8,30} Theoretical calculations suggest that the

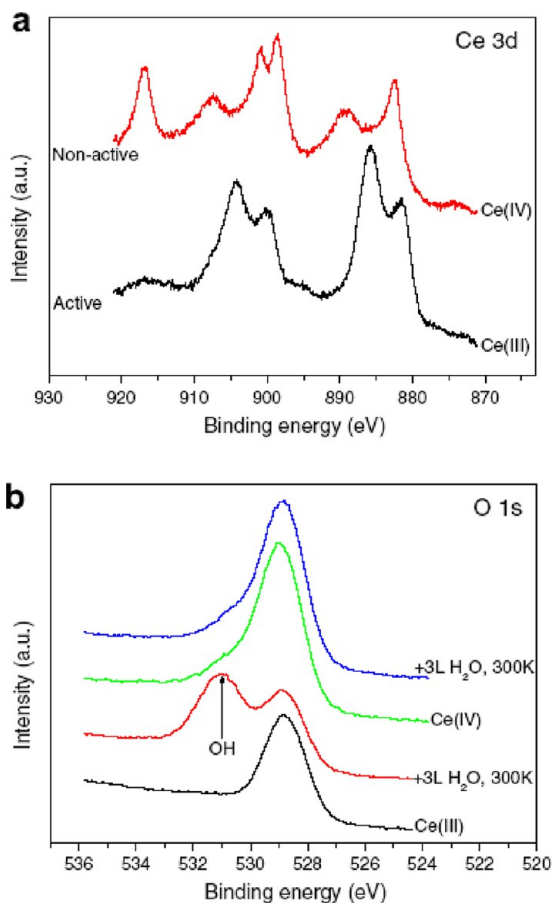


FIGURE 6. (a) Two typical Ce 3d core level spectra for Ce^{4+} from $\text{CeO}_2/\text{Au}(111)$ and Ce^{3+} from $\text{Ce}_2\text{O}_3/\text{Au}(111)$. (b) Two sets of O 1s core level spectra obtained from $\text{CeO}_2/\text{Au}(111)$ and $\text{Ce}_2\text{O}_3/\text{Au}(111)$ before and after dosing 3 L of water at 300 K. Taken from ref 38. Copyright 2007 Elsevier.

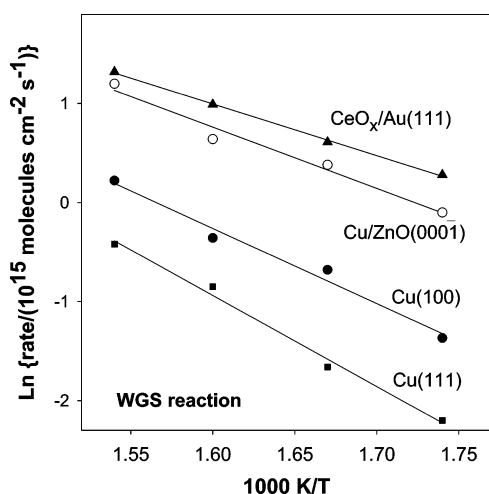


FIGURE 7. Arrhenius plot for the WGS reaction rate on Cu(111), Cu(100), Cu/ZnO(000 $\bar{1}$), and Au(111) surface approximately 20% covered by ceria. The data were acquired with a pressure of 20 Torr of CO and 10 Torr of H_2O and temperatures of 575, 600, 625, and 650 K. Taken from ref 30. Copyright 2010 Elsevier.

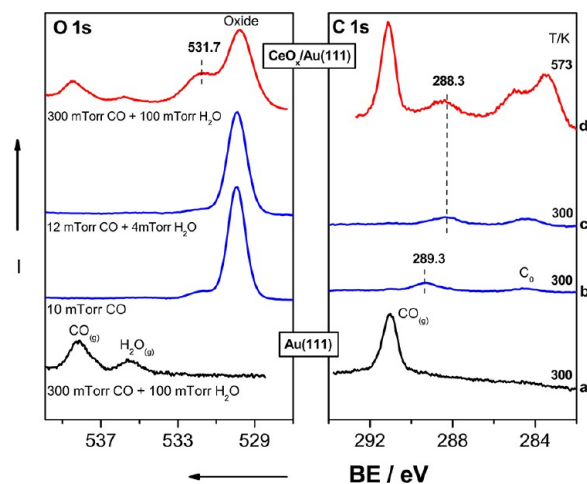
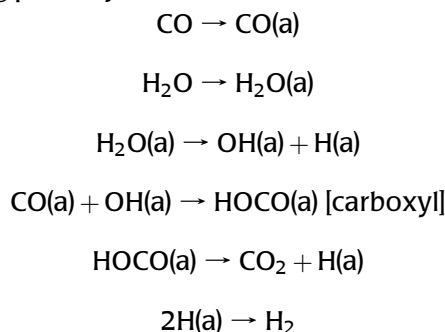


FIGURE 8. Ambient-pressure XPS data from Au(111) and $\text{CeO}_x/\text{Au}(111)$ under WGS reaction conditions. Taken from ref 39. Copyright 2013 Wiley.

mechanism for the WGS in $\text{CeO}_x/\text{Au}(111)$ undergoes the following pathway:^{8,22}



Formate (HCOO) and carbonate (CO_3) also have been proposed as reaction intermediates in an associative mechanism.⁴⁰ Recently, ambient-pressure (AP) XPS was used to study the mechanism of the WGS on $\text{CeO}_x/\text{Au}(111)$.³⁹ Figure 8 displays O 1s and C 1s spectra collected during exposure of Au(111) and a $\text{CeO}_x/\text{Au}(111)$ surface to a mixture of CO and H_2O . The AP-XPS experiments at 300 mTorr of CO + 100 mTorr of H_2O showed no surface species on Au(111) in the temperature range of 300–573 K and this surface is not able to catalyze the WGS reaction. CeO_x nanoparticles deposited on the Au(111) surface were exposed to CO (10–300 mTorr) with annealing from 300 to 573 K. Figure 8b shows a peak at 289.3 eV (C 1s), which has been assigned to CO_3 or HCOO species formed on CeO_x .³⁹ Exposure to CO only lead to formation of this surface species and some C. Spectra in Figure 8c show the result of exposing the $\text{CeO}_x/\text{Au}(111)$ surface

to 12 mTorr of CO + 4 mTorr of H₂O at 300 K. Without the interference of gaseous reactants (CO_(g) or H₂O_(g)), the formation of surface species is visible. The main feature in the C 1s region at 288.3 eV, with a shoulder at higher BEs, is assigned to CO₂^{δ-} species.³⁹ At higher pressures and temperatures (Figure 8d), the presence of CO_(g), H₂O_(g), and changes in the main features are observed. A shift to higher BEs of the feature at 288.3 eV in the C 1s region can be explained by the presence of CO₂^{δ-} and the formation of HCOO on the ceria nanoparticles, which appears at ~289 eV.³⁹ In the O 1s region, a large feature is observed centered at 531.7 eV due to a combination of OH, HCOO, and CO₂^{δ-} species.³⁹ Based on DFT calculations, it is proposed that the CO₂^{δ-} trapped at the metal–oxide interface is a product of the decomposition of HOCO on the catalyst surface.³⁹ These AP-XPS studies show the importance of the metal–oxide interface for the WGS.

4. The Water-Gas Shift on Au/CeO_x/TiO₂(110) Surfaces and Au/CeO_x/TiO₂ Powders: Optimizing the Participation of Gold and the Oxide Support in the Catalytic Process

Since the discovery by Haruta et al. that oxide-supported Au nanoparticles are extremely active as CO oxidation catalysts,¹² many research groups have investigated the activity of gold nanostructures for various catalytic reactions.^{3,12,14,19,20,25–27} Gold on titania powder catalysts exhibit very high activity for the WGS reaction⁴¹ but have a low thermal stability.⁴² Studies have been published examining in detail the deposition of small amounts of Au on TiO₂(110) with STM.^{13,43,44} These studies indicate that Au grows on this oxide substrate forming three-dimensional (3D) particles. At 300 K, the Au clusters nucleate mainly on step sites or on defect sites present in the terraces of TiO₂(110). The interaction of Au with an ideally flat TiO₂(110) surface is quite weak,⁴⁵ and a substantial amount of particle sintering occurs when the system is annealed from 300 to 650 K.^{13,43,44}

It has been shown that the interaction of gold with ceria nanoparticles is significantly stronger than with bulk ceria.⁴⁶ Therefore, stabilizing both Au and ceria as nanoparticles in close proximity can potentially further modify the chemical properties of the combined system. Figure 9A shows an STM image acquired after depositing Ce on TiO₂(110) under an atmosphere of O₂.^{31,47} Most of the spots (~70%, labeled “a”) have a height of 1.3 ± 0.2 Å and correspond to small wires of CeO_x.³¹ A minority of the spots (~30%, labeled “b”) have a height of 1.9 ± 0.3 Å and probably correspond to (1 × 2)

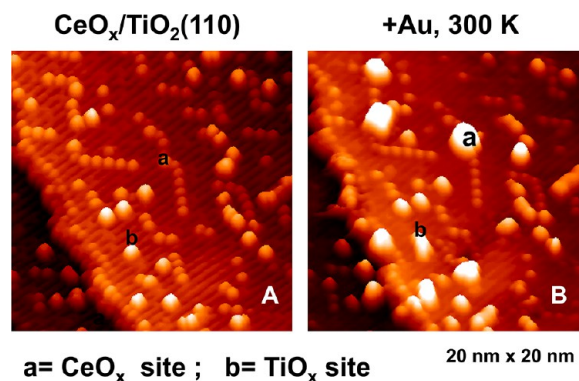


FIGURE 9. STM study of the morphology of Au/CeO_x/TiO₂(110). (A) STM image of a CeO_x/TiO₂(110) surface. Ce was deposited at 327 °C under an atmosphere of O₂ (~1 × 10⁻⁷ Torr) and then the sample was annealed at 900 K in O₂. (B) STM image obtained after deposition of gold on the CeO_x/TiO₂(110) surface that gave image A at room temperature with subsequent annealing at 600 K. Taken from ref 32. Copyright 2012 American Chemical Society.

reconstructions of TiO₂(110) induced by O₂ chemisorption.^{31,48} Figure 9B displays an STM image taken after deposition of ~0.25 ML of Au on the CeO_x/TiO₂(110) surface of Figure 9A. The deposition of Au was done at 300 K and the Au/CeO_x/TiO₂(110) system was subsequently heated to ~600 K. Large particles of Au formed and 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_x/TiO₂(110) substrate. When STM images for the Au/CeO_x/TiO₂(110) system are compared with those collected for plain Au/TiO₂(110),^{13,43,44} 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/TiO₂(110). As we will see below, the close contact between Au and CeO_x leads to a very high catalytic activity and also to long-term stability.

At small coverages of ceria on TiO₂(110), the CeO_x nanoparticles have an unusual coordination mode.^{31,47} STM and DF calculations point to the presence of Ce₂O₃ dimers, which form diagonal arrays that have specific orientations of 0, 24°, and 42° with respect to the [1 $\bar{1}$ 0] direction of the titania substrate.^{31,47} The ceria–titania interactions induce a change in the relative stability of the Ce³⁺/Ce⁴⁺ oxidation states that leads to a significant enhancement in the reactivity of the oxide surface toward water.⁴⁷ DF calculations for the dissociation of water on the Ce₂O₃/TiO₂(110) system showed an exothermic process ($\Delta E = -0.7$ eV) with a very small activation energy ($E_a = 0.04$ eV), Figure 10.⁴⁷ Photoemission experiments have confirmed the facile dissociation of

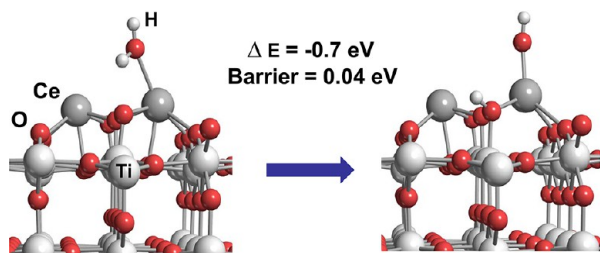


FIGURE 10. Initial and final geometries for the dissociation of a H₂O molecule on Ce₂O₃/TiO₂(110). Taken from ref 47. Copyright 2010 American Chemical Society.

water at 300 K on CeO_x/TiO₂(110) surfaces.⁴⁷ Once the CeO_x/TiO₂ is coupled to Au nanoparticles, one can envision the reaction of the OH formed by the dissociation of water with CO bound to the Au nanoparticles to produce the HOCO and CO₂^{δ-} intermediates seen in the metal–oxide interface present in CeO_x/Au(111).³⁹ A theoretical study predicts that the corner and edge atoms present in Au nanoparticles are better for binding CO and forming an HOCO intermediate than the atoms in extended Au(111) or Au(100) surfaces.^{8,22} Thus, in Au/CeO_x/TiO₂(110), one has the optimal configuration for the gold and oxide support.

Figure 11 displays Arrhenius plots for the WGS on Au/TiO₂(110) and Au/CeO_x/TiO₂(110) catalysts, $\theta_{\text{Au}} \approx 0.4$ ML in both cases, together with reported data for Cu(100) and Cu(111), a commonly used material for the WGS.³² As mentioned above, Au(111) or polycrystalline Au does not have any catalytic activity for the WGS. The same is valid for CeO_x/TiO₂(110). In Figure 11, Au/CeO_x/TiO₂(110) is the best WGS catalyst at all temperatures. The Au nanoparticles supported on CeO_x/TiO₂(110) produce a catalyst that is 12 (at 650 K) to 33 times (at 575 K) more active than Cu(111), a typical benchmark for WGS studies.^{32,49} Au/TiO₂(110) is not as good a catalyst as Au/CeO_x/TiO₂(110), but its performance is still quite remarkable because Au alone is not able to catalyze the WGS reaction. Figure 11 includes the apparent activation energies for the 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/TiO₂(110) and 7 kcal/mol on Au/CeO_x/TiO₂(110). The catalyst that has the highest activity in Figure 11 has also the lowest apparent activation energy. These data illustrate the benefits of co-depositing Au and ceria nanoparticles on the titania support. With respect to TiO₂(110), CeO_x/TiO₂(110) favors the dispersion of Au and water dissociation.⁴⁷

As a follow-up to the studies with the model Au/CeO_x/TiO₂(110) catalysts,^{31,47} powder catalysts of the Au/CeO_x/TiO₂

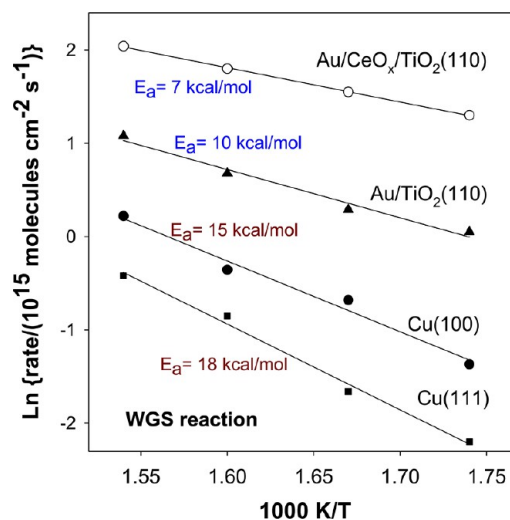


FIGURE 11. Arrhenius plots for the WGS on Au/TiO₂(110) and Au/CeO_x/TiO₂(110) catalysts (20 Torr of CO and 10 Torr of H₂O). Surfaces of metallic Au are not active for the WGS reaction. For comparison results are included for the WGS reaction on Cu(100) and Cu(111) surfaces, common benchmarks in catalytic studies. Taken from ref 32. Copyright 2012 American Chemical Society.

type were prepared.³² CeO_x nanoparticles were deposited on an anatase powder. Depending on the loading of ceria, one could see variations in the relative concentration of clusters, chains, and 3D nanoparticles on the titania (Figure 12).⁵⁰ Results of STEM-EELS and NEXAFS indicate that the oxide–oxide interface in these systems was rich in Ce³⁺ centers.⁵⁰ HRTEM showed that the Au particles were anchored near the ceria nanoparticles and on defects of the titania substrate.³² The steady-state “light-off” profiles of the powder Au/CeO_x/TiO₂ catalysts are shown in Figure 13.³² Both ceria-containing samples exhibited much higher activities than the plain Au–TiO₂ catalyst. Furthermore, in a test of stability it was found that a Au–CeO_x/TiO₂ catalyst showed only minor signs of deactivation with a drop of ~15% in the conversion after 20 h under our reaction conditions. This is a very remarkable result since the major drawback of gold based catalysts is their stability problems due to the easiness of particle sintering.^{41,42} The strong interaction between gold and the ceria–titania support seems to prevent the agglomeration of gold particles.³²

In situ measurements of XAFS and XRD were used to study the structural transformations in the Au/TiO₂ and Au/CeO_x/TiO₂ catalysts during the WGS.³² The fresh samples consisted of AuO_x dispersed on the oxide supports. The XANES results in Figure 14 show the disappearance of the features for AuO_x when a AuO_x/CeO_x/TiO₂ catalyst is exposed to a mixture of the reactants at temperatures around 150 °C. An analysis of the coordination number of the generated Au particles gave a particle size of ~2.0 and 2.5 nm.³²

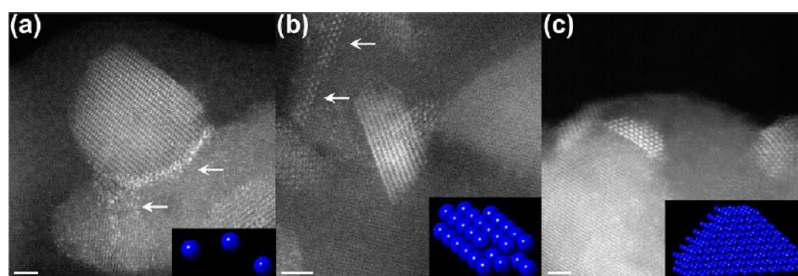


FIGURE 12. HAADF STEM images showing the different morphologies of ceria that can be found in a $\text{CeO}_x/\text{TiO}_2$ sample: clusters (a), constrained structures (chains) (b), and nanoparticles (c) (scale bars = 2 nm). Insets in the lower right corner are atomic models. Taken from ref 50. Copyright 2013 American Chemical Society.

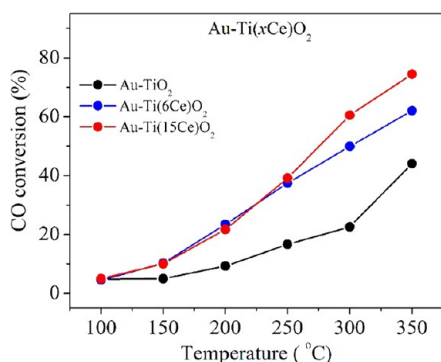


FIGURE 13. Steady-state “light off” profiles of Au/TiO_2 and $\text{Au}/\text{CeO}_x/\text{TiO}_2$ catalysts for the WGS reaction. Testing conditions: 1% $\text{CO}/3\% \text{H}_2\text{O}/\text{He}$, 10 mL/min. Taken from ref 32. Copyright 2012 American Chemical Society.

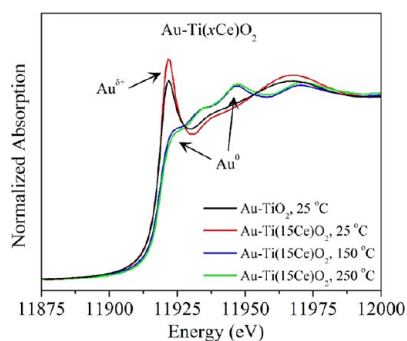


FIGURE 14. *In situ* XANES (Au L-III edge) spectra for Au/TiO_2 and $\text{Au}/\text{CeO}_x/\text{TiO}_2$ samples. The spectra were collected at 300, 450, and 550 K. Testing conditions: 1% $\text{CO}/3\% \text{H}_2\text{O}/\text{He}$, 30 mL/min. Taken from ref 32. Copyright 2012 American Chemical Society.

The results of *in situ* XRD measurements showed the existence of a very large concentration of Ce^{3+} sites that promoted the dissociation of water. Thus, there are several common features in the behavior and performance of $\text{Au}/\text{CeO}_x/\text{TiO}_2(110)$ and $\text{Au}/\text{CeO}_2/\text{TiO}_2$ powder catalysts. The phenomena observed in the model $\text{Au}/\text{CeO}_x/\text{TiO}_2(110)$ catalysts did provide useful concepts for the design and preparation of highly active and stable powder catalysts for the WGS reaction.

5. Conclusions

The combined results from experimental and theoretical studies for water adsorption show that $\text{Au}(111)$ is hydrophobic. Neither $\text{Au}(111)$ nor Au nanoparticles are able to break the $\text{O}-\text{H}$ bonds in water. The coupling of gold to ceria produces a bifunctional metal–oxide interface that is able to dissociate water, and thus, one can take advantage of the chemical properties of gold. $\text{Au}/\text{CeO}_x/\text{TiO}_2$ is an excellent catalyst for the water–gas shift reaction. It illustrates the benefits that can be obtained by optimizing the oxide component in metal–oxide catalysts for the WGS reaction.

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FOOTNOTES

The authors declare no competing financial interest.

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