Water-gas Shift Reaction over Gold Nanoparticles Dispersed on Nanostructured CeO_x-TiO₂(110) Surfaces: Effects of High Ceria Coverage

D. C. Grinter^a, J. B. Park^a, S. Agnoli^a, J. Evans^b, J. Hrbek^a, D. J. Stacchiola^a, S.D. Senanayake^a and J. A. Rodriguez^{a*}

^a Department of Chemistry, Brookhaven National Laboratory, Upton, NY, USA, NY 11973-5000

^b Facultad de Ciencias, Universidad Central de Venezuela, Caracas, 1020 A, Venezuela

Abstract

Scanning tunnelling microscopy has been used to study the morphology of an overlayer of ceria in contact with a TiO₂(110) substrate. Two types of domains were observed after ceria deposition. An ordered ceria film covered half of the surface and high-resolution imaging suggested a near-c(6 × 2) relationship to the underlying TiO₂(110)-(1 × 1). The other half of the surface comprised CeO_x nanoparticles and reconstructed TiO_x supported on TiO₂(110)-(1 × 1). Exposure to a small amount of gold resulted in the formation of isolated gold atoms and small clusters on the ordered ceria film and TiO₂(110)-(1 × 1) areas, which exhibited significant sintering at 500 K and showed strong interaction between the sintered gold clusters and the domain boundaries of the ceria film. The Au/CeO_x/TiO₂(110) model system proved to be a good catalyst for the water-gas shift (WGS) exhibiting much higher turnover frequencies (TOFs) than Cu(111) and Pt(111) benchmarks, or the individual Au/TiO₂(110) and Au/CeO₂(111) systems. For Au/CeO_x/TiO₂(110) catalysts, there was a decrease in catalytic activity with increasing ceria coverage that correlates with a reduction in the concentration of Ce³⁺ formed during WGS reaction conditions.

Keywords: STM, TiO₂(110), CeO₂, Gold, Water-gas shift

* Corresponding author, rodrigez@bnl.gov

Introduction

In recent years, mixed-metal oxides which contain ceria are receiving a lot of attention due to their applications in catalysis, materials science, photochemistry and the control of environmental pollution [1,2]. CeO_x-TiO₂ has shown to be an excellent substrate for the dispersion of metals used in the oxidation of CO, the water-gas shift reaction, the hydrogenation of CO₂ to alcohols, the splitting of water and the selective reduction of NO_x species [3,4,5,6,7,8]. For example, it has been found that systems of the M/CeO_x/TiO₂ (M = Au, Cu, or Pt) type produce H₂ by the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) or the photocatalytic splitting of water ($\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + 0.5\text{O}_2$) with considerably better activity than either of the individual oxide counter parts [3,7]. The origin of this notable enhancement can be traced to a combination of structural and electronic properties unique to the CeO_x-TiO₂ interfacial region [3,7].

When considering the CeO_x/TiO₂ system, the two oxide components are prototypical lanthanide (CeO₂) and transition metal (TiO₂) compounds and have been extensively studied on their own. Catalytically, both offer excellent redox chemical properties including reducibility, stable oxidation states (Ce⁴⁺/Ce³⁺, Ti⁴⁺/Ti³⁺), and oxygen storage capacity. However, both structurally (CeO₂ – fluorite versus TiO₂ – anatase lattice) and electronically (Ce-4f versus Ti-3d valence levels), there are substantial differences between these two materials. The characterization of CeO_x/TiO₂ powders with high-resolution transmission electron microscopy (HR-TEM) and electron energy loss spectroscopy (EELS) has shown a lot of intermixing at the oxide-oxide interface with an stabilization of the Ce³⁺ state with respect to Ce⁴⁺ [9]. Density functional theory (DFT) calculations indicate an energetic preference for the formation of O vacancies and the corresponding Ce³⁺ sites at the ceria-titania interface [9]. Efforts are needed to understand the fundamental properties of this interface to better interpret its catalytic behaviour and to improve the design of new catalysts.

In previous works, scanning tunnelling microscopy (STM) was used to study the growth mode of small ceria nanostructures on the $\text{TiO}_2(110)$ surface [3,4]. The STM images point to the presence of Ce_2O_3 dimers on top of the titania substrate. These dimers are ideal nucleation sites for gold clusters helping in the formation of highly active $\text{Au/CeO}_x/\text{TiO}_2(110)$ catalysts [3,10]. In this work, we investigate the dispersion and catalytic activity of gold nanoparticles on high coverages ($> 30\%$ of the substrate covered) of ceria in contact with $\text{TiO}_2(110)$. The ceria overlayers produce unique structures on the titania template which are better supports for metal catalysts than clean $\text{TiO}_2(110)$ or $\text{CeO}_2(111)$.

Experimental Methods

The STM experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr containing an Omicron variable temperature STM operated using chemically etched W tips [3,4]. The single crystal $\text{TiO}_2(110)$ substrate was prepared by cycles of Ar sputtering and annealing in UHV to ~ 1000 K until a surface comprised of large, atomically flat terraces was obtained with no appreciable contamination observed in STM imaging. Here, high coverages ($> 30\%$ of the substrate covered) of ceria were deposited on the titania sample. Cerium was evaporated from an e-beam evaporator (Focus EFM-3) onto the $\text{TiO}_2(110)$ surface in 2×10^{-7} torr O_2 at 650 K, followed by annealing to 950 K in the same oxygen pressure [3]. The coverage of ceria and gold is expressed in monolayers (ML) relative to the Ti atom density at the $\text{TiO}_2(110)$ surface: $6.6 \times 10^{14} \text{ cm}^{-2}$. This was estimated by extrapolation from earlier studies where small amounts of metallic cerium were deposited onto $\text{TiO}_2(110)$ such that the Ce cluster height, diameter, and number density could be measured by STM.[1] Gold was evaporated *in-situ* in the STM stage onto the ceria/ $\text{TiO}_2(110)$ at 300 K.

The catalytic studies were performed in a system which combines a batch reactor and a UHV chamber [3,4,10]. It is equipped with instrumentation for low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS) and

temperature programmed desorption (TPD). The sample could be transferred between the reactor and UHV chamber without exposure to air. In the kinetic measurements the sample was transferred to the batch reactor at ~ 300 K, then the reactant gases were introduced (20 Torr of CO and 10 Torr of H₂O) and the sample was rapidly heated to the reaction temperature of 625K. The amount of molecules produced was normalized by the active area exposed by the sample [3,4,10]. In our reactor a steady-state regime for the production of H₂ and CO₂ was reached after 2-3 minutes of reaction time.

Results and Discussion

A. Morphology of CeO_x/TiO₂(110)

As shown previously, at small coverages, ceria grows on TiO₂(110) forming Ce₂O₃ dimers [3,4]. These dimers exhibit a height that is quite different from that of TiO_x features and can agglomerate in different ways on the titania substrate (Figure 1) [3,4]. They can form diagonal arrays, small nanowires, that have specific orientations of 0, 24 and 42° with respect to the [1-1 0] direction of the titania substrate [4]. The stability of different dimer configurations was examined with DFT calculations [4]. With respect to the atoms in the O bridging rows of the TiO₂(110) surface, the dimers could adopt a horizontal or a diagonal configuration. The results of DFT calculations indicate that a diagonal dimer has a formation energy 2.6 eV more exothermic than the formation energy of a horizontal dimer. Thus, the dimers associate on the titania surface adopting the configurations show at the bottom of Figure 1 (A, B, C, D) [3,4].

Once that the ceria coverage becomes large, the simple arrays of the nanowires disappear and more complex structures are seen. A typical STM image of this type of ceria/TiO₂(110) system is displayed in Figure 2A. The system is composed of two distinct phases covering equal areas of the surface. One of these consists of bright, ordered regions (labelled I) with widths of 50-100 nm, which display dark disordered patches oriented roughly along [001] and dark linear depressions oriented at approximately $\pm 45^\circ$ to [001]. The rest of the surface is composed of regions which

exhibit a low degree of order (labelled II) and are decorated with a high density of small, bright features. Higher resolution STM images of the ‘ordered’ ceria regions are displayed in Figure 2B and 2C obtained at negative (-2.6 V) and positive (+1.0 V) sample biases to provide filled and empty states imaging, respectively. The domain boundaries within the ordered ceria regions are characterized by linear depressions in both filled and empty states images, permitting mapping of the atomic structures in both. (blue lines in Figure 2B, C) From the filled states image in Figure 2B, pairs of atomic-sized features are present in ‘dumbbell’ shapes, with alternate dumbbells rotated $\sim 90^\circ$ to each other, and the long axis of each dumbbell aligned at $\pm 40\text{-}50^\circ$ from the [001] direction. A non-primitive rectangular surface unit cell (white highlight in Figure 2B) has been constructed between these with dimensions of $1.7 (\pm 0.1) \text{ nm} \times 1.3 (\pm 0.1) \text{ nm}$, very close to a $c(6 \times 2)$ periodicity relative to the $\text{TiO}_2(110)\text{-(}1 \times 1\text{)}$ (unit cell: $0.296 \text{ nm} \times 0.649 \text{ nm}$), as was also observed in our previous study of this system [11]. In the empty states image (Figure 2C) an equivalent unit cell (black rectangle) can be constructed between the bright protrusions (displayed as black dots). Overlaying the dumbbell shapes from the filled states image, it is clear that each dumbbell is associated with a single bright spot in the empty states image. The structure of this ordered ceria phase, as recognized in our earlier paper, does not correspond to any particular surface of CeO_2 , rather the growth of the overlayer appears to be templated by the $\text{TiO}_2(110)$ substrate [11]. The high density of domain boundaries and generally small domain sizes (up to $\sim 50 \text{ nm}$) indicates a degree of strain within the ordered ceria layers. The precise composition and structure of the ceria layers on $\text{TiO}_2(110)$ appears to be extremely sensitive to the coverage and preparation conditions, especially the temperature, as demonstrated in previous studies of this system [4,11] as well as other mixed metal oxides [12]. Figure 2D shows an atomically resolved empty states image obtained from within one of the disordered regions (labelled II) in Figure 2A. The typical structure of the $\text{TiO}_2(110)\text{-(}1 \times 1\text{)}$ surface is observed, with bright rows along [001] corresponding to the Ti_{5c} sites at the surface [13]. A number of large bright strands (one example highlighted with a rectangle in Figure 2D) are present on the surface, these can be attributed to reconstructed TiO_x species, formed

by the diffusion of Ti^{3+} to the surface during the annealing process to form the ceria [4,11]. Additional smaller bright features are found situated on top of the Ti_{5c} rows (hexagonal highlight in Figure 2D) – our previous studies of this system have identified these as CeO_x nanoparticles (monomers and dimers) [4,11]. A number of bridging oxygen vacancies ($\text{O}_b\text{-vac}$, example marked with a circle in Figure 2D) are also found in these regions. The presence of such vacancies is somewhat surprising because the exposure to oxygen during the ceria growth procedure, even at an elevated temperature (950 K), would normally be sufficient to annihilate them [14]. There are clear similarities when comparing the features seen in Figure 2D to those observed in Figure 1 for a low coverage of ceria on titania. The surface in Figure 2D may be the prelude to the massive reconstruction that produces the ordered surfaces displayed in Figs. 2A and 2C. When the ceria coverage was increased from above 0.2 ML, this type of surface coexisted with titania terraces that had undergone reconstruction.

B. Morphology of $\text{Au/CeO}_x/\text{TiO}_2(110)$

Figure 3A depicts the large-scale morphology of the ceria/ $\text{TiO}_2(110)$ surface, demonstrating the equal areas of ordered ceria and ceria-decorated $\text{TiO}_2(110)$, prior to gold deposition. To prepare the model catalyst system, ~1% ML gold was deposited onto this area in-situ in the STM at room temperature. The result of this is shown in Figure 3B. Small bright gold clusters are observed to uniformly decorate the terraces of the ceria/ TiO_2 , with no preference for nucleation at the step edges of either the ordered or decorated regions. The gold adsorption behaviour on the ceria-decorated TiO_2 is consistent with that for reduced or fully-oxidised “clean” $\text{TiO}_2(110)$ surfaces and indicates a low concentration of hydroxyl groups whose presence would favour the formation of large clusters located at under-coordinated step edge sites [15]. In order to more fully examine the size distribution of the gold, magnified STM images are presented in Figure 4A. In this, we can see that the gold is not homogeneous in size on the ordered ceria but rather consists of many individual atomic-sized species (indicated by a circle in inset image in Figure 4A) with heights of ~0.2 nm,

and some larger clusters (example highlighted with a hexagon in inset image in Figure 4A) with heights up to a maximum of 0.45 nm. A histogram of the particle heights is presented in Figure 5 (blue bars). The smaller particle sizes are consistent with single atoms or clusters containing just a couple of atoms of gold [16], an exact measurement of their shape is complicated by convolution effects with the STM tip. The height distribution implies three-dimensional gold cluster morphology, as observed on ceria films with a $\text{CeO}_2(111)$ termination [17,18]. By assuming fcc type packing within these clusters, the largest (0.45 nm tall) can be considered to be 2 layers thick, and as such contain up to ~ 10 atoms. The gold atoms and clusters are relatively homogeneously distributed across the ordered ceria film with some nucleating within the domain boundaries and others in the middle of the domains. The morphology and location of the gold on the ceria-decorated $\text{TiO}_2(110)$ is more difficult to elucidate due to the presence of the CeO_x clusters and TiO_x reconstructed areas, although the taller clusters (>0.3 nm) can be clearly distinguished in Figure 4A.

The thermally-activated sintering of gold clusters and atoms on $\text{TiO}_2(110)$ is well established now under a variety of conditions and is shown to be dependent on a number of factors, including the sample preparation and especially the presence or lack thereof of O_{bvac} , OH_{b} and O_{ads} species [15,19,20,21,22]. In order to probe the temperature-stability of the gold atoms and clusters supported on our mixed ceria/titania system it was annealed to 500 K in UHV for 10 mins, the results of which are displayed in Figure 4B. (Note that the images displayed in Figure 4 are from slightly different areas of the sample due to the heating setup in our instrument.) Considering the ordered ceria phase first, by comparing the inset images in Figure 4A and 4B significant changes are observed. All of the small single atoms gold species are no longer present, and the clusters have increased in size (example highlighted with a square in the inset image in Figure 4B). This change in heights is clearly illustrated in the histogram in Figure 5 where the red bars correspond to the annealed surface. There are almost no clusters under 0.4 nm, and the tallest now approaches 1 nm (~ 4 atomic layers). The overall particle density for the larger clusters (>0.35 nm) has halved, going from 0.013 nm^{-2} to 0.06 nm^{-2} . After annealing, the large gold clusters are located primarily at the

vertices of the linear depressions caused by domain boundaries within the ordered ceria regions, although some are found at the step edges. The measurement of changes to the gold located on the $\text{TiO}_2(110)$ areas is again complicated by the presence of other similarly-sized features, but for particles >0.35 nm again there is significant sintering, with the density decreasing from 0.029 nm^{-2} to 0.010 nm^{-2} . These sintered particles are distributed evenly across the $\text{TiO}_2(110)$ terraces with no aggregation at the step edges, suggesting they are pinned either at the small CeO_x particles or the TiO_x reconstructed areas (see Figure 2D). No significant changes to the structure of the ordered ceria phase, or the $\text{TiO}_2(110)$ are observed after annealing to 500 K indicating the good thermal stability of the ceria layer.

In general our present (high ceria coverage) and previous results (low ceria coverage) [3,4] of STM for the $\text{Au/CeO}_x/\text{TiO}_2(110)$ systems show a strong interaction between the gold and the domain boundaries of the ceria overlayer. This was seen after depositing small (Figs 3-5) or large amounts of gold on the $\text{CeO}_x/\text{TiO}_2(110)$ substrate. The ceria nanostructures acted as nucleation sites for the growth of small or large particles of Au. Either at low [3] or high coverages of ceria (Figures 3 and 4), a gold-ceria interface was generated that can be useful as a catalyst for the water-gas shift reaction and other chemical transformations.

C. Catalytic activity of $\text{Au/CeO}_x/\text{TiO}_2(110)$ for the water-gas shift

We investigated the WGS reaction on $\text{Au/CeO}_x/\text{TiO}_2(110)$ model catalysts changing the amount of Au and ceria present in the catalyst. In previous works, we have studied the behaviour of these catalysts at low coverages (< 0.15 ML) of ceria when this oxide is present on the titania substrate in the form of nanowires (see Figure 1) and the ceria-titania interface has a limited size [3,10]. By working with $\text{CeO}_x/\text{TiO}_2(110)$ systems such as those depicted in Figures 3 and 4 one is enhancing the amount of exposed ceria to the reactants. The ceria in these systems is structurally and electronically perturbed with respect to bulk $\text{CeO}_2(111)$ and the ceria nanowires shown in Figure 1.

Neither Au(111) nor CeO_x/TiO₂(110) catalyse the WGS. However, Au nanoparticles dispersed on plain TiO₂(110) or CeO_x/TiO₂(110) are good catalysts. Figure 6 compares the catalytic activity of Au/TiO₂(110) and Au/CeO_x/TiO₂(110) catalysts in which the titania substrate was covered 12 or 55% by ceria (as measured by ion-scattering spectroscopy [3]). Maximum catalytic activity is observed for small or medium Au coverages (< 0.8 ML) on the oxide supports. STM indicates that at these coverages the average Au particle size is below 3 nm. As Au is added the catalytic activity reaches a maximum and then decreases. The position of the maximum for activity is around a gold coverage of 0.4 ML on TiO₂(110) and 0.6-0.8 ML on CeO_x/TiO₂(110). Since the number of nucleation sites for Au is bigger in the CeO_x/TiO₂(110) surfaces, the dispersion of Au in these systems is expected to be more efficient than on TiO₂(110) leading to smaller metal particles at high coverages on a mixed-oxide substrate.

Assuming that all the metal atoms deposited on TiO₂(110) and CeO_x/TiO₂(110) participate in the reaction, a common assumption in these type of studies [21], we estimated the turnover frequencies (TOFs) shown in Figure 7. These TOFs are much larger than the values found in previous studies for the WGS reaction on benchmark surfaces such as Cu(111) or Pt(111) [23,24], where the TOFs are always smaller than 1 molecule / metal site sec.

Two things are particularly interesting in Figures 6 and 7. First, both Au/CeO_x/TiO₂(110) surfaces exhibit a catalytic activity higher than that of Au/TiO₂(110) or Au/CeO₂(111) [25]. Thus, the generation of a ceria-titania interface always has a positive effect. Second, the catalytic activity significantly decreases when going from a titania surface covered 12% with ceria to a surface covered 55% with ceria. A comparison of the STM images in Figure 1 and 2 clearly shows the big differences in surface morphology when the ceria coverage increases. The small ceria nanowires in Figure 1 seem to be more active than the ceria overlayer in Figure 2. Using Ce 3d XPS spectra, one can quantify by deconvolution the amount of Ce³⁺ and Ce⁴⁺ species present on the Au/CeO_x/TiO₂(110) catalysts after reaction [3,26,27]. Each of these oxidation states of cerium has a distinctive Ce 3d XPS line-shape and can be separated by curve fitting [3,26,27]. Figure 8 displays

the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio measured after reaction for titania surfaces covered with 12% and 55% of ceria, both of them with 0.5 ML of Au. In the case of the $\text{Au}/12\%-\text{CeO}_x/\text{TiO}_2(110)$ catalyst, the vast majority of the Ce is in a 3+ oxidation state. On the other hand, for the $\text{Au}/55\%-\text{CeO}_x/\text{TiO}_2(110)$ catalyst, there is a substantial drop in the concentration of Ce^{3+} . This drop could explain the decrease in activity since the Ce^{3+} cations deposited on titania are highly efficient for the dissociation of water and the formation of OH groups [4], a key step in the WGS reaction [25,26]. In any case, one can conclude that a $\text{CeO}_x\text{-TiO}_2$ substrate is an excellent support for WGS catalysts with structural and catalytic properties not seen for pure TiO_2 or CeO_2 .

Conclusions

We have prepared a mixed ceria-titania oxide system by depositing a medium-size coverage of ceria on a $\text{TiO}_2(110)$ surface. STM images showed two types of domains. An ordered ceria film covered half of the surface and high-resolution imaging suggested a near- $c(6 \times 2)$ relationship to the underlying $\text{TiO}_2(110)-(1 \times 1)$. The other half of the surface comprised CeO_x nanoparticles and reconstructed TiO_x supported on $\text{TiO}_2(110)-(1 \times 1)$. Exposure to a small amount of gold resulted in the formation of isolated gold atoms and small cluster on the ordered ceria film and $\text{TiO}_2(110)-(1 \times 1)$ areas, which underwent significant sintering at 500 K and showed strong interaction between the sintered gold clusters and the domain boundaries of the ceria film.

The $\text{Au}/\text{CeO}_x/\text{TiO}_2(110)$ model system with medium-size coverage of ceria proved to be a good catalyst for the WGS exhibiting much higher activity than $\text{Cu}(111)$ and $\text{Pt}(111)$ benchmarks, or the individual $\text{Au}/\text{TiO}_2(110)$ and $\text{Au}/\text{CeO}_2(111)$ systems. For $\text{Au}/\text{CeO}_x/\text{TiO}_2(110)$ catalysts, there was a decrease in catalytic activity with increasing ceria coverage that correlates with a reduction in the concentration of Ce^{3+} formed during WGS reaction conditions.

Acknowledgements

The authors are grateful to S. Ma for his help in STM experiments examining the behavior of moderate coverages of ceria on titania. The research carried out in this manuscript was performed at Brookhaven National Laboratory, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, and Catalysis Science Program under contract No. DE-SC0012704. The work done at the Universidad Central de Venezuela was partially financed by INTEVEP and IBD.

Figures

Figure 1. Top: STM image of a $\text{TiO}_2(110)$ surface with a small coverage of ceria (~ 0.1 monolayer) of ceria. The image corresponds to an area of 20×20 nm and imaging conditions of $V_t = 1.5$ V and $I_t = 0.03$ nA. Bottom: Models for the growth configurations of CeO_x dimers on the titania surface (labelled as A, B, C and D). Taken from ref. [3], Copyright 2009 Proceedings of the National Academy of Science (PNAS).

Figure 2. STM images showing the morphology of 0.5 ML CeO_x on $\text{TiO}_2(110)$. **(A)** Large area image (150×150 nm², $V_s = +1.9$ V, $I_t = 0.04$ nA) showing the presence of two phases at the surface: (I) ordered ceria regions with linear depressions running through them, and (II) triangles of $\text{TiO}_2(110)$ -(1×1) decorated with small ceria particles. **(B)** Filled-states STM image (30×15 nm², $V_s = -2.6$ V, $I_t = 0.04$ nA) of the ordered ceria phase. **(C)** Empty-states STM image (30×15 nm², $V_s = +1.0$ V, $I_t = 0.02$ nA) of the ordered ceria phase. **(D)** Empty-states STM image (30×15 nm², $V_s = +1.74$ V, $I_t = 0.04$ nA) of the $\text{TiO}_2(110)$ between the ordered ceria phases. The circle and hexagon highlight examples of oxygen vacancies and CeO_x nanoparticles, respectively.

Figure 3. STM images (300×300 nm², $V_s = +2.7$ V, $I_t = 0.03$ nA) of 0.5 ML $\text{CeO}_x/\text{TiO}_2(110)$ before **(A)** and after **(B)** the evaporation of 1% ML gold *in situ* at 300 K.

Figure 4. **(A, B)** STM images (150×150 nm², inset: 20×20 nm², $V_s = +2.5$ V, $I_t = 0.03$ nA) demonstrating the sintering effects of annealing 1% ML Au supported on $\text{CeO}_x/\text{TiO}_2(110)$ at 500 K for 10 minutes in UHV.

Figure 5. Histogram of Au cluster heights for the experiment in Figure 4. Blue bars (as deposited Au) and red bars (after annealing the Au overlayer at 500 K for 10 minutes).

Figure 6. Water-gas shift activity of $\text{Au}/\text{TiO}_2(110)$ and two $\text{Au}/\text{CeO}_x/\text{TiO}_2(110)$ surfaces as a function of gold coverage. The area of titania covered by ceria was measured with ISS, before depositing gold, and found to be 12 and 55% of the clean substrate. The reported values for the production of H_2 (blue curve) and CO_2 (black curve) were obtained after exposing the catalysts to 20 Torr of CO and 10 Torr of H_2O at 625 K for 5 min. The number of H_2 and CO_2 molecules produced is normalized by the sample surface area. The data for $\text{Au}/\text{TiO}_2(110)$ and Au on 12%- $\text{CeO}_x/\text{TiO}_2(110)$ were taken from ref. [3].

Figure 7. Estimated TOFs for Au/TiO₂(110) and Au/CeO_x/TiO₂(110) catalysts as a function of Au coverage. Each surface was exposed to a mixture of 20 Torr of CO and 10 Torr of H₂O at 625 K.

Figure 8. Post-reaction Ce³⁺/Ce⁴⁺ ratio measured with XPS for Au/CeO_x/TiO₂(110) catalysts containing 0.5 ML of Au with 12% or 55% of the titania covered by ceria. Errors bars are indicated at the top of the grey bars. Ce³⁺ and Ce⁴⁺ have distinctive line-shapes in the Ce 3d region of XPS and can be separated by curve fitting [26,27].

References

1. M. Melchiona and P. Fornasiero, *Materials Today*, 17 (2014) 349
2. A. Trovarelli, *Catal. Rev. Sci. Eng.* 38 (1996) 439.
3. J.B. Park, J. Graciani, J. Evans, D. Stacchiola, S. Ma, P. Liu, A. Nambu, J. Fernandez-Sanz, J. Hrbek, and J.A. Rodriguez, *Proceedings of the National Academy of Science (PNAS)*, 106 (2009) 4975.
4. J.B. Park, J. Graciani, J. Evans, D. Stacchiola, S.D. Senanayake, L. Barrio, P. Liu, J.F. Sanz, J. Hrbek, and J.A. Rodriguez, *J. Am. Chem. Soc.*, 132 (2010) 356-363.
5. K.A. Michalow-Mauke, Y. Lu, K. Kowalski, T. Graule, M. Nachtegaal, O. Kröcher and D. Ferri, *ACS Catalysis*, 5 (2015) 5657.
6. S. Kundu, J. Ciston, S.D. Senanayake, D.A. Arena, E. Fujita, D. Stacchiola, L. Barrio, R.M. Navarro, J.L.G. Fierro, and J.A. Rodriguez, *J. Phys. Chem. C*, 116 (2012) 14062.
7. J. Strunk, W.C. Vining, and A.T. Bell, *ACS Catalysis*, 115 (2011) 4114.
8. J. Graciani, K. Mudiyanse, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz and J. A. Rodriguez, *Science*, 345 (2014) 546.
9. A.C. Johnston-Peck, S. D. Senanayake, J.J. Plata, S. Kundu, W. Xu, L. Barrio, J. Graciani, J. Fdez. Sanz, R.M. Navarro, J.L.G. Fierro, E. A. Stach, and J. A. Rodriguez, *J. Phys. Chem. C*, 117 (2013) 14463.
10. R. Si, J. Tao, J. Evans, J.B. Park, L. Barrio, J.C. Hanson, Y. Zhu, J. Hrbek and J.A. Rodriguez, *J. Phys. Chem. C*, 116 (2012) 23547.
11. S. Agnoli, A.E. Reeder, S.D. Senanayake, J. Hrbek, J.A. Rodriguez, *Nanoscale* 6 (2014) 800.
12. J.A. Rodriguez, D. Stacchiola, *Phys. Chem. Chem. Phys.* 12 (2010) 9557.

-
13. C.L. Pang, R. Lindsay, G. Thornton, *Chem. Rev.* 113 (2013) 3887.
 14. C.L. Pang, R. Lindsay, G. Thornton, *Chem. Soc. Rev.* 37 (2008) 2328
 15. D. Matthey, J.G. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Laegsgaard, B. Hammer, F. Besenbacher, *Science* 315 (2007) 1692.
 16. Y. Pan, Y. Cui, C. Stiehler, N. Nilius, H.-J. Freund, *J. Phys. Chem. C* 117 (2013) 21879.
 17. Y. Pan, N. Nilius, H.-J. Freund, J. Paier, C. Penschke, J. Sauer, *Phys. Rev. Lett.* 111 (2013) 206101.
 18. D.C. Grinter, C. Muryn, B. Santos, B.-J. Shaw, T.O. Menteş, A. Locatelli, G. Thornton, *J. Phys. Chem. C* 118 (2014) 19194.
 19. X. Tong, L. Benz, S. Chretien, H. Metiu, M.T. Bowers, S.K. Buratto, *J. Phys. Chem. C* 114 (2010) 3987.
 20. M. Chen, D.W. Goodman, *Science* 306 (2004) 252.
 21. M. Valden, X. Lai, D.W. Goodman, *Science* 281 (1998) 1647.
 22. E. Wahlstrom, N. Lopez, R. Schaub, P. Thostrup, A. Rønnau, C. Africh, E. Lægsgaard, J. K. Nørskov, and F. Besenbacher, *Phys. Rev. Lett.* 90 (2003) 026101.
 23. J. Nakamura, J.M. Campbell, and C.T. Campbell, *J. Chem. Soc. Faraday Trans.* 86 (1990) 2725.
 24. D.W. Flaherty, W.-Y. Yu, Z.D. Pozun, G. Henkelman, and C.B. Mullins, *J. Catal.* 282 (2011) 278.
 25. J.A. Rodriguez, P. Liu, J. Hrbek, J. Evans and M. Pérez, *Angew. Chem. Int. Ed.* 119 (2007) 1351.
 26. J.A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans and M. Pérez, *Science*, 318 (2007) 1757.
 27. A. Pfau and K.D. Schierbaum, *Surf. Sci.* 321 (1994) 71-80.

Figure(s)

Fig 1

Fig 2

Fig 3

500 K
↓
10 mins

Fig 4

Fig 5

Fig 6

Fig 7

Fig 8

Graphical abstract