High catalytic activity of Au/CeOₓ/TiO₂(110) controlled by the nature of the mixed-metal oxide at the nanometer level

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Mixed-metal oxides play a very important role in many areas of chemistry, physics, materials science, and geochemistry. Recently, there has been a strong interest in understanding phenomena associated with the deposition of oxide nanoparticles on the surface of a second (host) oxide. Here, scanning tunneling microscopy, photoemission, and density-functional calculations are used to study the behavior of ceria nanoparticles deposited on a TiO₂(110) surface. The titania substrate imposes nontypical coordination modes on the ceria nanoparticles. In the CeOₓ/TiO₂(110) systems, the Ce cations adopt an structural geometry and an oxidation state (+3) that are quite different from those seen in bulk ceria or for ceria nanoparticles deposited on metal substrates. The increase in the stability of the Ce³⁺ oxidation state leads to an enhancement in the chemical and catalytic activity of the ceria nanoparticles. The codeposition of ceria and gold nanoparticles on a TiO₂(110) substrate generates catalysts with an extremely high activity for the production of hydrogen through the water–gas shift reaction (H₂O + CO → H₂ + CO₂) or for the oxidation of carbon monoxide (2CO + O₂ → 2CO₂). The enhanced stability of the Ce³⁺ state is an example of structural promotion in catalysis described here on the atomic level. The exploration of mixed-metal oxides at the nanometer level may open avenues for optimizing catalysts through stabilization of unconventional surface structures with special chemical activity.

Experimental and Theoretical Methods

Microscopy, Photoemission, and Catalytic Tests. The microscopy studies were carried out in an Omicron variable temperature STM system that is directly attached to a main ultrahigh vacuum (UHV) chamber equipped with optics for low-energy electron diffraction, instrumentation for Auger electron spectroscopy and surface cleaning facilities (9, 14). Chemically etched W tips were used for imaging the surfaces. The TiO₂(110) crystal was cleaned by several cycles of Ne⁺ sputtering (1 keV, 40 min) and annealing (950 K, 5 min), and XPS/AES studies confirmed that there were no surface contaminants after this treatment (15).

Further, the high-resolution STM images of the surface exhibited bright Ti rows separated by 6.5 Å, as typically observed for TiO₂(110)-(1x1) (16). Photoemission studies were performed at beamline U7A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (9) by using a photon energy of 625 eV to collect the O 1s and Ti 2p regions, and 325 eV to collect the Ce 4d, Au 4f, and valence regions. In a separate UHV chamber, we acquired XPS spectra (Ce 3d, Ti 2p, O 1s, and Au 4f regions) and UPS spectra (valence region) using Mg Kα and He-I radiation, respectively. Ce and Au were deposited on TiO₂(110) by using metal evaporators (9, 14, 17). The flux of the Au doser was calibrated by depositing Au onto a Mo(100) crystal and measuring the thermal desorption spectra of the admetal (17). The area of the titania surface covered by ceria different crystal lattices in their most stable bulk phases, fluorite and rutile, respectively (2, 13). Within the fluorite structure each Ce atom is bonded to 8 O atoms, whereas 6 O atoms surround the Ti atoms in the rutile structure. One of the most interesting properties of ceria is its ability to undergo a conversion between ‘‘+4’’ and ‘‘+3’’ formal oxidation states (13). The surface chemistry and catalytic properties of CeO₂ depend on the formation of Ce³⁺ ions (13), and different approaches are followed to maximize their concentration (4, 5, 8). In the CeOₓ/TiO₂(110) systems, the titania substrate imposes on the ceria NPs nontypical coordination modes with a subsequent change in the relative stability of the Ce³⁺/Ce⁴⁺ oxidation states that leads to a significant enhancement in chemical activity. Furthermore, the deposition of gold NPs on CeOₓ/TiO₂(110) produces surfaces with an extremely high catalytic activity for the water–gas shift reaction and the oxidation of CO. This is quite remarkable because neither Au/TiO₂(110) nor Au/CeO₂(111) come close to matching the catalytic activity of Au/CeO₂/TiO₂(110).

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and gold was estimated by using STM images or a combination of ion-scattering spectroscopy (ISS) and photoemission (9, 17).

The catalytic studies were carried out in a system that combines a batch reactor and a UHV chamber (9, 17). The sample could be transferred between the reactor and UHV chamber without exposure to air. Typically, it was transferred to the batch reactor at ~298 K, and then the reactant gases were introduced (water−gas shift: 20 Torr of CO and 10 Torr of H2O; CO oxidation: 4 torr of CO and 2 Torr of O2). The catalytic activity for the water−gas shift was measured at 625 K (9, 17), with a bright spot having an average height of 1.4 ± 0.2 Å over the flat terrace and correspond to clusters of cerium oxide. The corresponding XPS and UPS spectra indicated that cerium was in an oxidation state of +3, and, consequently, its deposition led to the partial reduction of titanium cations with the appearance of Ti3+. Fig. 2 Left shows a typical UPS spectrum for this type of Ce/TiO2(110) surface. The features ~1 eV can be assigned to Ti3+ centers (1, 16), whereas those at ~2−3 eV correspond to Ce3+ centers (21). The existence of Ce3+ is corroborated by the Ce 3d XPS data in Fig. 2 Right. The Ce 3d XPS spectrum for the as-prepared Ce/TiO2(110) surface has the distinctive line shape of Ce3+ species (21, 22). Using DFT calculations, we investigated the bonding of Ce atoms to the TiO2(110) surface. The Ce atoms prefer the bonding configuration shown at the bottom of Fig. 2, interacting simultaneously with bridging and in-plane O atoms of the titania substrate. Upon adsorption, Ce formally releases 3 electrons to the oxide host, which move from the 6s and 5d levels in Ce to the lower-energy 3d levels in Ti, reducing 3 Ti4+ cations to Ti3+. The fourth valence electron from Ce is in a 4f level of lower energy than the 3d from Ti and therefore is not transferred, leaving the oxidation state of Ce as 3+. The adsorption of oxygen on the Ce/TiO2(110) surfaces led to the disappearance of Ti3+ sites in the XPS/UPS spectra and in the DFT-calculated density of states. The stability of the Ce3+ cations was verified by their resistance to oxidation under UHV conditions, as we had to expose the Ce/TiO2(110) surfaces to an O2 pressure of 1 Torr in the batch reactor to obtain the typical Ce 3d XPS spectrum of Ce4+ cations (21, 22), see Fig. 2 Right.

To avoid the reduction of the titania substrate, Ce atoms were deposited at 600 K and annealed to 900 K under O2 (~1 × 10−7 Torr) for 5 min. This led to the image shown in Fig. 1B. In this image, the features unrelated to the ideal TiO2(110) surface can be separated according to their height, as seen in Fig. 1C. Most of the spots (~80%) have a height of 1.3 ± 0.2 Å. These spots

Fig. 1. STM results illustrating morphological changes of CeOx on the TiO2(110) surface. (A) STM image (15 × 15 nm) taken after depositing Ce atoms at 298 K in UHV (V = 1.3 V and i = 0.05 nA). (B) STM image (15 × 15 nm) acquired after depositing Ce atoms at 600 K and subsequent annealing at 900 K in O2 (PO2 = 1 × 10−7 Torr) (~1.2 V and i = 0.07 nA). (C) Height distribution for the spots seen in B, D and E zoomed-in STM images (3.5 × 3.5 nm) of a diagonal array of CeOx, taken at different imaging condition of 1.2 V, 0.06 nA and 0.4 V, 0.06 nA, respectively. (F) Model showing possible orientations for the bright protrusions of CeOx in D and E. The dimers of ceria are shown as a combination of white and yellow spheres.

Growth of Ceria on TiO2(110)

In Fig. 1, we show STM images acquired after depositing cerium on TiO2(110) under different conditions. Fig. 1A corresponds to an image obtained after dosing Ce atoms under ultrahigh vacuum (UHV) at a sample temperature of 298 K. The bright spots have an average height of 1.4 ± 0.2 Å over the flat terrace and correspond to clusters of cerium oxide. The corresponding XPS and UPS spectra indicated that cerium was in an oxidation state of +3, and, consequently, its deposition led to the partial reduction of titanium cations with the appearance of Ti3+. Fig. 2 Left shows a typical UPS spectrum for this type of Ce/TiO2(110) surface. The features ~1 eV can be assigned to Ti3+ centers (1, 16), whereas those at ~4−5 eV correspond to Ce3+ centers (21). The existence of Ce3+ is corroborated by the Ce 3d XPS data in Fig. 2 Right. The Ce 3d XPS spectrum for the as-prepared Ce/TiO2(110) surface has the distinctive line shape of Ce3+ species (21, 22). Using DFT calculations, we investigated the bonding of Ce atoms to the TiO2(110) surface. The Ce atoms prefer the bonding configuration shown at the bottom of Fig. 2, interacting simultaneously with bridging and in-plane O atoms of the titania substrate. Upon adsorption, Ce formally releases 3 electrons to the oxide host, which move from the 6s and 5d levels in Ce to the lower-energy 3d levels in Ti, reducing 3 Ti4+ cations to Ti3+. The fourth valence electron from Ce is in a 4f level of lower energy than the 3d from Ti and therefore is not transferred, leaving the oxidation state of Ce as 3+. The adsorption of oxygen on the Ce/TiO2(110) surfaces led to the disappearance of Ti3+ sites in the XPS/UPS spectra and in the DFT-calculated density of states. The stability of the Ce3+ cations was verified by their resistance to oxidation under UHV conditions. We had to expose the Ce/TiO2(110) surfaces to an O2 pressure of 1 Torr in the batch reactor to obtain the typical Ce 3d XPS spectrum of Ce4+ cations (21, 22), see Fig. 2 Right.

To avoid the reduction of the titania substrate, Ce atoms were deposited at 600 K and annealed to 900 K under O2 (~1 × 10−7 Torr) for 5 min. This led to the image shown in Fig. 1B. In this image, the features unrelated to the ideal TiO2(110) surface can be separated according to their height, as seen in Fig. 1C. Most of the spots (~80%) have a height of 1.3 ± 0.2 Å. These spots
can be attributed to CeO$_x$ after comparing with the image in Fig. 1A for Ce/TiO$_2$(110). A minority of the spots (≈20%) in Fig. 1B have a height of 1.9 ± 0.3 Å. These features were not seen for Ce/TiO$_2$(110) and probably correspond to (1 × 2) reconstructions of TiO$_2$(110) induced by O$_2$ chemisorption (11, 16). They are a consequence of the migration of interstitial Ti atoms from the bulk to the surface of the titania crystal (11, 16). We found them also in blank experiments for O$_2$/TiO$_2$(110). In Fig. 1B, the spots due to CeO$_x$ are arranged forming units that are oriented ≈48°, 66°, or 90° with respect to the Ti rows of the oxide substrate. These units were not seen in blank experiments for Ce/TiO$_2$(110) or O$_2$/TiO$_2$(110) and are characteristic of the O$_2$/CeO$_x$/TiO$_2$(110) systems. Close-up images of a ≈44° aligned unit are shown in Fig. 1D and E. In Fig. 1D, the bright ceria spots are centered on 5f Ti rows and all have a height close to 1.35 Å and a diameter of 6.8 Å. Their size and position suggests that each spot may contain 2 Ce atoms located in between the O bridging and 5f Ti rows. This is confirmed by scanning the same feature with lower imaging bias (0.4 V instead of 1.2 V), where the electron tunneling occurs at different density of states in CeO$_x$/TiO$_2$(110) systems (Fig. 1E). From the STM data, one can construct a structural model consisting of an array of dimers of ceria as displayed in Fig. 1F. According to our measurements of core and valence photoemission, the oxidation state of the Ce atoms inside the dimers is essentially +3. Thus, in the CeO$_x$/TiO$_2$(110) systems, the Ce cations adopt a structural geometry and an oxidation state that are quite different from those seen in bulk ceria (2, 13) or for NPs of ceria deposited on metal substrates (7, 9).

Using DFT, we investigated the process of adsorption–oxidation for Ce deposited on TiO$_2$(110). Fig. 3 shows the calculated energy pathway for such a process. The adsorption energy of atomic Ce is very high (ΔE = −7.23 eV). On its most stable adsorption site, Ce interacts with 2 bridging and 1 in-plane O atoms (Fig. 3, step 1). The fact that 3 electrons move from high to lower energy levels, Ce(5d$^1$6s$^2$) → Ti(3d$^1$), explains in part the high adsorption energy of Ce. The adsorption process of atomic Ce could be described as

\[ \text{Ce} + 3\text{Ti}^{4+}(\text{TiO}_2) \rightarrow \text{Ce}^{3+} + 3\text{Ti}^{3+}(\text{TiO}_2) \quad \text{[1]} \]

The dissociation of O$_2$ near the adsorbed Ce is a highly exothermic process (ΔE = −6.66 eV). The final structure is a unit of CeO$_2$ over TiO$_2$(110), where the O atoms are adsorbed on top of in-plane Ti atoms and strongly interact with the Ce atom (Fig. 3, step 2). The oxidation state of the Ce in this configuration is 4+

\[ \text{Ce}^{3+} + 3\text{Ti}^{3+}(\text{TiO}_2) + \text{O}_2 \rightarrow \text{CeO}_2(\text{Ce}^{4+})/\text{TiO}_2 \quad \text{[2]} \]

Such CeO$_2$ monomers could be assigned to the smallest spots observed in STM at very low coverages of ceria. For the surface in Fig. 1B, possible CeO$_2$ monomers are denoted by arrows and, as predicted by the DFT calculations, they are not located at the center of the Ti rows. The CeO$_2$ monomers are excellent sites for...
the adsorption of a second Ce atom to form dimers (Fig. 3, step 4). The increment in the adsorption energy with respect to the adsorption on a clean surface is due to the fact that 1 of the 3 electrons released by the incoming Ce does not go to the high-energy 3d levels of Ti but rather to the 4f of Ce$^{4+}$ from the CeO$_2$ monomer, which is reduced to Ce$^{3+}$

$$\text{CeO}_2(\text{Ce}^{4+})/\text{TiO}_2 + \text{Ce}$$

$$+ 2\text{Ti}^{4+}(\text{TiO}_2) \rightarrow \text{Ce}_2\text{O}_2(\text{Ce}^{3+}) \text{ on TiO}_2 + 2\text{Ti}^{3+}(\text{TiO}_2)$$

$$[3]$$

The addition of oxygen to the Ce$_2$O$_2$ unit generates Ce$_2$O$_3$.

$$\text{Ce}_2\text{O}_2(\text{Ce}^{3+})/\text{TiO}_2 + 2\text{Ti}^{3+}(\text{TiO}_2) + \frac{1}{2} \text{O}_2 \rightarrow \text{Ce}_2\text{O}_3(\text{Ce}^{3+})$$

$$[4]$$

on TiO$_2$, and the ceria dimer adopts a configuration (Fig. 3, step 5) where shared oxygen leads to a diagonal arrangement in agreement with the results of STM (Fig. 1 E and F). In the presence of oxygen, the complete oxidation of Ce has to be considered, going from a Ce$_2$O$_3$ dimer to 2 CeO$_2$ monomers (Fig. 3, step 6). Differently from the previous step, here, there are not high-energy Ti 3d electrons but 2 electrons in low-energy Ce 4f states. The process is exothermic but only by $-0.92$ eV, 3 times less than the energy released in the previous step. This means that as long as Ti$^{3+}$ species exist, O$_2$ will prefer to adsorb and dissociate on them because the stabilization energy for the system is much higher. Therefore, even though the oxidation process of dimers is favorable, the other site is preferred for the adsorption and dissociation of O$_2$. This illustrates the complex interplay that one can have when dealing with the electronic and chemical properties of a mixed-metal oxide.

For applications in catalysis, the relative stability of the Ce$^{3+}$/Ce$^{4+}$ oxidation states of ceria is a very important issue (1, 4–6, 13, 23, 24). We calculated the energy released by the reactions

$$\text{CeO}_2 + \frac{1}{2} \text{O}_2 \rightarrow 2\text{CeO}_2$$

$$[5]$$

$$2\text{CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2$$

$$[6]$$

for both bulk ceria and CeO$_2$ dimers deposited on TiO$_2$(110). The $\Delta E$ for the oxidation process, (the reaction shown in 5), was $-2.56$ eV in the case of bulk CeO$_2$ and $-0.92$ eV for the CeO$_2$ dimers bonded to titania. The reduction of CeO$_2$/TiO$_2$(110) by CO$_2$ (the reaction shown in 6), was a very exothermic process with a $\Delta E$ of $-2.35$ eV. In contrast, the $\Delta E$ for the corresponding reaction of bulk CeO$_2$ was $-0.71$ eV. These trends were confirmed by comparing reduction/oxidation experiments on CeO$_2$(111) and CeO$_2$/TiO$_2$(110). For example, a CeO$_2$(111) surface did not undergo reduction under an atmosphere of 20 Torr of CO at 400 K (17), but a CeO$_2$/TiO$_2$(110) surface (formed by exposing CeO$_2$/TiO$_2$(110) to 1 Torr of O$_2$ at 298 K) was completely transformed into CeO$_2$/TiO$_2$(110). The high stability of the Ce$^{3+}$ cations in CeO$_2$/TiO$_2$(110) is a consequence of their nontypical coordination mode and the effect of Ce (4f)–O (2p)–Ti (3d) bonding interactions.

**Catalytic Activity of Au/CeO$_2$/TiO$_2$(110)**

The WGS reaction is a critical catalytic process for the production of clean hydrogen in the chemical industry (4, 5). There is a continuous search for catalysts with a better WGS activity (4–6, 9). As shown below, the deposition of gold NPs on CeO$_2$/TiO$_2$(110) yielded surfaces with an extremely high catalytic activity for the WGS. Fig. 4 displays STM images acquired from the same surface area before (Fig. 4A) and after (Fig. 4B) depositing gold on CeO$_2$/TiO$_2$(110) at 298 K with subsequent annealing to 600 K (Fig. 4C). The CeO$_2$/TiO$_2$(110) was preannealed under O$_2$ ($=1 \times 10^{-7}$ Torr) at 900 K and had a morphology similar to that seen in Fig. 1B. The deposition of Au at room temperature, $0.2$ monolayer, produced 3-dimensional metal particles anchored to steps of the titania surface, “a” sites, to the (1 $\times$ 2) reconstructions of TiO$_2$(110), “b” sites, and to the CeO$_2$ dimers, “c” sites. Annealing to 600 K produced large particles of Au that were simultaneously located on b and c sites. Au NPs with a diameter as large as 5.9 nm and a height of 1.3 nm were seen, but smaller metal particles were also present on the CeO$_2$/TiO$_2$(110) surface. On this surface, the dispersion of the Au NPs was substantially larger than seen on a pure TiO$_2$(110) surface where Au mainly binds to the steps (10, 15).

Neither CeO$_2$/TiO$_2$(110) nor Au(111) were able to catalyze the WGS. However, Au/CeO$_2$/TiO$_2$(110) surfaces are outstanding catalysts for the WGS as shown in Fig. 5. We performed test experiments in which Au/TiO$_2$(110) surfaces were prepared following the same steps used for the synthesis of Au/CeO$_2$/TiO$_2$(110) but without the deposition of cerium. The Au/TiO$_2$(110) systems were good WGS catalysts, see Fig. 5 Upper, but they did not come close to match the activity of Au/CeO$_2$/TiO$_2$(110). The same is valid when comparing with the WGS activities of Au/CeO$_2$(111) (17), CeO$_2$/Au(111) (9), Cu/ZnO(0001) (17), and copper single crystals (17, 25). Cu/ZnO is the most common WGS catalyst used in the industry (5, 17, 25), and copper is the best pure-metal catalyst (25, 26). For the Au/CeO$_2$/TiO$_2$(110) catalyst in Fig. 5, one could assume that the concentration of active sites is proportional to the number of ceria regions in contact with gold NPs. Because only 12% of the titania support was covered by ceria, as measured by XPS, and the ceria coverage must be at least 300 times more active than a Cu(100) surface on a per-active-site basis. *

Postreaction characterization of the Au/CeO$_2$/TiO$_2$(110) surfaces with XPS showed the presence of metallic Au and Ce$^{3+}$ cations. An identical result was found in situ measurements of X-ray absorption spectroscopy for Au/CeO$_2$/TiO$_2$ powders under

*It is usually assumed that all atoms of a flat Cu(100) surface, 1.53 $\times 10^{15}$ atoms cm$^{-2}$, are active in the WGS reaction (25). The structural model in Fig. 1F was used to calculate the area occupied by a Ce$_2$O$_3$ dimer on the TiO$_2$(110) surface. Using this and the ceria coverage determined from XPS measurements (~12% of the titania surface was covered), we find that the concentration of Ce in the Au/CeO$_2$/TiO$_2$(110) catalyst of Fig. 5 was in the order of 0.03 $\times 10^{15}$ atoms cm$^{-2}$. This is an upper limit to the actual concentration of the active sites, because not all of the Ce atoms had a Au particle nearby (see Fig. 4 B and C). After subtracting the WGS activity of Au/TiO$_2$(110) from that of Au/CeO$_2$/TiO$_2$(110), one finds that the Au/ceria sites are at least 300 times more active than the atoms in a Cu(100) surface.
WGS reaction conditions. The high catalytic activity of Au/CeO₂/TiO₂(110) can be attributed to the special chemical properties of the supported CeO₂ dimers and cooperative effects at ceria–gold interfaces. Usually, the rate-determining step in the WGS reaction is the dissociation of water (9, 17, 26). Isolated NPs of gold cannot dissociate this molecule (27, 28). We found that the Ce³⁺ sites present in CeO₂/TiO₂(110) easily dissociate water, but, upon exposure to CO, highly stable HCOₓ species were formed on the oxide surface and there was no production of H₂ or CO₂ gas. In Au/CeO₂/TiO₂(110), one has a bifunctional catalyst: The adsorption and dissociation of water takes place on the oxide, CO adsorbs on gold NP sites, and all subsequent reaction steps occur at oxide–metal interfaces. Au NPs do catalyze the reaction of OH with CO to yield a HOCO intermediate and then H₂ and CO₂ (27). Previous studies for the WGS on Au–CeO₂ catalysts point to a direct participation of the oxide in the reaction process (4, 5, 9). Our results illustrate the tremendous impact that an optimization of the chemical properties of nanoceria can have on the activity of a WGS catalyst.

Nowadays, the oxidation of CO on Au/TiO₂ catalysts is receiving a lot of attention (1, 10, 29, 30). Fig. 6 displays the CO oxidation activity of Au/TiO₂(110) and Au/CeO₂/TiO₂(110) as a function of Au coverage. The area of TiO₂(110) covered by CeO₂ was measured with ISS, before depositing gold, and found to be ~16% of the clean substrate. The reported values for the production of CO₂ were obtained after exposing the catalysts to 4 Torr of CO and 2 Torr of O₂ at 300 K for 5 min. The number of CO₂ molecules produced is normalized by the sample surface area.

Fig. 6. CO oxidation activity of Au/TiO₂(110) and Au/CeO₂/TiO₂(110) as a function of Au coverage. The area of TiO₂(110) covered by CeO₂ was measured with ISS, before depositing gold, and found to be ~16% of the clean substrate. The reported values for the production of CO₂ were obtained after exposing the catalysts to 4 Torr of CO and 2 Torr of O₂ at 300 K for 5 min. The number of CO₂ molecules produced is normalized by the sample surface area.
Our results illustrate the high impact that an optimization of the chemical properties of nanoceria can have on the activity of a WGS or CO oxidation catalyst. This approach should be valid in general for catalysts that contain ceria as part of a mixed-metal oxide (4–7), opening new directions for tuning catalytic activity by coupling appropriate pairs of oxides. The key issue is to take advantage of the complex interactions that occur in a mixed-metal oxide at the nanometer level.


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