Formation and Thermal Stability of \( \text{Au}_2\text{O}_3 \) on Gold Nanoparticles: Size and Support Effects

Luis K. Ono and Beatriz Roldan Cuenya*

Department of Physics, University of Central Florida, Orlando, Florida 32816

Received: November 28, 2007; In Final Form: January 9, 2008

Gold nanoparticles with two different size distributions (average sizes of \( \sim 1.5 \) and \( \sim 5 \) nm) have been synthesized by inverse micelle encapsulation and deposited on reducible (\( \text{TiO}_2 \)) and nonreducible (\( \text{SiO}_2 \)) supports. The thermal and chemical stability of oxidized gold species formed upon cluster exposure to atomic oxygen have been investigated in ultrahigh vacuum using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy (XPS), as well as temperature-programmed desorption (TPD).

Our work demonstrates that (a) low-temperature (150 K) exposure to atomic oxygen leads to the formation of surface as well as subsurface gold oxide on Au nanoparticles, (b) the presence of the reducible TiO\(_2\) substrate leads to a lower gold oxide stability compared to that on SiO\(_2\), possibly because of a TiO\(_2\) oxygen vacancy-mediated decomposition process, (c) heating to 550 K (Au/SiO\(_2\)) and 300 K (Au/TiO\(_2\)) leads to a near-complete reduction of small (\( \sim 1.5 \) nm) NPs while a partial reduction is observed for larger clusters (\( \sim 5 \) nm), and (d) the desorption temperature of O\(_2\) from preoxidized Au clusters deposited on SiO\(_2\) depends on the cluster size, with smaller clusters showing stronger O\(_2\) binding.

Introduction

Bulk gold is known as one of the most inert metals in the periodic table.\(^1\) This trait is attributed to the lack of interaction between the orbitals of adsorbates and the filled \( d \) states of gold.\(^2,3\) The high value of the enthalpy of oxygen chemisorption by gold to form its oxide \( \text{Au}_2\text{O}_3 \) (\( \Delta H = +19.3 \text{ kJ/mol} \)) also indicates its chemical inertness.\(^4\) However, pioneering work by Haruta et al. has demonstrated that highly dispersed Au nanoparticles (NPs) (<10 nm) supported on TiO\(_2\) are considerably active for the low-temperature oxidation of CO\(^5\) and C\(_2\)H\(_6\) epoxidation.\(^6\) Since then, the topic of gold in catalysis has received significant attention. Despite the large number of reports currently available, the microscopic origin of gold’s heterogeneous catalytic activity is still poorly understood, and lack of consensus prevails with respect to the nature of the active sites,\(^7–9\) the chemical state of the active gold species (metallic vs ionic gold),\(^10–12\) as well as the relative importance of the different oxygen species (chemisorbed oxygen, surface oxide, subsurface oxygen) that might be present on these catalysts under realistic reaction conditions.\(^13,14\)

Several authors attribute the enhanced chemical reactivity of gold NPs to the presence of ionic gold; however, whether anionic or cationic (\( \text{Au}^{5−}, \text{Au}^{6+} \)) gold species are preferable is still a matter of debate.\(^11,12,14–17\) The presence of cationic interfacial gold species has been inferred on catalytically active systems such as Au deposited on reduced TiO\(_2\).\(^18\) This is contrary to the traditional picture involving electron transfer from oxide supports to Au NPs. Positively charged atoms at the metal−support interface have been observed, and their presence has been correlated to the enhanced catalytic activity of the system.\(^19,20\) The active role of these cationic gold species on the water−gas shift reaction (WGS) has been demonstrated recently by Fu et al.\(^21\) In that work, similar activities for the WGS reaction were obtained on gold NPs supported on La-doped CeO\(_2\) before and after the removal of the metallic gold species.\(^21\) This result suggested a strong interaction of ionic gold with the ceria support, and the authors claimed that the presence of metallic NPs was not necessary for this catalytic reaction.\(^22\)

On the theoretical side, several density functional theory (DFT) works have investigated the strength of the binding of CO,\(^23,24\) O\(_2\),\(^25,26\) propene,\(^27\) and methanol\(^28\) to nonmetallic Au clusters. Here, a common trend was found, with reactant molecules showing stronger binding energy to anionic and cationic gold species, as compared to metallic gold. Recent hybrid DFT calculations carried out by Okumura et al.\(^8\) suggested that although O\(_2\) activation occurs on anionic Au cationic Au atoms show stronger bonding to CO. The authors proposed a model of dynamic charge polarization in which a strong heterojunction between Au clusters and their support is indispensable for the activation of oxygen species. The presence of negatively charged atoms in the perimeter region of Au NPs was attributed to localized Coulomb blockade effects. Furthermore, this surface negative charge was found to increase with decreasing cluster size,\(^29\) in agreement with the known enhanced catalytic activity observed for small Au clusters.

Several experimental studies have been dedicated to the electronic and chemical characterization of oxidized gold species on Au single crystals,\(^30–32\) polycrystalline films,\(^33,34\) and the surface of Au NPs.\(^35,36\) The instability of \( \text{Au}_2\text{O}_3 \) formed upon exposing a gold film (100 nm) to O\(_2\) plasma has been reported by Tsai et al.\(^37\) In this work, an activation energy of 57 kJ/mol was extracted for the decomposition of gold oxide from the correlation of electrical resistance measurements, conducted in air at room temperature (RT), and X-ray photoelectron spectroscopy (XPS) investigations after several time intervals. A nonmonotonic interaction of size-selected gold clusters with atomic oxygen was found by Boyen et al.\(^38\) More specifically, 1.4 nm clusters (55 atoms, closed-shell electronic structure) were found to be resistant to oxidation. However, when larger (> 1.6
TABLE 1: Summary of the Parameters Tuned and Average Height and Diameter of Au Nanoparticles Deposited on SiO₂ and TiO₂

<table>
<thead>
<tr>
<th>sample</th>
<th>substrate</th>
<th>PS/P2VP molecular weight (g/mol)</th>
<th>HAuCl₄/P2VP ratio</th>
<th>height (nm)</th>
<th>diameter (nm)</th>
<th>interparticle distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. 1</td>
<td>SiO₂</td>
<td>53 000/43 800</td>
<td>0.4</td>
<td>4.9 ± 1.6</td>
<td>16 ± 3</td>
<td>50 ± 6</td>
</tr>
<tr>
<td>no. 2</td>
<td>TiO₂</td>
<td>53 000/43 800</td>
<td>0.4</td>
<td>5.4 ± 1.2</td>
<td>19 ± 5</td>
<td>51 ± 18</td>
</tr>
<tr>
<td>no. 3</td>
<td>SiO₂</td>
<td>820/3800</td>
<td>0.05</td>
<td>1.7 ± 0.8</td>
<td>12 ± 4</td>
<td>24 ± 4</td>
</tr>
<tr>
<td>no. 4</td>
<td>TiO₂</td>
<td>820/8300</td>
<td>0.05</td>
<td>1.4 ± 0.5</td>
<td>10 ± 4</td>
<td>59 ± 40</td>
</tr>
</tbody>
</table>

nm and smaller clusters (<1.3 nm) were exposed to an identical treatment, Au(core)/Au₂O₃(shell) structures with oxide shell thicknesses on the order of 0.7 nm were obtained.

Recently, a number of experimental studies discussing the chemical reactivity of gold surfaces precoated with atomic oxygen have been published. Min et al. reported the existence of three types of oxygen species on Au(111): (i) chemisorbed oxygen (oxygen bound to gold that is not part of an ordered phase), (ii) oxygen in surface oxide (well-ordered two-dimensional phase), and (iii) subsurface oxygen or bulk oxide (three-dimensional phase). On the basis of CO oxidation studies, the authors found the following relation among the reactivity of the different oxygen species: chemisorbed oxygen > oxygen in surface oxide > oxygen in bulk gold oxide. The role played by these species in the thermodynamics and kinetics of oxidation/reduction reactions is a major challenge for the microscopic understanding of gold catalysis. This understanding becomes highly challenging when small NPs are considered because of the added complexity of the presence of different facets, kinks, and steps and substantial interactions with the support. As an example, on ~6 nm Au NPs deposited on highly ordered pyrolytic graphite (HOPG), Lim et al. observed by XPS the formation of a single oxygen species upon exposure to atomic oxygen under ultrahigh-vacuum (UHV) conditions. This species was ascribed to chemisorbed oxygen because it was found to readily react with CO producing CO₂. Interestingly, two different oxygen species were identified on similarly treated but smaller gold NPs (~3 nm). In this case, one of the oxygen species was assigned to chemisorbed oxygen, which decomposes rapidly upon CO exposure, and the other to subsurface oxygen, inert toward reaction with CO.

Our work intends to address the following questions: (1) under which conditions is gold oxide stable on a gold nanomaterial, (2) how are the chemical kinetics of gold oxide decomposition affected by the size of the particles and the nature of their metal oxide support, and (3) is more than one gold oxide species (surface and subsurface) stable on NPs? In order to gain insight into these topics, we have used micelle encapsulation methods to synthesize size- and shape-selected gold nano-clusters supported on thin SiO₂ and TiO₂ films. Morphological characterization was conducted by atomic force microscopy (AFM), and the decomposition of oxidized gold species, formed upon in situ O₂ plasma exposure, was investigated in UHV by XPS. Temperature-programmed desorption (TPD) measurements provided information on the reaction order and activation energy for molecular oxygen desorption from Au₂O₃(shell)/Au(core) NPs supported on SiO₂. Finally, CO exposure experiments were conducted to distinguish surface oxides from subsurface oxides.

Experimental Section

Size-selected Au nanoparticles were synthesized by inverse micelle encapsulation on polystyrene-block-poly(2-vinylpyridine) diblock copolymers [PS(53000)/P2VP(43800)]. When the PS-P2VP polymers are dissolved in toluene, inverse micelles are formed with the polar units (P2VP) constituting the core and the nonpolar polystyrene (PS) tails extending outward. Subsequently, chloroauric acid (HAuCl₄·3H₂O) is added to the polymeric solution and AuCl₄⁻ compounds attach to the pyridine groups in the P2VP core. The micelles containing Au NPs are deposited onto different substrates by dip-coating at a speed of 1 μm/min. The NP size can be tuned by changing the molecular weight of the polymer (P2VP) as well as the metal salt/P2VP concentration ratio. The length of the polymer tail (PS) determines the interparticle distance. In this study, the following two polymers have been used: PS(53000)/P2VP(43800) and PS(8200)/P2VP(8300).

Naturally oxidized Si(111) wafers and ultrathin Ti films (15 nm) electron-beam deposited on Si(111) have been used as NP supports. Further details on this preparation method can be found in refs 43–48. A summary of the synthesis parameters used is given in Table 1.

The characterization of the sample morphology was performed ex situ by AFM in tapping-mode (Digital Instruments, Multimode). The ex situ prepared samples were mounted on a molybdenum sample holder with a K-type thermocouple located directly underneath the sample and transferred into a modular UHV system (SPECS GmbH) for polymer removal and electronic/chemical characterization. The system is equipped with an hemispherical electron energy analyzer (Phoibos 100, SPECS GmbH) and a dual-anode (Al Kα, 1486.6 eV and Ag Kα, 2984.4 eV) monochromatic X-ray source (XR50M, SPECS GmbH) for XPS, and a differentially pumped quadrupole mass spectrometer (QMS, Hiden Analytical, HAL 301/3F) with an electron-beam sample heating system connected to a PID temperature controller (Eurotherm, 2048) for TPD experiments. The base pressure in this chamber is 1–2 × 10⁻¹⁰ mbar.

Polymer removal from the Au NP’s surface was conducted by O₂ plasma exposure (Oxford Scientific, OSMiPlas) at low temperature (150 K) at a pressure of 5.5 × 10⁻⁵ mbar for 100 min. The polymer is removed during the first 20–30 min of this treatment, and further O₂ plasma exposure results in the formation of Au=O compounds. The XPS measurements, conducted immediately after the O₂ plasma treatments, were done with the sample at a temperature lower than 200 K. For the temperature-dependent decomposition of gold oxide (XPS), a linear heating ramp with β = 3 K/s was used. Because all of our annealing treatments were conducted in vacuum, lower decomposition temperatures for gold oxide are expected in our case as compared to similar studies conducted under higher partial O₂ pressure.

The XPS binding energy (BE) scale has been calibrated using the Ti-2p₂/3 peak on Ti (454.2 eV) and Si-2p₂/3 peak on Si (99.3 eV) substrates as references. We can see the Ti⁷⁺ and Si⁷⁺ peaks because of the ultrathin nature of our TiO₂/TiO₂(6 nm)/Ti(9 nm)/SiO₂/Si(111) and SiO₂/SiO₂(4 nm)/Si(111) support films. From cross-sectional TEM measurements (not shown), the thicknesses of the TiO₂ and SiO₂ films are 6.0 ± 0.5 nm and 3.8 ± 0.5 nm, respectively. Because Au₂O₃ is known to decompose under intense X-ray exposure within hours, a control experiment was conducted to ensure that no gold oxide decomposition occurred during our XPS acquisition time (~10 min). A maximum decrease in the Au³⁺ signal of 2% was observed under
our measurement conditions (Al Kα radiation, 1486.6 eV at a power of 300 W). For the analysis of peak positions, line widths, and relative areas of the Au⁰ and Au³⁺ components, the raw XPS spectra were fitted with two (Au⁰) or four (Au⁰, Au³⁺) Gaussian functions after linear background subtraction. During the fitting, the intensity ratio between the Au-4f½ and Au-4f½ peaks was fixed to 0.75, and the full width at half-maximum (fwhm) of the different components was 1.3 ± 0.3 eV (Au⁰) and 1.7 ± 0.5 eV (Au³⁺).

Prior to the TPD measurements, the polymer-free Au NPs were flash-annealed to 700 K. This procedure reduced the residual gas background significantly at high temperatures without inducing any significant changes in the NP size distribution. Subsequently, the samples were exposed to atomic oxygen at a pressure of 2.3 × 10⁻³ mbar for 15 min. For the TPD studies, the samples were kept at RT during O₂ plasma exposure because a cold plasma treatment resulted in an increase of the background of the TPD spectra. Subsequently, the samples were placed ~3 mm away from the mass spectrometer glass shield opening (5 mm aperture) and heated at a rate of 5 K/s.

In order to investigate if for a given particle size and support combination, both surface and subsurface gold oxide species were formed upon exposure to atomic oxygen at low temperature (150 K), the samples were dosed with CO (P₃CO = 1.0 × 10⁻⁵ mbar for 10 min, 4500 L), and the Au³⁺ XPS signal was monitored before and after CO exposure. All samples were dosed with CO at RT except sample no. 4, for which the CO dosing was conducted at ~150 K (and XPS measured at ~200 K) in order to prevent significant thermal decomposition of the relatively unstable oxide formed on this sample.

**Results and Discussion**

(a) **Morphological Characterization (AFM).** Figure 1 displays AFM micrographs of Au NPs with two different size distributions synthesized using diblock copolymers with different molecular weights: PS(53000)−P2VP(43800) (Figure 1a−d), and PS(8200)−P2VP(8300) (Figure 1e and f). The particles were deposited on SiO₂, Figure 1a and e (samples 1 and 3) and on TiO₂, Figure 1c and f (samples 2 and 4), and all images were taken after polymer removal using O₂ plasma. In addition, the influence of annealing in UHV to 700 K (sample no. 1) and 500 K (sample no. 2) on the nanoparticle size was monitored, Figure 1b and d, respectively. No significant size changes were observed in any of the samples upon annealing. The sizes of the Au NPs estimated by AFM after O₂ plasma are given in Table 1. Particles with similar size distributions (4.9−5.4 nm height for samples 1 and 2, and 1.4−1.7 nm for samples 3 and 4) were found on both substrates when the same encapsulating polymer was used in the synthesis. Because of the AFM tip convolution effects (tip radius ~7 nm), the average NP height was used as the characteristic size parameter.

(b) **Electronic Characterization (XPS).** The thermal decomposition of oxidized gold species in core(Au⁰)/shell(Au³⁺) nanoparticles was monitored in situ (UHV) by XPS. Figure 2 shows XPS spectra from the Au-4f core level region of our four samples as a function of the annealing temperature. Spectra (i) were measured at ~200 K directly after a low-temperature (~150 K) O₂ plasma treatment. Spectra ii and iii were acquired after isothermal sample annealing for 10 min at 400 and 500 K respectively, followed by a fast cool down to room temperature using liquid nitrogen flow. The two doublets observed with maxima at (84.6 ± 0.3, 88.4 ± 0.3 eV) and (86.9 ± 0.2, 90.6 ± 0.2 eV) were assigned to the 4f½/2 and 4f½ core levels of Au⁰ and Au³⁺ in Au₂O₃. The vertical reference lines in...
commonly attributed to initial and final state effects. In addition, DFT calculations by Yang et al. suggested that positive core-level shifts measured for Au NPs supported on MgO(001) and TiO2 (110) could be related to the presence of oxygen vacancies in the supports.

(c) Temperature Dependence of the Thermal Decomposition of Au2O3.

Size Effects. It is known that the particle size affects the reduction rate of metal nanocatalysts, and two models based on geometrical and electronic effects have been proposed. In the geometrical model, different oxygen adsorption sites are available for differently sized clusters. In the electronic model, size-dependent changes in the electronic structure of small clusters are believed to play a role in the stability of metal oxide cluster shells. For our large NPs (~5 nm), geometrical effects should dominate, while electronic effects may also play a role in the reduction of our small clusters (~1.5 nm).

The influence of the particle size on the thermal stability of Au2O3 can be inferred by comparing XPS spectra taken on samples with two different particle size distributions supported on the same substrate (Figure 2a and c for Au/SiO2 and Figure 2b and d for Au/TiO2). In order to estimate the thickness of the gold oxide formed upon low-temperature O2 plasma exposure, the model described by Nanda et al. and Wu et al. in refs 57 and 58 was used. Following this model, the NP shape is assumed to be spherical and composed of a metallic core (Au) and an oxidized shell (Au2O3). The ratio of the intensities of the photoelectron peaks (4f 7/2 in our analysis) from the Au0 core and Au3+ shell is given by

\[
\frac{I_{Au_2O_3}(\theta)}{I_{Au}(\theta)} = \frac{K_{Au_2O_3}}{K_{Au}} \frac{\int_{R_1}^{R_2} \int_{0}^{\pi} \exp\left(\frac{r \cos \theta - \sqrt{R_2^2 - r^2 \sin^2(\theta)}}{\lambda_2}\right) r^2 \sin(\theta) \, d\theta \, dr}{\int_{0}^{\pi} \exp\left(\frac{r \cos \theta - \sqrt{R_1^2 - r^2 \sin^2(\theta)}}{\lambda_1}\right) r^2 \sin(\theta) \, d\theta} \]

where \( R_1 \) is the radius of the NP core and \( R_2 \) is the total radius of the NP (measured by AFM). The inelastic mean free path (IMFP) of electrons in metallic Au (\( \lambda_1 \)) is 1.781 nm. Using NIST software and a gold oxide density of 13.675 g/cm3 (see ref 60 for details on the structure of Au2O3), we estimated an IMFP (\( \lambda_2 \)) of 1.937 nm for Au2O3. The constants \( K_{Au_2O_3} \) and \( K_{Au} \) are related to the distinct elemental sensitivities and instrumental factors. A value of \( K_{Au_2O_3}/K_{Au} = 0.32 \) was used in our studies.

Equation 1 was evaluated numerically, and the \( R_1 \) value was varied until the \( I_{Au_2O_3}(\theta)/I_{Au}(\theta) \) ratio matched the intensity ratio measured by XPS.

Figure 3 shows the calculated Au2O3 shell thicknesses as a function of temperature. As described above, all samples were annealed for 10 min at the respective temperatures and the XPS spectra were measured subsequently at room temperature. The maximum thicknesses of the Au2O3 shell formed on the large NPs deposited on SiO2 (sample no. 1) and TiO2 (sample no. 2) after O2 plasma were 0.79 \pm 0.02 nm and 0.83 \pm 0.02 nm, respectively. For the small clusters, the initial maximum Au2O3 thicknesses were 0.38 \pm 0.02 nm (sample no. 3, SiO2) and 0.31 \pm 0.01 nm (sample no. 4, TiO2). For NPs deposited on both substrates, a clear size-dependence of the stability of Au2O3 can be inferred from Figure 3.

For the Au/TiO2 system, the Au oxide shell was found to be more stable on the large NPs (sample no. 2), with a 50%
decomposition of the Au$_2$O$_3$ shell obtained at $\sim$310 K as compared to $\sim$265 K for the smaller clusters (sample no. 4). The higher surface/volume ratio present in the small clusters should contribute to their faster reduction. Nearly complete disappearance of the Au$^{3+}$ signal ($<14\%$ of the initial Au$_2$O$_3$ thickness remaining) was observed at 300 K for the small clusters on TiO$_2$ (sample no. 4), while a substantial Au$^{3+}$ signal ($\sim66\%$ of the initial Au$_2$O$_3$ thickness) could still be detected on the surface of the large clusters (sample no. 2) at 300 K and $\sim25\%$ Au$^{3+}$ signal at 500 K. A similar size-dependent trend was observed by our group during the reduction of surface Pt-oxides (PtO and PtO$_2$) on Pt NPs supported on anatase TiO$_2$ powders.$^{61}$ These results are also in agreement with data obtained by Suuronen et al.$^{62}$ on oxidized Rh clusters supported on different oxide powders, where faster reduction rates were measured for smaller clusters.

For the Au/SiO$_2$ system, the Au$_2$O$_3$ shell on smaller NPs displayed a slightly higher thermal stability at low temperature than the large NPs, with a 50% decay in the Au$^{3+}$ signal on small clusters (sample no. 3) at 430 K as compared to a similar decay at 410 K for the large clusters (sample no. 1). On this system, a nearly complete decomposition of the Au$_2$O$_3$ shell (within the experimental error margin) was observed for the small clusters after 10 min annealing at 550 K (sample no. 3), while a $\sim0.2$ nm-thick gold oxide layer was still present at that temperature on the large clusters (sample no. 1). The dramatic differences in the stability of Au$_2$O$_3$ on small NPs deposited on SiO$_2$ and TiO$_2$ will be discussed in the next section, where the role of the cluster support will be considered.

It is noteworthy that on both substrates only a partial reduction of the Au$_2$O$_3$ layer is observed for our large NPs (samples 1 and 2) up to an annealing temperature of $\sim$550 K (10 min), where a $\sim0.2$-nm-thick Au$_2$O$_3$ shell remains on both SiO$_2$ and on TiO$_2$. Further annealing ($>600$ K, not shown) resulted in a slow decomposition of this oxide component. However, for the smaller NPs supported on both substrates, complete Au$^{3+}$ reduction is observed below 550 K, Figure 3. This difference can be attributed to the presence of more than one gold oxide species (surface and subsurface oxide) in these NPs and to a distinct thermal stability of such species. This is discussed in more detail in Section e. For bulk systems, typical values for the decomposition temperature of gold oxide Au$_2$O$_3$ is in the range of 360–450 K. However, the existence of a more stable form of gold oxide on Au(111), stable up to 1073 K, has also been reported by Chesters et al.$^{63}$

Support Effects. In addition to size effects, the influence of the oxide support on the decomposition of surface oxides on metal nanoparticles cannot be neglected. As an example, Schalow et al.$^{14}$ attributed the more facile reduction of preoxidized, small ($<3$ nm) Pd NPs supported on Fe$_3$O$_4$/Pt(111) as compared to larger clusters (10–100 nm) because of the stronger metal–support interactions expected for small clusters.

In the current study, a drastic difference in the stability of Au$_2$O$_3$ over NPs with similar size distributions but deposited on different substrates was observed. As an example, the Au$_2$O$_3$ thicknesses obtained from the analysis of Figure 2a(ii) and 2b–(ii) (large particles, $\sim5$ nm height) after annealing at 400 K for 10 min were 0.56 $\pm$ 0.04 nm for Au/SiO$_2$ and 0.22 $\pm$ 0.04 nm for Au/TiO$_2$. Similarly, after annealing the small NPs ($\sim1.5$ nm) at 350 K for 10 min, gold oxide shells with thicknesses of 0.28 $\pm$ 0.04 nm for Au/SiO$_2$ (not shown) and 0.0 $\pm$ 0.04 for Au/TiO$_2$ [Figure 2d(iii)] were obtained. As can be seen in Figure 3, for both particle sizes, Au$_2$O$_3$ is more easily decomposed (at lower temperature) when the NPs are supported on reducible TiO$_2$ substrates. A tentative explanation for this distinct behavior involves oxygen spillover from the oxidized Au NP shell to the TiO$_2$/Ti substrate. This model is based on the well-known facile reduction of the TiO$_2$ support at low temperature. Oxygen vacancies created in the TiO$_2$ upon sample annealing might be replenished by oxygen from the gold oxide NP shell. Such a mechanism is not possible in the case of SiO$_2$ because it only becomes reduced well above the temperatures employed here (maximum annealing temperature of 600 K). Oxygen vacancies in the support are known to be favorable sites for strong interactions with Au NPs,$^{5,64,65}$ becoming preferential sites for the nucleation of metal clusters.$^{66}$ Furthermore, a stronger binding of Au clusters to reduced TiO$_2$ films as compared to bulk TiO$_2$ has been measured,$^{67}$ and charge-transfer phenomena from oxygen vacancies in the reduced TiO$_2$ supports to metal clusters have been discussed.$^{18,68}$ In our studies, it appears that a strong metal–support interaction for the Au/TiO$_2$ system could be responsible for the decomposition of gold oxide on TiO$_2$ at a lower temperature than that on SiO$_2$.

Interestingly, Chang et al.$^{59}$ observed that the thermal decomposition of Ta$_2$O$_5$ was faster when it was deposited directly on Ti as compared to structures where an intermediate oxygen diffusion barrier (TiN) was present (Ta$_2$O$_5$/TiN/Ti). They concluded that oxygen diffuses from the Ta$_2$O$_5$ film to the underlying Ti layers and that the Ti contributes to its reduction. Furthermore, when the Ta$_2$O$_5$ film was in direct contact with Si, no enhanced reduction was detected. Finally, it should be noted that the influence of a reducible support on oxide decomposition depends on the relative stability of the oxides involved. For example, there are reports indicating a slower decomposition rate of RhO$_2$ clusters when deposited on partially reduced Ce–Zr powders.$^{62}$ Here, the reducible oxide support is believed to act as a local supplier of oxygen, slowing down the metal oxide decomposition. This is, however, a different experimental system because, contrary to the case of Au on TiO$_2$, where the enthalpy of formation of Au$_2$O$_3$ is very high, Rh forms a much more stable oxide.

Because the size-dependent Au$_2$O$_3$ decomposition behavior is different for similarly sized Au clusters deposited on our two different substrates, a distinct underlying mechanism is expected. Assuming that oxygen vacancies in the oxide support play a role in the stability of the Au oxide in the Au/TiO$_2$ system, the higher stability of Au$_2$O$_3$ in large Au NPs (sample no. 2) as compared to smaller NPs (sample no. 4) could indicate that a rate-limiting step for the decomposition of Au$_2$O$_3$ is the diffusion of atomic oxygen to the Au/TiO$_2$ interface. Following this model, larger diffusion barriers to the NP/support interface must be present in the case of large Au clusters.

A schematic summary of the mechanisms proposed here for the decomposition of the Au oxide shell, formed on size-selected Au NPs supported on SiO$_2$ and TiO$_2$ upon atomic oxygen exposure, is given in Figure 4. In the SiO$_2$ case, desorption of atomic (labeled as process 1) and molecular oxygen (upon recombination, process 2) from the oxide shell are depicted. Furthermore, for the large NPs, the diffusion of subsurface oxygen to the NP surface is also considered (3). On TiO$_2$, one additional decomposition pathway (4) is proposed, where O vacancies created in the TiO$_2$ substrate during annealing are continually replenished by oxygen atom spillover from the Au oxide NP shell.

In order to demonstrate that a relatively large number of oxygen vacancies were present in our TiO$_2$ support after annealing at low temperature, we have conducted in situ XPS studies on the uncoated TiO$_2$ support after O$_2$ plasma exposure...
Formation and Thermal Stability of \( \text{Au}_2\text{O}_3 \)

Figure 4. Schematic model illustrating different mechanisms for \( \text{Au}_2\text{O}_3 \) decomposition on large and small NPs supported on SiO\(_2\) and TiO\(_2\). Four processes are depicted: (1) direct desorption of atomic oxygen, (2) recombination of atomic oxygen and desorption as molecular oxygen, (3) segregation of subsurface oxygen to the NP's surface, and (4) atomic oxygen from the NP shell spills over to the TiO\(_2\) substrate and replenishes oxygen vacancies created on TiO\(_2\) upon sample annealing.

Figure 5. XPS spectra (Al K\(_\alpha = 1486.6\) eV) corresponding to the Ti-2p core level of a gold-free TiO\(_2\) substrate. Chemical composition changes on Ti–O compounds were monitored after different annealing treatments at different temperatures in UHV for 10 min. The raw data were deconvoluted with Ti\(_{0}^{3+}\), Ti\(_{2}^{2+}\), Ti\(_{3}^{+}\), and Ti\(_{4}^{+}\) fitting components. Reference lines for the Ti-2p\(_{3/2}\) XPS peak of the different Ti species are indicated.

Figure 7 shows how the thickness of the \( \text{Au}_2\text{O}_3 \) shell (Au\(^{3+}\) XPS signal) decreases as a function of annealing time for the following temperatures: 350, 375, and 400 K. The data in Figure 7 were obtained from the analysis of XPS spectra similar to the ones displayed in Figure 6 using eq 1. This study has been carried out only on samples 1, 2, and 3 (Figures 7a, b, and c). The Au\(^{3+}\) reduction in sample no. 4 (small particles on TiO\(_2\)) was so fast that a meaningful dataset could not be obtained using this procedure because the decomposition occurred in a time interval on the order of our experimental time error. This experimental error is related to the time required to increase and decrease the sample temperature from RT to the desired annealing value and back to RT for XPS analysis.

The data in Figure 7 show that the oxide decomposition slows down as the oxide shell thickness decreases (note the logarithmic time axis). Tsai et al.\(^{37}\) conducted a similar study on an Au film (100 nm thick) exposed to an O\(_2\) plasma treatment (for 1 min) based on resistance measurements performed in air (45% moisture content) at temperatures of 295, 323, 348, and 400 K. The authors discussed that the decomposition of surface \( \text{Au}_2\text{O}_3 \) in air followed first-order rate kinetics with an activation energy of 57 kJ/mol (\(-0.59\) eV). In contrast, the XPS results in Figure 7 cannot be fitted with simple rate equations for several reasons: (i) more than one gold oxide species is present in our samples (chemisorbed O\(_2\), surface oxide, subsurface oxide), (ii) the nanoparticle size affects the stability of each of these species, (iii) the nature of the oxide support affects the decomposition of surface \( \text{Au}_2\text{O}_3 \).
kinetics (Au/TiO$_2$). In the following, we discuss the curves in Figure 7 in more detail.

Support Effects. For samples with identical size distributions (samples 3 and 4, ~1.5 nm), a faster Au$_3^+$ decomposition rate was observed for the NPs supported on TiO$_2$ (sample no. 4), Figure 6d as compared to NPs on SiO$_2$ (sample no. 3), Figures 6c and 7c. Although less drastic, the same observation was made for the samples containing the larger NPs (~5 nm, sample no. 2), Figures 6a and 7a (SiO$_2$) and 6b and 7b (TiO$_2$). We attribute this effect to the strong metal-support interaction characteristic of the Au/TiO$_2$ system as also discussed in the temperature-dependent studies described above. Furthermore, our results indicate that such interactions affect small clusters more significantly than larger particles.14

Size Effects. According to previous literature,72 the initial thickness of the Au$_2$O$_3$ shell formed on each sample should be taken into consideration in order to understand the kinetics of the thermal decomposition of oxides. Sayan et al.72 investigated the decomposition of HfO$_2$ deposited on SiO$_2$/Si and found a nearly linear relationship between the HfO$_2$ thickness and the decomposition time. Furthermore, they observed that the thickness of the SiO$_2$ support did not affect the stability of HfO$_2$. In our experiments, thicker Au$_2$O$_3$ films were formed on the larger clusters (i.e., 0.8 ± 0.1 nm and 0.3 ± 0.1 nm for ~5 nm and ~1.5 nm Au NPs on TiO$_2$, respectively), where slower Au$_3^+$ decomposition rates were measured. An exception is the Au/SiO$_2$ system, where Au$_2$O$_3$ seems to be slightly more stable on small NPs below 550 K. As mentioned above, geometric (stronger oxygen adsorption sites on small clusters) and

Figure 6. XPS spectra (Al Kα = 1486.6 eV) corresponding to the Au-4f core level of samples with two different average Au nanoparticle sizes: (a and b) ~5 nm and (c and d) ~1.5 nm supported on SiO$_2$ (a and c) and TiO$_2$ (b and d). All data were acquired after isothermal sample annealing in UHV at 350 K for different time intervals. For reference, XPS spectra measured directly after O$_2$ plasma exposure are also shown.

Figure 7. Time dependence of the decomposition of Au$_2$O$_3$ obtained from the XPS spectra shown in Figure 6 for three different samples: (a) sample no. 1 (Au/SiO$_2$, 4.9 nm), (b) sample no. 2 (Au/TiO$_2$, 5.4 nm), and (c) sample no. 3 (Au/SiO$_2$, 1.7 nm). The temperatures during isothermal annealing are indicated.
Formation and Thermal Stability of Au$_2$O$_3$

electronic effects can influence the decomposition behavior on such small clusters.

In order to explain the complex kinetics of Au$_2$O$_3$ decomposition on differently sized Au NPs exclusively based on size effects, two different models can be considered: (i) the formation of an intermediate gold oxide compound$^{33}$ (e.g., Au$^{3+}$ decomposition to Au$^+$) and (ii) the presence of subsurface oxygen. Although literature reports that favor each of these options exist, and both models are described below, our experimental evidence supports the presence of subsurface oxide.

The presence of Au$^+$ species was suggested by Pireaux et al.$^{39}$ after monitoring the decomposition of gold oxide on Au(111) in UHV by XPS. The authors obtained atomic Au/O ratios of $\approx 0.6$ right after oxidation and $\approx 1.4$ after annealing to 340 K and concluded that Au$_2$O$_3$ (auric oxide, Au$^{3+}$) is formed immediately after atomic oxygen exposure, whereas the reduction process at 340 K resulted in Au$_2$O (aurous oxide, Au$^+$). However, recent DFT calculations on the stability of different gold oxides indicate that Au$_2$O$_3$ is more stable than Au$_2$O.$^{60}$

Whether subsurface oxygen is present in gold films and particles upon exposure to atomic oxygen is still a matter of controversy. Lim et al.$^{74}$ used XPS to investigate the oxidation of Au NPs with different sizes supported on HOPG. Upon exposing large NPs ($\approx 7$ nm) to atomic oxygen, a single peak of O-1s at 530 eV was recorded. Subsequent sample exposure to CO (3000 L) at RT resulted in the reduction of the particles. However, for smaller NPs ($\approx 3$ nm), two different oxidation states (530 and 532 eV) were observed in the O-1s core level. Following the findings by Min et al.$^{42}$ for small Au NPs supported on TiO$_2$(110). Subsurface oxygen (bulk oxide) species have also been identified on Au(111) by Min et al.$^{42}$ and their relative stability was found to depend on the sample temperature during atomic oxygen exposure (ozone) as well as on the oxygen coverage. In fact, surface and subsurface gold oxide species as well as chemisorbed oxygen were found in bulk systems exposed to atomic oxygen at low temperature (200 K), whereas at high temperature (400 K), only surface gold oxide species were observed. Following the findings by Min et al.$^{42}$ a reason for the discrepancies found in the previous literature reports might be the different procedures used to deposit atomic oxygen on gold surfaces (coverage and sample temperature).

(e) Stability of Gold Oxide upon CO Dosing: Surface versus Subsurface Oxide. In order to gain insight into whether surface and subsurface gold oxide species coexist in our preoxidized size-selected Au nanoparticles supported on SiO$_2$ and TiO$_2$, we dosed the samples with CO and monitored the decomposition of gold oxide species by XPS. Figure 8 shows XPS spectra from the Au-4f core level region of our four samples (see Table 1 for details) after O$_2$-plasma at 150 K (i) and after subsequent 4500 K (ii) and 9000 L (iii) CO dosing at room temperature (samples 1, 2, and 3) and at 200 K (sample no. 4). Because the gold oxide compounds formed on sample no. 4 were found to decompose thermally upon annealing at RT, in order to separate gas from thermally induced decomposition of gold oxide, the CO dosing on sample no. 4 was done at 200 K.

In Figure 8a [sample no. 1, Au($\approx 5$ nm)/SiO$_2$], it can be seen that the relative Au$^{3+}$ contribution to the XPS spectra decreases upon CO dosing (ii) because of Au$_2$O$_3$ decomposition as a result of CO$_2$ formation. Note, however, that the Au$^{3+}$ signal does not disappear completely, even after a 9000 L CO exposure (iii), suggesting that subsurface Au-oxide species are present. For sample no. 1, the intensity ratio of the Au$^{3+}$/Au$^0$ 4f$_{7/2}$ core levels is 1.05 $\pm$ 0.04 after O$_2$ plasma (i), 0.68 $\pm$ 0.03 after 4500 L CO dosing (ii), and 0.52 $\pm$ 0.02 after a subsequent 4500 L CO exposure (iii). As expected, the decrease in the Au$^{3+}$ intensity is accompanied by an increase in the Au$^0$ XPS signal. A similar trend was observed for sample no. 2 [Au($\approx 5$ nm)/TiO$_2$] in Figure 8b, although the decay in the Au$^{3+}$/Au$^0$ ratio after 4500 L CO dosing was smaller (from 0.66 $\pm$ 0.04 after O$_2$ plasma to 0.56 $\pm$ 0.03 after CO dosing). Samples 3 [Au($\approx 1.5$ nm)/SiO$_2$] and 4 [Au($\approx 1.5$ nm)/TiO$_2$] display Au$^{3+}$/Au$^0$ ratios of 1.8 $\pm$ 0.3 and 1.7 $\pm$ 0.2 immediately after O exposure (i) and 1.0 $\pm$ 0.2 and 1.4 $\pm$ 0.3 after CO exposure (ii), respectively. Because CO is only expected to react with weakly bound oxygen species and surface gold oxide,$^{42,74}$ the residual Au$^{3+}$ signal measured for all samples after high CO dosing indicates that subsurface oxygen is present in all samples.

Recent DFT calculations by Shi and Stampfl$^{75}$ on O/Au(111) revealed that the most energetically favorable configuration is an ultrathin surface-oxide-like structure ($\approx 0.31$ ML oxygen coverage) with O atoms quasi-threefold coordinated to Au, and gold atoms at the surface twofold linearly coordinated to O. This structure was found to be significantly more stable (up to 420 K at atmospheric pressure and up to 200 K under ultrahigh vacuum conditions) than on-surface chemisorbed oxygen or atomically adsorbed oxygen. Furthermore, for higher oxygen coverages ($\approx 0.5$ ML, as is our case), mixed on-surface + subsurface structures were found to be more favorable than pure on-surface adsorption.
The size-dependent differences in the reduction of Au-O compounds, formed upon room temperature atomic oxygen exposure, were studied by TPD. Figure 9a and b shows O$_2$ desorption signals (open circles) measured on (a) sample no. 1 (Au/SiO$_2$, 4.9 nm) and (b) sample no. 3 (Au/SiO$_2$, 1.7 nm) after an O$_2$ plasma treatment ($P_{O_2} = 2.3 \times 10^{-5}$ mbar for 15 min). The dashed lines display control experiments conducted on gold-free SiO$_2$ substrates exposed to analogous O$_2$ plasma treatments.

Two major differences between our XPS and TPD investigations should be noted. First, the XPS samples were exposed to atomic oxygen at 150 K, while the TPD samples were dosed with O at 300 K (in order to minimize the residual gas background). According to previous studies, after such RT plasma treatment the formation of bulk gold oxide is not favorable, and the TPD features described below should be attributed mainly to the desorption of chemisorbed oxygen and the decomposition of surface Au$_2$O$_3$. Second, while the TPD samples were subjected to a fast annealing cycle (80 s), the XPS samples were successively annealed from 300 to 600 K maintaining the sample temperature fixed for 10 min at 350, 400, 450, 500, 550, and 600 K, Figure 3.

A desorption peak at 401 K ($\sigma$ state) was observed for the SiO$_2$ substrate, Figure 9a and b. Oxidized Au NPs on SiO$_2$ showed two characteristic desorption peaks: one at $\sim$404 K ($\sigma$ state from the substrate), and another ($\gamma$ state) at $\sim$555 K for sample no. 1 ($\sim$5 nm Au clusters) and $\sim$584 K for sample no. 3 ($\sim$1.5 nm Au clusters). Our TPD data indicate a size-dependent O$_2$ desorption in which smaller NPs show higher desorption temperatures ($\gamma$ state). As expected, this size dependence is observed only for the $\gamma$ state because the $\sigma$ state was assigned to O$_2$ desorption from the substrate and the same SiO$_2$ support was used for both samples. This is in agreement with previous O$_2$ TPD desorption studies conducted by Bondzie et al. on Au evaporated on TiO$_2$(110). They observed higher desorption temperatures (645 K) for smaller Au NPs ($\sim$0.35 ML Au coverage) as compared to larger Au NPs (520–545 K) ($\sim$6 ML Au).

In order to obtain the reaction order for O$_2$ desorption, we employed the method described by Saliba et al. in ref 77. Figure 9c and d shows plots of $[\ln(\alpha/\alpha_0) - n \ln \theta]$ versus $1/T$ for several choices of desorption kinetic order “n” for two average particle sizes of Au nanoparticles deposited on SiO$_2$: (c) $\sim$5 nm and (d) $\sim$1.5 nm.

(f) Size-Dependent O$_2$ Desorption (TPD). The size-dependent differences in the reduction of Au–O compounds, formed upon room temperature atomic oxygen exposure, were studied by TPD. Figure 9a and b shows O$_2$ desorption signals (open circles) measured on (a) sample no. 1 (Au/SiO$_2$, 4.9 nm) and (b) sample no. 3 (Au/SiO$_2$, 1.7 nm) after an O$_2$ plasma treatment ($P_{O_2} = 2.3 \times 10^{-5}$ mbar for 15 min). The dashed lines display control experiments conducted on gold-free SiO$_2$ substrates exposed to analogous O$_2$ plasma treatments.
oxygen coverages) by Saliba et al. 77 and Sault et al. 79 Similar results were obtained recently by Deng et al. 78 based on O2 TPD studies on Au(111). In the latter case, the peak temperature of O2 desorption at 550 K was independent of oxygen coverage, and it was attributed to a pseudo-first-order reaction.

In contrast, for small NPs, Figure 9d, the best fit was tentatively given by two desorption orders: \( n = 1.5 \) or \( n = 2 \), with desorption energies of 1.2 ± 0.1 and 1.6 ± 0.1 eV, respectively. The data in Figure 9d could not be fitted by first-order desorption kinetics. Despite the good agreement of the respective. The data in Figure 9d could not be fitted by first-order determined for sample no. 3 is due to the presence of different adsorption sites (steps, kinks, terraces), vacancy creation upon annealing, lateral interactions between adsorbates, and adsorbate diffusion are neglected. In our case, the situation is further complicated by metal—support interactions that appear to play a role in the \( \text{Au}_3\text{O}_3 \) decomposition as well as by the presence of two different gold oxide species.

Our findings could have important implications on the performance of real-world catalysts. First, the catalytic activity of clusters is known to depend on their oxidation state, making knowledge of the stability of oxide phases at elevated temperatures and on different substrates of great technological relevance. Second, it has also been suggested that the toxicity of certain catalytic metal clusters upon release into the environment may depend on their oxidation state. Future work will focus on the influence of the oxidation state on the catalytic activity of these size-selected nanoscale systems.

Conclusions

Thermal decomposition studies on O-precovered (150 K) gold NPs supported on SiO2 and TiO2 have been conducted by XPS. Clear differences in the stability and decomposition kinetics of \( \text{Au}_3\text{O}_3 \) were found as a function of the average particle size and nature of the oxide support. The effect of the substrate was evidenced by a reduced stability of gold oxide on Au NPs supported on TiO2, a system where strong metal—support interactions are expected. Here, oxygen spillover from the cluster’s oxidized surface shell to O vacancies formed in the reducible TiO2 substrate upon annealing is suggested as a possible decomposition pathway. Although both nanoparticle size and support were found to influence the stability of \( \text{Au}_3\text{O}_3 \), the support effect is more pronounced, as evidenced by a very fast reduction of \( \text{Au}^{3+} \) in Au/TiO2, and enhanced gold oxide stability in Au/SiO2. Furthermore, nearly complete reduction of small (~1.5 nm diameter) NPs was observed at 300 K for Au/TiO2 and at 550 K for Au/SiO2. In contrast, for larger clusters only partial \( \text{Au}_3\text{O}_3 \) decomposition was observed up to 600 K. This suggests that at least on the large NPs two different oxygen species are present: surface gold oxide that decomposes at temperatures below 600 K and bulk or subsurface oxide that is stable well above 600 K. In addition, for the small clusters, the presence of surface and subsurface oxide was confirmed by CO dosing experiments. A decrease in the \( \text{Au}^{3+} \) signal and an increase in Au0 upon CO exposure indicated the reduction of surface gold oxide. The observation of incomplete \( \text{Au}^{3+} \) reduction for CO dosings as large as 9000 L provided clear support for the presence of a stable subsurface gold oxide species in all samples. Finally, TPD data obtained after room temperature atomic oxygen exposure revealed distinct O2 desorption temperatures on differently sized Au nanoparticles supported on SiO2. A higher desorption temperature (584 K) was observed for ~1.5 nm clusters, as compared to 555 K for ~5 nm large clusters. These results indicate that the stability of gold oxide species strongly depends on the cluster size.

Acknowledgment. We acknowledge financial support by the National Science Foundation (NSF-CAREER award, 0448491).

Supporting Information Available: Histograms of the particle height distributions and XPS spectra of the Au-4f region acquired after different X-ray exposure times. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes
