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## Interaction of Gold with Cerium Oxide Supports: $CeO_2(111)$ Thin Films vs $CeO_x$ Nanoparticles

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Morphology, electronic structure, and CO adsorption of gold supported on well-ordered CeO<sub>2</sub>(111) thin films and CeO<sub>x</sub> nanoparticles were studied by scanning tunneling microscopy (STM), photoelectron spectroscopy (XPS), and infrared reflection absorption spectroscopy (IRAS). Ceria nanoparticles grown on crystalline thin silica films possess Ce in both the 3+ and 4+ oxidation states, with the former dominating in smaller particles. Upon deposition on CeO<sub>2</sub>(111) films, most of the Au particles are formed at the step edges. The particles on terraces grow presumably through the decoration of point defects, which are more numerous on reduced surfaces. Combined XPS and IRAS data show that partially charged Au<sup> $\delta$ +</sup> species are formed by deposition at low temperatures (~100 K) and low coverages on both ceria supports. Formation of Au<sup> $\delta$ +</sup> on CeO<sub>2</sub>(111) films is kinetically limited and is attributed to the interaction of the gold ad-atoms with defects. In variance to extended ceria surfaces, where only metallic Au nanoparticles are observed at 300 K, the "cationic" gold species are formed in abundance on nano-CeO<sub>x</sub> and exhibit enhanced thermal stability. It is shown that nanoceria stabilizes small Au clusters, which may even be incorporated into the ceria nanoparticles at elevated temperatures.

#### 1. Introduction

Chemical reactions on gold surfaces have recently received much attention owing to the unusual catalytic properties observed for highly dispersed gold in various reactions such as preferential and total CO oxidation, the water gas shift (WGS) reaction, etc.<sup>1-4</sup> In spite of a huge number of studies in this field, the nature of the active sites in oxide supported Au catalysts remains a controversial issue (see refs 1-16 and references therein). Among the reaction mechanisms proposed in the literature, there are some involving positively charged, "cationic" gold species, which have been invoked in particular after experimental observations by Flytzani-Stephanoupolus and co-workers of enhanced reactivity for cyanide-leached Au/CeO<sub>2</sub> catalysts in the WGS reaction.<sup>6,7</sup> Gates and co-workers, using X-ray absorption techniques, also showed the importance of the cationic gold in CO oxidation over Au/MgO catalysts.<sup>8,9</sup> Finally, Corma's group observed that nanocrystalline ceria ("nanoceria") as a support remarkably increased the activity of gold as compared to conventional ceria supports.<sup>10-13</sup> The effect was attributed to the presence of cationic (Au<sup>+</sup>, Au<sup>3+</sup>) surface species.

On the other hand, Behm and co-workers showed that  $Au^{3+}$  species in the leached Au/CeO<sub>2</sub> catalysts readily transform under the WGS reaction conditions into small metallic aggregates, with the mass-normalized activity being significantly lower than on the nonleached catalysts.<sup>17</sup> This finding is consistent with the studies of Rodriguez and co-workers on a reaction-induced reduction of gold in ceria-supported catalysts.<sup>18</sup> Moreover, this group has recently demonstrated that high activity in the WGS reaction can even be achieved on the Au(111) single crystal surface covered by islands of Ce oxide, thus indicating that it is the structure of the Au/oxide interface rather than the dimensions of Au particles that governs this reaction.<sup>19</sup>

The oxidation state of Au species in the real catalysts is very often deduced on the basis of the infrared spectra of CO (e.g., see refs 4, 7, 13, and 20-26). It is well-established that metallic gold exhibits a CO stretching band at around 2110 cm<sup>-1</sup>. The absorption bands in the 2200-2150 cm<sup>-1</sup> region, i.e., blueshifted with respect to CO in the gas phase (= $2143 \text{ cm}^{-1}$ ), are usually assigned to Au<sup> $\delta+$ </sup>-CO bonds. Negatively charged Au<sup> $\delta^-$ </sup>-CO species are shown to explain the bands in the region between 2050 and 1800 cm<sup>-1</sup>.<sup>23,24</sup> Less understood are the "intermediate" bands between 2110 and 2140 cm<sup>-1</sup>. Some research groups associate these bands with partially oxidized gold,<sup>7,11</sup> while others with CO adsorption on small metallic Au clusters.4,25 In addition, Hadjiivanov and co-workers have proposed that the bands at  $\sim 2140 \text{ cm}^{-1}$  could be the Au<sup>+</sup> adsorption sites dispersed not on the oxide support but on the surface of the metallic Au particles.<sup>21,22</sup> After the recent review of Mihaylov et al.26 on CO IR studies of gold, it appears that Au<sup>3+</sup> and Au<sup>+</sup> species can indeed be stabilized as isolated species on oxides; however, the examples have been limited to Au supported on zeolites.

It is well-known that gold exhibits a high electronegativity and high ionization potential, which make it a poor electron donor. As a result, gold weakly interacts with many oxides. Not surprisingly, defects such as oxygen vacancies play an important role in the adsorption of gold on oxide surfaces. In particular, the vacancies in ceria result in localization of charge over the cations surrounding the vacancy (see, for instance, refs 27, 28 and references therein). It is obvious that preparation methods, pretreatments, and reaction mixtures can all influence the structure of supported gold catalysts. The lack of knowledge of the atomic structure of the powdered Au/oxide catalysts and difficulties to control the morphology, particle size, degree of hydration, etc., necessitate basic research studies. The studies on the model systems involving metal particles supported on planar oxide substrates <sup>4,5,29–33</sup> under well-controlled conditions

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have been envisioned to provide fundamental knowledge on relationships between the atomic structure and the chemical properties of supported gold clusters.

Recently, we have reported on the morphology of the Au particles, deposited by physical vapor deposition (PVD) onto well-ordered CeO<sub>2</sub>(111) films, and their structural changes at elevated ambient pressures using scanning tunneling microscopy (STM).<sup>34,35</sup> The results suggested that gold most strongly interacts with defects on terraces typically associated with oxygen vacancies. Also, Weststrate et al. have studied the electronic structure of Au particles on CeO<sub>2</sub>(111) films and CO adsorption using X-ray photoelectron spectroscopy (XPS) with synchrotron light.<sup>36</sup> The results are in line with previous observations that CO adsorbs primarily on low-coordinated sites on gold particles.<sup>4,25</sup>

In continuation of our previous works, here we focus on understanding the role of ceria support dimensions on structural, electronic, and CO adsorption characteristics of gold. In this paper, we have studied the interaction of gold with CeO<sub>2</sub>(111) as well as ceria nanoparticles grown on thin silica films. XPS, STM, and infrared reflection absorption spectroscopy (IRAS) were employed for this comparative study. Data clearly show that the morphology of a ceria support strongly affects the structure of gold. The results may shed light on the structural aspects of catalysis over ceria-supported gold and may in addition aid in deeper understanding of promotional effects of ceria additives to metal catalysts.

#### 2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure below  $1 \times 10^{-10}$  mbar), equipped with a low energy electron diffraction (LEED, Omicron), an X-ray photoelectron spectrometer with a Scienta SES-200 analyzer, an IR spectrometer (Bruker IFS 66v/s), and an STM (Omicron). In addition, XP spectra were measured using the synchrotron light at BESSY II, Berlin (beamline UE52-PGM1).

The Ru(0001) single crystal (10 mm diameter, from Mateck) was clamped to a Mo holder and heated from the backside of the crystal using electron bombardment. The temperature was controlled by a feedback control system (Schlichting Phys. Instrum.) with a type K thermocouple spot-welded to the edge of the crystal. The clean Ru surface was prepared using cycles of  $Ar^+$  sputtering followed by annealing in UHV to 1300 K.

The preparation of ultrathin silica films on Mo(112) includes PVD of Si in oxygen ambient and subsequent high temperature annealing, as described in details elsewhere (ref 37 and references therein). The quality of the films was inspected each time prior to use. Among other thin films used in our previous studies,<sup>24,25,32</sup> the silica films have been chosen because of their chemical inertness toward gold.<sup>38</sup> Therefore, we expected that gold deposited on the ceria/silica surface would preferentially interact with ceria nanoparticles rather than silica.

Ce and Au (both 99.9%, Goodfellow) were vapor-deposited from W crucibles using an e-beam-assisted evaporator (Focus EFM3). During evaporation the sample was biased at the same potential as the metal source (typically  $\sim$ 800 V) to prevent accelerating of the metal ions toward the sample that may create defects on a support in a noncontrollable manner. Indeed, preliminary results showed different thermal desorption spectra of CO on alumina-supported gold particles deposited without sample biasing. The effect of biasing was not studied in detail in this study. Both XPS spectrometers at BESSY and FHI were calibrated with gold foil by setting the Au  $4f_{7/2}$  level to 84.0 eV. XPS measurements were performed immediately after preparation of the ceria films and particles and, in addition, prior to Au deposition. The spectra did not reveal a reduction of the ceria surface upon staying in vacuum, at least for the time of the experiments.

The STM images presented here were obtained with Pt–Ir tips at tunneling currents of  $\sim$ 0.1 nA and positive sample bias of  $\sim$ 2 V.

Preparation of Ceria Supports. The preparation of ceria films on a Ru(0001) single crystal, originally suggested by Mullins et al.,  $^{39}$  includes PVD of Ce in  ${\sim}5 \times 10^{-7}$  mbar  $O_2$  at T > 700 K and subsequent annealing in oxygen at ~980 K.<sup>34</sup> Due to a large lattice mismatch ( $\sim 40\%$ ) between CeO<sub>2</sub>(111) and Ru(0001) (as well as other typical metal substrates), growth of the Ce oxide films goes through the formation of ceria particles like a granular film,<sup>40</sup> which must be further annealed at high temperatures to make the film surface smooth and wellordered. It is well-known that growth of oxide films is governed to a large extent by the adhesion energy between an oxide and a substrate. In the case of ceria on metals, the interfaces suffer from a large mismatch. In attempts to overcome this issue, we employed a kinetically limited growth at low temperatures to facilitate the formation of the first, interfacial ceria layer. We oxidized Ru(0001) in  $10^{-6}$  mbar of O<sub>2</sub> at 600 K and first deposited Ce in 10<sup>-6</sup> mbar of O<sub>2</sub> at 100 K (i.e., in contrast to the 700 K used previously<sup>34,39</sup>) in amounts approximately equivalent to form 4-5 monolayers of CeO<sub>2</sub>(111) on Ru(0001). Subsequently, the temperature was increased at a rate of 1 K s<sup>-1</sup> and kept at 700 K during deposition of the next several layers. After deposition, the sample was further oxidized at  $\sim$ 980 K at the same oxygen pressure. LEED showed a sharp  $Ru(0001) - (1.4 \times 1.4)$  pattern characteristic for ceria films.<sup>39</sup> From the attenuation of Ru 3d XPS signals, the average film thickness was estimated to be about 3 nm.

Different recipes were used here for preparation of ceria nanoparticles supported on thin silica films. In order to mimic preparation of real catalysts, we mostly used water-assisted deposition (WAD) that included PVD of Ce on top of ice films, produced by adsorption of 10 L (1 L =  $10^{-6}$  torr s) of water at 100 K. The sample was then slowly heated to 600 K in  $10^{-6}$  mbar of O<sub>2</sub>. The unreacted water desorbs intact from the silica films at ~160 K.<sup>41</sup> Another preparation involved PVD of Ce in  $10^{-7}$  mbar of O<sub>2</sub> at 100 K followed by slow heating to 300 K, which will be referred to as "direct" PVD to discriminate from the WAD primarily used in this study.

#### 3. Results and Discussion

**3.1. Morphology.** Figure 1a shows a room temperature STM image of Au particles deposited at 100 K onto freshly prepared, fully oxidized  $CeO_2(111)$  films. Wide, atomically flat terraces of the ceria films are clearly observed. The terraces often consisted of several domains, with the domain boundaries visible in STM as irregularly shaped trenches. At this coverage, the majority of the particles were formed at the step edges due to weak interaction of Au ad-atoms with the O-terminated  $CeO_2(111)$  terraces. Only a few Au particles were found on the terraces, which most likely decorated the point defects, typically associated with oxygen vacancies.<sup>27,28,34,40</sup> Note that the particles on the terraces are considerably larger than at the steps.

The particles distribution on the surface changed substantially when the ceria films were annealed in UHV at 950 K for 5 min prior to the Au deposition (cf. Figure 1a-d). At the same Au



Figure 1. Room temperature STM images of Au particles deposited at 100 K on the fully oxidized (a, b) and partially reduced (c, d)  $CeO_2(111)$  films.

coverage, more particles were observed on terraces, and fewer particles were found on steps. The particles on terraces are certainly smaller than those on the fully oxidized films. These morphological changes can be explained by creating oxygen vacancies on terraces upon high temperature vacuum annealing, which then serve as nucleation sites for gold. Consequently, at a given Au coverage, the particle density increases and the mean particle size decreases accordingly. The defects trap the majority of the Au ad-atoms migrating on the terraces, ultimately leaving less gold to be adsorbed at the steps.

We now address the morphology of the ceria supported on silica films. Independently of whether ceria was deposited by PVD directly onto the films or using water as a buffer layer, STM images revealed formation of nanosized particles. In the case of direct PVD, the particles were randomly distributed on the surface probably due to the strong interaction of Ce adatoms with silica films. At a given amount of ceria, the WAD samples showed 3-4 times lower particle density and larger particle size. The particles were mostly found at the steps as shown on Figure 2a. The formation and aggregation of particles on ice films is a complex process that is driven by the dewetting, islanding, and sublimation of ice on heating<sup>42</sup> and is beyond the scope of this paper. It was suggested by Gross et al., studying WAD of gold on silica films,<sup>43</sup> that one can independently control particle size and only change particle density by repeating the whole deposition procedure. Figure 2b shows STM images of the sample, prepared in two sequential WAD steps and possessing 50% more ceria than in Figure 2a. Indeed, the particle density is increased from 0.027 to 0.035 particles/nm<sup>2</sup>, while the size is only slightly increased.

Deposition of ~0.15 ML of gold (1 ML =  $1.4 \times 10^{15}$  atoms/ cm<sup>2</sup>) at ~100 K and then heating to 300 K (for STM measurements) produced subtle changes in the particle density. Annealing to 600 K in the course of thermal stability studies of the Au/nanoceria systems (see below) caused 20-30% reduction of the particle density probably due to coalescence of adjacent particles. Certainly, the particles gain size as shown in Figure 2c, d. The comparison of STM images of the pristine CeO<sub>x</sub> and Au/CeO<sub>x</sub> particles did not reveal any features which could be interpreted as individual Au particles that stuck to ceria particles. Therefore, the STM results suggest that (i) gold nucleates exclusively on the ceria nanoparticles and (ii) Au species are interacting with ceria and probably covering ceria particles rather than forming Au particles bordering the ceria particles.

**3.2. Electronic Structure: XPS Study.** The electronic structure of ceria-based systems was studied by photoelectron



**Figure 2.** (a) STM image of ceria nanoparticles grown on ultrathin silica films using water-assisted deposition (WAD, see text). The WAD was repeated in (b) by adding 50% more ceria than in (a). The surface (a) was dosed with 0.15 ML Au at 100 K and stepwise annealed up to 600 K, and the resulting surface is shown in (c). The surface (b) was dosed with 0.23 ML Au at 100 K and annealed to 600 K as shown in (d). Image size 100 nm  $\times$  100 nm.

spectroscopy using a standard dual anode X-ray source as well as synchrotron light. The latter was used to increase spectral resolution, necessary in particular for the very complex spectra of ceria. Figure 3 shows the Ce 3d region for a thin ceria film (top spectrum) and silica-supported ceria at increasing coverage (bottom spectra) at  $h\nu = 1020$  eV. The spectrum for the ceria film is usually rationalized in terms of the spin orbital pairs of the Ce3d<sup>9</sup>4f<sup>0</sup>O2p<sup>6</sup>, Ce3d<sup>9</sup>4f<sup>1</sup>O2p<sup>5</sup>, and Ce3d<sup>9</sup>4f<sup>2</sup>O2p<sup>4</sup> final states,<sup>44–46</sup> which are labeled in the figure as 4f', 4f'', and 4f''', respectively. (However, we recently noticed that this assignment is questionable, and a more thorough study is underway.<sup>47</sup>)

The highest binding energy (BE) peak at  $\sim$ 917 eV is not observed for Ce<sup>3+</sup> compounds and is therefore used to differentiate  $Ce^{4+}$  from  $Ce^{3+}$ . The latter species manifest itself by the Ce 3d<sub>5/2</sub> signals at 880 and 885 eV, which correspond to the 4f" and 4f" final states of Ce<sup>3+</sup>, respectively.<sup>44</sup> These peaks are obviously missing in the spectra of the ceria films. Therefore, XPS data support the LEED and STM results on the formation of the fully oxidized  $CeO_2(111)$  films, where the presence of small amounts of Ce<sup>3+</sup> cations can only be determined by spectral deconvolution, which typically includes Gaussian-Lorentzian fitting after removal of a Shirley background. Although precise determination of the degree of reduction from Ce 3d data is not always straightforward (for example, see discussion in ref 48), using the approach suggested in refs 49 and 50 we have estimated the  $Ce^{3+}/(Ce^{3+} + Ce^{4+})$  ratio to be ~0.1. One should, however, keep in mind that ceria, as a reducible oxide, may undergo an X-ray-induced surface reduction. Therefore, this value can be considered as the upper limit in fully oxidized films.

Vacuum annealing at 950 K for 5 min results in an increase of  $Ce^{3+}$  in the films. This is consistent with the STM results showing a higher density of defects decorated by gold in the annealed samples. We will refer to the vacuum-annealed ceria films as the "reduced" ones for brevity.



**Figure 3.** Ce 3d region of XPS spectra (photon energy 1020 eV) measured on fully oxidized CeO<sub>2</sub>(111) films (top spectrum) and ceria nanoparticles at increasing coverage (bottom spectra). Spectral deconvolution into Ce<sup>4+</sup> and Ce<sup>3+</sup> related signals is shown only for the highest Ce coverage. (See text for the peak assignment.)

The XP spectra of ceria nanoparticles are very different from those of  $CeO_2(111)$  films. Figure 3 shows the spectra, recorded at BESSY, of ceria deposited on silica films at 100 K in an oxygen ambient for different coverages. By comparing these spectra with those recorded in another setup equipped with conventional XPS and also with STM, we found that the highest coverage in this study (see bottom spectrum in Figure 3) corresponds to the ceria particles of  $\sim$ 5 nm in size, on average. The spectra clearly show that the contribution of the Ce<sup>3+</sup> states to the overall signal is significant. Due to broadening of the peaks and a relatively low signal-to-noise ratio as compared to those in the films, the spectral deconvolution is not trivial. In the first approximation, we have only increased the full width half-maximum (fwhm) of the peaks by comparing the 4f' components (at 917 eV) in the ceria films and the  $\sim$ 5 nm particles (bottom spectrum in Figure 3) and fixed the peak positions derived from spectral deconvolution of the films. Then, we also let the peak positions deviate slightly (within  $\sim$ 300 meV) from those in the films. In both cases, we found that Ce states in the nanoparticles can in principle be obtained by a superposition of the  $Ce^{4+}$  and  $Ce^{3+}$  states with a respective weighing factor, whereby broadening reflects different surroundings of the Ce atoms in the nanoparticles. The analysis revealed that the  $Ce^{3+}/(Ce^{3+} + Ce^{4+})$  ratio increases from 40  $\pm$  1 to 50  $\pm$  2 and finally to 67  $\pm$  10% upon decreasing the ceria coverage, as shown in Figure 3. Basically, the same trend is observed using water-assisted preparation; smaller ceria particles exhibit larger contributions of the Ce<sup>3+</sup> state.



**Figure 4.** Ce 4d region of XPS spectra measured on  $CeO_2(111)$  films (top spectrum) and ceria nanoparticles (bottom spectra) at different photon energies as indicated. The spectra are offset for clarity. (See text for the peak assignment.)

The partial reduction of ceria nanoparticles is also reflected in the Ce 4d spectra as shown in Figure 4. In analogy with Ce 3d spectra, the highest BE peaks at ~123 and ~126 eV, which are missing in the Ce(III) oxide, are typically assigned to Ce<sup>4+</sup> with a Ce4d<sup>9</sup>4f<sup>0</sup>O2p<sup>6</sup> final state (marked as 4f ' in Figure 4) with a spin-orbit splitting of 3.3 eV. There is no agreement for the assignment of the other peaks due to a strong coupling between the Ce4d and Ce 4f levels that results in the multiplet splitting, which has a magnitude comparable to the spin-orbit splitting, thus rendering the full analysis very complex. Following Mullins et al.,<sup>44</sup> one should assign the peaks indicated by arrows in Figure 4 (top) as Ce<sup>4+</sup> with Ce4d<sup>9</sup>4f<sup>1</sup>O2p<sup>5</sup> and Ce4d<sup>9</sup>4f<sup>2</sup>O2p<sup>4</sup> final states, but again this assignment is questionable.<sup>47</sup>

It has turned out that the Ce 4d spectra of ceria nanoparticles are strongly dependent on the photon energy as shown in the bottom part of Figure 4. At 230 eV only the Si 2p peak at 102.5 eV could be detected in this region, with no signal corresponding to the Ce 4d levels. With stepwise increasing of the photon energy from 230 to 1487 eV, the Ce 4d signals first grow in intensity and then attenuate, while the Si 2p peak decreases monotonously. Such behavior cannot be explained solely by escape depth effects (via increasing the kinetic energy of the photoelectrons at higher photon energy), thus reflecting the elemental composition depth profile in the surface region. Indeed, at the same kinetic energy (~100 eV), the Ce 4d spectrum reveals almost no Ce on the surface while the Ce 3d spectrum does (see Figure 3). In fact, the photon energy dependence of the Ce 4d spectra can be explained by the nonlinear dependence of the photoionization cross section of the Ce 4d level exhibiting the so-called Cooper minimum<sup>51</sup> at low energies (i.e., in variance to the Si 2p that has the highest cross section at low photon energy which monotonously decreases at higher energies<sup>52</sup>). The fact that the spectrum at 700 eV looks somewhat better than the one at 380 eV may be indicative of the escape depth effect in this case.

The presence of the BE states above 120 eV of a relatively high intensity in the Ce 4d spectrum of ceria particles is fully consistent with the corresponding Ce 3d spectrum of the same sample (see bottom spectrum in Figure 3) showing primarily  $Ce^{4+}$  species. The differences in the peak intensity ratios observed in the low BE region as compared to the fully oxidized  $CeO_2$  film indicate a significant contribution of the  $Ce^{3+}$ 



**Figure 5.** Au 4f (a) and Ce 3d (b) regions of XPS spectra (Mg K $\alpha$  source, 1487 eV) for 0.15 ML Au deposited at 100 K on CeO<sub>x</sub>/SiO<sub>2</sub>. The spectra were measured at 100 K after heating to the indicated temperatures. The deconvolution of the Au 4f spectra is shown only for the spectra at 100 and 600 K, for clarity. The Ce 3d spectrum for the pristine CeO<sub>x</sub> is also shown, for comparison.

photoelectrons at ~114, ~112, and ~109 eV reported by Mullins et al<sup>44</sup> for Ce(III) oxide.

Our XPS data are in full agreement with the results reported by Tsunekawa et al.53 for monodisperse CeO<sub>2-x</sub> particles produced by a size-fractionation method in emulsion, with the mean particle size ranging between 2.2  $\pm$  0.3 and 3.8  $\pm$  0.6 nm. Also, Wang et al.<sup>50</sup> studied electrodeposited CeO<sub>2</sub> films with the mean crystallite size of 6-10 nm, as measured by X-ray diffraction, and observed a  $Ce^{3+}:Ce^{4+}$  ratio  $\sim 0.2$ . On the other hand, the XP spectra reported by Qiu et al.<sup>54</sup> for nanocrystalline ceria powders of 10-25 nm in average size as determined by electron microscopy were in fact very similar to those of fully oxidized CeO<sub>2</sub>, and only Ar<sup>+</sup> sputtering could produce substantial amounts of Ce<sup>3+</sup> cations on the surface. Therefore, the XPS studies suggest that  $\sim$ 5 nm is probably the particle size below which ceria exhibits a significant degree of reduction. Indeed, recent theoretical calculations of unsupported  $Ce_nO_{2n-x}$ (n = 19, 44, 85) clusters by Loschen et al.<sup>55</sup> showed the formation of Ce<sup>3+</sup> ions on the corner and edge sites, the relative amount of which increases with decreasing particle size.

In the next step, we compare electronic properties of gold deposited onto well-ordered CeO<sub>2</sub>(111) films and silica-supported CeO<sub>x</sub> nanoparticles. Gold deposition on the CeO<sub>2</sub>(111) films at 100 K (not shown) results in the relatively broad Au 4f signal centered at 84.3 eV for the Au 4f<sub>7/2</sub> component (to which we will only refer in the text), which shifts to 84.0 eV (i.e., characteristic for the bulk gold) upon heating to 300 K. Similar results were obtained for gold deposited onto pristine silica films (not shown). The shift to lower BEs upon heating can be assigned to final state effects in small Au particles that undergo sintering at 300 K. Note that Weststrate et al. also observed values between 84.2 and 84.0 eV for gold deposited on CeO<sub>2</sub> films at 300 K.<sup>36</sup>

The XP spectra of Au/nano-CeO<sub>x</sub> substantially differ from those of Au/CeO<sub>2</sub>(111). Figure 5a shows a Au 4f spectrum measured for "as-deposited" gold and a series of those following CO adsorption at 100 K and subsequent heating to the indicated temperatures (in the course of the IRAS studies, see below). At 300 K, the Au  $4f_{7/2}$  peak shifts to 84.6 eV. Heating to 400 and 600 K gradually shifts the peak to 84.4 and 84.3 eV, respectively, which are still remarkably higher than 84.0 eV found for Au/CeO<sub>2</sub>(111) already at 300 K.

A broad Au  $4f_{7/2}$  signal centered at 85.3 eV, observed upon deposition at 100 K, is at about 1 eV higher energies than for Au particles on ceria and silica films. The signal broadening, which is quite symmetric, can in principle be attributed to a broad size distribution of gold species attached to the ceria nanoparticles. Alternatively, one can decompose the Au states by deconvoluting spectra using parameters obtained for a clean gold foil and/or Au nanoparticles formed on CeO<sub>2</sub> films at 300 K as references. The best fit was obtained with the three states, i.e., at 84.0, 85.1, and 86.1 eV for the Au  $4f_{7/2}$  component as shown in Figure 5a, bottom spectrum. Stepwise heating to 600 K leads to an increasing contribution of the metallic state at 84.0 eV (from 18 to 57%) and a simultaneous vanishing of the component at 86.1 eV (from 36 to 4% at 300 K). Meanwhile, the intensity of the  $\sim$ 85 eV component stays relatively constant (46-39%). This indicates that a significant part of the Au species, even annealed to 600 K, exhibits BEs as high as 85 eV, which is  $\sim 1$  eV higher than in gold nanoparticles formed on the CeO<sub>2</sub> films.

In principle, both initial and final state effects can be responsible for the BE shifts observed on small Au clusters. The former includes metal oxidation, charge transfer, reduced metal-metal coordination, etc., while the final state effects are caused by screening and delocalization of the hole formed during the photoionization of the core electrons. It has previously been shown in our group<sup>31,56,57</sup> that metal (Pd, Rh) particles of mean particle size (d) supported on alumina films exhibit a  $d^{-1}$ dependence of the BE shift, thus indicating that the Coulomb energy of the final state is decisive. The slope of the BE vs  $d^{-1}$ curve reflects the efficiency of hole screening by the valence electrons which is in turn higher for the s orbitals.<sup>57</sup> As Rh has a 5s<sup>1</sup>4d<sup>8</sup> electron configuration and Pd has a 4d<sup>10</sup> configuration, the BE shifts for Rh particles are significantly smaller than for Pd of a given particle size (the slopes  $\Delta BE/\Delta(d^{-1})$  are ~10 and  $\sim 5.5 \text{ eV} \times \text{ Å}$  for Pd and Rh, respectively<sup>31</sup>). To the best of our knowledge, the BE(d) relationship for Au is not available, although BE vs Au coverage data were reported in the literature.58 However, one would reasonably expect that screening for Au having a 6s15d10 configuration should even be more efficient than for Rh. The combined STM and XPS results on Au/CeO<sub>2</sub>(111) clearly demonstrate that 3 nm Au particles already show the same value (84.0 eV) as in the Au bulk. Therefore, the BE shifts to 85.3 eV, on average, as observed on Au/nanoceria, would result in the Au particle size below or close to a single atom if we assume the  $d^{-1}$  dependence as for Rh. Therefore, the very high BE values observed for Au are attributed to initial state effects, indicating the formation of positively charged gold species when deposited on nanoceria at 100 K.

This finding basically supports the STM-based conclusion that gold does not form its own particles under the conditions studied, but strongly interacts with ceria nanoparticles. The interaction also manifests itself in the corresponding Ce 3d spectra (Figure 5b), showing that the amount of Ce<sup>4+</sup> in nanoceria decreases upon deposition of Au at 100 K as monitored by the signals at ~917 and ~882 eV (highlighted in Figure 5b). Note that heating to 300 K causes no visible changes, thus suggesting that it is not CO that reduces ceria. The Ce<sup>4+</sup> signals attenuate further after heating to 400 and 600 K. Therefore, the results indicate that gold may reduce ceria nanoparticles at these conditions. This is fully consistent with our analysis of the Au 4f spectra showing significant amounts of oxidized Au species on ceria nanoparticles.



**Figure 6.** Series of IRAS spectra of CO adsorbed at 100 K on 0.1 ML of Au deposited on fully oxidized (left panel) and reduced (right panel)  $CeO_2(111)$  films with increasing CO exposure (a, d). Spectra recorded during slow heating to 300 K are shown in (b, e). The samples were then reexposed to 5 L CO at 100 K, and the resulting spectra are shown in (c, f).

Basically, the same behavior was observed for nanoceria prepared by direct PVD (not shown here). For low amounts of gold deposited at 100 K, the broad peak at 85.2 eV shifted to 84.8 eV upon heating to 300 K. At higher Au coverage, the signal centered at 85.3 eV shifted to 84.5 eV at 300 K. Again, heating to 400 K caused significant reduction of the Ce<sup>4+</sup> state.

**3.3. CO Adsorption: IR Study.** CO adsorption on ceria has been previously studied by Fourier transform IR spectroscopy of CeO<sub>2</sub> powders (see refs 59, 60 and references therein). In most cases, the FTIR studies were performed at room temperature in CO ambient at pressures in the millibar range. For example, Li et al. reported that CeO<sub>2</sub> powders, outgassed at 1000 K for 30 min, showed two absorption bands at 2177 and 2156 cm<sup>-1</sup> for CO stretch vibrations.<sup>59</sup> Those are simultaneously vanishing upon pumping CO out, thus indicating weak adsorption of CO on ceria. The bands were assigned to CO linearly adsorbed on Ce<sup>4+</sup> and Ce<sup>4+</sup> in a more unsaturated coordination state created by severe degassing at 1000 K, respectively. No CO adsorption was observed on the hydroxylated ceria surfaces. The authors also observed that CO partially reduced the ceria even at room temperature.

CO adsorption studies on ceria at low temperatures ( $\sim$ 77 K) followed by evacuation ( $\sim$ 10<sup>-4</sup> mbar) resulted in coveragedependent bands at 2168 and 2157 cm<sup>-1</sup>, as reported by Lavalley and co-workers.<sup>60</sup> Again, the high frequency band was assigned to CO coordinated to Ce<sup>4+</sup>, while the band at 2157 cm<sup>-1</sup> to physisorbed CO interacting with surface OH species.

Our IRAS study of the fully oxidized ceria films and ceria nanoparticles showed essentially no absorption bands upon exposure of 20 L (1 L =  $10^{-6}$  torr s) CO at ~100 K. This is in apparent disagreement to the IR studies on powders cited above. The discrepancy may have different origins. It may come from

the fact that the IRAS experiments involve CO pressures by at least 6 orders of magnitude lower than typically used in the FTIR experiments on powders. In contrast to CO adsorption on metals, where the IR results on real and model systems are basically consistent (e.g., see ref 20 for Au), this issue may be particularly important for the oxide surfaces where the CO sticking coefficient is usually low. In addition, we employed IR spectroscopy in the reflection mode from a metal substrate underneath oxide. Therefore, the so-called metal selection rules must be applied whereby CO molecules parallel to the surface will be not detected in the spectra.<sup>61</sup> Finally, the discrepancy may also stem from the differences in preparation and surface structures of powders and model systems. Indeed, CO adsorption on the  $CeO_2(111)$  surface, which is O-terminated, must be closely related to the atomic structure of the defects such as O-vacancies, the density of which in our thin films is low, as judged by STM and XPS. In addition, surface contaminations on powders may play a role, which is not an issue for the model systems. Therefore, the comparison with results on well-defined model systems in fact aids in a deeper understanding of the assignment of the IR bands on powders. The efficiency of this approach has been recently shown for CO adsorption on MgO surfaces (ref 62 and references therein), where the agreement between powders, single crystals, and thin films was only possible by performing experiments at cryogenic temperatures due to the different populations of the various low-coordinated adsorption sites.

Figure 6 shows IRA spectra following 5 L CO exposure to Au particles supported on  $CeO_2(111)$  films at 100 K. On the fully oxidized film (left panel), the absorption band at 2124 cm<sup>-1</sup> grows in intensity with increasing CO exposure. At saturation CO coverage, this peak apparently "disproportionates" into two

bands, centered at 2130 and 2117  $cm^{-1}$ , probably due to restructuring of the adsorbed CO molecules.

Slow heating to 300 K caused basically the reverse behavior following CO desorption (Figure 6b). Heating to 300 K is accompanied by morphological changes manifested by the BE shifts in XPS (see section 3.2). Indeed, subsequent CO exposure resulted in a single band at 2109 cm<sup>-1</sup> (Figure 6c), which is characteristic of metallic Au surfaces.

The CO IRA spectra for the same amounts of gold deposited on the reduced ceria film (right panel in Figure 6) are very similar to those on the fully oxidized film, except that the intensity ratio between the bands at 2130 and 2117 cm<sup>-1</sup> increased, and a weak shoulder at 2152 cm<sup>-1</sup> emerges at saturation CO coverage. Again, after heating to 300 K and subsequent CO exposure, all bands converge into the one at 2112 cm<sup>-1</sup> (Figure 6f), characteristic of metallic gold.

Regarding the weak signal at  $\sim 2150 \text{ cm}^{-1}$ , this band could in principle be assigned to the partially charged Au<sup> $\delta$ +</sup> species formed upon interaction of the Au single atoms with surface defects at low temperatures, whereby the formation of large Au aggregates is limited by a low diffusivity of Au ad-atoms. However, this feature can also be associated with the gold nucleating in the "holes" in the ceria films not detectable by CO IRAS. (As discussed above, the ceria films may suffer from the film discontinuity arising due to the large misfit with the substrate.) Indeed, the experiments with Au deposited on ceriafree and partially covered Ru surfaces, treated in the same manner as in the preparation of ceria films, revealed a very strong band at 2155 cm<sup>-1</sup>; yet, the origin of this band is unclear. Assuming that a signal intensity is proportional to CO population, the shoulder at 2152 cm<sup>-1</sup> seen in Figure 5d will correspond to  $\sim 5\%$  of the surface area, which can reasonably be assigned to O/Ru open areas in the films. In any case, this band irreversibly disappears after first heating to 300 K.

Thus, the IRAS results combined with XPS and STM data for Au/CeO<sub>2</sub>(111) can be rationalized in terms of small Au clusters at 100 K readily sintering at 300 K, ultimately forming Au metallic nanoparticles. Since the particles formed on the reduced films were, on average, smaller than on the fully oxidized films (see Figure 1), small variations in frequencies for Au metallic particles (2112 vs 2109 cm<sup>-1</sup>) can be attributed to the particle size effect such that smaller particles exhibit higher CO stretching frequencies (see also ref 25).

Gold aggregates into metallic clusters even at  $\sim 10 \text{ K}^{38}$  on pure silica thin films used as a support for ceria nanoparticles. Therefore, at the deposition temperature 100 K used here, one would expect formation of exclusively metallic Au aggregates. Indeed, IRA spectra for 0.1 ML Au deposited at 100 K on silica films showed a single peak at 2113 cm<sup>-1</sup> that shifts to 2109 cm<sup>-1</sup> upon heating to 300 K as a result of Au sintering.

In the next step, we analyze CO adsorption on Au/nano-CeO<sub>x</sub> systems. Figure 7a shows the IRAS results for 10 L of CO adsorbed on 0.15 ML Au deposited at 100 K and stepwise annealed to 600 K. For an as-deposited sample, the broad signal centered at 2124 cm<sup>-1</sup> is observed, which in principle resembles those observed on Au/CeO<sub>2</sub>(111). However, heating to 300 K and CO reexposure at 100 K only slightly shift the peak to the lower frequency (2120 cm<sup>-1</sup>) which is much higher than the  $\sim$ 2110 cm<sup>-1</sup> observed on Au/CeO<sub>2</sub>(111). Heating to 400 and 600 K causes further red-shifting and signal narrowing but cannot reach the values at  $\sim$ 2110 cm<sup>-1</sup> typical for metallic Au. Therefore, it is clear that ceria nanoparticles stabilize gold in nanosized form, i.e., in contrast to extended ceria surfaces where only metallic Au nanoparticles are observed at room temperature.



**Figure 7.** IRA spectra of 20 L CO adsorbed on two 0.15 ML Au/ CeO<sub>x</sub>/SiO<sub>2</sub> samples. The sample (b) possesses 50% more ceria than (a). The samples were heated to the indicated temperature and reexposed to CO at 100 K. All spectra were obtained at 100 K. The spectra are offset for clarity.

Since gold nucleates exclusively on ceria particles, the size of Au clusters at a given amount of Au should depend on the particle density, which can be varied in our experiments by repeating the WAD procedure. As shown in Figure 2, the particle density is increased by  $\sim 30\%$  after depositing 50% more ceria in two sequential WAD steps, without significant change of the mean particle size. Deposition of the same amounts of gold (0.15 ML) onto this support revealed the IR band at 2130 cm<sup>-1</sup> (see Figure 7b), i.e., at higher frequencies than in the previous experiment (2124 cm<sup>-1</sup>), in line with smaller Au species being formed. Surprisingly, heating to 300 K did not cause the band shift, but rather reduction of the peak intensity. Further heating to 400 K reduced intensity even more. Practically no CO was observed in the spectra after CO exposure to the sample heated to 600 K. Either CO does not adsorb on this surface at 100 K or CO is adsorbing parallel to the metal substrate surface and becomes invisible due to the metal selection rules.<sup>61</sup>

Following the above results, that the interaction depends on the relative amounts of gold and ceria, we have increased the amounts of gold by the same 50% (totally to  $\sim$ 0.22 ML) as done previously for ceria. The IRAS results were found to be very similar to that shown in Figure 7a; i.e., no CO uptake reduction was observed upon heating, thus supporting the hypothesis that at low Au coverage Au more strongly interacts with ceria, including possibly being incorporated into the ceria particles. Postcharacterization of the annealed samples by XPS revealed the Au 4f7/2 BEs at 84.5-84.3 eV, which is still significantly higher than in Au nanoparticles (84.0 eV) and, therefore, consistent with the IRAS results. Again, the Ce 3d spectra of Au/nano-CeO<sub>x</sub> revealed reduction of the Ce<sup>4+</sup> states upon heating. It appears that the interaction of Au with nano- $CeO_x$  involves strong charge redistribution in the ceria nanoparticles. However, elaborate theoretical calculations and proper modeling are necessary to validate this hypothesis.

#### 4. Summary

We have performed a comparative study of gold supported on well-ordered CeO<sub>2</sub>(111) thin films and CeO<sub>x</sub> nanoparticles using STM, XPS, and IRAS of CO. On the CeO<sub>2</sub>(111) films, Au nanoparticles are primarily formed at the step edges in addition to those on the terraces via decoration of point defects, the amount of which increases on partially reduced films. Ceria particles, supported on thin silica films, possessed Ce both in the 3+ and 4+ oxidation states as detected by XPS with the former dominating at the low coverage.

Combined XPS and CO IRAS data show that partially charged  $Au^{\delta+}$  species are formed upon deposition at low temperature (~100 K) and at low coverage, most likely due to interaction of gold single atoms with the ceria surface. On CeO<sub>2</sub>(111) films these species readily transform into metallic Au particles upon heating to 300 K. In contrast to extended ceria surfaces, the  $Au^{\delta+}$  species, observed in abundance on the nano-CeO<sub>x</sub> support, are resistant toward sintering at 300 K, but strongly interact with ceria nanoparticles such that Au may even be incorporated into ceria at elevated temperatures. The latter finding may have a strong impact on catalytic properties of gold as suggested by Metiu and co-workers on the basis of theoretical calculations.<sup>63,64</sup>

The results suggest that the interaction of Au with nano- $\text{CeO}_x$  involves strong charge redistribution in the ceria nanoparticles, resulting in positively charged Au species. Thorough theoretical calculations and proper modeling are necessary to validate this hypothesis.

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