

Do Quantum Size Effects Control CO Adsorption on Gold Nanoparticles?*

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Size effects in adsorption and reactivity of supported metal particles have been observed for at least two decades.^[1,2] In recent years, gold nanoparticles have received attention for their extraordinary catalytic activity for reactions such as low temperature CO oxidation.^[3-5] A number of different theories have been advanced to explain this reactivity in terms of special reaction sites created by the metal-support interface.^[3-5] Goodman's group invoked quantum effects to explain a maximum in CO oxidation activity^[6,7] and suggested that particle thickness, in this case two atomic layers, may be the key parameter. Herein, through a combination of scanning tunneling microscopy (STM), temperature programmed desorption (TPD), and infrared reflection absorption spectroscopy (IRAS), we report the first experimental evidence that thin islands of gold in fact have the same CO adsorption behavior as large gold particles and extended gold surfaces. Therefore observed differences in reactivity of gold nanoparticles are proposed to arise from the presence of highly uncoordinated gold atoms.

We have previously found that palladium exhibits two-dimensional (2D) growth on a FeO(111) thin film, forming large monolayer islands,^[8] which display CO adsorption behavior that is different from bulk palladium.^[9] However, we have found in the case of gold that the transition from 2D- to 3D-growth occurs at a very low coverage (≈ 0.1 monolayers).^[10] Therefore, in the present work, we re-examine the situation at these low coverages to determine whether 2D gold structures also show deviations in CO adsorption behavior from the bulk.

For coverage up to 0.1 \AA (effective thickness), gold forms islands of monolayer height (Figure 1 a). The inset in Figure 1 a shows that these monolayer islands are well shaped. At further increasing coverage the nucleation density remains fairly constant and two-layer particles form. Finally, at highest coverage studied ($\approx 2 \text{ \AA}$), Au deposits of up to 7 nm in diameter and 4-5 layers in height are seen (Figure 1 b). Note that unlike many other cases of nucleation and growth on oxide films^[11] the metal particles nucleate on regular sites of the FeO films.^[8] This implies that one may study the role of layer thickness independently of the influence of defects.

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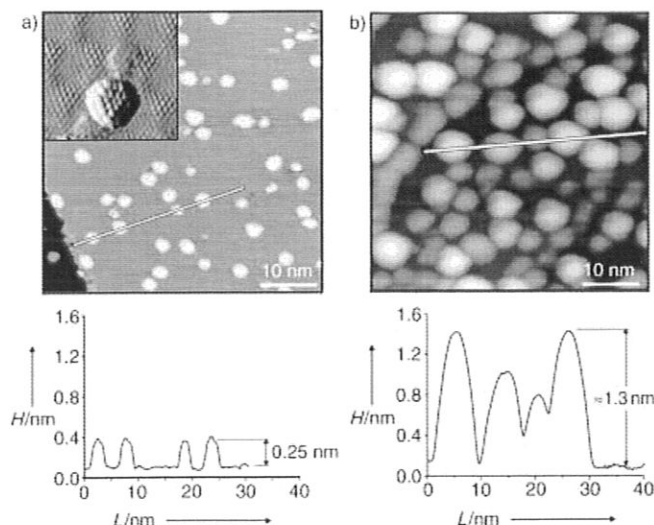


Figure 1. Room temperature STM images of Au deposited on FeO(111) and annealed to 500 K at different Au coverages: a) 0.1 Å, b) 2.0 Å. The line scans below the images clearly show islands of one atomic layer in height (in a) and 3D-particles up to five layers in height (in b). The inset in (a) shows a high-resolution STM image of the individual monolayer island (image size $7 \times 7 \text{ nm}^2$). Tunneling parameters: $V_{\text{tip}} = 200 \text{ mV}$, $J = 0.8 \text{ nA}$.

Although particle size effects in CO adsorption have previously been observed for Au on other oxides,^[10,12] the comparison of TPD spectra (Figure 2a) shows for thin islands of gold and large particles on FeO(111) that the desorption of CO is essentially independent of particle thickness. In all spectra, a low temperature feature at 130 K and a second feature at 200 K are observed, their relative intensities increase with increasing gold coverage.

The presence of two desorption peaks (at 140 and 185 K) in the CO TPD spectra has been observed for highly stepped

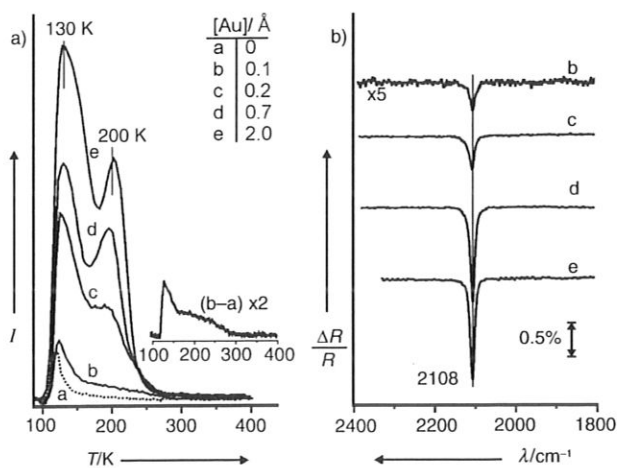


Figure 2. CO TPD (a) and IRAS (b) spectra comparing CO adsorption behavior for gold deposits as a function of Au coverage (in Å) following exposure of 1.5 Langmuir CO at 90 K. As FeO is inert to CO adsorption,^[8,9] a small feature in the TPD detected at approximately 120 K is assigned to desorption from the sample holder. The difference spectrum is shown for the lowest coverage, for clarity.

Au(332) surfaces.^[13] Gottfried et al. observed only a single peak at 140 K for CO chemisorption on Au(110),^[14] a second, higher desorption-temperature feature grew after the surface was roughened by ion bombardment. This suggests that our low temperature feature may be associated with terrace sites while CO desorption at a higher temperature is associated with sites of lower gold coordination, such as the particle edges.

A theoretical examination of the effects of dimensionality, has shown that unsupported gold monolayer islands should not adsorb CO at all.^[15] However, it was noted that strain effects induced by an underlying support could lead to stronger adsorption behavior.^[16,17] When grown on various substrates in an epitaxial manner gold has been found to exhibit both the lattice constant for Au(111)^[18,19] and deformed-lattice constants^[20,21]. Therefore, our observations could also be dependent upon the support. However, it seems unlikely that strain is playing a significant role in the adsorption of CO as the TPD spectra shown in Figure 2a are essentially identical not only to one another but also not significantly different from spectra obtained from CO desorption from single-crystal surfaces Au(332)^[13] and from 3D gold particles on alumina.^[10] In addition, the reactivity in real gold catalysts has been shown to be relatively independent of the support when the particles are properly dispersed.^[3,4,22]

The IRAS spectra comparing CO adsorption states on thin Au layers and large Au particles on FeO(111) reveal only one signal at 2108 cm^{-1} regardless of the Au coverage (Figure 2b). Again, this result matches data previously obtained for "bulk" single-crystal gold surfaces^[13,23,24] and large 3D particles.^[25] However, particle size effects have been observed for varying gold coverages on alumina^[25,26] and titania^[12] which show red and blue shifts, respectively, of the CO signal as particle size is decreased. Although these shifts were only of the order of 10 cm^{-1} , for a system that is as notoriously insensitive as CO on Au, this represents evidence that the small particles supported on these supports may undergo changes in electronic structure as their size changes. As this is not the case for the monolayer islands observed here, one can conclude that issues of quantum confinement are not likely to be the determining factor.

To determine the origin of the two separate peaks in the TPD spectra (see Figure 2a), CO was dosed at 90 K on a sample with monolayer gold islands (0.1 Å coverage) which was subsequently examined by IRAS following heating to various temperatures (Figure 3). A thermal flash to 150 K revealed that the IRAS signal at 2108 cm^{-1} is not significantly reduced, although all CO from the low-temperature state of the TPD experiment must practically be desorbed. We continue to observe measurable IRAS intensity all the way up to 200 K with a slight blue shift of the band to 2115 cm^{-1} . As similar behavior was observed for larger gold particles (not shown), we assign the single IRAS peak observed (see Figure 2b) to the high-temperature desorption state (185 K) in TPD spectra (Figure 2a). This suggests that the quite intense desorption signal below 150 K in the TPD spectra for annealed samples is from CO molecules with no or low IRAS intensity.

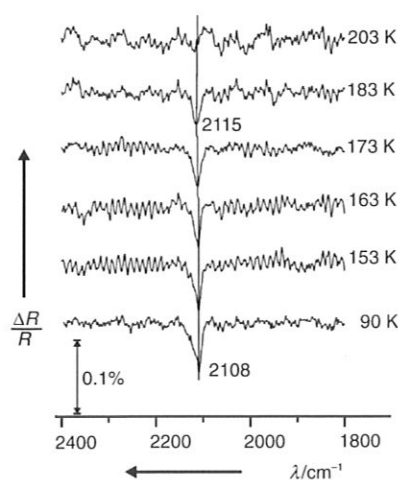


Figure 3. IRAS spectra for monolayer islands formed by deposition of 0.1 Å of gold. The sample was exposed to 1.5 Langmuir CO at 90 K and then heated to the listed temperature. All measurements were made at 90 K.

According to selection rules applied in an IRAS experiment,^[27] only vibrations having a dipole moment perpendicular to the surface are excited. Therefore, it is probable that the low-temperature desorption state is due to CO weakly adsorbed parallel to the gold surface. This conclusion is supported by the observations of Dumas et al., whereby saturation of the IRAS signal at 2110 cm^{-1} was found at a CO coverage of 0.25 monolayers on a rough gold film. The appearance of signals for physisorbed CO was not seen until 0.6 monolayers, thereby suggesting adsorption of CO in this intermediate coverage regime occurred in a non-IR sensitive configuration.^[24] Recent UV photoemission spectroscopy measurements of CO on Au(110) suggest that the majority of the chemisorbed CO may indeed be lying parallel to the surface.^[14] The blue shift of the CO IR signal at increasing temperature (or decreasing CO coverage) is atypical of CO adsorption on other metal surfaces such as Pt or Pd.^[28,29] However, this trend has been observed on other gold surfaces^[13,25] and is generally attributed to the lack of back-donation of electrons from the metal to CO.^[30]

Our data indicates that earlier hypotheses surrounding unusual adsorption/reaction properties of gold particles of particular thickness^[6,7] are not valid for CO adsorption. It is possible to come to this conclusion because the gold particles nucleate on regular lattice sites of the FeO(111) film, unlike gold on other oxide surfaces, such as TiO₂, where gold exhibits a strong preference for defects.^[31,32] Therefore, the influence of defects on the electronic structure of the particles may be excluded.

One could attribute the size effects observed to the interaction of such thin islands with oxygen. Campbell and co-workers^[33] have reported that monolayer gold particles adsorb atomic oxygen with up to 40% higher binding energies than larger particles. However, as no detailed structural characterization of the particles was made, conclusions tied only to particle thickness are difficult.

From theoretical studies, the presence of highly uncoordinated gold atoms has been proposed to effect the strength

of the adsorption of CO and oxygen,^[15,34] and this has been demonstrated for the adsorption of CO on gold step and edge sites by using high resolution electron energy loss spectroscopy (HREELS) in an examination of Au films on Pd(111).^[35,36] A single adsorption state at approximately 2120 cm^{-1} and the adsorption intensity could be correlated with the film deposition temperature and therefore the film roughness. That the desorption state extended to 300 K for CO from "as deposited" gold particles on an FeO(111) film^[10] implies that in the process of annealing to 500 K, the highly uncoordinated atoms that are responsible for the presence of this high-temperature state are lost owing to sintering and restructuring effects. In turn, this indicates that the presence of defects in the substrate (which are absent in our system) may determine the reactivity and adsorption properties of gold, perhaps by stabilizing particles with a larger number of low-coordinated atoms.

In summary, using CO as a probe molecule we have found that monolayer islands of gold do not, in fact, have different adsorption properties to bulk gold. The exceptional activity of gold nanoparticles for the low-temperature CO oxidation reaction probably does not arise from quantum size effects as a result of particle thickness, but rather the presence of highly uncoordinated atoms.

Experimental Section

The work was performed in two separate ultrahigh vacuum (UHV) chambers (base pressure below 2×10^{-10} mbar) which were both equipped with differentially pumped quadrupole mass spectrometers (Hiden Analytical) for TPD measurements. The TPD spectra could be used for comparing and combining the STM structural data (measured in the first chamber) and spectroscopic (IRAS) data (measured in the second chamber).

Thin FeO(111) films were prepared on a Pt(111) single crystal by literature methods.^[37-40] Gas exposures were performed with a directional doser. Gold was evaporatively deposited on the FeO film with a rate of ca. 0.1 Å min^{-1} (effective thickness) as calibrated by a quartz microbalance. A retarding potential was applied to the sample to avoid any sputtering caused by acceleration of the metal ions towards the sample. The Au coverage was measured in nominal thickness (in Å). For each measurement an Au/FeO sample, a new film was grown. After deposition of gold, the sample was heated to 500 K to thermally stabilize the system for TPD experiments. For CO desorption measurements, the sample was cooled to about 90 K, placed about 0.5 mm in front of the spectrometer shield (6 mm aperture) and heated with a rate of 5 K s^{-1} . IRAS data (Mattson RS-1 FTIR, spectral resolution 2 cm^{-1}) presented are transmission spectra in which the ratio of the signal with and without CO is given. All measurements were performed at 90 K. Exposure of the sample to CO did not result in any CO₂ formation and therefore there was no reduction of the oxide support. TPD and IRAS measurements could be repeated many times, which indicates that the surface did not undergo any changes.

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