

Cryogenic CO Oxidation on TiO₂-Supported Gold Nanoclusters Precovered with Atomic Oxygen

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Bulk gold has long been regarded as a “noble” metal, having very low chemical and catalytic activity.^{1,2} However, largely through the work of Haruta and co-workers, metal oxide-supported gold particles, particularly those that are less than 5 nm in diameter, have been found to have remarkable catalytic properties.³ In recent years, gold clusters supported on titania (Au/TiO₂) have been shown to be very active catalysts for selective oxidation of propene, nitrogen oxide reduction, and relatively low-temperature CO oxidation.^{3,4} However, a microscopic understanding of these reactions on Au/TiO₂ has yet to be attained, as the effect of gold particle size and details regarding the reaction mechanism remain unresolved.

In this study we show that impinging gas-phase CO molecules react readily with oxygen adatoms (O_a) preadsorbed on Au/TiO₂-(110) planar model catalysts to produce CO₂ under ultrahigh-vacuum conditions in which the sample is cryogenically cooled. On hydrated Au/TiO₂ powder catalysts prepared by the deposition–precipitation method followed by calcination, Boccuzzi et al. have shown that with preadsorption of CO on the catalyst the reaction with molecular O₂ will produce CO₂ at 90 K, whereas with molecular oxygen preadsorption, the reaction is completely inhibited.⁵ To focus on the reactivity of oxygen adatoms, and since the dissociation probability of molecular oxygen on our samples is immeasurably low, we expose the surface to an atomic oxygen source to populate the surface with oxygen adatoms. Bondzie et al. have previously shown that CO is oxidized rapidly on the oxygen adatom precovered Au/TiO₂ model catalyst surface at room temperature.⁶ Here we extend their results to sample temperatures as low as 65 K and also investigate the effects of gold cluster size and oxygen adatom coverage on the CO oxidation reaction.

The experiments were conducted in a molecular beam surface scattering apparatus consisting of an ultrahigh-vacuum scattering chamber⁷ equipped with an Auger electron spectrometer, low-energy electron diffraction optics, quadrupole mass spectrometer (QMS), quartz crystal microbalance (QCM), and a custom-built metal doser which is used for vapor-depositing gold on TiO₂. The TiO₂(110) crystal is mounted on a tantalum plate that can be resistively heated and is in thermal contact with a liquid nitrogen bath. A type K thermocouple is spot-welded to the backside of the tantalum plate to monitor the temperature of the sample.

Gold nanoclusters are deposited on TiO₂ at 300 K by carefully following a procedure published by Lai et al.,⁸ who have shown via scanning tunneling microscopy that the size of gold nanoclusters grown on TiO₂ can be controlled by varying the amount of vapor-deposited gold. In this study, the quantity of gold deposited, reported in monolayers (ML), is determined by using the QCM. Here, 1 ML of gold refers to a single atomic layer of close-packed gold (1.387 × 10¹⁵ atoms/cm²), which has a thickness of approximately 2.35 Å. A supersonic beam of oxygen atoms produced from a radio frequency (RF)-generated plasma source^{9,10} is directed at the surface

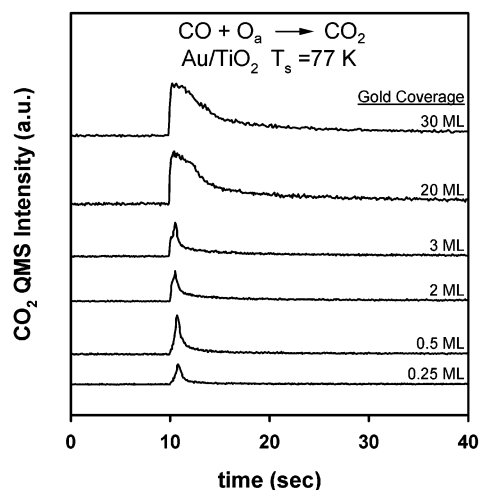


Figure 1. Evolution of CO₂ from various amounts of gold on TiO₂ at 77 K. For all samples oxygen atoms were preadsorbed prior to impinging a continuous CO beam (starts at $t = 10$ s.) on the surface.

to preadsorb oxygen adatoms. Although we see immeasurable adsorption of molecular oxygen from exposure to an O₂ molecular beam, the RF plasma jet source may generate some excited oxygen molecules, which could have an enhanced molecular adsorption probability. To check that the surface was exclusively precovered with oxygen adatoms after exposure to the RF plasma jet source, the sample was heated to 400 K, a temperature well below the associative desorption peak temperature (~600 K, heating rate = 5 K/s) for atomic oxygen on the Au/TiO₂ surface, to induce either dissociation or desorption of any molecularly adsorbed oxygen species: this annealing process did not change the reactivity of the surface. Finally, a continuous molecular beam of pure carbon monoxide (flux ≈ 9 × 10¹³ molecules/cm²·s) is impinged upon the surface immediately after oxygen atom adsorption (without annealing) to study the reaction of CO with oxygen adatoms on the various Au/TiO₂ model surfaces.

Figure 1 shows a series of experiments, performed in the manner described above, for gold coverages ranging from 0.25 to 30 ML.¹¹ As shown in Figure 1, CO oxidation occurs even at a temperature of 77 K when the carbon monoxide beam impinges on the oxygen precovered Au/TiO₂(110) surface. Similar results, not shown here, have been obtained with sample temperatures as low as 65 K. These model catalyst samples were precovered with a comparable percentage (50–70% of saturation coverage) of oxygen adatoms prior to directing the carbon monoxide beam at the Au/TiO₂ surface.¹¹ Carbon monoxide molecules adsorb on the surface and react with oxygen adatoms to produce CO₂, which then promptly desorbs from the surface. Apparently, atomic oxygen is bound weakly enough on gold such that an adsorbed CO can abstract an O atom with a very small activation barrier.¹² Blank experiments

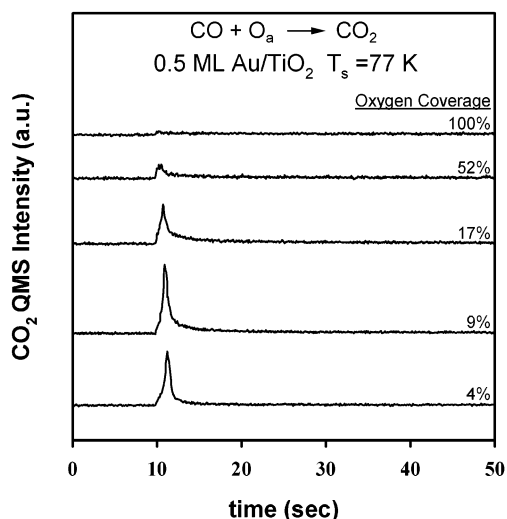


Figure 2. Evolution of CO₂ from a 0.5 ML of gold on TiO₂ with different oxygen atom coverages at 77 K. For all samples oxygen atoms were preadsorbed prior to impinging a continuous CO beam (starts at $t = 10$ s) on the surface.

employing an inert flag that can be placed in front of the sample verify that the CO₂ production is directly related to CO impinging on the Au/TiO₂ surface. In our experiments, carbon dioxide is produced only if gold has been deposited on the TiO₂(110) surface and oxygen adatoms are preadsorbed on the model catalyst sample.

Although the surfaces with more gold (i.e., 20 and 30 ML) produce more CO₂ as seen from the integrated area of the CO₂ signal, this is likely because most of the surface is covered by gold, hence more oxygen atoms adsorbed on gold are available for reaction with CO. Nevertheless, rapid CO₂ production is clearly seen on all surfaces with different particle sizes, including the surfaces nominally covered by continuous gold films (20 and 30 ML). While Valden et al., in their studies of CO oxidation employing *molecular oxygen*, report a strong size effect in which a maximum in activity was observed at an average gold particle diameter of 3.5 nm followed by a drastic drop in activity for average particle sizes larger than 6 nm,¹³ we see little change in CO₂ production from *atomically adsorbed oxygen* with different particle sizes. As noted by Bondzie et al.⁶ regarding CO oxidation employing gaseous *molecular oxygen*, our findings support the notion that if reactive oxygen is supplied mainly through dissociation of oxygen molecules on the surface, the rate-limiting step in CO oxidation over gold is likely the dissociation of molecular oxygen, and the particle size effect seen by Haruta, Goodman, and co-workers^{3,13} may be due to this elementary step.

Figure 2 shows CO₂ production as a function of oxygen coverage with 0.5 ML (~3.1 nm diameter on average)⁸ of gold on TiO₂ at 77 K. As more atomic oxygen is preadsorbed, above a coverage of ~10% relative to saturation, less CO₂ is produced with a continuous

CO beam of the same intensity. The CO uptake by the surface also decreases as the oxygen coverage increases from 4% relative coverage to saturation coverage, thus explaining some of the decrease in CO₂ production seen with higher oxygen coverages. It may be that when the oxygen coverage is relatively high, there are fewer sites for CO to adsorb upon, thus resulting in less CO₂ production or that oxygen adatoms change the electronic properties of the gold particles so that CO adsorption and reaction is hindered.

We note that even though CO₂ production drastically drops after approximately 3–5 s of exposure to the CO beam, there is still a considerable amount of oxygen remaining on the sample (as determined from desorption measurements). Also, the reaction probability of an adsorbed CO molecule to convert to carbon dioxide is only on the order of ~5%. Why the remaining oxygen is not reacting more rapidly with adsorbed or impinging CO molecules is not currently understood and remains a subject of further investigation. It is possible that the remaining unreactive oxygen atoms are in the bulk of the gold particle or on surface sites that are not particularly reactive at 77 K.

In conclusion, we have shown that CO reacts readily with preadsorbed oxygen atoms on a Au/TiO₂ planar model catalyst to produce CO₂ even at temperatures as low as 65 K. Gold particle size seems to have little effect on the CO oxidation reaction when oxygen adatoms are preadsorbed. We have also shown that as the oxygen adatom coverage increases, the rate of CO oxidation decreases on Au/TiO₂ at cryogenic temperatures.

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