

CO Oxidation on Au_n/TiO₂ Catalysts Produced by Size-Selected Cluster Deposition

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Since the discovery that supported gold nanoparticles show surprising catalytic activity,¹ considerable effort has gone into probing the effects of particle size. For bulk catalysts, peak activity is typically found for particle sizes in the 2–5 nm range (hundreds to thousands of atoms), as measured by transmission electron microscopy (TEM). TEM is insensitive to particles smaller than ~1 nm and may overlook smaller active species. Indeed, Fu et al.² recently showed that activity for the water gas shift reaction on Au/CeO₂ and Pt/CeO₂ catalysts was unchanged when the nanoparticles were removed, leaving only ionic metal species on the surface. There have been a number of planar model catalyst studies where Au particles are grown on single crystal or thin film oxide, with size characterized by STM.^{3–5} CO oxidation on Au/rutile TiO₂ (110) has been particularly well studied, and activities typically are found to peak for Au_n in the few nanometer size range. Such experiments allow detailed probing of physical and chemical properties for nanometer size particles, but are not as well suited to studying particles in the subnanometer range. Heiz and co-workers⁶ used deposition of size-selected cluster cations to study CO oxidation on Au_n/MgO, observing significant reactivity for clusters as small as Au₈. Here, we present a study of room-temperature CO oxidation on planar model Au_n/TiO₂ catalysts prepared by deposition of size-selected Au_n⁺, *n* = 1, 2, 3, 4, 7. Activity is strongly dependent on deposited cluster size, with substantial activity for Au_n as small as three atoms.

The instrument and procedures used for the deposition studies have been described previously.^{7,8} In brief, Au_n⁺ samples are prepared by laser vaporization of gold into a helium flow, which then expands into vacuum. Ions are collected by a quadrupole ion guide, mass selected, and then deposited onto TiO₂ in an ultrahigh vacuum (UHV-base pressure ≈ 1 × 10⁻¹⁰ mbar). The kinetic energy spread of the Au_n⁺ beam is less than 1 eV, and clusters were deposited at an energy of 1 eV/atom. All samples had 1.39 × 10¹⁴ Au atoms/cm² (~0.1 of a monolayer) deposited as clusters, except for Au₇, where the density was 10 times smaller. Single-crystal rutile TiO₂ (110) was cleaned by 1 keV Ar⁺ sputtering, followed by 850 K annealing in UHV, following a common preparation method for rutile TiO₂.^{5,9} X-ray photoelectron spectroscopy (XPS) of the TiO₂ prior to deposition⁸ is consistent with near-stoichiometric TiO₂ containing 7–8% of oxygen vacancies. (The XPS vacancy estimate was calibrated by a separate water dissociation experiment.) The issue of what sample morphology results from deposition of Au_n⁺ is discussed below. For notational convenience, we will refer to a sample prepared by Au_n⁺ deposition as Au_n/TiO₂. Upon Au_n deposition, XPS indicates that all Au is formally in its zero oxidation state. Ti XPS shows a slight intensity reduction in the spectral range associated with Ti³⁺ centers, suggesting that Au is binding at surface oxygen vacancies. This conclusion is consistent with the results of Wahlström et al. who observe Au_n to bind over oxygen vacancies.³

O₂ has a low sticking probability on TiO₂ and Au/TiO₂, and, for that reason, most model catalyst studies done under UHV conditions

have used atomic oxygen.^{4,10} We used temperature-programmed desorption (TPD) and low-energy ion scattering spectroscopy (ISS) to study binding of O₂ to the catalysts. For low doses of O₂, no significant O₂ thermal desorption is observed in the 300–800 K range. After a 600 L dose of ¹⁸O₂ on Au_n/TiO₂, ISS indicates that ~9% of the top layer O atoms originated from the ¹⁸O₂ dose. ISS does not address the nature of the ¹⁸O₂ binding; however, XPS suggests that the ¹⁸O₂ binds at oxygen vacancies. Studies using temperature-dependent O₂ adsorption/TPD⁹ and STM¹¹ indicate that 300 K O₂ adsorption leads to dissociation. DFT calculations indicate several stable O and O₂ binding arrangements in association with vacancies.¹²

In the work of Bondzie et al.,¹⁰ atomic O was found to bind to nanometer size Au particles on Au/TiO₂ model catalysts, as shown by ~40% attenuation of Au ISS signal following O exposure. ISS signal recovered upon CO dosing, as CO reactively removed O; however, large (>100 L) CO exposures were required. For O₂, we find a 24% percent attenuation of Au ISS signal following a 600 L ¹⁸O₂ dose for all cluster sizes, suggesting that some oxygen is adsorbed on the gold. For subsequent CO exposures of up to ~20 L, we see no recovery in the Au ISS signal, even though some reactive surface oxygen is being removed (see below). The Au ISS recovery seen by Bondzie et al. presumably reflects their much higher CO dose.

The effect on the ISS spectra of CO exposure by itself was also studied. For Au and Au₂, 5 L (~1.2 ML) CO exposure results in a ~20% attenuation of the Au signal. If CO adsorbed efficiently atop Au, much larger Au signal attenuation would result.⁸ The implication is either that only a fraction of the Au sites are occupied by CO, or that CO binds to Au, but not directly on top. The behavior for Au₃ is quite different. No attenuation of Au ISS signal is observed, but there is a ~5% attenuation of the O and Ti signals. The absence of Au ISS attenuation indicates that CO does not bind atop Au for Au₃ deposits, at least on the 5 min time scale of the experiment. The Ti and O attenuation indicates that CO is blocking scattering from the substrate, either by binding at the Au–substrate interface or at TiO₂ vacancies. The former interpretation is supported by the fact that we do not see similar Ti and O attenuations for CO on clean TiO₂ at room temperature.

To study CO oxidation, we used a pulse dosing technique similar to that recently described by Judai et al.¹³ 600 L of ¹⁸O₂ is pre-dosed onto the model catalysts at room temperature, and then the O₂ is shut off. Subsequently, C¹⁶O is admitted through a pulsed valve/dosing tube, calibrated to deliver ~0.2 L (0.05 ML) pulses to the surface, with a width of ~150 ms. C¹⁶O, C¹⁸O, and C¹⁶O¹⁸O leaving the surface are measured by a mass spectrometer collimated to collect only species desorbing from the cluster-containing spot on the surface. The CO dose magnitude is calibrated by desorption from Ni(100).¹⁴

Figure 1 shows C¹⁶O¹⁸O intensities versus time from reaction on clean TiO₂, and TiO₂ with 0.1 ML of Au deposited as Au_n⁺, *n*

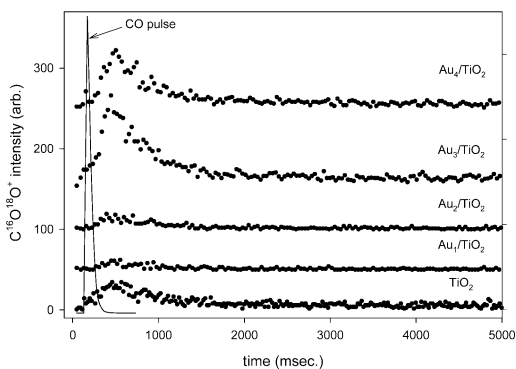


Figure 1. CO₂ evolution following 0.2 L CO pulse on Au_n/TiO₂.

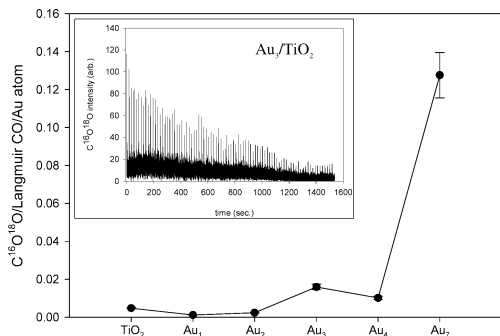


Figure 2. Size dependence of CO oxidation activity. Inset: Effects of 100 CO pulses on Au₃/TiO₂.

= 1–4. No signal is seen for C¹⁸O, indicating that CO does not dissociate on the surface. Note that there is some CO oxidation even from clean TiO₂, reflecting the presence of reactive oxygen species on the surface. When Au or Au₂ are deposited, the reactivity is strong. XPS suggests that Au binds at vacancy sites, and ISS indicates that they bind CO. These Au species do not catalyze CO oxidation themselves, however, and block CO oxidation that would otherwise occur on clean TiO₂. When Au₃ and Au₄ are deposited, however, CO oxidation activity is substantially greater than on clean TiO₂; that is, gold clusters as small as the trimer form surface structures that catalyze CO oxidation. Figure 2 summarizes the C¹⁶O¹⁸O production activity for Au_n, $n = 1-4,7$. Activity is given as C¹⁶O¹⁸O molecules produced per Langmuir CO per deposited Au atom. The uncertainty in comparing samples is estimated to be about 20%, with absolute uncertainty of a factor of 3, because of collection efficiency and mass spectrometer sensitivity considerations. Clearly, activity is strongly dependent on deposited cluster size, presumably because both electronic and geometric structures are size-dependent. The inset to Figure 2 shows the decay in C¹⁶O¹⁸O production during a series of 100 CO pulses (0.2 L each), following a 600 L ¹⁸O₂ exposure. The signal recovers to nearly its original intensity if the surface is redosed with ¹⁸O₂, indicating that the decay is mostly attributable to depletion of reactive surface oxygen.

Another interesting point is the time dependence of CO₂ evolution (Figure 1). The CO₂ rise time is ~300 ms, and CO₂ continues to evolve for about 1 s. Slow CO₂ evolution might reflect diffusion kinetics of the reactive surface oxygen or CO/Au_n reactants. In that case, one might expect slower CO₂ evolution at the end of the 100 CO pulses, as the reactant pool is depleted. No change is observed. Slow CO₂ evolution might simply reflect desorption kinetics;

however, we note that CO₂ desorbs from Au(111) and oxygen-covered Au below 120 K,¹⁵ and from mixed Au–TiO₂ films below ~250 K.¹⁶ CO₂ evolution might be controlled by reaction kinetics or by desorption of the CO reactant. The ISS results are interesting in this regard. CO is observed to bind stably to atop Au for the nonreactive Au and Au₂ samples, but not for the reactive samples prepared with Au₃ and larger clusters. The inactivity of Au or Au₂ samples may reflect too-strong CO–Au binding.

None of our results directly address the question of what happens to the gold clusters upon deposition. A few points are clear. CO binding and oxidation activity are strongly dependent on deposited cluster size. The Au surface structures formed are stable enough to give constant CO oxidation behavior over several cycles of O₂ exposure followed by 100 CO pulses. The implication is that the samples do not reach an equilibrium state, which would depend only on Au concentration, not Au_n⁺ size. This result is interesting in light of STM data from Wahlström et al.,³ who evaporated Au atoms onto TiO₂ (110) in varying doses and at varying temperatures and determined the average Au cluster size that formed. Extrapolation of their results suggests that we should see an average cluster size of tens of atoms, indicative of extensive diffusion and sintering. Such sintering is clearly inconsistent with the strong dependence of reactivity on deposited cluster size. The most obvious differences between our experiment and theirs are as follows: We deposit preformed clusters, rather than atoms. Our impact energy (1 eV/atom) is well above the thermal energies in their experiment. We deposit cations, rather than neutrals. We might expect preformed clusters to diffuse and sinter differently than atoms, because clusters are inherently more stable. It is not clear, however, why deposition of Au⁺ does not appear to grow a distribution of large (and therefore reactive) clusters. Here, and perhaps also for the larger Au_n⁺, the higher impact energy, and energy available from neutralization, must result in reduced tendency to diffuse and sinter. Presumably, the stabilization comes from defects created by the impact process.

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