

Reaction of CO with Molecularly Chemisorbed Oxygen on TiO₂-Supported Gold Nanoclusters

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The chemistry of supported gold catalysts^{1,2} has proven to be complex, and details regarding a reaction as superficially simple as CO oxidation are still not fully understood. One important issue that remains unresolved is the identity of the active oxygen species involved in the reaction. It is well-known that bulk gold will not readily dissociate oxygen,^{3–5} yet atomic oxygen species adsorbed on gold surfaces have been observed to be highly reactive toward CO.^{3–9} It has been speculated that the unique catalytic behavior of gold nanoclusters is related to their reduced dimensionality resulting in properties suitable for the dissociation of oxygen.^{6,10} However, this picture is in contrast with (i) results from theory that show oxygen dissociation on any gold system, including small gold clusters, is highly activated (activation energies ~ 1 eV)^{11–14} and (ii) null experimental results regarding the dissociation of oxygen on gold systems.^{3–6,8}

Interestingly, some density functional theory (DFT) calculations indicate that molecularly chemisorbed oxygen is stable on strained gold surfaces and steps, as well as on small gold clusters,^{11–15} and ultraviolet photoemission spectroscopy measurements have indicated that small, gas-phase gold clusters, Au_{*n*} (*n* = 2–20), will adsorb oxygen molecularly.^{16,17} Gas-phase gold clusters that are known to adsorb oxygen molecularly have also provided experimental evidence for oxidation of CO,¹⁸ and DFT calculations regarding the reaction of CO with molecularly chemisorbed oxygen on gold have predicted that the reaction is relatively facile.^{10,15,19,20} Liu et al. have calculated that molecularly chemisorbed oxygen at the Au–TiO₂ interface will readily react with CO to form CO₂.¹⁹ Molina et al. have also presented similar results showing that CO will react with molecularly chemisorbed oxygen at the Au–TiO₂ interface with an activation barrier of 0.15 eV.²⁰ Lopez and Nørskov report calculations that show that molecular oxygen adsorbed on a 10 atom gold cluster is as reactive as atomically adsorbed oxygen for CO oxidation.¹⁰ Sanchez et al. have also presented DFT results in which they determine that CO will react spontaneously with molecularly chemisorbed oxygen on Au₈ clusters supported on MgO.¹⁵

As of yet, no conclusive experimental evidence has been presented regarding the reactivity of molecularly chemisorbed oxygen on extended gold surfaces or on supported gold clusters larger than ~ 20 atoms. Previously, we showed that exposing a Au/TiO₂ model catalyst sample to a radio frequency (RF)-generated plasma-jet resulted in the population of molecularly chemisorbed oxygen (O_{2,a}) on the sample along with atomically adsorbed oxygen (O_a).²¹ In this paper we present results from an investigation of the reactivity of O_{2,a} on an oxygen-covered Au/TiO₂ model catalyst. We observe that samples that are populated with both O_a and O_{2,a} consistently result in greater CO₂ production than samples populated with an equivalent O_a coverage but without O_{2,a}. For the data presented in this paper, we observe a 41% difference in CO₂

production between a sample populated with only O_a and one populated with both O_a and O_{2,a}.

The experiments were performed in an ultrahigh-vacuum molecular beam surface scattering apparatus that has been described in detail previously.^{9,21,22} The sample assembly consists of Au(111) and TiO₂(110) single crystals that are mounted on opposite faces of a tantalum plate that is in thermal contact with a liquid nitrogen reservoir and that can be resistively heated. Gold is vapor-deposited on the TiO₂(110) sample as described previously.^{9,21} Mixtures of 8% oxygen in Ar are dosed via a supersonic, RF-generated plasma-jet source with a dissociation fraction of $\sim 40\%$ as determined via time-of-flight.²³ All oxygen coverages reported on Au/TiO₂ are defined as the coverage relative to saturation and are determined by integration of the recombinative thermal desorption spectra of oxygen from the Au particles. Energetic beams of Kr (~ 1 eV) and Ar (~ 0.5 eV), formed by supersonic expansion in a 98% He mixture, are used for the collision-induced desorption (CID) experiments.^{21,24,25} The same apertures are used for defining beams of C¹⁶O, Kr, and the oxygen-plasma-jet, and the spot size produced is smaller than the crystal faces, thus minimizing direct exposure to surfaces other than the sample.

In our previous study,²¹ we noted that the ratio of O_{2,a} adsorbed on the sample during the plasma exposure to the O_a on the sample is relatively small ($\sim 10\%$ for 2 ML [monolayers] Au/TiO₂). For the experiments presented in this paper, it was desirable to increase this ratio to facilitate measurement of the reactivity of O_{2,a}. A procedure utilizing isotopically labeled oxygen was devised: (i) the sample (*T_s* = 77 K) was exposed to a plasma-jet formed using ¹⁶O₂ to a coverage of $\sim 50\%$; (ii) the sample was heated to 300 K to desorb ¹⁶O_{2,a}; and after cooling to 77 K, (iii) the ¹⁶O_a-covered sample was exposed to a plasma-jet formed using ¹⁸O₂ (exposure equivalent to $\sim 25\%$ coverage on a clean 1 ML Au/TiO₂ sample). By preadsorbing ¹⁶O_a on the sample, we could limit the available sites for ¹⁸O_a adsorption and thus increase the ratio of ¹⁸O_{2,a} to ¹⁸O_a on the sample. For the 1 ML Au/TiO₂ sample discussed here the ratio was increased from ~ 0.34 to ~ 0.75 . We observe some formation of mass 34 species (¹⁶O¹⁸O) on the sample, but the quantity formed is small compared to the amount of mass 36 (¹⁸O_{2,a}) species and its effect on the measurement of the reactivity of molecularly chemisorbed oxygen is immeasurable.

Following the preparation of the oxygen-covered sample described above, two separate experiments were performed to determine if ¹⁸O_{2,a} reacted with C¹⁶O. One experiment required the removal of ¹⁸O_{2,a} via CID, followed by a C¹⁶O exposure to measure the amount of C¹⁶O¹⁸O produced from reaction of C¹⁶O with ¹⁸O_a. The second experiment consisted of exposing the oxygen-covered sample to C¹⁶O to determine the quantity of C¹⁶O¹⁸O produced from reaction with both ¹⁸O_a and ¹⁸O_{2,a}. A difference in the C¹⁶O¹⁸O produced during the two experiments could be associated with the

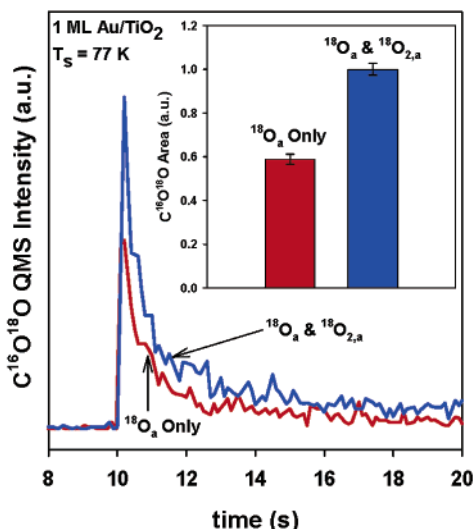


Figure 1. $C^{16}O^{18}O$ production at 77 K from a 1 ML Au/TiO₂ sample populated with both $^{18}O_a$ and $^{18}O_{2,a}$ (blue curve) and $^{18}O_a$ only (red curve) upon exposure to a pure CO beam at 10 s. Inset shows average values and uncertainties of $C^{16}O^{18}O$ produced from a series of three identical measurements such as the ones shown.

presence of $^{18}O_{2,a}$ since both surfaces are populated with the same initial amount of $^{18}O_a$.

Figure 1 shows the mass 46 ($C^{16}O^{18}O$) produced during experiments representative of both CO oxidation scenarios discussed above. The upper blue curve in Figure 1 shows the mass 46 production from the sample with both $^{18}O_a$ and $^{18}O_{2,a}$ species present on the sample, and the lower red curve shows the mass 46 production from a surface that has been cleared of $^{18}O_{2,a}$ via CID. Both reactions show behavior typical of the CO oxidation reaction with preadsorbed oxygen atoms reported previously.^{8,9} However, comparison of the two $C^{16}O^{18}O$ production curves in Figure 1 shows that the sample with both of the oxygen species present on the sample results in more $C^{16}O^{18}O$ production (average values and uncertainties from three identical experiments are shown in the inset). On average, a difference of $41 \pm 2\%$ in the $C^{16}O^{18}O$ production is observed between the two samples. Similar results have been obtained on a 2 ML Au covered TiO₂ surface ($\sim 18\%$ difference). It should be noted that no mass 48 species is observed evolving from the sample, indicating that the original $C^{16}O$ bond remains intact.

In principle, the difference in the $C^{16}O^{18}O$ production shown above cannot be totally ascribed to reaction of $C^{16}O$ with $^{18}O_{2,a}$. When $^{18}O_{2,a}$ reacts with $C^{16}O$, the $^{18}O_a$ remaining could also react to make $C^{16}O^{18}O$. However, a large accumulation of additional $^{18}O_a$ on the sample reduces the reactivity of the sample in this O_a coverage regime, as shown previously.⁸

A key assumption in the interpretation of our experimental results is that Kr CID does not affect the reactivity of the atomic oxygen overlayer. To verify the validity of this assumption, we repeated the experiments shown in Figure 1 using energetic Ar (~ 0.5 eV) for CID measurements. Results essentially identical to those presented in Figure 1 were obtained.

To further address the effect of Kr CID on the reactivity of O_a , an experiment was performed on $^{16}O_a$ -covered Au/TiO₂ in which the sample was (i) exposed to the plasma-jet at 77 K and (ii) heated to 170 K to desorb $^{16}O_{2,a}$, and after the sample cooled to 77 K, (iii) Kr CID was performed (as expected, no CID of $^{16}O_{2,a}$ was observed) and (iv) the CO₂ production was measured. For comparison, a similar experiment was conducted, with the exception that step iii was not performed. The difference in the CO₂ production between

these two experiments was found to be negligible ($<3\%$), further verifying that Kr CID does not alter the reactivity of the atomic oxygen overlayer. Similar results are observed on Au(111).

Finally, in all the experiments used for the data in Figure 1, the mass 44 ($C^{16}O_2$) produced was the same (within $\sim 5\%$), again suggesting that Kr CID does not measurably affect the reactivity of the preadsorbed, annealed ^{16}O atoms.

A determination of the reaction probability of the $O_{2,a}$ on the sample is difficult since both the TiO₂ and Au clusters are populated with $O_{2,a}$ as discussed in our previous publication.²¹ However, considering its smaller population relative to the O_a species, it appears that $O_{2,a}$ is at least comparable in reactivity to the O_a on the sample.

In conclusion, we have investigated the CO oxidation reaction on a Au/TiO₂ model catalyst populated with both O_a and $O_{2,a}$ and compared it to the reactivity of a Au/TiO₂ model catalyst sample populated with only O_a . We observe that samples populated with both oxygen species consistently result in more CO₂ production than samples with only O_a . We observe a difference of $41 \pm 2\%$ in the CO₂ production from samples with both oxygen species compared to samples with just atomic oxygen. We interpret this result as evidence that molecularly chemisorbed oxygen can directly participate in the CO oxidation reaction on Au/TiO₂ model catalyst systems with particles in the 2–5 nm size range, revealing a reaction channel that does not require the dissociation of oxygen.

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