Evidence for Molecularly Chemisorbed Oxygen on TiO$_2$ Supported Gold Nanoclusters and Au(111)

James D. Stiehl, Tae S. Kim, Sean M. McClure, and C. Buddie Mullins*

Department of Chemical Engineering, The University of Texas at Austin, Center for Nano- and Molecular Science and Technology, and Texas Materials Institute, 1 University Station CO400, Austin, Texas 78712-0231

Received October 24, 2003; E-mail: mullins@che.utexas.edu

It is well documented from experiment that O$_2$ does not readily chemisorb on gold single crystals[1−3] or titania supported gold clusters larger than ∼1 nm[4] either dissociatively or molecularly. Additionally, and consistent with experiment, density functional theory (DFT) calculations suggest that the barrier to dissociative chemisorption of oxygen on gold is very high and also that molecularly chemisorbed oxygen is not stable on clean Au(111).[5,6] However, some DFT calculations indicate that molecularly chemisorbed oxygen is stable on strained gold surfaces and steps, as well as on small gold clusters.[5−9] Indeed, ultraviolet photoemission spectroscopy measurements have indicated that small gas-phase gold clusters, Au$_n$ ($n = 2−20$), will adsorb molecular oxygen.[10,11] The nature of chemisorbed oxygen on gold, either atomically or molecularly adsorbed, is important in elucidating the unique chemistry that has been observed over supported gold catalysts in the 1−5 nm diameter range (such as the oxidation of carbon monoxide).[12] It is known from experiment that atomically adsorbed oxygen will readily oxidize CO,[4,13] and DFT calculations regarding gold clusters suggest that molecularly chemisorbed oxygen is stable and oxidizes CO with virtually no activation barrier.[7,9] However, no conclusive experimental evidence has been presented regarding the existence, stability, or reactivity of molecularly chemisorbed oxygen on extended gold surfaces or on supported gold clusters larger than ∼20 atoms. Herein, we present evidence from thermal desorption (TDS), adsorption/reaction-induced desorption, and collision-induced desorption (CID) spectra, indicating the presence of molecularly chemisorbed oxygen (O$_{2,a}$) on both gold clusters supported on TiO$_2$(110) as well as on Au(111), after exposure to an oxygen plasma-jet molecular beam.

The experiments were performed in an ultrahigh vacuum molecular beam surface scattering apparatus that has been described in detail previously.[14] The sample assembly consists of Au(111) and TiO$_2$(110) single crystals which 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. Titania supported Au nanoclusters are created by vapor deposition of gold on the TiO$_2$-(110) sample.[13] Oxygen is dosed via a supersonic, radio frequency generated plasma-jet source with a dissociation fraction of ∼40% as determined via time-of-flight.[19] A 60% relative oxygen coverage is used in all of the experiments reported for the 2 ML Au/TiO$_2$ sample, and the experiments reported on the Au(111) single crystal were given an equivalent oxygen exposure (∼1.3 ML). A high kinetic energy beam of Kr (∼1 eV), formed by supersonic expansion of a 2% Kr in He mixture, is used for the CID experiments.[15] The same apertures are used for defining beams of CO, Kr, and the O-plasma-jet, and the spot size produced is much smaller than the crystal faces to minimize exposure of these gases to surfaces other than the sample.

Figure 1a shows the TDS obtained immediately after exposing the 2 ML Au/TiO$_2$ sample, held at 77 K, to the oxygen plasma-jet
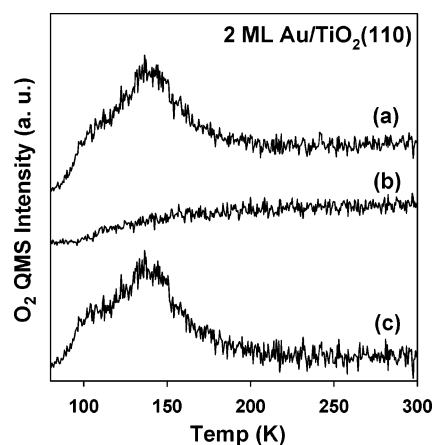

Figure 1. TDS from a 2 ML Au/TiO$_2$ sample (a) following exposure to the oxygen plasma-jet, (b) following exposure to the plasma-jet and then CID of O$_{2,a}$, and (c) difference spectra of (a) and (b).

source. A low-temperature desorption feature indicative of molecularly chemisorbed oxygen is evident in the spectrum. Figure 1b shows a TDS taken after the same oxygen exposure as in Figure 1a but with removal of the O$_{2,a}$ via CID (as discussed later). The TDS feature observed in Figure 1b is significantly decreased in intensity as compared to Figure 1a. Figure 1c shows the difference spectrum of the two TDS and clearly reveals a desorption peak at ∼145 K, which, assuming first-order desorption, corresponds to a binding energy of approximately 0.35 eV. This peak desorption temperature is comparable to that measured in O$_{2,a}$ desorption from Pt(111) (150 K)[16] and Ag(110) (190 K).[17] The quantity of O$_{2,a}$ is only ∼10% of the amount of O$_2$ that desorbs as a result of recombinative desorption of O atoms from the 2 ML Au/TiO$_2$ surface.

Figure 2 shows a series of experiments that further suggest the existence of an O$_{2,a}$ species on the samples following exposure to the plasma-jet. Figure 2a shows a CID measurement of an oxygen covered 2 ML Au/TiO$_2$ sample. At time $t = 10$ s, the Kr beam was directed at the sample and a prompt increase in the mass 32 quadrupole mass spectrometer (QMS) signal is observed, followed by a decay to the background level. Either (i) O$_{2,a}$ is desorbed upon impingement of the Kr beam, or (ii) two oxygen adatoms recombine and desorb due to the Kr−surface collision. Evidence for the former mechanism is depicted in Figure 2b, which shows the results of a CID measurement following (i) exposure of the sample to the plasma-jet followed by (ii) heating the sample to 300 K prior to (iii) impingement of the Kr beam. Note that a mass 32 signal is not observed in Figure 2b, indicating that heating to 300 K, a temperature ∼300 K below the recombinative thermal desorption temperature of O$_a$ from gold, was sufficient to remove the O$_{2,a}$. Finally, further support for CID of O$_{2,a}$ and not recombination of O adatoms was obtained by re-exposing the sample to the Kr beam
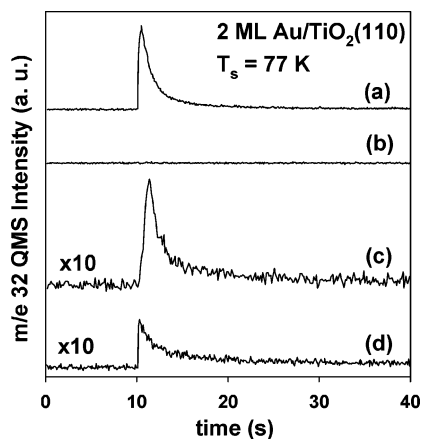
Figure 2. O_2 evolution at 77 K (a) from CID from a 2 ML Au/TiO$_2$ sample after exposure to O$_2$ plasma-jet, (b) from CID from a 2 ML Au/TiO$_2$ sample after exposure to O$_2$ plasma-jet and heating to 300 K, (c) during impingement of a CO beam on an oxygen covered 2 ML Au/TiO$_2$ sample, and (d) from CID from Au(111) following exposure to plasma-jet.

following the experiment shown in Figure 2(a): no further CID of a mass 32 species is observed. Additionally, we note that TDS measurements in the 300−700 K range reveal that the O$_a$ population is unchanged, within experimental uncertainty, by CID of O$_{2,a}$. Also, the quantity of O$_{2,a}$ observed during CID is consistent with the amount seen in low-temperature TDS, within the experimental uncertainties. CID of O$_{2,a}$ has been observed previously in a study on Pt(111).[15]

Figure 2c shows the mass 32 signal detected while dosing CO (CO beam impinges on sample at $t = 10$ s) on an oxygen covered 2 ML Au/TiO$_2$ surface. Interestingly, a small amount of mass 32 evolves from the surface upon impingement of CO. Apparently, the heat of adsorption of CO and/or the heat of reaction of CO with adsorbed oxygen is sufficient to induce desorption of weakly bound di-oxygen. No mass 32 signal is observed in similar experiments if either (i) Kr CID or (ii) annealing of the sample to ∼300 K is performed to remove O$_{2,a}$ prior to CO beam impingement. Adsorption/reaction-induced desorption of O$_{2,a}$ is also observed on Au(111) (not shown) when impinging a CO beam on the oxygen plasma-jet exposed Au(111) surface. We note that adsorption-induced desorption of O$_{2,a}$ has been observed on Pt-(111) previously.[18,19]

Oxygen is known to adsorb molecularly on TiO$_2$,[20] and impingement of Kr on the oxygen plasma-jet dosed, Au-free TiO$_2$(110) surface results in CID of O$_{2,a}$. Thus, it is important to determine if any of the oxygen evolving during the CID measurement on the Au/TiO$_2$ sample shown in Figure 2a is associated with Au clusters. Although the time-integrated quantity of O$_{2,a}$ on the bare TiO$_2$ sample is ∼30% greater than that from a 2 ML Au/TiO$_2$ sample for equivalent exposures of oxygen, 2 ML of Au is expected to cover ∼70% of the TiO$_2$(110) crystal (based on STM data from Lai et al.[21]), strongly suggesting that some of the O$_{2,a}$ is associated with gold clusters. Low-temperature TDS of O$_{2,a}$ from gold-free TiO$_2$ as compared to 2 ML Au/TiO$_2$ shows behavior similar to that just discussed regarding the CID measurements. Further proof of O$_{2,a}$ being associated with gold is evidence for adsorption/reaction-induced desorption of O$_{2,a}$ from Au(111) as mentioned previously.

CID of di-oxygen is also observed from the Au(111) single crystal upon impingement by energetic Kr as shown in Figure 2d. The amount of mass 32 species that evolves from the Au(111) single crystal in CID is much smaller than that from the 2 ML Au/TiO$_2$ sample for equivalent plasma jet exposures. Perhaps O$_{2,a}$ adsorbs much more readily on the Au particles than on the Au(111) surface due to an increased concentration of low coordination sites as compared to Au(111).[5,6]

Attempts to populate O$_{2,a}$ on the Au/TiO$_2$ sample without using the plasma-jet were unsuccessful. A 2 ML Au/TiO$_2$ sample was exposed to 100 L (1 L $= 1 \times 10^{-6}$ Torr s) of O$_2$ at a surface temperature of 77 K, and O$_{2,a}$ was undetectable in CID experiments (as was O$_a$). Additionally, the 2 ML Au/TiO$_2$ sample was (i) exposed to the plasma-jet of oxygen followed by (ii) heating to 300 K to desorb any O$_{2,a}$ and then (iii) exposed to 100 L of oxygen followed by (iv) CID in an attempt to determine if preadsorbed oxygen adatoms would enhance adsorption and/or stabilize O$_{2,a}$. This experiment also resulted in no detectable O$_{2,a}$.

Finally, the mechanisms for formation of O$_{2,a}$ on either sample upon exposure to the plasma-jet oxygen source are not currently well understood and are the subject of ongoing investigation.

In conclusion, we have shown evidence for the presence of O$_{2,a}$ on Au(111) and on Au clusters supported on a TiO$_2$(110) surface following exposure of these samples to a plasma-jet source of oxygen. We have detected and identified O$_{2,a}$ from thermal desorption spectra, collision-induced desorption spectra, and heat of adsorption/reaction-induced desorption spectra.

References
(1) Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 351.
(2) Parker, D. H.; Koel, B. E. *J. Vac. Sci. Technol., A* **1990**, *8*, 2585.
(3) Gottfried, J. M.; Schmidt, K. J.; Schroeder, S. L. M.; Christmann, K. *Surf. Sci.* **2002**, *511*, 65.
(4) Bondzie, V. A.; Parker, S. C.; Campbell, C. T. *Catal. Lett.* **1999**, *63*, 143.
(5) Xu, Y.; Mavrakakis, M. *J. Phys. Chem. B* **2003**, *107*, 9298.
(6) Mills, G.; Gordon, M. S.; Metiu, H. *J. Chem. Phys.* **2003**, *118*, 4198.
(7) Lopez, N.; Nørskov, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 11262.
(8) Liu, Zhi-Pan; Hu, P.; Alavi, A. *J. Am. Chem. Soc.* **2002**, *124*, 14770.
(9) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W.-D.; Häkkinen, H.; Barnett, R. N.; Landman, U. *J. Phys. Chem. A* **1999**, *103*, 9573.
(10) Stolcic, D.; Fischer, M.; Ganterför, G.; Kim, Y. D.; Sun, Q.; Jena, P. *J. Am. Chem. Soc.* **2003**, *125*, 2848.
(11) Kim, Y. D.; Fischer, M.; Ganterför, G. *Chem. Phys. Lett.* **2003**, *377*, 170.
(12) Haruta, M. *Catal. Today* **1997**, *36*, 153; *CATTECH* **2002**, *6*, 102.
(13) Kim, T. S.; Stiehl, J. D.; Reeves, C. T.; Meyer, R. J.; Mullins, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 2018.
(14) Wheeler, M. C.; Seets, D. C.; Mullins, C. B. *J. Chem. Phys.* **1996**, *105*, 1572.
(15) Åkerlund, C.; Zorić, I.; Kasemo, B. *J. Chem. Phys.* **1996**, *104*, 7359.
(16) Gland, J. *Surf. Sci.* **1980**, *93*, 487.
(17) Barteau, M. A.; Madix, R. J. In *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodriff, D. P., Eds.; Elsevier: Amsterdam, 1982; Vol. 4, Chapter 4.
(18) Rettner, C. T.; Lee, J. J. *J. Chem. Phys.* **1994**, *101*, 10185.
(19) Wheeler, M. C.; Seets, D. C.; Mullins, C. B. *J. Chem. Phys.* **1997**, *107*, 1672.
(20) Henderson, M. A.; Epling, W. S.; Perkins, C. L.; Peden, C. H. F.; Diebold, U. *J. Phys. Chem. B* **1999**, *103*, 5328.
(21) Lai, X.; St. Clair, T. P.; Valden, M.; Goodman, D. W. *Prog. Surf. Sci.* **1998**, *59*, 25.

JA039214H