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Communication

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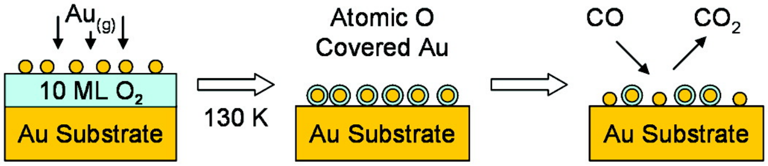

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Cryogenic CO_2 Formation on Oxidized Gold Clusters Synthesized via Reactive Layer Assisted Deposition

Jooho Kim, Zdenek Dohnálek, and Bruce D. Kay*

Chemical Sciences Division, Fundamental Science Directorate, Pacific Northwest National Laboratory,
PO Box 999, Mail Stop K8-88, Richland, Washington 99352

Received August 22, 2005; E-mail: Bruce.Kay@pnl.gov

The catalytic chemistry of gold is a topic of great current interest.[1−8] Specifically, supported gold clusters have been shown to catalyze the oxidation of CO to CO_2 at low temperature.[6,7] It is believed that the rate-limiting step in this reaction is the dissociative chemisorption of molecular oxygen.[3] Recent studies employing an atomic oxygen beam to oxidize Au have shown that CO_2 formation can occur at temperatures as low as 65 K.[6] In this Communication, we report studies where gas-phase Au atoms are deposited onto a multilayer film of molecular oxygen and demonstrate that this technique produces oxidized gold clusters. This method of producing oxidized gold clusters is an extension of our earlier work synthesizing MgO nanostructures using a technique termed Reactive Layer Assisted Deposition (RLAD).[9−11] Employing a combination of temperature programmed desorption (TPD) and molecular beam techniques, we show that the oxidized gold clusters readily react with CO to produce CO_2 at temperatures as low as 35 K.

Experiments were conducted in a molecular beam-surface scattering apparatus described elsewhere.[9] Key elements of this instrument include capabilities for cryogenic (<30 K) thin film synthesis, TPD, X-ray photoelectron spectroscopy (XPS), and effusive beam atomic gold deposition monitored via a quartz crystal microbalance (QCM). In these studies, a thick gold film deposited on a Mo(100) single crystal is used as a substrate to deposit multilayers of O_2 and atomic Au.[9] The substrate is resistively heated, and its temperature is measured using a W-5% Re/W-26% Re thermocouple. Additionally, a thermal CO beam is used to study the reactivity of the oxidized gold deposits.

Figure 1A, traces (a) and (b), display O 1s XPS spectra for molecularly physisorbed and atomic chemisorbed oxygen on the underlying gold substrate, respectively. Trace (a) is obtained after deposition of 10 monolayers (ML) of O_2 at 22 K. The observed feature at 537.0 eV corresponds to molecular oxygen. Trace (b) shows the XPS spectrum taken after heating the film displayed in trace (a) to 130 K. Noticeable are the absence of the molecular state (537.0 eV) and the appearance of the atomic state (529.0 eV). The atomic state is due to an X-ray induced dissociation of molecular oxygen. Control experiments (not shown) indicate that an identical O_2 multilayer film heated to 130 K prior to X-ray irradiation exhibits no detectable oxygen, thereby demonstrating that the atomic state is X-ray induced. The radiation induced dissociation of oxygen on gold has been extensively studied and is discussed in detail elsewhere.[12] Trace (c) displays the XPS spectrum for a 10 ML O_2 film exposed to 1 ML of atomic gold at 22 K and subsequently heated to 130 K prior to acquiring the XPS spectrum. The XPS spectrum (c) clearly indicates the presence of atomic oxygen and conclusively demonstrates that the 1 ML of gold deposited on top of the O_2 multilayer leads to O_2 dissociation.

The dissociation of O_2 is further confirmed by TPD. Figure 1B(d) displays the O_2 TPD spectrum from 10 ML of physisorbed O_2 on the gold substrate, that is, no atomic Au deposited on O_2. This spectrum exhibits two peaks corresponding to desorption of multilayer (35 K) and monolayer (45 K) molecular oxygen. The absence of O_2 desorption at high temperature (~500 K) indicates that O_2 does not dissociate on the Au substrate. Figure 1B(e) displays the O_2 TPD spectrum from 1 ML of Au deposited onto 10 ML of physisorbed O_2. The low temperature multilayer and molecular monolayer portion of the TPD spectrum is omitted for clarity. The high temperature region exhibits an atomic oxygen recombinative desorption peak at 510 K. The presence of this peak and the XPS spectrum displayed in Figure 1A(c) clearly demonstrate that the deposition of atomic Au dissociates O_2.

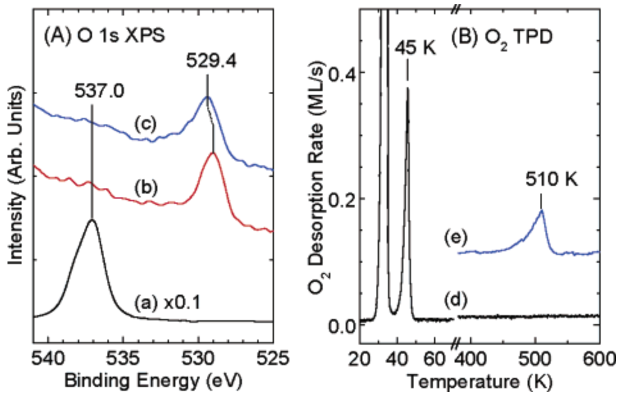

Figure 1. (A) O 1s X-ray photoelectron spectra from (a) a 10 ML thick O_2 film deposited on the Au substrate at 22 K; (b) a 10 ML thick O_2 film exposed to the X-rays to acquire XPS spectrum (a) followed by annealing to 130 K to remove molecularly bound O_2, and leave atomic O; (c) 1 ML of atomic Au deposited on 10 ML of O_2 at 22 K and annealed to 130 K. All the XPS spectra were acquired at 22 K. (B) O_2 temperature programmed desorption spectra from (d) a 10 ML thick O_2 film deposited on the Au substrate, and (e) 1 ML of atomic Au deposited on 10 ML of O_2 at 22 K. Low (<130 K) and high (>130 K) temperature regions of the TPD spectra are acquired at ramp rates of 0.6 and 3 K/s, respectively. There are no desorption features observed in the temperature range between 70 and 400 K. The coverage of both molecular and atomic oxygen is expressed relative to the area of the 45 K O_2 TPD feature, which we define as 1ML.

Prior studies of mass-selected Au clusters, both in the gas phase[3,13] and supported on the oxide substrates,[4] suggested that a partial negative charge was required to strongly bind O_2 and mediate the CO oxidation reaction. In the experiments presented here, we utilize charge-neutral Au atoms and demonstrate that negatively charged Au is not required to facilitate O_2 dissociation and subsequent CO oxidation.

The reactivity of CO with atomic oxygen bound to gold clusters was examined after depositing 1 ML of Au onto a 10 ML thick O_2 film at 22 K and heating the film to 130 K to desorb any excess unreacted O_2 as well as any molecular oxygen chemisorbed to the gold.[14−17] This sample was again cooled to 22 K, exposed to a 1 ML dose of CO, and heated at a ramp rate of 0.6 K/s. The resulting CO_2 TPD spectrum is displayed in Figure 2A(a). At 35 K, well

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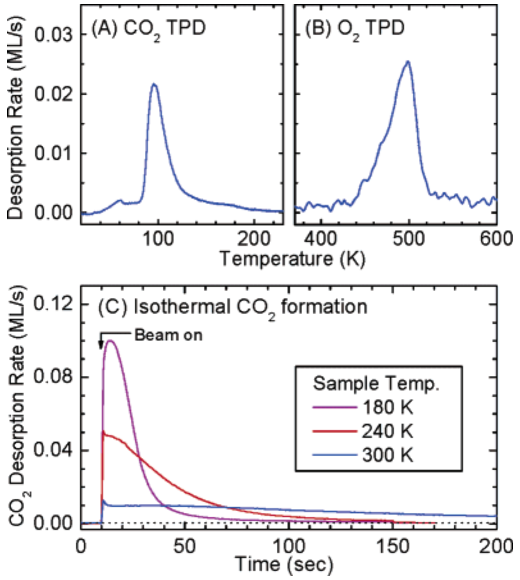

Figure 2. (A) CO$_2$ and (B) O$_2$ temperature programmed desorption spectra after the exposure of the Au clusters covered with atomic oxygen (prepared as in Figure 1A(c)) to 1 ML of CO at 22 K. Low (<300 K) and high (>300 K) temperature regions of the TPD spectra are acquired at ramp rates of 0.6 and 3 K/s, respectively. The CO$_2$ yield in this experiment is ~0.7 ML. (C) CO$_2$ desorption monitored during the exposure of atomic oxygen covered Au clusters to a molecular beam of CO at substrate temperatures of 180, 240, and 300 K. The initial reaction yield is ~50% at 180 K, and the reaction is driven to stoichiometric completion at all three temperatures, yielding 1.9 ML of CO$_2$.

below that observed for desorption of CO$_2$ multilayer (~82 K), a small amount of CO$_2$ is observed. This CO$_2$ probably arises from a small fraction of reaction products which fail to dissipate the reaction exothermicity into and thermally equilibrate with the substrate prior to desorption. There is a dramatic increase in the CO$_2$ desorption above 85 K. Desorption of a monolayer of CO$_2$ adsorbed on the clean gold substrate occurs at ~85 K (not shown), suggesting that below this temperature most of the CO$_2$ produced by CO oxidation should remain adsorbed. The CO$_2$ desorption rate reaches a maximum at ~95 K and decays predominantly by 120 K with reduced yet measurable desorption lingering to ~200 K. Further heating to 600 K results in the recombinative desorption of O$_2$ at ~500 K (Figure 2B), indicating the presence of unreacted atomic oxygen on gold. Quantitative analysis indicates that ~45% of the initial atomic oxygen remains unreacted. Additionally, a significant fraction of the adsorbed CO desorbs (not shown) without undergoing reaction. Repeated CO exposures at 22 K, followed by heating to 200 K (not shown), result in complete removal of atomic oxygen via the formation of CO$_2$.

The reactivity of atomic oxygen with CO can be studied isothermally using molecular beam techniques. In these studies, the clusters are exposed to CO while monitoring the evolution of CO$_2$ mass spectrometrically. Figure 2C displays the observed CO$_2$ production rate for temperatures of 180, 240, and 300 K. The initial CO$_2$ production rate decreases with increasing temperature due to a kinetic competition between CO desorption and reaction.[18] The maximum desorption rate observed at 180 K corresponds to an initial reaction probability of ~0.5, indicating that the oxidation reaction is extremely efficient. For all of these temperatures, the isothermal oxidation reaction runs to completion, resulting in a clean gold surface. In related experiments, the clusters were pre-annealed to 350 K prior to exposure to the CO beam. These experiments (not shown) exhibit the same qualitative dependence on surface temperature, thereby ruling out sintering as the cause of the reduced reactivity observed at higher temperature. Even at 120 K (data not shown), the reaction runs to near completion (~85%) during exposure to the CO beam. The remaining 15% of the CO$_2$ product desorbs upon subsequent heating of the sample. It is not clear whether this remaining CO$_2$ is formed during exposure to the CO beam at 120 K or due to a reaction between adsorbed O and CO during subsequent heating.

In conclusion, we have shown the deposition of atomic, charge-neutral gold onto a multilayer of O$_2$ at 22 K forms atomic oxygen. While the structure and size distribution of these gold−oxygen clusters remain to be determined, they readily catalyze the formation of CO$_2$ at temperatures as low as 35 K. Furthermore, above 120 K, the reaction runs to near completion during exposure to gas-phase CO with initial reaction yields as high as 50%.

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