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Water Activated by Atomic Oxygen on Au(111) to Oxidize CO at Low Temperatures

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Since Haruta's discovery of the exceptional reactivity of gold nanoclusters nearly 20 years ago,[1] there has been an exponential growth in the study of catalytic chemistry on metal oxide-supported small gold particles including low-temperature CO oxidation,[2−8] direct propylene epoxidation,[9−11] and the water gas shift reaction.[12−14] Although 2−5 nm diameter gold nanoparticles exhibit interesting and important catalytic reactivity in many heterogeneous chemical reactions, oftentimes, details regarding the reaction mechanism remain uncertain. Notably, catalytic CO oxidation over gold clusters requires the presence of water to proceed at appreciable rates.[15,16] It has been postulated that water may assist in either activating the molecular oxygen or decomposing carbonates formed on the surface.[16,17] Both hypotheses suggest that water is not directly involved but rather only indirectly promotes the reaction.

Here we show that a Au(111) surface populated with atomic oxygen [^{16}O] and oxygen-labeled water [$H_2{}^{18}O$] produces both $C^{16}O^{16}O$ and $C^{16}O^{18}O$ while impinging $C^{16}O$ at low surface temperatures, indicating the direct involvement of water in CO oxidation with OH as a possible reaction intermediate.

The reaction of CO and OH leading to CO_2 formation is widely studied in gas-phase chemistry due to the pivotal role of OH radicals in atmospheric chemistry.[18,19] There are also several investigations of CO and OH reaction on metal surfaces,[20−22] primarily related to electrochemistry. In an ultrahigh vacuum (UHV) study, Bergeld et al. showed that water can promote CO oxidation on oxygen-covered Pt(111). They showed that when water is coadsorbed prior to a temperature-programmed reaction of a Pt(111) surface populated with CO and oxygen, a previously unobserved CO_2 desorption peak near 200 K appears. This new peak has been attributed to CO reacting with OH groups on the surface.[22] It is possible that a similar reaction occurs on oxygen-covered Au(111) where hydroxyls formed from water splitting are reacting with CO to form CO_2 at low surface temperatures.

The experiments were performed in a molecular-beam surface-scattering chamber that has been described elsewhere[7,23] but is briefly summarized here. The apparatus consists of a UHV scattering/analysis section and a quadruply differentially pumped molecular beam source section. The sample consists of a Au(111) single crystal (11 mm in diameter, 1.5 mm thick) mounted to a tantalum plate that can be resistively heated and is in thermal contact with a liquid nitrogen bath, and the temperature of the surface is monitored with a type K thermocouple. Oxygen atoms were deposited on the surface using a radio frequency (RF) generated plasma source that produced a supersonic beam of ^{16}O atoms from an 8% (vol.) $^{16}O_2$ in Ar gas mixture. All three beams (oxygen, water, and CO) were expanded from the same nozzle through the same apertures to ensure that the beam spots on the gold sample were the same in size and coincident. The beam spot (~3 mm in diameter) was much smaller than the sample size to minimize effects from impinging gas interacting with other surfaces in the chamber. The Au(111) surface was cleaned employing standard methods[7,23] until no appreciable impurity could be detected by Auger electron spectroscopy.

Figure 1 demonstrates how CO can react with water when oxygen adatoms are present to activate the water on Au(111) at 77 K. In Figure 1a, a beam of CO is impinged on a 0.18 ML (1 ML = 1.387×10^{15} (atoms or molecules)/cm^2) atomic oxygen [^{16}O]-covered surface. As can be seen, only mass 44 $C^{16}O_2$ is observed during the CO impingement. In Figure 1b, the CO beam is impinged on Au(111) covered by 0.1 ML of isotopically labeled $H_2{}^{18}O$. Without preadsorbed oxygen, CO_2 is not formed on the surface. In Figure 1c, 0.1 ML of $H_2{}^{18}O$ is dosed over 0.18 ML of atomic oxygen on Au(111), followed by exposure to a CO beam. As can be seen from the data of Figure 1c, in addition to mass 44 $C^{16}O_2$, a small amount (27% of total CO_2 production) of mass 46 $C^{16}O^{18}O$ is observed, indicating that oxygen originating from water is directly involved in CO oxidation at 77 K on Au(111) when atomic oxygen is preadsorbed on the surface. Another notable feature in this quadrupole mass spectrometer (QMS) spectrum regards the rapid CO_2 signal decay, although there is still a considerable amount of surface oxygen remaining on the surface (based on subsequent temperature programmed desorption (TPD)). This is due to unreacted CO covering the surface (verified from TPD), limiting further reaction.

To further explore the details of this reaction, we compare the total amount of CO_2 produced from our Au(111) surface solely covered by oxygen with that of the surface covered with both atomic oxygen and water. As mentioned earlier, not all surface oxygen is consumed when a CO beam is impinged on the surface at 77 K. To avoid accumulation of CO on the surface, we ran the reaction at $T_s = 140$ K, a temperature well below the desorption peak temperature (175 K) of water on oxygen-covered Au(111) but above the desorption peak temperature (108 K) for CO (to avoid limiting the extent of reaction).

In Figure 2a, a CO beam is impinged on Au(111) with 0.08 ML of oxygen at 140 K. The area underneath the curve between 10 and 40 s represents the amount of mass 44 CO_2 produced as shown in the inset. No mass 46 CO_2 is detected in this case. In Figure 2b, a CO beam is impinged on a surface where 0.08 ML of oxygen is initially dosed, followed by the addition of 0.1 ML of $H_2{}^{18}O$. The red curve represents the amount of mass 44 CO_2 production, and the blue curve represents the amount of mass 46 CO_2 [i.e., $C^{16}O^{18}O$] produced during CO impingement. The inset shows the total amount of CO_2 produced for each case in a bar chart, with the red bar representing mass 44 CO_2 and the blue bar representing mass 46 $C^{16}O^{18}O$. As shown, with the same amount of preadsorbed ^{16}O on the surface, 77% more CO_2 production is observed with water added to the surface, similar to what Bergeld et al. have seen on Pt(111).[22]

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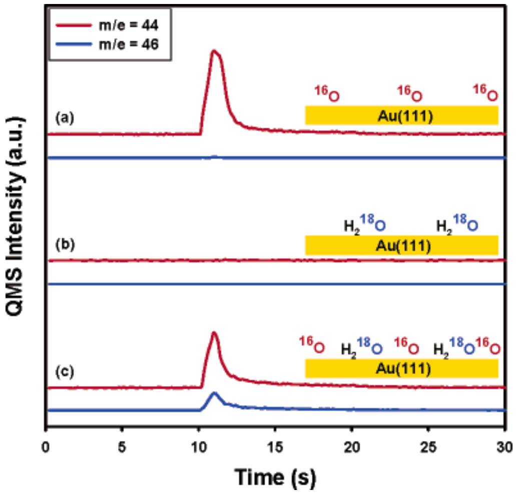

Figure 1. Evolution of CO_2 at 77 K while impinging a continuous CO beam (from 10 to 20 s) at the surface. The red curve represents mass 44 $C^{16}O^{16}O$ and the blue curve represents mass 46 $C^{16}O^{18}O$ with (a) 0.18 ML of ^{16}O atoms preadsorbed, (b) 0.1 ML of $H_2{}^{18}O$ preadsorbed, and (c) 0.1 ML of $H_2{}^{18}O$ in addition to 0.18 ML of ^{16}O atoms preadsorbed on Au(111) at 77 K. We note that all procedures were performed with the surface temperature at 77 K.

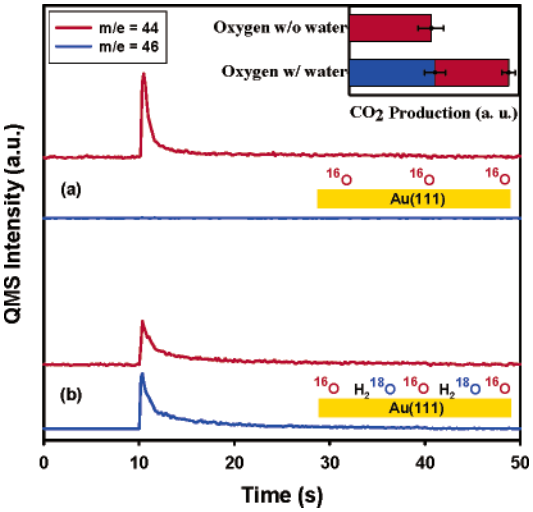

Figure 2. Evolution of CO_2 at 140 K while impinging a continuous CO beam (from 10 to 40 s) at the surface. The red curve represents mass 44 $C^{16}O^{16}O$ and the blue curve represents mass 46 $C^{16}O^{18}O$ with (a) 0.08 ML of ^{16}O preadsorbed and (b) 0.1 ML $H_2{}^{18}O$ in addition to 0.08 ML of ^{16}O atoms preadsorbed on Au(111) at 77 K.

Based on subsequent TPD measurements (not shown), there was no detectable atomic oxygen left on the surface after the CO impingement at 140 K. However a small amount (~0.03 ML) of $H_2{}^{18}O$ and $H_2{}^{16}O$ (produced from oxygen scrambling between ^{16}O and $H_2{}^{18}O$) was observed that was not consumed during the reaction. Once the oxygen atoms that activate water are completely consumed either by directly reacting with CO or reacting with CO as hydroxyls, the remaining water on the surface does not react with CO. This is in agreement with the results shown in Figure 1b in which adsorbed water alone does not oxidize CO. No hydrogen or hydrogen-containing species (other than water) were detected either during the CO impingement phase of the experiment or in subsequent TPD's.

From these results, we speculate that OH groups, formed from water interacting with atomic oxygen on Au(111), participate in oxidizing CO to produce CO_2 on the surface. We have shown that oxygen from adsorbed water will scramble with preadsorbed oxygen atoms on Au(111) and that it is very likely that some water will form hydroxyl on the surface during this oxygen scrambling.[24] This hydroxyl may be responsible for the mass 46 $C^{16}O^{18}O$ observed here. If the mass 46 CO_2 was solely from CO reacting with atomic oxygen (resulting from disproportionation of OH), we would expect to see an equal amount of CO_2 production compared to the surface reaction without water because there would still be approximately the same amount of atomic oxygen on the surface (even if hydrogen atoms from water molecules moved from ^{18}O to ^{16}O). But we clearly see an increase in the total amount of CO_2 produced, indicating that water is activated by atomic oxygen on the surface to take part in the CO oxidation at surface temperatures as low as 77 K.

In conclusion, we observe involvement of water in oxidizing impinging CO on oxygen atom-precovered Au(111) at low temperatures. CO_2 production was greatly increased with the addition of water on the same oxygen precoverage, and we interpret these results as being due to CO reacting directly with activated water or OH groups formed from water interacting with atomic oxygen on Au(111).

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References

(1) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405.
(2) Lin, S. D.; Bollinger, M.; Vannice, M. A. *Catal. Lett.* **1993**, *17*, 245.
(3) Tsubota, S.; Cunningham, D. A. H.; Bando, Y.; Haruta, M. *Stud. Surf. Sci. Catal.* **1995**, *91*, 227.
(4) Epling, W. S.; Hoflund, G. B.; Weaver, J. F.; Tsubota, S.; Haruta, M. *J. Phys. Chem.* **1996**, *100*, 9929.
(5) Schumacher, B.; Plzak, V.; Kinne, M.; Behm, R. J. *Catal. Lett.* **2003**, *89*, 109.
(6) Daniells, S. T.; Makkee, M.; Moulijn, J. A. *Catal. Lett.* **2005**, *100*, 39.
(7) Kim, T. S.; Stiehl, J. D.; Reeves, C. T.; Meyer, R. J.; Mullins, C. B. *J. Am. Chem. Soc.* **2003**, *125*, 2018.
(8) Stiehl, J. D.; Kim, T. S.; McClure, S. M.; Mullins, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 13574.
(9) Stangland, E. E.; Stavens, K. B.; Andres, R. P.; Delgass, W. N. *J. Catal.* **2000**, *191*, 332.
(10) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566.
(11) Mul, G.; Zwijnenburg, A.; van der Linden, B.; Makkee, M.; Moulijn, J. A. *J. Catal.* **2001**, *201*, 128.
(12) Liu, Z.-P.; Jenkins S. J.; King D. A. *Phys. Rev. Lett.* **2005**, *94*, 196102.
(13) Andreeva, D.; Idakiev, V.; Tabakova, T.; Ilieva, L.; Falaras, P.; Bourlinos, A.; Travlos, A. *Catal. Today* **2002**, *72*, 51.
(14) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. *Science* **2003**, *301*, 935.
(15) Date, M.; Haruta, M. *J. Catal.* **2001**, *201*, 221.
(16) Date, M.; Okumura, M.; Tsubota, S.; Haruta, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2129.
(17) Boccuzzi, F.; Chiorino, A. *J. Phys. Chem. B* **2000**, *104*, 5414.
(18) Lester, M. I.; Pond, B. V.; Anderson, D. T.; Harding, L. B.; Wagner, A. F. *J. Chem. Phys.* **2000**, *113*, 9889.
(19) Rockmann, T.; Brenninkmeijer, C. A. M.; Sauerssig, G.; Bergamaschi, P.; Crowley, J. N.; Fischer, H.; Cruutzen, P. J. *Science* **1998**, *281*, 544.
(20) Hayden, B. E.; Rendall, M. E.; South, O. *J. Am. Chem. Soc.* **2003**, *125*, 7738.
(21) Lei, T.; Zei, M. S.; Ertl, G. *Surf. Sci.* **2005**, *581*, 142.
(22) Bergeld, J.; Kasemo, B.; Chakarov, D. V. *Surf. Sci.* **2001**, *495*, L815.
(23) Wheeler, M. C.; Seets, D. C.; Mullins, C. B. *J. Chem. Phys.* **1996**, *105*, 1572.
(24) Kim, T. S.; Gong, J.; Ojifinni, R. A.; White, J. M.; Mullins, C. B. In preparation.

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