Gold Catalysis

DOI: 10.1002/anie.201104694

Mechanism and Active Sites of the Oxidation of CO over Au/TiO_2**

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Dedicated to the Fritz Haber Institute, Berlin, on the occasion of its 100th anniversary

Gold nanoparticles supported on titanium oxides are highly active catalysts for the oxidation of CO even at low temperature.[1,2] Despite extensive research to determine the reaction mechanism and the active sites on a molecular scale, there is still no consensus about 1) the the active sites and the mechanism of activation of O_2 molecules and 2) the role of moisture and its influence on the activity of the catalysts.

For instance, although most research groups agree that small Au^0 nanoparticles are the predominant catalytic species,[3–5] other groups have proposed that cationic gold species,[6–8] undercoordinated sites on the gold nanoparticles,[9–11] or electron-rich gold nanoparticles play an essential role in the reaction.[12] Furthermore, dissociation of O_2 has been reported to occur when undercoordinated gold atoms are present on extended gold surfaces under model conditions.[13,14] On the basis of high-intensity in situ X-ray absorption near-edge structure analysis, van Bokhoven and co-workers indicated that O_2 molecules can dissociate on gold nanoparticles supported on Al_2O_3 and TiO_2 substrates.[15] In contrast, Liu et al. calculated that the barrier to dissociation of O_2 on unsupported gold is >2 eV and that even at the Au/TiO_2 interface, the dissociation barrier is still 0.52 eV.[16] These values indicate that O_2 interacts weakly with gold, and thus spontaneous dissociation of O_2 molecules on the gold surface is not energetically favorable. Recently, Behm and co-workers found that the amount of active oxygen species on the Au/TiO_2 surface is linearly related to the number of perimeter sites at the interface between the oxide support and the gold nanoparticles, indicating that the gold-support interface plays a dominant role in O_2 activation.[17]

Furthermore, the oxidation of CO is greatly influenced by moisture in the reactant gas.[18–21] Date et al. proposed on the basis of their research and that of others that moisture has two effects: it activates O_2 molecules, and it decomposes a carbonate species.[20] However, the mechanistic details of the promotional effect of moisture are not fully understood. Here, we describe the reaction mechanism and active sites for the oxidation of CO over Au/TiO_2, along with the role of moisture, on a molecular scale.

First, we investigated the effect of moisture on the oxidation of CO over $Au/TiO_2(110)$ (Figure 1). The gold coverage of all samples was fixed at one monolayer equivalent (MLE). The reaction was carried out at a typical reaction temperature of 300 K and the features for the oxidation of CO appeared remarkably. We used quadrupole mass spectrometry to monitor the CO_2 signal at $m/q = 44$. In the absence of moisture, formation of CO_2 was not observed, indicating that the oxidation of CO did not proceed under these reaction conditions. However, in the presence of H_2O, formation of CO_2 increased linearly with the reaction time. Increasing the H_2O pressure increased the amount of CO_2 formed at H_2O pressures up to 0.1 Torr, but the amount of CO_2 decreased at 0.5 Torr of H_2O.

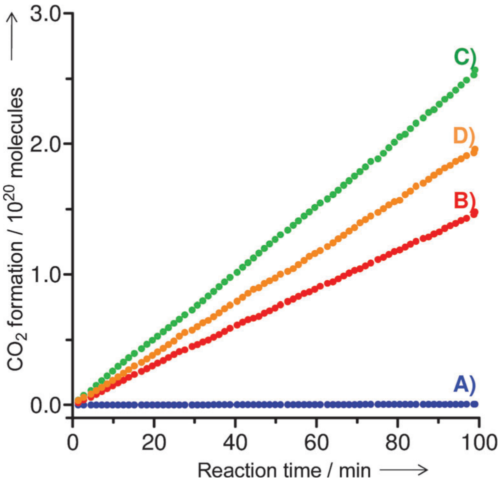

Figure 1. Effect of the H_2O partial pressure on the formation of CO_2 over one MLE of $Au/TiO_2(110)$ at 300 K: A) 0 Torr, B) 0.01 Torr, C) 0.1 Torr, and D) 0.5 Torr. The oxidation of CO was performed in batch mode under 25 Torr of CO and 625 Torr of O_2.

We next examined the relationship between the rate of CO_2 formation (r_{CO_2} as indicated by the slopes of the lines in Figure 1) and the H_2O partial pressure at two reaction temperatures, 300 and 400 K (Figure 2). At 300 K, the rate of CO_2 formation increased significantly with increasing H_2O partial pressure. The rate peaked at 0.1 Torr of H_2O and then gradually decreased with increasing H_2O pressure. In contrast, at 400 K, the oxidation of CO proceeded without moisture, and the rate of CO_2 formation did not depend on the H_2O partial pressure. These results indicate that moisture promoted the oxidation of CO over the $Au/TiO_2(110)$ surface

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[**] We are grateful to Prof. M. Haruta at Tokyo Metropolitan University for his constructive discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104694.

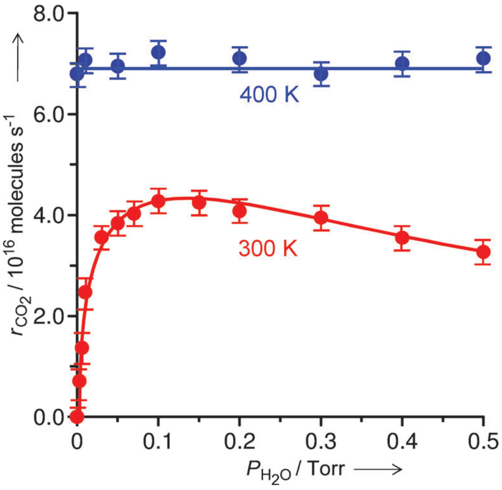

Figure 2. Rate of CO_2 formation (r_{CO_2}) over one MLE of $Au/TiO_2(110)$ as a function of the H_2O partial pressure at 300 (●) and 400 K (●). The oxidation of CO was performed in batch mode under 25 Torr of CO and 625 Torr of O_2.

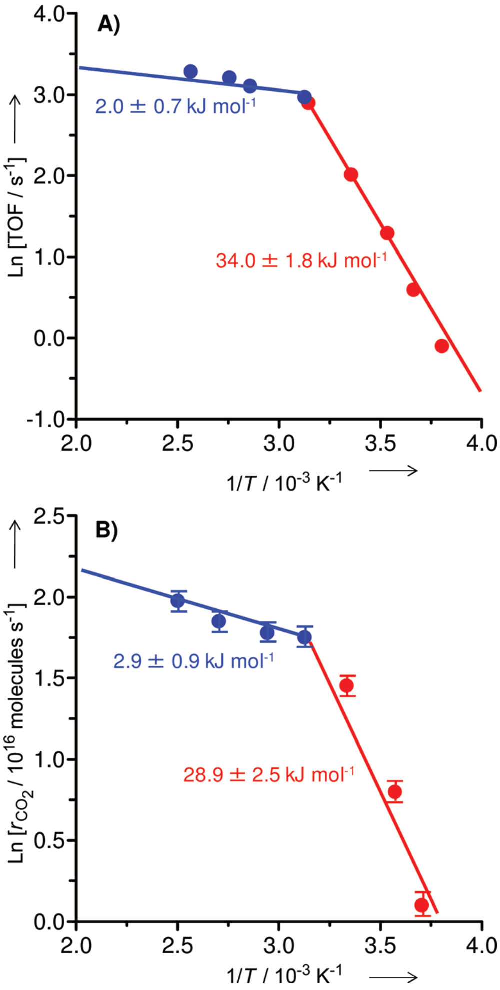

Figure 3. Arrhenius plots for the formation of CO_2 over A) a powdered Au/TiO_2 catalyst[22] and B) one MLE of $Au/TiO_2(110)$. The oxidation of CO was performed in batch mode under 25 Torr of CO, 625 Torr of O_2, and 0.1 Torr of H_2O.

only at low temperatures. This important observation suggests that the mechanisms for the oxidation of CO over $Au/TiO_2(110)$ at 300 and 400 K differed. We propose that the process by which O_2 molecules were activated strongly depends on the reaction temperature. That is, O_2 molecules were activated directly over the $Au/TiO_2(110)$ surface at high temperatures, whereas moisture took part in the activation at low temperatures.

In early studies, Haruta[22] demonstrated that the mechanism for the oxidation of CO over a gold catalyst may depend on the reaction temperature. The apparent activation energy for CO oxidation over powdered Au/TiO_2 changed drastically with the reaction temperature (Figure 3 A): the activation energy was estimated to be (2.0 ± 0.7) kJ mol^{-1} at temperatures above 320 K, whereas the activation energy at temperatures below 320 K was estimated to be (34.0 ± 1.8) kJ mol^{-1}. Here, we examine the temperature dependence of the rate of CO_2 formation over a $Au/TiO_2(110)$ model surface in the presence of H_2O. The Arrhenius plot of the data (Figure 3 B) clearly shows a sudden change in the slope at around 320 K. The apparent activation energies above and below 320 K were estimated to be (2.9 ± 0.9) and (28.9 ± 2.5) kJ mol^{-1}, respectively. These values and the overall dependence on the reaction temperature agreed well with the results obtained for a powdered Au/TiO_2 catalyst, indicating that $Au/TiO_2(110)$ is a good model surface for powdered Au/TiO_2 and that the active sites and the reaction mechanism over the $Au/TiO_2(110)$ surface might change at 320 K.

We previously reported that the diameters of gold particles deposited on a single crystal of TiO_2 can be controlled in the range of 1–10 nm (see Figure S1 in the Supporting Information).[23] Here, we prepared $Au/TiO_2(110)$ surfaces bearing gold particles of different sizes and then measured the rates of CO_2 formation at 300 and 400 K over the surfaces. The rate of CO_2 formation increased with decreasing particle size and increased markedly at particle sizes below 2 nm at both temperatures (see Figure S2 in the Supporting Information).

We examined the turnover frequencies (TOFs) for the formation of CO_2 at the two reaction temperatures as a function of the mean gold particle diameter (Figure 4). To determine whether the active sites for the oxidation of CO were exposed gold atoms on the gold particles or perimeter sites at the interface between the gold particles and the TiO_2 support, we calculated the TOFs in two ways: 1) by normalizing the number of CO_2 molecules formed per second to the total number of exposed Au atoms at the gold particles (TOF-S) and 2) by normalizing the number of CO_2 molecules formed per second to the total number of gold atoms at the perimeter interfaces (TOF-P). The number of gold atoms at the interfaces was estimated from the perimeter length of the particles and the gold interatomic distance (0.288 nm). The results clearly showed that the relationship between TOF and mean gold particle diameter depends strongly on the reaction temperature. At 300 K, TOF-S decreased with increasing mean gold particle diameter, whereas TOF-P remained

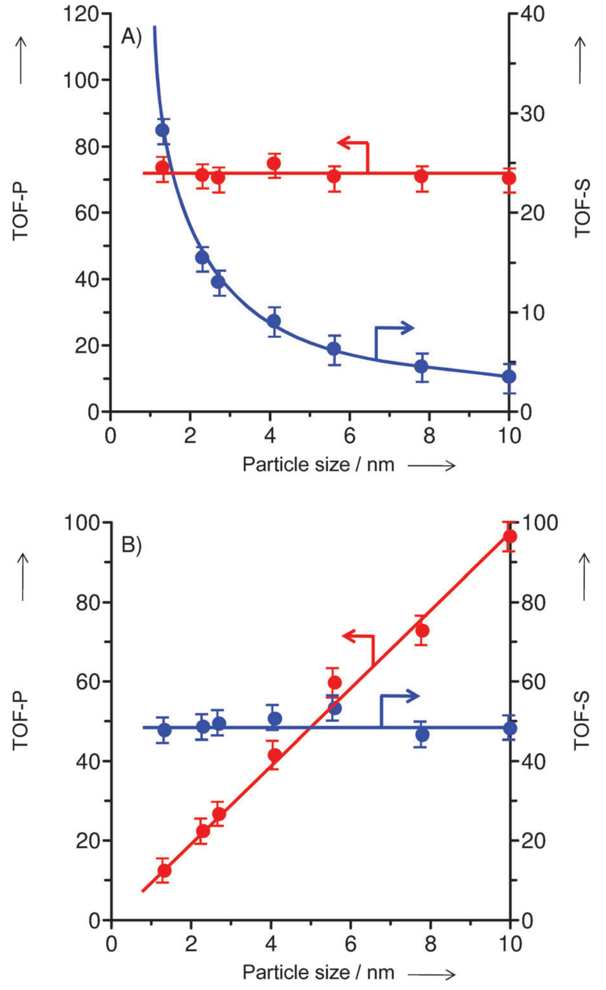

Figure 4. TOFs for the formation of CO_2 over one MLE of Au/TiO_2-(110) as a function of the mean diameter of the gold particles at A) 300 and B) 400 K. ●) by normalizing the number of CO_2 molecules formed per second to the total number of gold atoms at the perimeter interfaces (TOF-P) and ●) by normalizing the number of CO_2 molecules formed per second to the total number of exposed Au atoms at the gold particles (TOF-S).

nearly constant regardless of the particle diameter (Figure 4 A). These results suggest that the active sites for CO oxidation are the gold atoms located at the periphery of the gold particles attached to TiO_2 and that the catalytic activity for CO oxidation correlates neither to a change in the fraction of edge or corner sites nor to a change in the electronic structure of the gold particles induced by quantum size effects. In contrast, TOF-S at 400 K remained nearly constant regardless of the mean gold particle diameter (Figure 4 B), suggesting that the active sites for CO oxidation are newly created on the gold metal surface at high temperature. Thus, we can conclude that both the reaction mechanisms and the active sites differed between the low (<320 K) and the high temperature regions (>320 K).

To obtain more information about the active sites for CO oxidation on the Au/TiO_2 catalyst and the underlying mechanism of the reaction, we examined the kinetics of CO oxidation over a Ti-deposited gold single-crystal surface (see Figures S3 and S4 in the Supporting Information). An inversely supported model gold catalyst, TiO_2/Au(111) was prepared by depositing Ti on Au(111) using an electron beam evaporator. The coverage of Ti on Au(111) (Θ_{Ti}) was estimated from the Ti $2p_{3/2}$/Au $4f_{7/2}$ X-ray photoelectron spectroscopy (XPS) ratio. At 300 K, no CO_2 formed over the clean Au(111) surface (i.e. prior to Ti deposition), whereas at 400 K, CO oxidation proceeded at an estimated rate of $(6.7\pm0.4)\times10^{16}$ molecules s^{-1}. The TOF, which was calculated by normalizing the number of CO_2 molecules formed per second to the total number of surface gold atoms (1.39×10^{15} atoms cm^{-2}), was estimated to be (48.2 ± 2.9) molecules $site^{-1}s^{-1}$. Furthermore, the activation energy for CO_2 formation over Au(111) was determined to be (3.5 ± 0.3) kJ mol^{-1} at the high-temperature region. These kinetic data are consistent with those for the reaction over Au/TiO_2(110), indicating that CO oxidation at high temperatures takes place on the metallic gold surface. The presence of low-coordinated gold atoms on the surface of the nanoparticles may contribute to the high activity of CO oxidation.[9,10] We believed that during CO oxidation at high temperatures, the Au(111) surface was reconstructed and that low-coordinated gold atoms appeared. In contrast, formation of CO_2 was observed for the TiO_2-deposited Au(111) surface at low temperatures. The CO_2 formation rate increased with increasing Ti coverage, and the optimum rate was obtained at $\Theta_{Ti}=0.65$. In our previous study,[24] we found that monolayer TiO_2 islands with diameters of about 20 nm form on the Au(111) surface and that the number of TiO_2 islands increases with increasing Ti coverage below $\Theta_{Ti}=0.65$. We estimated the TOF for CO_2 formation over TiO_2/Au(111), which was calculated from the length of the perimeter interface between the TiO_2 islands and the gold substrate. The TOF for TiO_2/Au(111) at $\Theta_{Ti}=0.65$ (78.6 ± 6.8 molecules $site^{-1}s^{-1}$) is consistent with that for Au/TiO_2(110). Furthermore, the activation energy for CO_2 formation over TiO_2/Au(111) (26.1 ± 2.7 kJ mol^{-1}) agrees well with that for Au/TiO_2(110). We thus believe that the active site for CO oxidation at low temperatures is the perimeter interface between the gold nanoparticles and the TiO_2 support and that moisture plays an essential role in low-temperature CO oxidation over Au/TiO_2.

At low temperatures (<320 K), H_2O plays an essential role in promoting the oxidation of CO. Theoretical calculations and experimental data demonstrate that over gold clusters the hydroperoxide species can be produced directly from the reaction of O_2 with H_2O.[25–27] The O–O bond in the hydroperoxide species is activated, and consequently the reaction with CO to form CO_2 occurs with a small activation barrier. Thus, O_2 reacts with H_2O at the perimeter interface between the gold nanoparticles and the TiO_2 support to produce hydroperoxide species, which react with CO over gold clusters to form CO_2 at low temperatures. In contrast, at high temperatures, low-coordinated gold atoms build up on the surface as a result of surface reconstruction because of their exposure to oxygen. The low-coordinated gold atoms adsorb and even dissociate O_2, which then oxidizes CO on the metallic gold surface.

Experimental Section

The experiments were performed in an ultrahigh vacuum apparatus composed of three chambers: a preparation chamber ($<5\times10^{-10}$ Torr) equipped with an ion gun for Ar^+ sputtering, a cathodic arc plasma source, and an evaporator for Ti deposition. An analysis chamber ($<1\times10^{-10}$ Torr) held equipment for X-ray photoelectron spectroscopy, low-energy electron diffraction, Auger electron spectroscopy, and quadrupole mass spectroscopy. A reaction chamber ($<1\times10^{-9}$ Torr) was connected to the analysis chamber through a leak valve, to measure the reaction gases by quadrupole mass spectrometry. X-ray photoelectron spectra were measured with $Mg_{K\alpha}$ radiation. Low-energy electron diffraction patterns were obtained at a gun emission current of about 2 μA at energies of 50–60 eV.

Single crystals of $TiO_2(110)$ ($8\times8\times0.5$ mm^3, 99.999% purity) were used as supports for the Au/TiO_2 model catalysts, which were cleaned by three cycles of Ar^+ sputtering and annealing at 900 K under vacuum after oxidation at 900 K for 90 min at 200 Torr of oxygen. A single-crystal disc of Au(111) (8 mm diameter, 1 mm thickness, 99.999% purity) was polished only on one side. The surface was cleaned by Ar^+ sputtering and annealing at 900 K under vacuum.

Gold was deposited on the $TiO_2(110)$ surfaces by means of cathodic arc plasma deposition (ULVAC, ARL-300) at 300 K, at 70 V of arc voltage, and 360–2200 μF of condenser capacity at a pressure of 10^{-9} Torr. We estimated the number of deposited gold atoms using a quartz microbalance. Then, XPS measurements were performed on the surface-deposited gold atoms under the same conditions to study the Au $4f_{7/2}$ peak area. A coverage of one MLE corresponds to a Au(111) surface atom density of 1.39×10^{15} atoms cm^{-2}. We fixed the gold coverage at one MLE by controlling the generation frequency of the arc. Titanium was deposited on Au(111) surfaces by evaporation from a Ti rod (1.5 mm in diameter) with an electron beam evaporator (AVC AEV-1). The Ti coverage (Θ_{Ti}) was estimated by XPS measurements on the basis of the saturation coverage of atomic oxygen produced by exposure of the Au(111) surface to ozone at 323 K; $\Theta=1$ corresponded to a Au(111) surface atom density of 1.39×10^{15} atoms cm^{-2}. The Ti and O coverages were determined from the Ti $2p_{3/2}$/Au $4f_{7/2}$ and O 1s/Au $4f_{7/2}$ peak area ratios, respectively, using the O 1s/Au $4f_{7/2}$ peak area ratio obtained from the coverage of saturation oxygen ($\Theta_O=1.1$) by ozone exposure and the sensitivity factors for O 1s and Ti $2p_{3/2}$. The Ti deposition rate was 0.05 min^{-1} at a constant flux of 10 nA. The TiO_2/Au(111) model surfaces were produced by oxidizing the Ti-deposited Au(111) surface at 700 K for 10 min in 3×10^{-7} Torr of O_2.

CO oxidation was carried out under 25 Torr of CO, 625 Torr of O_2, and 0.1 Torr of H_2O at a sample temperature of 270–400 K in a batch reactor. We examined the dependence of the CO_2 formation rates on the CO and O_2 pressures. The CO_2 formation rate was of zero order on CO pressures above 3 Torr, and on O_2 pressures above 12 Torr. We selected the reaction conditions in a way that the CO_2 formation rate did not dependent on the CO and O_2 pressures. As a result, we determined the CO pressure to be 25 Torr. Furthermore, the O_2 pressure was determined to be 625 Torr because the ratio of $CO:O_2$ in the real catalyst reaction system was normally 1:25. The sample was mounted using two 0.25 mm diameter tantalum wires for resistive heating. The temperature of the sample was measured by a alumel–chromel thermocouple spot-welded to the back of the crystal. The stainless steel walls of the reactor and the sample holder were found to show no activity for CO oxidation in the blank test, that is, reaction with the $TiO_2(110)$ sample over the temperature range of 270–400 K. The CO, O_2, and CO_2 concentrations were determined by monitoring the pressures at mass numbers 28, 32, and 44, respectively, by quadrupole mass spectrometry.

Received: July 7, 2011
Revised: September 6, 2011
Published online: September 16, 2011

Keywords: gold · heterogeneous catalysis · nanoparticles · oxidation

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