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Article (Special Issue on Gold Catalysis)

Mechanism and active sites of CO oxidation over single-crystal Au surfaces and a Au/TiO₂(110) model surface

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ARTICLE INFO

Article history:

Received 8 April 2016

Accepted 27 July 2016

Published 5 October 2016

Keywords:

Gold

Model catalyst

CO oxidation

Reaction mechanism

Active sites

ABSTRACT

We describe the reaction mechanism and active sites for CO oxidation over a Au/TiO₂(110) model surface and Au single-crystal surfaces, along with the role of H₂O, on a molecular scale. At low temperature (< 320 K), H₂O played an essential role in promoting CO oxidation, and the active site for CO oxidation was the perimeter of the interface between the gold nanoparticles and the TiO₂ support (Au^{δ+}–O^{δ-}–Ti). We believe that the O–O bond was activated by the formation of OOH, which was produced directly from O₂ and H₂O at the perimeter of the interface between the gold nanoparticles and the TiO₂ support, and consequently OOH reacted with CO to form CO₂. This reaction mechanism explains the dependence of the CO₂ formation rate on O₂ pressure at 300 K. In contrast, at high temperature (> 320 K), low-coordinated gold atoms built up on the surface as a result of surface reconstruction due to exposure to CO. The low-coordinated gold atoms adsorbed O₂, which then dissociated and oxidized CO on the metallic gold surface.

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1. Introduction

Gold nanoparticles supported on titanium oxides are highly active catalysts for CO oxidation even at low temperature [1,2]. Haruta [3] reported that the catalytic performance of gold nanoparticles was controlled by three major factors: the structure of the contact between the gold and the oxide support, the nature of the support, and the particle size, with the contact structure being the most important factor. Despite extensive research on the reaction mechanism and the nature of the active sites on a molecular scale, no consensus has been reached about (i) the nature of the active sites and the mechanism of activation of O₂ molecules and (ii) the role of H₂O and its influence on the activities of the catalysts. The origins of the catalytic activity of gold are considered to stem from some combination of contributions from quantum size effects, the presence of low-coordination gold sites, charge transfer between the sup-

port and gold, and the formation of a perimeter of the interface between gold and the oxide support.

Although most investigators agree that small metallic gold nanoparticles are the predominant catalytic species [4–6], others have proposed that cationic gold species [7–9], undercoordinated sites on the gold nanoparticles [10–12], or electron-rich gold nanoparticles [13] play an essential role in the reaction. Furthermore, O₂ dissociation reportedly occurs when undercoordinated gold atoms are present on extended gold surfaces under model conditions [14,15]. On the basis of high-intensity in situ X-ray absorption near-edge structure analysis, van Bokhoven et al. [16] indicated that O₂ molecules could dissociate on gold nanoparticles supported on Al₂O₃ and TiO₂ substrates. Goodman and coworkers [17,18] claimed that the TiO_x support acted mainly as a dispersant and a promoter and that a bilayer of gold that blocks direct access of the reactants to the support was responsible for CO oxidation. Fur-

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This work was financially supported by JST-CREST.

DOI: 10.1016/S1872-2067(16)62516-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 10, October 2016

thermore, Liu et al. [19] calculated that the barrier to dissociation of O_2 from unsupported gold was > 2 eV and that even at the Au/TiO₂ interface, the dissociation barrier was still 0.52 eV. These values indicate that O_2 interacts weakly with gold, and thus spontaneous dissociation of O_2 molecules from the gold surface is not energetically favorable. The perimeter of the interface sites between gold nanoparticles and the oxide support have been recently considered as reaction sites for CO oxidation [20–24]. Behm et al. [21] found that the amount of active oxygen species on the Au/TiO₂ surface was 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. Yates et al. [22] reported that CO oxidation over a Au/TiO₂ catalyst at low temperature (120 K) occurred at a perimeter zone or on the support surfaces. Theoretical studies [25–27] have also highlighted the importance of the periphery of gold particles.

Furthermore, CO oxidation is greatly influenced by H₂O in the reactant gas [28–31]. Dte et al. [30], on the basis of their research and that of others, proposed that H₂O had two effects: it activates O_2 molecules, and it decomposes a carbonate species. However, the mechanism of the promotional effect of H₂O is not fully understood. Here, we describe the reaction mechanism and active sites of CO oxidation over Au/TiO₂, along with the role of H₂O, on a molecular scale.

2. Experimental

The experiments were performed in an ultra-high-vacuum apparatus composed of three chambers: a preparation chamber ($< 3 \times 10^{-10}$ Torr) equipped with an ion gun for Ar⁺ sputtering, a cathodic arc plasma source, and an evaporator for Ti deposition. An analysis chamber ($< 1 \times 10^{-10}$ Torr) held equipment for X-ray photoelectron spectroscopy (XPS) and quadrupole mass spectrometry (QMS). A reaction chamber ($< 1 \times 10^{-9}$ Torr) was connected to the analysis chamber via a leak valve, to measure the reaction gases by QMS. XPS were measured with Mg K α radiation.

Single crystals of TiO₂(110) (8 × 8 × 0.5 mm, 99.999% purity, SPL) were used as supports for the Au/TiO₂ model catalyst, and the crystals were cleaned by three cycles of Ar⁺ sputtering and annealing at 900 K under a vacuum after oxidation at 900 K for 90 min under 200 Torr of O₂. Single-crystal discs of Au(111) and Au(100) (8 mm diameter, 1 mm thickness, 99.999% purity, SPL) were polished on only one side. The polished surface was cleaned by Ar⁺ sputtering and annealing at 900 K under vacuum.

Gold was deposited on the TiO₂(110) surface with a cathodic arc plasma gun (ULVAC, ARL-300) at 300 K, an arc voltage of 70 V, a condenser capacity of 360–2200 μ F, and a pressure of 10^{-9} Torr. The size of the gold particles could be tuned by adjusting the condenser capacity of the arc plasma gun [20,32]. For example, when a condenser capacity of 360 μ F was used, gold nanoparticles with a mean particle diameter of 1.3 nm (composed of approximately 55 atoms) were observed on the TiO₂(110) surface. At a condenser capacity of 2200 μ F, the size

distribution of gold particles was bimodal (4.3 and 5.8 nm with a calculated mean particle diameter of 5.6 nm) [32]. For all condenser capacities used, the deposited gold particles were almost hemispherical, and the shape was confirmed by atomic force microscopy. Thus, the size of gold particles deposited on a single crystal of TiO₂ could be controlled in the range of 1–10 nm.

We estimated the number of deposited gold atoms using a quartz microbalance. Then, the XPS of the surface-deposited gold on TiO₂(110) were measured under the same deposition conditions to obtain the Au 4f_{7/2} peak areas. A coverage of 1 monolayer equivalent corresponded a Au(111) surface atom density of 1.39×10^{15} atoms cm⁻². We fixed the gold coverage at 1 monolayer equivalent by controlling the generation frequency of the arc.

We also prepared an inverse catalyst by depositing titanium on a Au(111) surface by evaporation from a Ti rod (1.5 mm diameter) with an electron beam evaporator (AVC AEV-1). The Ti coverage 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; a coverage of 1 corresponded to a Au(111) surface atom density of 1.39×10^{15} atoms cm⁻². We determined the Ti and O coverages from the Ti 2p_{3/2}/Au 4f_{7/2} and O 1s/Au 4f_{7/2} peak area ratios, respectively, by using the O 1s/Au 4f_{7/2} peak area ratio obtained at saturation oxygen coverage ($\theta_0 = 1.1$) produced 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 TiO₂/Au(111) surface was produced by oxidizing the Ti-deposited Au(111) surface at 700 K for 10 min in 3×10^{-7} Torr of O₂.

CO oxidation reaction was carried out under 1–25 Torr of CO, 1–625 Torr of O₂, and 0–0.5 Torr of H₂O at a sample temperature of 270–400 K in a batch reactor. The sample was mounted with two 0.25 mm diameter tantalum wires for resistive heating. The temperature of the sample was measured with an alumel-chromel thermocouple spot-welded to the back of the crystal. The stainless steel walls of the reactor, the sample holder, and tantalum wires showed no activity for CO oxidation in a blank test, that is, reaction with a TiO₂(110) sample at 270–400 K. The reaction gases were introduced into the analysis chamber at a constant pressure of 4×10^{-9} Torr through a leak valve, and the pressures of CO, O₂, and CO₂ were measured in real time during the reaction by monitoring of mass numbers 28, 32, and 44, respectively. The concentrations of CO, O₂, and CO₂ were calculated from the pressure of each gas and sensitivity factors of 1.06, 1.0, and 1.4, respectively.

3. Results and discussion

3.1. CO oxidation over a Au/TiO₂(110) model surface

First, we investigated the effect of H₂O on CO oxidation over Au/TiO₂(110) at 300 K, a reaction temperature at which the typical properties of the Au/TiO₂ catalyst with respect to CO oxidation can be observed [20]. In the absence of H₂O, no CO₂ formed, indicating that CO was not oxidized under these reac-

tion conditions. However, in the presence of H₂O, the amount of CO₂ formed increased linearly with reaction time. The rate of CO₂ formation increased with increasing H₂O pressure up to 0.1 Torr of H₂O, but the amount of CO₂ formed decreased at 0.5 Torr of H₂O. CO oxidation over gold catalysts is known to be strongly influenced by H₂O in the reactant gas [29,33], indeed our results strongly indicate that CO oxidation did not proceed in the absence of H₂O.

To clarify the role of H₂O in the CO oxidation, we examined the relationship between the CO₂ formation rate and the H₂O partial pressure at two reaction temperatures, 300 and 400 K (Fig. 1). At 300 K, the rate initially increased substantially with increasing H₂O partial pressure, peaked at 0.1 Torr of H₂O, and then gradually decreased with increasing H₂O pressure. In contrast, at 400 K, CO oxidation proceeded even in the absence of H₂O, and the CO₂ formation rate did not depend on the H₂O partial pressure. The observation that H₂O promoted CO oxidation over the Au/TiO₂(110) surface only at low temperature suggests that the mechanisms of CO oxidation at 300 and 400 K differed. We propose that the process by which O₂ molecules were activated strongly depended on the reaction temperature. That is, at high temperature, O₂ molecules were activated directly over the Au/TiO₂(110) surface, whereas at low temperature, H₂O took part in the activation.

In early studies, Haruta [34] suggested that the mechanism of CO oxidation over a gold catalyst depended on reaction temperature. Haruta found that the apparent activation energy of CO oxidation over powdered Au/TiO₂ changed drastically with reaction temperature (Fig. 2(A)): the estimated activation energy is 2.0 ± 0.7 kJ mol⁻¹ above 320 K, whereas the estimated activation energy below 320 K is 34.0 ± 1.8 kJ mol⁻¹. In this study, we examined the temperature dependence of the rate of CO₂ formation over Au/TiO₂(110) in the presence of H₂O (Fig. 2(B)). An Arrhenius plot of the data clearly showed a sudden change in slope at around 320 K, and we estimated the apparent activation energies above and below 320 K to be 2.9 ± 0.9 and 28.9 ± 2.5 kJ mol⁻¹, respectively. These values and the overall dependence on reaction temperature agreed well with Haruta's results for a powdered Au/TiO₂ catalyst, indicating that Au/TiO₂(110) was a good model surface for powdered

Fig. 1. Rate of CO₂ formation (r_{CO_2}) from CO over 1 monolayer equivalent of Au/TiO₂(110) as a function of H₂O partial pressure ($P_{\text{H}_2\text{O}}$) at 300 K (■) and 400 K (●). The oxidation of CO was performed in batch mode under 25 Torr of CO and 625 Torr of O₂. Reproduced from Ref. [20].

Au/TiO₂ and that the active site and the reaction mechanism over the Au/TiO₂(110) surface might change at 320 K.

We next examined the dependence of CO₂ formation rate on CO and O₂ partial pressures at 300 and 400 K. Increasing the CO partial pressure increased the CO₂ formation rate at CO pressures up to 3 Torr, and the reaction order at both temperatures was estimated to be 0.96 at CO pressures below 3 Torr (Fig. 3). Previously, we investigated CO adsorption on Au(111) and Au(100) single-crystal surfaces using polarization modulation infrared reflection absorption spectroscopy and found that CO adsorption on both surfaces showed similar CO-pressure dependences: the peak intensities increase with increasing pressure up to 3 Torr and then remain constant at pressures above 3 Torr [35]. In the same study, we also found that CO adsorption over the gold surfaces showed first-order dependence on CO pressure. Thus, the dependence of the CO₂ formation rate on CO pressure observed for Au/TiO₂(110) was in good agreement with our previously reported results for CO surface coverage, indicating that the CO₂ formation rate was strongly governed by the CO surface coverage. However, the dependence of the CO₂ formation rate on CO partial pressure

Fig. 2. Arrhenius plots for the formation of CO₂ from CO over (A) powdered Au/TiO₂ catalyst and (B) 1 monolayer equivalent of Au/TiO₂(110). The oxidation of CO was performed in batch mode under 25 Torr of CO, 625 Torr of O₂, and 0.1 Torr of H₂O. Reproduced from Ref. [20].

Fig. 3. Dependence of the CO₂ formation rates (r_{CO_2}) on the CO partial pressure (P_{CO}) at 300 (■) and 400 K (●). The oxidation of CO was performed in batch mode under 1–25 Torr of CO, 625 Torr of O₂, and 0.1 Torr of H₂O.

became zero order at CO pressures above 3 Torr, because CO adsorption became saturated at 3 Torr. These results indicate that CO adsorbed on the gold surface was converted to CO₂ at both reaction temperatures.

In contrast, the dependence of the CO₂ formation rate on O₂ partial pressure changed with reaction temperature (Fig. 4). The rate of CO₂ formation increased with increasing O₂ partial pressure up to 12 Torr at both temperatures. At 300 K, the reaction order was estimated to be 0.97 from the slope of the straight line, whereas at 400 K, the reaction order was estimated to be 0.51, which was approximately half of that at 300 K. This result supports the idea that the mechanism of O₂ activation strongly depended on reaction temperature.

We also examined the rates of CO₂ formation at 300 and 400 K over Au/TiO₂(110) surfaces deposited gold particles of different mean particle diameters (Fig. 5). At 300 K, the CO₂ formation rate sharply increased when the particle diameter dropped below 2 nm, whereas at 400 K, the rate increase with

Fig. 4. Dependence of the CO₂ formation rates (r_{CO_2}) on the O₂ partial pressure (P_{O_2}) at 300 (■) and 400 K (●). The oxidation of CO was performed in batch mode under 25 Torr of CO, 1–625 Torr of O₂, and 0.1 Torr of H₂O.

Fig. 5. Rate of CO₂ formation (r_{CO_2}) from CO over 1 monolayer equivalent of Au/TiO₂(110) as a function of mean particle diameter of gold at 300 (■) and 400 K (●). The oxidation of CO was performed in batch mode under 25 Torr of CO, 625 Torr of O₂, and 0.1 Torr of H₂O.

decreasing particle size was more gradual. The difference in the particle diameter dependences at the two reaction temperatures suggests that the active sites for CO oxidation at 300 and 400 K differed. Furthermore, we estimated the apparent activation energies of CO₂ formation over Au/TiO₂(110) surfaces at various mean particle diameters and found that the slopes of the Arrhenius plots were nearly the same at all the particle diameters (Fig. 6). The apparent activation energies for CO oxidation above and below 320 K were estimated to be about 4 and 30 kJ mol^{−1}, respectively, and were independent of the gold particle diameter. This result strongly suggests that the nature of the active sites for CO oxidation on Au/TiO₂(110) did not vary with the particle diameter.

To investigate the active sites for CO₂ formation, we plotted the turnover frequencies (TOFs) for CO₂ formation at the two reaction temperatures as a function of mean gold particle diameter (Fig. 7). To determine whether the active sites for CO oxidation were exposed gold atoms on the gold particles or

Fig. 6. Arrhenius plots for the formation of CO₂ from CO over 1 monolayer equivalent of Au/TiO₂(110) at 1.3 (○, ●), 2.5 (□, ■), and 4.2 nm (△, ▲) of mean gold particle diameters. The oxidation of CO was performed in batch mode under 25 Torr of CO, 625 Torr of O₂, and 0.1 Torr of H₂O.

Fig. 7. Turnover frequencies (TOFs) for the formation of CO₂ over 1 monolayer equivalent of Au/TiO₂(110) as a function of the mean diameter of the gold particles at (A) 300 and (B) 400 K. Data were obtained by normalizing the number of CO₂ molecules formed per second to (■) the total number of gold atoms at the perimeter interfaces (TOF-P) and (●) the total number of exposed Au atoms at the gold particles (TOF-S). Reproduced from Ref. [20].

perimeter sites at the interface between the gold particles and the TiO₂ support, we calculated the TOFs in two ways: (i) by normalizing the number of CO₂ molecules formed per second to the total number of exposed gold atoms on the gold particles (TOF-S) and (ii) by normalizing the number of CO₂ molecules formed per second to the total number of gold atoms at the perimeter of the interfaces (TOF-P). The number of gold atoms at the interface perimeter was estimated from the length of the perimeter and the gold interatomic distance (0.288 nm). The results clearly show that the relationship between TOF and mean gold particle diameter depended strongly on reaction temperature. At 300 K, TOF-S decreased with increasing particle diameter, whereas TOF-P remained nearly constant regardless of particle diameter (Fig. 7(A)). These results suggest that the active sites for CO oxidation were gold atoms located at the perimeter of the gold particles attached to TiO₂ and that the catalytic activity for CO oxidation was correlated neither to a change in the fraction of edge or corner sites nor to a change in the electronic nature of gold particles induced by the quantum size effect. In contrast, TOF-S at 400 K remained nearly constant regardless of the mean gold particle diameter (Fig. 7(B)), suggesting that the active sites for CO oxidation were newly created on the gold metal surface at this temperature. Thus, we concluded that both the reaction mechanisms and the active sites differed between the low-temperature region (< 320 K) and the high-temperature region (> 320 K).

3.2. CO oxidation over Au single-crystal and TiO₂/Au(111) surfaces

To obtain more information about the active sites, we investigated the kinetics of CO oxidation over an inverse catalyst, that is, a Ti-deposited gold single-crystal surface. First, we carried out the CO oxidation reaction over Au(111), Au(100), and TiO₂(110) single-crystal surfaces (Table 1). No CO₂ formed over the Au(111) and Au(100) surfaces (surfaces not modified with Ti) at 300 K, even when H₂O was present in the reaction gas. In

contrast, at 400 K, CO oxidation proceeded on both gold surfaces at an estimated rate of 6.4×10^{16} to 6.7×10^{16} molecules s⁻¹. The TOFs, which were calculated by normalizing the number of CO₂ molecules formed per second to the total number of surface gold atoms, over Au(111) and Au(100), were estimated to be 48.2 and 52.5 molecules site⁻¹ s⁻¹, respectively; and these values were in good agreement with the value for the Au/TiO₂(110) surface (47.8 molecules site⁻¹ s⁻¹). Furthermore, we compared the activation energies for CO oxidation over Au(111) and Au(100) with the activation energy over a Au/TiO₂(110) surface at high temperature (> 320 K). From the slopes of Arrhenius plots of the CO₂ formation rates (Fig. 8), we determined the activation energies for CO₂ formation on Au(111) and Au(100) to be 3.5 ± 0.3 and 4.5 ± 0.9 kJ mol⁻¹, respectively. These activation energies were almost the same as the activation energy for the reaction over the Au/TiO₂(110) surface (2.9 ± 0.9 kJ mol⁻¹). These kinetic data for the Au single-crystal surfaces and the Au/TiO₂(110) surface were consistent, indicating that at high temperature, CO was oxidized on the metallic gold surface. Some investigators have suggested that the presence of low-coordinated gold atoms on the surface of nanoparticles may contribute to their high activity for CO oxidation [10,11]. We believed that during CO oxidation at high temperature, the Au(111) and Au(100) surfaces were reconstructed and that low-coordinated gold atoms appeared. The

Table 1

CO oxidation reaction over Au(111), Au(100), and TiO₂(110) single-crystal surfaces.

Surfaces	CO ₂ formation rate / $\times 10^{16}$ molecules s ⁻¹		TOF / molecules site ⁻¹ s ⁻¹	
	300 K ^a	400 K ^b	300 K ^c	400 K ^d
Au(111)	0.0	6.7	0.0	48.2
Au(100)	0.0	6.4	0.0	52.5
TiO ₂ (110)	0.0	0.0	0.0	0.0
Au/TiO ₂ (110) ^e	4.3	6.7	73.7	47.8

^a CO: 25 Torr, O₂: 625 Torr, H₂O: 0.1 Torr; ^b CO: 25 Torr, O₂: 625 Torr;

^c CO₂ formation/perimeter Au atoms; ^d CO₂ formation/surface Au atoms;

^e Au: 1.3 nm, 1 monolayer equivalent.

Fig. 8. Arrhenius plots for the formation of CO₂ from CO over the Au(111) (▲), Au(100) (■), and Au/TiO₂(110) (●) surfaces. The oxidation of CO was performed in batch mode under 25 Torr of CO and 625 Torr of O₂.

low-coordinated gold atoms adsorbed O₂, which then dissociated and oxidized CO on the metallic gold surface. That is, CO oxidation over the Au/TiO₂ catalyst proceeded by the Langmuir-Hinshelwood mechanism, which explains the observed reaction order with respect to O₂ partial pressure for CO oxidation at 400 K (CO + 1/2O₂ → CO₂).

In contrast, we observed CO₂ formation over the TiO₂-deposited Au(111) surface at low temperature with H₂O in the reaction gas. At 400 K, the CO₂ formation rate decreased with increasing Ti coverage, and no CO₂ formation was observed at coverages of > 1.2 (Fig. 9). The relationship between the CO₂ formation rate and Ti coverage agreed well with the relationship between the number of exposed gold atoms and the Ti coverage over TiO₂/Au(111). Furthermore, the TOFs for TiO₂/Au(111) at 400 K were estimated to be 40.2–44.4 molecules site⁻¹ s⁻¹ (Table 2), and these values are in agreement with those for the Au/TiO₂(110) and gold single-crystal surfac-

Fig. 9. Rate of CO₂ formation over the TiO₂-deposited Au(111) surface as a function of Ti coverage at 300 (■) and 400 K (●). The oxidation of CO was performed in batch mode under 25 Torr of CO, 625 Torr of O₂, and 0.1 Torr of H₂O.

Table 2

CO oxidation reaction over the TiO₂/Au(111) surface with various Ti coverage.

Ti coverage (θ)	CO ₂ formation rate / ×10 ¹⁶ molecules s ⁻¹		TOF / molecules site ⁻¹ s ⁻¹	
	300 K ^a	400 K ^b	300 K ^c	400 K ^d
0.21	0.12	4.9	77.4	44.4
0.39	0.21	3.4	73.4	40.7
0.65	0.33	2.0	78.6	40.2
Au/TiO ₂ (110) ^e	4.3	7.2	73.7	47.8

^aCO: 25 Torr, O₂: 625 Torr, H₂O: 0.1 Torr; ^bCO: 25 Torr, O₂: 625 Torr;

^cCO₂ formation/perimeter Au atoms; ^dCO₂ formation/surface Au atoms;

^eAu: 1.3 nm, 1 monolayer equivalent.

es. The agreement demonstrates that the active sites for CO oxidation over the Au/TiO₂(110) surface were identical to the metallic gold sites. In contrast, at 300 K, the CO₂ formation rate initially increased with increasing Ti coverage, and the rate peaked at a coverage of 0.65. This result clearly indicates that the TiO₂ deposited on the gold surface directly promoted CO oxidation at 300 K at a coverage range from 0 to 0.65. However, the deposited TiO₂ inhibited the CO₂ oxidation reaction at high coverage.

If the perimeter interface between TiO₂ islands and the Au substrate acted as the active site for CO oxidation, the TOF (the CO₂ formation rate per Au atom at the perimeter of the interface) over the TiO₂/Au(111) surface must agree with the TOF for Au/TiO₂(110). Thus, we estimated the TOFs for CO₂ formation over the TiO₂/Au(111) surface at various Ti coverages (Table 2). In our previous study, we found that monolayer TiO₂ islands with diameters of about 20 nm formed on Au(111); the number of TiO₂ islands increased with increasing Ti coverage below 0.65, and as the coverage was increased further, multi-layer islands of TiO₂ began to form [36]. Then, we determined the number of gold atoms from the length of the perimeter interface between TiO₂ islands and the gold substrate; the length of the perimeter was calculated from the mean diameter and the number of TiO₂ islands observed by noncontact atomic force microscopy. The TOFs for TiO₂/Au(111) at 300 K were nearly independent of Ti coverage and were estimated to be 73.4–78.6 molecules site⁻¹ s⁻¹, which were consistent with that for Au/TiO₂(110). Furthermore, the activation energies for CO₂ formation over the TiO₂-deposited Au(111) surface were examined at low temperature (Fig. 10). The activation energies for CO₂ formation over TiO₂/Au(111) at Ti coverages of 0.39 and 0.65 were estimated to be 25.1 ± 2.3 and 26.1 ± 2.7 kJ mol⁻¹, respectively. These values are in good agreement with the Au/TiO₂(110) value. Thus, the kinetic data for the reaction over TiO₂/Au(111) agreed well with those for the reaction over Au/TiO₂(110), strongly supporting the idea that the active site for CO oxidation at low temperature was the perimeter interface between the gold nanoparticles and the TiO₂ support and that H₂O played an essential role in low-temperature CO oxidation on Au/TiO₂.

3.3. Reaction mechanism of CO oxidation

Both theoretical calculations and experimental data have

Fig. 10. Arrhenius plots for the formation of CO₂ from CO over Au/TiO₂(110) (■) and TiO₂/Au(111) at Ti coverages of 0.39 (▲) and 0.65 (●). The oxidation of CO was performed in batch mode under 25 Torr of CO, 625 Torr of O₂, and 0.1 Torr of H₂O.

demonstrated that over gold clusters, OOH can be produced directly from O₂ and H₂O [37–39]. We thus proposed the reaction mechanism as follows:

First, H₂O dissociated to OH and H over the perimeter of the interface between the gold nanoparticles and the TiO₂ support (Au^{δ+}–O^{δ–}–Ti). The H atom reacted with O₂ to form OOH. The O–O bond was activated by the formation of OOH, and that the reaction with CO to form CO₂ occurred subsequently. Recently, Lyubinetzky et al. [40] reported two pathways for H₂O interaction with oxygen adatoms on TiO₂(110); these investigators observed the recombination reaction of two OH molecules to form H₂O and oxygen adatoms over rows of Ti⁴⁺. Thus, we believe that in our system, two OH molecules were converted to H₂O and O₂ by a recombination reaction on Ti⁴⁺ sites over the Au/TiO₂ surface. However, the O₂ molecules formed on the TiO₂ surface were not involved in the CO oxidation reaction, because CO cannot be adsorbed on TiO₂. This reaction mechanism explains the dependence of the CO₂ formation rate on O₂ pressure at 300 K (CO + O₂ → CO₂ + 1/2O₂).

4. Conclusions

The reaction mechanism and active sites for CO oxidation over a Au/TiO₂ model surface, gold single-crystal surfaces, and a Ti-deposited gold single-crystal surface, along with the role of H₂O, were investigated on a molecular scale. At low temperature (< 320 K), H₂O played an essential role in promoting CO oxidation. The active site for CO oxidation at low temperature was the perimeter of the interface between the gold nanoparticles and the TiO₂ support (Au^{δ+}–O^{δ–}–Ti). We believe that the O–O bond was activated by the formation of OOH, which was produced directly from O₂ and H₂O at the perimeter of the interface between the gold nanoparticles and the TiO₂ support,

and consequently OOH reacted with CO to form CO₂. This reaction mechanism explains the dependence of the CO₂ formation rate on O₂ pressure at 300 K. In contrast, at high temperature, low-coordinated gold atoms built up on the surface as a result of surface reconstruction due to exposure to CO. The low-coordinated gold atoms adsorbed O₂, which then dissociated and oxidized CO on the metallic gold surface.

Acknowledgments

We are grateful to Professor M. Haruta at Tokyo Metropolitan University for constructive discussions.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 1676–1683 doi: 10.1016/S1872-2067(16)62516-0

Mechanism and active sites of CO oxidation over single-crystal Au surfaces and a Au/TiO₂(110) model surface

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At low temperature (< 320 K), the active sites were the perimeter of the interface between gold nanoparticles and TiO₂ support. In contrast, low-coordinated gold atoms were the active sites at high temperature (> 320 K).

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单晶Au表面和Au/TiO₂(110)模型催化剂表面CO氧化反应机理和活性位

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摘要: 在分子尺度上介绍了Au/TiO₂(110)模型催化剂表面和单晶Au表面CO氧化反应机理和活性位、以及H₂O的作用。在低温(< 320 K), H₂O起着促进CO氧化的作用, CO氧化的活性位位于金纳米颗粒与TiO₂载体界面(Au^{δ+}–O^{δ-}–Ti)的周边。O₂和H₂O在金纳米颗粒与TiO₂载体界面边缘处反应形成OOH, 而形成的OOH使O–O键活化, 随后OOH与CO反应生成CO₂。300 K时CO₂的形成速率受限于O₂压力与该反应机理相印证。相反, 在高温(> 320 K)下, 因暴露于CO中而导致催化剂表面重组, 在表面形成低配位金原子。低配位的金原子吸附O₂, 随后O₂解离, 并在金属金表面氧化CO。

关键词: 金; 模型催化剂; 一氧化碳氧化; 反应机理; 活性位

收稿日期: 2016-04-08. 接受日期: 2016-07-27. 出版日期: 2016-10-05.

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