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Investigation of CO Oxidation Transient Kinetics on an Oxygen Pre-covered Au(211) Stepped Surface

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Abstract The desire to explain the origin(s) of the unexpected catalytic activity of oxide-supported Au nanoparticles for CO oxidation discovered by Haruta and coworkers has stimulated numerous experimental and theoretical studies of Au nanoclusters in the gas phase and on metal oxide supports, and on Au single-crystal surfaces. In order to explore further the reactivity of low-coordination Au step sites, we have performed transient kinetics studies of CO oxidation on an O-precovered, stepped Au(211) single crystal surface. We found behavior similar to that observed previously on flat Au(111) and (110) surfaces; i.e., there is no evidence in these transient kinetics for any special reactivity associated with this stepped Au surface. The CO oxidation reaction rate was highly dependent on the initial oxygen coverage, and we determined an apparent activation energy for CO oxidation of -7.0 kJ mol^{-1} for $\theta_{\mathrm{O}}^{\mathrm{init}} = 0.9$ ML. Within the Langmuir-Hinschelwood (LH) reaction scheme, we estimate an activation energy of $E_{\mathrm{LH}} = 20$–43 kJ mol^{-1} on this surface for CO oxidation via this pathway. This is somewhat below the value of 67 kJ mol^{-1} predicted by recent theoretical calculations.

Keywords Gold · Au(211) · Stepped surface · Chemisorption · Ozone · CO oxidation · Temperature programmed desorption (TPD)

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1 Introduction

While Au catalysts were known to be able to carry out a number of selective oxidation reactions, the discovery several years ago by Haruta and coworkers [1–3] of facile, low-temperature CO oxidation catalysis over supported Au nanoparticles rekindled an interest in Au catalysis and motivated an intense effort to investigate and explain the activity of these new catalysts. Numerous studies were initiated on Au single crystal surfaces and on Au clusters in the gas phase and deposited or grown on metal oxide supports. These studies have supported the early results in which, despite the fact that bulk Au is quite inert, nano-sized clusters of Au supported on metal oxides show catalytic activity for CO oxidation and also selective hydrocarbon oxidation [4].

Many explanations have been suggested to enlighten this remarkable activity of supported Au nanoclusters and the difficulty of explicitly probing and testing these explanations has hampered progress. One possibility that was suggested is that small nanoclusters can stabilize high concentrations of step sites or particular crystal planes (e.g., the Au(211) surface) that are highly active for such reactions [5–9]. To help evaluate this simple proposal, it is of interest to measure CO oxidation rates over bulk Au surfaces that present a high concentration of such reactive sites. While CO oxidation kinetics have been reported over Au(111) and Au(110)-(1 × 2) single crystal surfaces [10–13], no kinetics measurements of CO oxidation have been reported at stepped Au surfaces or, in particular, on the Au(211) crystal plane. In this letter, we report on our investigations of CO oxidation kinetics on an Au(211) surface. Because of the low dissociation probability of O_2 on this surface [14], we performed transient kinetic measurements of CO titration of a preadsorbed oxygen adlayer on the Au(211) surface.

2 Experimental

Experiments were conducted in a two-level stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. More details of the experimental setup can be found elsewhere [15]. The Au crystal could be heated resistively to 1,100 K and cooled to 85 K by liquid nitrogen. Temperature at the crystal was monitored by a chromel-alumel thermocouple pressed firmly using Au foil into a small hole in the side of the crystal. The uncertainty in the temperature measurements was ±2 K by means of this arrangement. High-purity CO (Matheson Gas Products, U.H.P. grade, 99.9% purity) was used without further purification. Ozone (O_3) used for dosing in UHV was prepared in our laboratory using a commercial ozone generator. All ozone exposures were carried out with the crystal held at 85 K, and then a subsequent flash of the sample to 300 K was made. Experiments carried out at other temperatures were performed by heating or cooling this surface to the indicated temperature. Temperature-programmed desorption (TPD) experiments were performed with the crystal in line-of-sight of the QMS ionizer and a heating rate of 3 K/s. Absolute coverages are referenced to the Au surface atom density such that $\theta = 1.0$ monolayer (ML) corresponds to 1.48×10^{15} atoms/cm^2 [14].

3 Results and Discussion

Oxygen adatoms with coverage θ_{O} were formed at the Au(211) surface at 85 K by dosing ozone in UHV [14], and then the oxygen-precovered surface was held at various temperatures during exposure to CO gas. As reported elsewhere [15], CO TPD curves obtained after large CO exposures on Au(211) show peaks at 130 and 190 K. IRAS spectra (not shown here) showed that almost no CO was stable in a coadsorbed layer on the surface after small exposures of CO on the O-precovered Au(211) surface at 85 K. After large CO exposures, facile CO reaction with oxygen adatoms on the surface at 85 K created empty sites which could then be occupied by coadsorbed CO.

Figure 1 shows O_2 TPD curves obtained after predosing ozone on a Au(211) surface to create an initial oxygen coverage of $\theta_{\mathrm{O}}^{\mathrm{init}} = 0.9$ ML and then exposing the surface at 300 K to CO at $P_{\mathrm{CO}} = 2.5 \times 10^{-7}$ Torr for a given time. This $\theta_{\mathrm{O}}^{\mathrm{init}}$ value corresponds to the saturation coverage of adsorbed oxygen on a gold surface with $\theta = 1.0$ ML. Oxygen predosed Au surfaces were regenerated to the initial oxygen coverage of $\theta_{\mathrm{O}}^{\mathrm{init}} = 0.9$ ML every time before exposing to CO. Surface oxygen is removed by CO oxidation reactions to form CO_2 which desorbs promptly. Subsequently, O_2 is desorbed upon heating in TPD due to recombination of oxygen adatoms. The area under each curve is proportional to the surface-bound oxygen concentration, this result was corroborated in a previous work by measuring the O(517 eV)/Au(240 eV) peak-to-peak height ratio by AES [14]. Therefore, the amount of unreacted oxygen remaining on the surface after a given CO exposure can be calculated from the O_2 TPD peak area. In addition to the peak shifting from 515 to 530 K, associated to terrace sites, a feature at 540 K, associated to step sites, is found at low coverages of unreacted oxygen [14], as shown in Fig. 1. The rate of CO oxidation for a given CO-dosing time, or at a particular value of θ_{O}, is obtained simply by the slope $\mathrm{d}\theta_{\mathrm{O}}/\mathrm{d}t$ of this $\theta_{\mathrm{O}}(t)$ curve. Figure 1 demonstrates that there is a high reactivity of the surface for oxidation of CO at the Au(211) surface at 300 K and the surface oxygen concentration is reduced substantially in only a few minutes by exposure at $P_{\mathrm{CO}} = 2.5 \times 10^{-7}$ Torr.

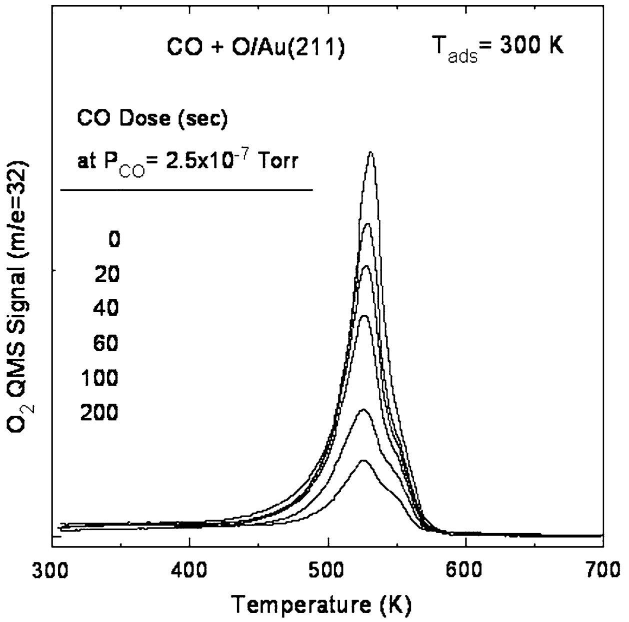

Fig. 1 O_2 TPD curves taken after CO exposures on an oxygen-precovered Au(211) surface at 85 K with $\theta_{\mathrm{O}}^{\mathrm{init}} = 0.9$ ML

For $\theta_{\mathrm{O}}^{\mathrm{init}}$ of 0.9 ML, as shown in Fig. 2a, the initial rate of CO oxidation was nearly constant until θ_{O} was reduced to about 0.3 ML, and then CO oxidation slowed dramatically for $\theta_{\mathrm{O}} \sim 0.2$ ML. A series of such transient CO oxidation curves were generated by repeating these experiments for different values of $\theta_{\mathrm{O}}^{\mathrm{init}} = 0.63$, 0.50, and 0.22 ML, and these results are also shown in Fig. 2a. Initial rates of CO oxidations calculated from data in Fig. 2a are gathered in Fig. 2b which indicates that CO oxidation initially proceeds much faster for lower initial coverages of oxygen. Not only does the CO oxidation rate depend on the surface oxygen concentration, but the rate constant strongly depends on the initial conditions [11], i.e., there is not a unique rate that corresponds to the value of θ_{O}, as shown first by Engel et al. [16].

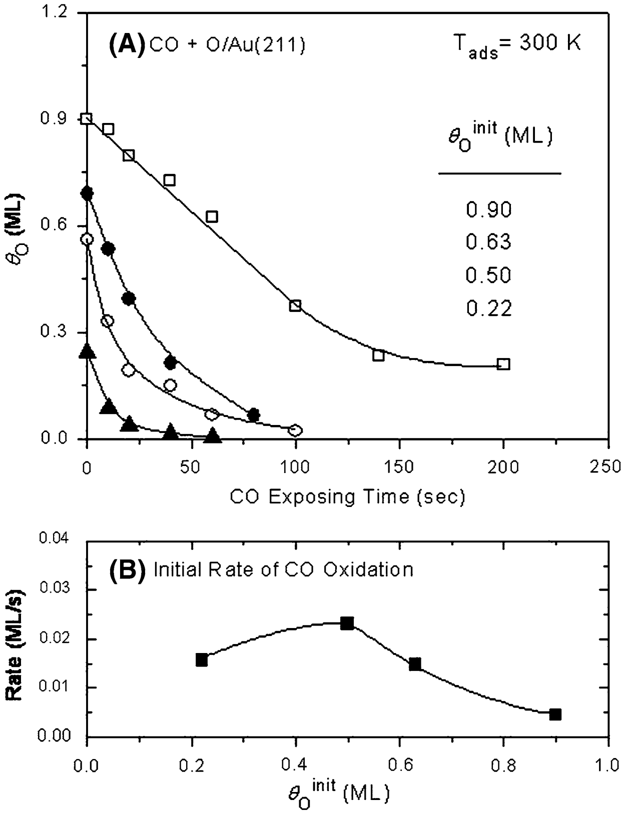

Fig. 2 **a** Plots of the oxygen coverage following CO doses on the O/Au(211) surface with different initial oxygen coverages. Values for θ_O were calculated from O_2 TPD peak areas. **b** Initial rates of CO oxidation calculated from data on plot (**a**) as a function of initial oxygen coverages, θ_O^{init}

In addition, the CO oxidation rate was measured on the oxygen-precovered Au(211) surface at 200, 300 and 400 K with $\theta_O^{init} = 0.9$ ML. This was investigated as before using O_2 TPD spectra that were obtained following CO exposures to measure the amount of unreacted surface oxygen. The results are given in Fig. 3a. The rate of CO oxidation on Au(211) at 200 K is higher than that at 400 K under these conditions, which means that the apparent activation energy E_{app} has a negative value. An Arrhenius plot from the data in Fig. 3a is shown in Fig. 3b. The slope of this plot gives $E_{app} = -7.0$ kJ mol^{-1}. A negative value indicates that some pre-equilibrium controls the reaction rate because a single elementary step cannot have negative activation energy.

A Langmuir-Hinschelwood (LH) mechanism for CO oxidation is often considered as follows:

$$\mathrm{CO(g)} \underset{k_{des}}{\overset{k_{ads}}{\Leftrightarrow}} \mathrm{CO(a)} \qquad (1)$$

$$\mathrm{CO(a)} + \mathrm{O(a)} \xrightarrow{k_{LH}} \mathrm{CO_2(a)} \qquad (2)$$

$$\mathrm{CO_2(a)} \rightarrow \mathrm{CO_2(g)} \qquad (3)$$

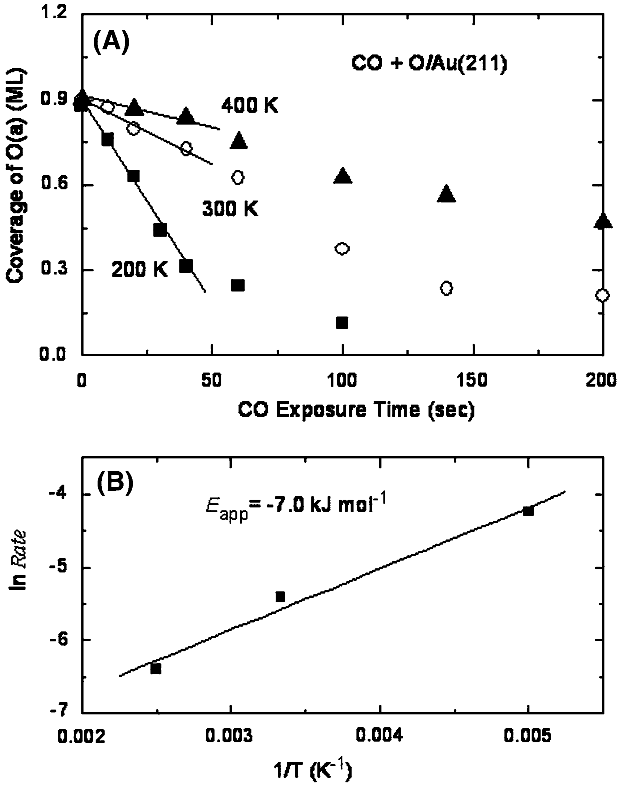

Fig. 3 **a** Plots of transient CO oxidation kinetics curves for $P_{CO} = 2.5 \times 10^{-7}$ Torr on the Au(211) surface at 200, 300 and 400 K. Oxygen coverages were calculated from O_2 TPD curves obtained after CO titrations. Initial reaction rates were calculated from data acquired up to 50 s of reaction time. **b** Arrhenius plot giving the apparent activation energy for CO oxidation on a Au(211) surface using initial reaction rates from the data in (**a**)

If the equilibrium between gaseous and adsorbed CO given in Eq. (1) is important for the rate of CO oxidation, then the value of E_{app} for the reaction is given by

$$E_{app} = E_{LH} - E_d(\mathrm{CO}) \qquad (4)$$

where E_{LH} is the activation energy for the L-H step in Eq. (2) and E_d(CO) is the activation energy for desorption of CO. In addition to the value of E_{app}, which controls the observed kinetics, one would also like to know the value of E_{LH} since this elementary step indicates additional information about the reactivity of the surface. The value of E_{LH} can be calculated from E_{app} if E_d(CO) is known. Because E_d(CO) = 27–50 kJ mol^{-1} depending on occupation of terrace or step sites, one can make an estimate of E_{LH} = 20–43 kJ mol^{-1} by assuming that there is no effect of O(a) on E_d(CO). This of course introduces uncertainty in the estimate of E_{LH}, but we expect that this is small.

Using similar transient kinetics techniques, negative values of E_{app} close to this value were previously reported on Au(111) where $E_{app} = -10.5$ kJ mol^{-1} [10] and on

Ag(110) where $E_{app} = -4.8$ kJ mol^{-1} [17]. On Au(111), CO does not adsorb at 100 K and so $E_d(CO) \leq 25$ kJ mol^{-1}. This leads to an estimate of $E_{LH} \leq 14.5$ kJ mol^{-1}. On Ag(110), $E_d(CO) = 27$ kJ mol^{-1} and so $E_{LH} = 22$ kJ mol^{-1}. A positive value of $E_{app} = 8.4$ kJ mol^{-1} at $\theta_O = 0.25$ ML was reported on Au(110) by Outka and Madix [11]. This led to $E_{LH} \leq 42$ kJ mol^{-1} considering $E_d(CO) \leq 34$ kJ mol^{-1} on Au(110). This report was disputed by Gottfried et al. [12] who reported values of $E_{app} = -1.8$ kJ mol^{-1}. Using their estimation of $E_d(CO) = 38$ kJ mol^{-1} [18], E_{LH} can be obtained as 36 kJ mol^{-1}. A lower limit for E_{LH} is expected to be about 16.7 kJ mol^{-1} which is the activation energy value for the gas phase reaction of O + CO [19]. Our E_{LH} value of 20–43 kJ mol^{-1} for CO oxidation is larger than that on Au(111) and Ag(111), but smaller than that of Au(110). All of these data are summarized in Table 1. Even though Au(211) is a stepped surface, we find that the activation energy for CO oxidation is not much different from “flat” Au (111) or (110) surfaces. In addition, this value can be compared to that of $E_{LH} = 67$ kJ mol^{-1} which was predicted by theoretical calculations by Liu et al. [9].

We set out to obtain some initial data that could be used to inform whether high concentrations of step sites, or in particular the presence of Au(211) crystal planes, might simply explain the high reactivity for CO oxidation exhibited by supported Au nanoclusters. We cannot identify experimentally any additional reactivity associated with step sites on the Au(211) surface and the values of both E_{app} and E_{LH} for CO oxidation on Au(211) were not much different from those on Au(111) or Au(110). One complication in these experiments is the restructuring of Au surfaces by oxygen adsorption, as we reported by LEED on Au(211) [14] and by LEED [20] and STM on Au(111) [21]. However, the initial reaction rate, as shown in Fig. 2b, is not highest at the smallest coverages where steps still exist. No clear evidence is established indicating a tendency for CO oxidation at step sites rather than terrace sites.

It is commonly considered that O_2 dissociation controls the overall CO oxidation reaction on Au surfaces and perhaps on Au catalysts. Our study here does not probe this important feature, addressing only the structure sensitivity of CO oxidation. Information on this elementary step is useful regarding a general characterization of the surface reactivity, and could be important directly if O_2 dissociation were to be activated sufficiently on the catalyst or if substantial oxygen spillover occurred. Turner et al. have recently reported on the ability of tiny particles containing as few as 55 Au atoms supported on SiO_2 and BN to catalyze the selective oxidation of alkenes by only O_2 [22].

Our previous studies begin to address O_2 dissociation on stepped Au surfaces, and we reported that no O_2 dissociation occurred on the Au(211) step surface under relatively high pressure conditions [14]. This behavior is similar to that on other Au single crystal surfaces. Thus far, we have found no evidence that steps, or this crystal plane, have much to do with the remarkable catalytic properties of supported Au nanoparticles. It is worth mentioning that Goodman and coworkers investigated the CO oxidation activity on the Au cluster sizes supported on planar TiO_2 and proposed that the structure sensitivity could be attributed to a quantum size effect [23, 24]. They also found that Au islands that were two atomic layers thick were the most effective catalyzing CO oxidation and possessed unusual electronic properties. These results were confirmed by Campbell et al. who found that even Au nanoparticles supported on $TiO_2(111)$ showed no preferential reactivity for the titration rate of preadsorbed oxygen by CO [25].

4 Summary

We have conducted transient kinetics studies of CO oxidation on a stepped Au(211) single crystal surface precovered with oxygen created by ozone dosing. CO oxidation on Au(211) does not appear to be significantly enhanced or otherwise different from that on Au(111) and (110) surfaces. CO titration of preadsorbed oxygen proceeds facilely below room temperature. The CO oxidation reaction rate was dependent on the initial oxygen coverage, and an apparent activation energy for CO oxidation was determined to be -7.0 kJ mol^{-1} for $\theta_O^{init} = 0.9$ ML using initial reaction rates. Our estimate of the Langmuir-

Table 1 Apparent activation energy of CO oxidation (E_{app}), desorption activation energy of CO (E_d(CO)), and Langmuir-Hinschelwood activation energy of CO oxidation (E_{LH}) on Au and Ag single cystal surfaces

	E_{app} (kJ mol^{-1})	E_d (CO) (kJ mol^{-1})	E_{LH} (kJ mol^{-1})	References
Au(111)	−10.5	≤25	≤14.5	[10]
Au(110)	8.4 (at $\theta = 0.25$ ML)	≤34	≤42	[11]
Au(110)	−1.8	38	36	[12, 18]
Ag(110)	−4.8	27	22	[17]
Au(211)			67	[9]
Au(211)	−7.0	27–50	20–43	This work

Hinschelwood (LH) activation barrier for CO oxidation of $E_{\mathrm{LH}} = 20$–$43\ \mathrm{kJ\ mol^{-1}}$ on the Au(211) surface is in between than that on Au(111) and Au(110), somewhat below the value of $67\ \mathrm{kJ\ mol^{-1}}$ predicted on Au(211) by theoretical calculations.

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