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## Oxidation of carbon monoxide over $Au(1 1 0) - (1 \times 2)$

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#### Abstract

We have studied the oxidation of carbon monoxide (CO) on an oxygen-precovered gold  $(1 \ 1 \ 0)$ - $(1 \times 2)$  surface. At low oxygen coverages, the reaction is first-order in the oxygen coverage and has an apparent activation energy of -1.8 kJ/mol. Assuming a Langmuir–Hinshelwood mechanism we evaluated a true activation energy of 57 kJ/mol. A complete reaction energy diagram of the CO oxidation on Au(110) is reported.

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#### 1. Introduction

A presently widely studied catalytic reaction is the CO oxidation over oxide-supported gold particles [1–3]. Research is stimulated (a) by the surprising fact that gold as the noblest metal shows appreciable catalytic activity and (b) because of the technically relevant low-temperature activity of this type of catalysts. Despite the indefatigable research efforts, the nature of the active species and the mechanism of the O<sub>2</sub> activation are still controversial. Apparently two major classes of systems exist for which completely different reaction mechanisms have been proposed. The one class of systems includes Au particles of 2–5 nm diameter supported on oxides of the first transition metal row. The chemical nature of the support (and traces of water) play a decisive role. It is assumed that a positively polarized Au species on the junction of metal and oxide is essential for the O2 activation ([1] and references therein). On the other hand, evidence has been obtained that negatively charged, very small  $Au_n^-$  (or  $Au_n^{\delta-}$ ) clusters catalyse the CO oxidation even in the gas phase [4] or on relatively inert substrates such as MgO or SiO<sub>2</sub>. The activity depends strongly on the cluster size and is highest for n = 8. The support, however, seems to play a minor role for this class of systems [5,6]. The possible coexistence of several completely different mechanisms for catalysis on (supported and unsupported) gold particles makes the situation more complicated than originally thought, but it may explain some contradictions in previous results (e.g. concerning the influence of reductive or oxidative pretreatment on the activity).

It has been pointed out that a further understanding of the nature of these gold-based catalysts

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requires thorough quantitative kinetic measurements [2]. While these are rare, there is also a lack of UHV reference studies on gold single-crystal surfaces. In one of the few previous investigations, Outka and Madix [7] oxidized CO on an oxygenprecovered Au(110) surface and evaluated an apparent activation energy of  $(8 \pm 4)$  kJ/mol for the overall reaction. A true activation energy of the surface reaction could not be determined because the CO desorption energy remained unknown.

In one of our recent reports on oxygen adsorption on Au(110)-(1×2) [8] we performed reactive thermal desorption measurements of the CO oxidation reaction and found a rate maximum at 175 K. Above this temperature the rate has a negative temperature coefficient. This result suggests a negative apparent activation energy and is thus at variance with the positive value reported by Outka and Madix. To clarify this point we now performed detailed kinetic measurements. The data obtained in this and our recent publications enable us to present a complete energy diagram of the CO oxidation over Au(110).

#### 2. Experimental

A detailed description of our sample and its preparation was given in Ref. [9], whereas the experimental details of the kinetic measurements can be found in Ref. [8].

The error of the pressure measurement amounts to 20%. The different gauge sensitivities for the particular gases were compensated by dividing the meter reading by the following factors: CO 1.1,  $O_2$  0.8 (values recommended by the manufacturer of the gauge).

#### 3. Results and discussion

Fig. 1 displays the CO<sub>2</sub> desorption rate,  $R_{CO_2}$ , as a function of time for various fixed temperatures between 60 and 400 K. In all measurements, the following procedure was applied: chemisorbed atomic oxygen (0.45 ML) was prepared by electron bombardment of physisorbed O<sub>2</sub> as described in Refs. [9,10]. To ensure a uniform oxygen phase in



approximately exponentially with time (Fig. 1). First, we qualitatively consider the initial rates (t = 0): in the low-temperature range between 60 and 160 K, the initial rate increases with temperature due to the usual rise of the reaction rate constant  $k_r$ . Above 180 K, however, the rate decreases, indicating a negative apparent activation energy. The most likely reason is a decrease of the CO equilibrium coverage with increasing temperature, which is not compensated by the increase of  $k_r$ .

Assuming a Langmuir–Hinshelwood mechanism, which is strongly suggested by the behaviour in the high-temperature range, we can derive a mechanism that allows a quantitative analysis and the determination of the true activation energy of the surface reaction. The following mechanism is proposed:

Fig. 1. CO oxidation over O/Au(110)-(1×2). CO<sub>2</sub> desorption rate as a function of time for temperatures between 60 and 400 K. Detected mass: m/z = 44 (CO<sub>2</sub><sup>+</sup>). Inset: semi-logarithmic plot.



$$O_2(g) \xrightarrow[k_{a,O_2}]{} O_2(ad)$$
(1)

$$O_2(ad) \xrightarrow{k_{diss,O_2}} 2O(ad)$$
(2)

$$\operatorname{CO}(g) \xrightarrow{k_{a,CO}} \operatorname{CO}(ad)$$
 (3)

$$\operatorname{CO}(\operatorname{ad}) + \operatorname{O}(\operatorname{ad}) \xrightarrow{k_{\mathrm{r}}} \operatorname{CO}_2(\operatorname{ad})$$
 (4)

$$\operatorname{CO}_2(\operatorname{ad}) \xrightarrow{k_{\operatorname{d}}\operatorname{CO}_2} \operatorname{CO}_2(\operatorname{g})$$
 (5)

Eqs. (1) and (2) can be excluded from our consideration, since O(ad) is not formed by spontaneous adsorption.

According to Eq. (5), the  $CO_2$  desorption rate is given by

$$R_{\rm CO_2} \equiv \frac{\mathrm{d}N_{\rm CO_2}}{A\mathrm{d}t} = k_{\rm d,CO_2}\Theta_{\rm CO_2} \tag{6}$$

Above the CO<sub>2</sub> desorption temperature on oxygen-precovered gold, which is found to be  $\approx 120$  K [11,12], the CO<sub>2</sub> equilibrium coverage,  $\Theta_{CO_2}$ , is certainly very low and obeys the steady-state condition:

$$\frac{\mathrm{d}\Theta_{\mathrm{CO}_2}}{\mathrm{d}t} = -k_{\mathrm{d},\mathrm{CO}_2}\Theta_{\mathrm{CO}_2} + k_\mathrm{r}\Theta_{\mathrm{CO}}\Theta_{\mathrm{O}} \cong 0 \tag{7}$$

Eliminating  $\Theta_{CO_2}$  from Eqs. (6) and (7) yields:

$$R_{\rm CO_2} = k_{\rm r} \Theta_{\rm CO} \Theta_{\rm O} = -\frac{\mathrm{d}\Theta_{\rm O}}{\mathrm{d}t} \tag{8}$$

With an excess of gas phase CO, we can now also eliminate  $\Theta_{CO}$  if we assume that the CO adsorption/desorption equilibrium is only minimally perturbed by the oxidation reaction, an assumption that is well-justified [11]. Thus, the CO coverage is given by the Langmuir isotherm, at least for a small coverage range in which the isosteric heat remains practically constant:

$$K \equiv \frac{k_{\rm a,CO}}{k_{\rm d,CO}} = \frac{\Theta_{\rm CO}}{p_{\rm CO}(1 - \Theta_{\rm CO})}$$
$$\approx \frac{\Theta_{\rm CO}}{p_{\rm CO}} \quad \text{for} \quad \Theta_{\rm CO} \ll 1 \tag{9}$$

At the given CO pressure and temperatures above 160 K, the equilibrium CO coverage is low,

e.g.,  $\approx 0.05$  ML at 180 K and  $p_{\rm CO} = 10^{-6}$  mbar (see Ref. [13]). Thus, we can neglect  $\Theta_{\rm CO}$  in the denominator on the right hand side of Eq. (9).

Combining Eqs. (8) and (9) (simplified) under elimination of  $\Theta_{CO}$  yields:

$$R_{\rm CO_2} = -\frac{\mathrm{d}\Theta_{\rm O}}{\mathrm{d}t} = \frac{k_{\rm a,CO}k_{\rm r}}{k_{\rm d,CO}}p_{\rm CO}\Theta_{\rm O} \equiv k_{\rm exp}\Theta_{\rm O} \qquad (10)$$

with the empirical rate constant  $k_{exp}$ . Thus, the mechanism in Eqs. (3)–(5) in combination with our additional assumptions predicts a pseudo-first-order reaction. Applying the Arrhenius equation to the individual rate constants in Eq. (10) leads to the following expression for  $k_{exp}$ :

$$k_{\exp} = k_{a,CO} p_{CO} \frac{v_{\rm r}}{v_{\rm d,CO}} e^{-(E_{\rm r} - E_{\rm d,CO})/RT}$$
(11)

with the CO desorption energy  $E_d$ , the activation energy of the oxidation step (Eq. (4))  $E_r$ , and the respective frequency factors  $v_{d,CO}$  and  $v_r$ . Eq. (11) shows that the apparent activation energy of the overall reaction,  $E_r - E_{d,CO}$ , can be obtained from the slope of a plot of ln  $k_{exp}$  vs. 1/T.

In order to evaluate  $k_{exp}(T)$  from the curves in Fig. 1, we integrate the rate equation Eq. (10) and, with this result, eliminate  $\Theta_0$  from Eq. (10):

$$R_{\rm CO_2} = -\frac{\mathrm{d}\Theta_{\rm O}}{\mathrm{d}t} \equiv k_{\rm exp}\Theta_{{\rm O},t=0}\mathrm{e}^{-k_{\rm exp}t} \tag{12}$$

with the initial oxygen coverage  $\Theta_{O,t=0}$ .

Thus,  $k_{exp}$  can be evaluated from the curves in Fig. 1 by the relation:

$$k_{\exp} = -\frac{\mathrm{d}\ln R_{\mathrm{CO}_2}}{\mathrm{d}t}.$$
 (13)

According to Eqs. (11) and (13), the slope of a plot of  $\ln \left(-\frac{\dim R_{CO_2}}{dr}\right)$  vs. 1/T is  $-(E_r - E_{d,CO})/R$ , i.e., it is equal to the apparent overall reaction activation energy. Such a plot for temperatures between 200 and 400 K is displayed in Fig. 2 and yields  $(E_r - E_{d,CO}) = (-1.8 \pm 0.9)$  kJ/mol, in agreement with the negative temperature coefficient of the rate above  $\approx 160$  K (see Fig. 1). Determination of the true activation energy,  $E_{r}$ , requires knowledge of the CO desorption energy,  $E_{d,CO}$ . In a recent paper [13], we evaluated the isosteric heat of CO adsorption at zero coverage,  $Q_{st} = (59 \pm 2)$  kJ/mol, which is, for a mobile

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Fig. 2. Plot of  $\ln(-d \ln R_{CO_2}/dt)$  vs. 1/T.

adsorbate layer, equal to the CO binding energy [11]. Since CO adsorption is non-activated (as shown in Ref. [13]) we can identify the binding energy with the desorption energy and thus obtain a value of  $E_r = (57 \pm 3)$  kJ/mol for the true activation energy. This value is higher than the activation energy for the gas phase reaction between CO and oxygen atoms, which is only 15 kJ/mol [14]. The difference between  $E_r$  and the gas phase value can be interpreted as the energy expense for the rehybridization of the adsorbate-substrate bonds of CO and oxygen in the activated complex.

A closer evaluation of the curves in Fig. 1 reveals that the plots of  $\ln R_{\rm CO_2}$  vs. 1/T actually deviate somewhat from linearity, especially in the low-temperature range below 180 K (Fig. 1, inset). In the following, we consider several possible reasons for these deviations which partly reflect the simplifications we applied for deriving Eqs. (11) and (13), and critically discuss further implicit assumptions of our model.

(a) We assumed that  $\Theta_{CO} \propto p_{CO}$  (Eq. (9)), which is only valid for small  $\Theta_{CO}$ . Furthermore, we assumed that the CO adsorption-desorption equilibrium is not perturbed by the reaction of CO with chemisorbed oxygen. Now we give up these simplifications and demonstrate that the 'complete' solution contains an additional term in which  $\Theta_0$  is proportional to time *t*. Assuming steady-state conditions for CO(ad) we obtain:

$$\frac{\mathrm{d}\Theta_{\mathrm{CO}}}{\mathrm{d}t} = k_{\mathrm{a,CO}}p_{\mathrm{CO}}(1 - \Theta_{\mathrm{CO}}) - k_{\mathrm{d,CO}}\Theta_{\mathrm{CO}} - k_{\mathrm{r}}\Theta_{\mathrm{CO}}\Theta_{\mathrm{O}} = 0$$
(14)

Herein, we still assume a constant  $k_{d,CO}$ , which requires a coverage-independent CO desorption energy, and a constant  $k_{a,CO}$ , which requires that the CO sticking coefficient is independent of temperature.

With Eq. (14), we eliminate  $\Theta_{CO}$  from Eq. (8) and obtain instead of Eq. (10):

$$R_{\rm CO_2} = -\frac{\mathrm{d}\Theta_{\rm O}}{\mathrm{d}t}$$
$$= \frac{k_{\rm a,CO}k_{\rm r}p_{\rm CO}}{k_{\rm a,CO}p_{\rm CO} + k_{\rm d,CO} + k_{\rm r}\Theta_{\rm O}}\Theta_{\rm O}$$
$$\equiv k_{\rm exp}\Theta_{\rm O} \tag{15}$$

Eq. (15) reveals that the experimental rate constant,  $k_{exp}$ , is actually not independent of the oxygen coverage  $\Theta_0$ . Integration yields:

$$\ln \frac{\Theta_{\rm O}}{\Theta_{\rm O,t=0}} + \frac{k_{\rm r}}{k_{\rm a,CO} + k_{\rm d,CO}} (\Theta_{\rm O} - \Theta_{\rm O,t=0})$$
$$= -\frac{k_{\rm r} k_{\rm a,CO} p_{\rm CO}}{k_{\rm a,CO} p_{\rm CO} + k_{\rm d,CO}} t$$
(16)

The second term on the left hand side of Eq. (16) leads to a deviation from the first-order kinetics. The occurrence of  $k_{a,CO} + k_{d,CO}$  in the denominator indicates that these deviations increase when the CO adsorption and desorption rates are small, i.e., at low-temperatures and low CO pressures (as can be seen in Fig. 1, inset).

(b) The CO sticking coefficient  $S_{\rm CO}$  and the desorption rate constant  $k_{\rm d,CO}$  may depend on oxygen coverage  $\Theta_{\rm O}$ , which decreases during the reaction.

(c) The Langmuir isotherm, which was used in Eqs. (9) and (14), is only valid for very CO coverages (e.g. at elevated temperatures) because the isosteric heat of CO is coverage-dependent (see Ref. [13]) and, thus,  $k_{d,CO}$  itself is a function of the CO coverage. Furthermore,  $k_{a,CO}$  contains the CO sticking coefficient  $S_{CO}$ . If  $S_{CO}$  is a function of temperature, the temperature dependence of  $k_{exp}$  is not restricted to the exponential term in Eq. (11),



Fig. 3. Quantitative energy diagram of the CO oxidation over Au(110)-( $1\times2$ ). All values concerning dioxygen adsorption are multiplied with 1/2 to account for the stoichiometry of the reaction which requires only 1/2 O<sub>2</sub> for the oxidation of one CO molecule. All values (apart from the standard gas phase reaction energy of 285 kJ/mol and the O<sub>2</sub> dissociation energy of 498 kJ/mol) were taken from this and our recent publications.

which was implicitly assumed when we derived the apparent activation energy from the plot in Fig. 2.

(d) The oxygen phase may be less homogeneous than the oxygen thermal desorption data in Ref. [10] suggest, leading to a variety of oxygen adsorption states with different reactivity towards CO. This idea is supported by the UPS measurements described in Ref. [11] and by the apparent contradiction between the relatively high activation energy of  $E_r = (57 \pm 3)$  kJ/mol and the fact that the reaction occurs already below 100 K.

Outka and Madix [7] reported an apparent activation energy of  $(8 \pm 4)$  kJ/mol for the CO oxidation on an oxidized Au(110)-(1×2) surface, a result which disagrees with our value of  $(-1.8 \pm 0.9)$ kJ/mol. A possible reason for this deviation may be the different methods for producing chemisorbed oxygen. Outka and Madix employed thermal dissociation of O<sub>2</sub> on a hot Pt wire in front of the sample. It cannot be excluded that a different oxygen species than with our method is generated in this way. Furthermore, impurities, especially Pt from the hot wire, may influence the reactivity of the chemisorbed oxygen (although no Pt contamination was found with AES).

# 4. Energetics and kinetics of the CO oxidation on gold

In our recent publications, we extensively studied the energetics and kinetics of the adsorption of oxygen [9,10,15], CO [13], and CO<sub>2</sub> [11,12] on Au(110). The respective data, complemented by the activation energies as evaluated in this work, enable us to report a complete energy diagram (Fig. 3) of the CO oxidation on Au(110). It is clear from Fig. 3 that the high activation barrier for the dissociative oxygen chemisorption prevents a direct catalytic reaction on the single-crystal surface. In the case of a real gold-based catalytic system, influences of the particle size or the support drastically reduce this barrier.

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