

Pd(111) versus Pd–Au(111) in carbon monoxide oxidation under elevated pressures

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The oxidation of CO on Pd(111) and Pd₇₀Au₃₀(111) has been studied under pressures upto 100 Torr. Gold is found to decrease the surface activity by inhibiting oxygen dissociation. For a sufficient conversion time depending on the CO coverage and the surface identity, a dramatic boost of activity occurs. This is ascribed to a switch from CO-induced inhibition of O₂ adsorption to a regime determined by CO adsorption. The other kinetic features are explained by oxidation of palladium and adsorption-induced restructuring of the surfaces.

KEY WORDS: model catalysts; single-crystal surfaces; palladium; gold; bimetallic alloys; CO oxidation.

1. Introduction

Platinum group metals are very efficient oxidation and hydrogenation catalysts. In particular, palladium is among the most active metals for CO oxidation. In addition to its scientific interest, this reaction is technologically important for car-exhaust emission control, CO₂ lasers, air purification, sensors and fuel cells.

Although many works concern CO oxidation over supported Pd catalysts [1–3], single-crystal surfaces [4–6] and planar supported model catalysts [7–9] under low pressure conditions (<10⁻² Torr), very few experimental studies have been performed at pressures relevant to catalysis. To our knowledge, the sole exceptions to this are the studies of Goodman and coworkers. These authors have investigated CO oxidation over Pd(110) [10], Pd(100) [11] and Pd(111) [12] and compared these surfaces to Pd/SiO₂/Mo(110) model catalysts [13] at pressures ranging from 10⁻⁹ to 10 Torr. In summary, CO oxidation on palladium proceeds through a Langmuir-Hinshelwood mechanism. CO adsorbs molecularly, possibly through a weakly bonded precursor state, and O₂ dissociates before the CO + O reaction occurs. At moderate temperatures, CO covers the surface and inhibits O₂ dissociation. Therefore, the reaction rate is determined by CO desorption. Furthermore, the reaction is only slightly structure-sensitive.

Pd–Au catalysts have recently been found superior to pure Pd or Au catalysts for several reactions, e.g., the direct synthesis of hydrogen peroxide [14] and the

ethylene acetoxylation to vinyl acetate for the VAM process [15]. In our own attempt to modify the catalytic reactivity of palladium surfaces by gold, we have investigated the hydrogenation of 1,3-butadiene [16], the oxidation of hydrogen [17] and here the oxidation of CO over single-crystal surfaces of the Pd₇₀Au₃₀ bulk alloy. In the case of CO oxidation and following theoretical predictions [18], gold may decrease the CO–Pd adsorption strength due to Au–Pd alloying effects (ligand and/or ensemble effects). The weaker CO–Pd interaction may favor the adsorption of O₂ and promote the oxidation of CO. Thus, the reaction may start at temperatures lower than the usual ones (~200 °C), just like on supported gold-based catalysts, which are active below room temperature [19–21].

In this Letter, we present new kinetic results concerning CO oxidation on Pd(111), under elevated pressures (upto 100 Torr) and highly oxidative conditions. Besides, we compare the catalytic properties of Pd₇₀Au₃₀(111) to those of Pd(111).

2. Experimental

We used an experimental set-up that includes facilities for sample preparation and analysis under ultrahigh vacuum (UHV), along with catalytic testing in a static reactor. This stainless-steel low-volume (120 cm³) reactor is UHV-compatible and can operate at gas pressures up to the atmospheric pressure and at temperatures between 20 and 200 °C. This apparatus has been described in details in Ref. [16].

The Pd(111), Au(111) and Pd₇₀Au₃₀(111) samples (10 mm diameter, 1 mm thickness, 5 N purity, 0.1°

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miscut, 0.1 μm polishing) were cleaned by repeated cycles of Ar ion sputtering and annealing at 660, 440 and 460 $^{\circ}\text{C}$, respectively. The surface quality was checked by Auger electron spectrometry (AES) and low energy electron diffraction (LEED). For all single-crystals, the indicators of surface cleanliness were the absence of carbon and sulfur contaminations and well-ordered LEED patterns. A fixed surface concentration (measured by the AES peak-to-peak intensity ratios: $R_{\text{Au/Pd}} = 0.4$, considering the NVV transition at 73 eV for Au and the MNN transition at 332 eV for Pd) was necessary to achieve reproducible experiments over the alloy single-crystal. As reported in Ref. [16], the clean $\text{Pd}_{70}\text{Au}_{30}(111)$ surface exhibits a (1×1) unreconstructed structure and a gold concentration of 75 ± 5 at % in the topmost atomic layer. The clean Pd(111) and Au(111) surfaces present a (1×1) structure and a herringbone-type $(22 \times \sqrt{3})$ pattern, respectively.

After cleaning, the samples were transferred from the preparation chamber to the reactor. The pressure remained in the 10^{-9} Torr range during the transfers. Gas mixtures containing high-purity CO, O_2 and Ar (neutral gas used for internal calibration) were introduced into the reactor. Then, the reactor content was sampled through a leak valve and analyzed with a quadrupole mass spectrometer. The stability of the catalytic surfaces was tested by performing repeated reaction cycles that included injection of the reactants, reaction, and evacuation of the reacted gases by turbomolecular pumping. After the experiments, the partial pressures of CO (p_{CO}), O_2 (p_{O_2}) and CO_2 (p_{CO_2}) were calculated from the mass spectrometer data corrected for ion fragmentation and spectrometer sensitivity.

3. Results

In the investigated temperature range ($T < 160$ $^{\circ}\text{C}$), the partial pressure ratios $p_{\text{CO}}/p_{\text{O}_2}$ were chosen according to Goodman and coworkers [10, 12] in order to optimize the CO_2 formation rate and, therefore, obtain measurable kinetics. Au(111) is inactive whatever the temperature. In all the investigated pressure conditions, Pd and Pd–Au are inactive at room temperature; their activity increases with temperature.

Figure 1 shows the evolution of p_{CO} and p_{CO_2} as a function of time during CO oxidation over Pd(111) and Pd–Au(111) at 150 $^{\circ}\text{C}$, $p_{\text{CO}}^0 = 0.1$ Torr and $p_{\text{O}_2}^0 = 10$ Torr (values of the partial pressures at $t = 0$). On both surfaces, the CO pressure decreases linearly (constant reaction rate, r_1). Below a certain value of p_{CO} , the rate suddenly increases to a constant rate r_2 . Pd–Au(111) is ~ 4 times less active than Pd(111). Moreover, both r_1 and r_2 are lower for the alloy.

We performed several reaction cycles. The kinetics is roughly stable over Pd–Au (that is why only a single run is reported in figure 1). Conversely, the catalytic activity

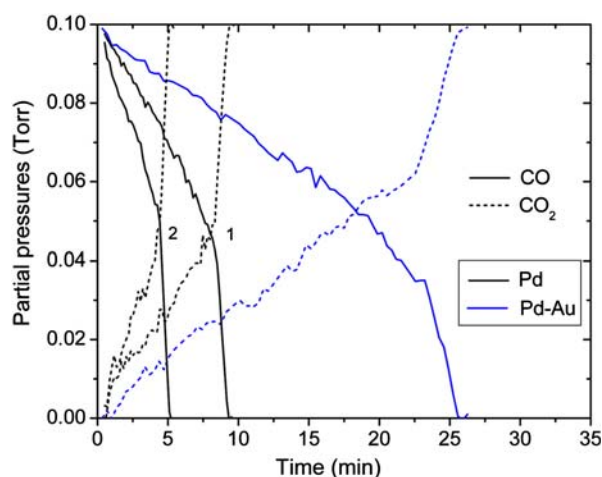


Figure 1. CO (solid lines) and CO_2 (dotted lines) partial pressures during two consecutive runs of CO oxidation on Pd(111) (black lines) and one run on Pd–Au(111) (blue lines). $p_{\text{O}_2}^0 = 10$ Torr, $T = 150$ $^{\circ}\text{C}$.

of Pd increases by a factor ~ 2 from one cycle to the next but only two cycles are necessary to reach a “steady state”. This boost in the CO oxidation activity concerns r_1 and, to a smaller extent, r_2 .

Table 1 summarizes our results. We report the $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$ ratio ($p_{\text{CO}}^{\text{th}}$ stands for the threshold CO pressure when the reaction accelerates and p_{CO}^0 is the initial CO pressure in the reactor) and the turnover frequency (TOF) of CO conversion, *i.e.* of CO_2 formation.

On Pd(111), at 160 $^{\circ}\text{C}$ ($p_{\text{CO}}^0 = 0.1$ Torr and $p_{\text{O}_2}^0 = 20$ Torr) the reaction was so fast that we were not able to measure any rate. Under these conditions, the reaction must instantaneously reach the second kinetic regime, *i.e.* $p_{\text{CO}}^{\text{th}} \geq p_{\text{CO}}^0$. On the other hand, at 120 $^{\circ}\text{C}$ (same pressure conditions) the reaction was quite slow (at least 100 min for total conversion). In this case, we observed a big boost ($r_2/r_1 = 15$) for $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0 = 0.4$. Pd–Au(111) was inactive at 120 $^{\circ}\text{C}$ but became active at 150 $^{\circ}\text{C}$. A slight boost ($r_2/r_1 = 2$) was observed for $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0 = 0.2$. In all the cases, r_2/r_1 is lower on Pd–Au than on Pd.

Now let us analyze the effect of the total pressure for a given $p_{\text{CO}}/p_{\text{O}_2}$ ratio (Table 1). For $p_{\text{CO}}/p_{\text{O}_2} = 0.01$ ($T = 150$ $^{\circ}\text{C}$) on the Pd(111) surface, the turnover frequencies, and obviously the r_2/r_1 ratios remain unchanged whatever the initial total pressure is. The turnover frequency is around 0.3 s^{-1} before the boost (TOF_1) and 7–9 times greater after it (TOF_2). Furthermore, $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$ decreases as both p_{CO}^0 and $p_{\text{O}_2}^0$ increase. Conversely, on Pd–Au(111) both the TOF and the $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$ ratio vary with the total pressure (keeping $p_{\text{CO}}/p_{\text{O}_2}$ constant). Besides, the turnover frequency increases with $p_{\text{O}_2}^0$ (at p_{CO}^0 fixed, 0.1 Torr), whereas $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$ decreases. At $p_{\text{O}_2}^0 = 20$ Torr, when p_{CO}^0 increases, the TOF and the $p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$ ratio slightly decrease.

Table 1

Kinetic parameters of CO oxidation over Pd(111) and Pd–Au(111). The TOF is the number of CO molecules converted per surface atom per second (surface density taken equal to 1.5×10^{15} atoms per cm^2). The 1 and 2 subscripts correspond to the kinetic regime. p_{CO}^0 and $p_{\text{CO}}^{\text{th}}$ stand for the CO initial pressure and the value of the CO pressure at the boost, respectively. The reported values concern steady-state reaction runs.

$p_{\text{CO}}^0(\text{Torr})/p_{\text{O}_2}^0(\text{Torr})$ (Temperature, °C)	Pd(111)		Pd–Au(111)	
	$p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$	TOF ₁ then TOF ₂ (s^{-1}) (r_2/r_1)	$p_{\text{CO}}^{\text{th}}/p_{\text{CO}}^0$	TOF ₁ then TOF ₂ (s^{-1}) (r_2/r_1)
0.1/20 (120)	0.40	0.027 then 0.40 (15)	Not relevant	~0
0.1/20 (160 for Pd, 150 for Pd–Au)	≥ 1	Not measurable	0.23	0.54 then 0.99 (2)
0.1/10 (150)	0.58	0.29 then 2.1 (7)	0.44	0.067 then 0.39 (6)
0.2/20 (150)	0.56	0.33 then 3.1 (9)	0.15	0.36 then 0.90 (3)
1/100 (150)	0.40	0.27 then 2.5 (9)		Not measured

Figure 2 plots $p_{\text{CO}}^{\text{th}}$ as a function of p_{CO}^0 ($p_{\text{O}_2}^0 = 20$ Torr, $T = 160$ °C) for Pd and Pd–Au. The threshold CO pressure increases with the initial CO pressure on both surfaces. In addition, as will be discussed below, $p_{\text{CO}}^{\text{th}}$ is lower for Pd–Au(111) than for Pd(111).

We also studied the influence of the CO pressure (at a given initial oxygen pressure) on the reaction rate. In figure 3, we report the turnover frequencies as a function of the CO pressure (TOF₁ as a function of p_{CO}^0 and TOF₂ as a function of $p_{\text{CO}}^{\text{th}}$). In the case of Pd(111), TOF₁ is almost independent of p_{CO} , whereas TOF₂ increases with p_{CO} . On the other hand, both TOF₁ and TOF₂ decrease slightly as a function of p_{CO} in the case of Pd–Au(111).

4. Discussion

The conversion of CO to CO₂ follows the same behavior on Pd(111) and Pd₇₀Au₃₀(111): $p_{\text{CO}}(t)$ decreases (rate r_1) until it reaches a threshold pressure ($p_{\text{CO}}^{\text{th}}$); then, the reaction accelerates (rate r_2). In the pressure and temperature ranges studied, CO is the

most abundant species on the surface during the first kinetic regime. Thus, O₂ can hardly find free sites to dissociate. However, the probability of O₂ dissociation is not zero, so the initial reaction rate r_1 is non-zero (see figure 1).

In addition, r_1 is roughly independent of p_{CO}^0 on Pd (figure 3). This means that this first kinetic regime is intermediate between that where CO desorption is rate-limiting (negative CO order) and that where CO adsorption is rate-limiting (positive CO order) [3, 4, 12]. When the CO coverage reaches a critical value, there is a sudden reaction light-off (see Ref. [6] for the determination of such a critical coverage on Pd(110)). At this moment, the reaction switches to a second kinetic regime controlled by the supply of CO. Furthermore, provided $p_{\text{CO}}/p_{\text{O}_2}$ is constant, the absolute rates (r_1 and r_2) do not depend on the partial pressures in the case of Pd (Table 1). This agrees with the proposed mechanism of CO-induced blocking of oxygen adsorption. Let us notice that this activity change does not seem to be due

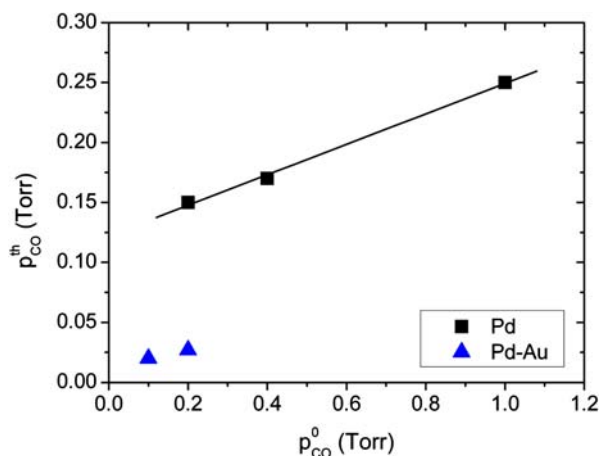


Figure 2. CO threshold pressure $p_{\text{CO}}^{\text{th}}$ (CO pressure remaining in the reactor at the time of the boost) as a function of the initial CO pressure p_{CO}^0 for CO oxidation on Pd(111) (black squares) and Pd–Au(111) (blue triangles). $p_{\text{O}_2}^0 = 20$ Torr, $T = 160$ °C (steady state). The slope of the black line is 0.13 ± 0.01 .

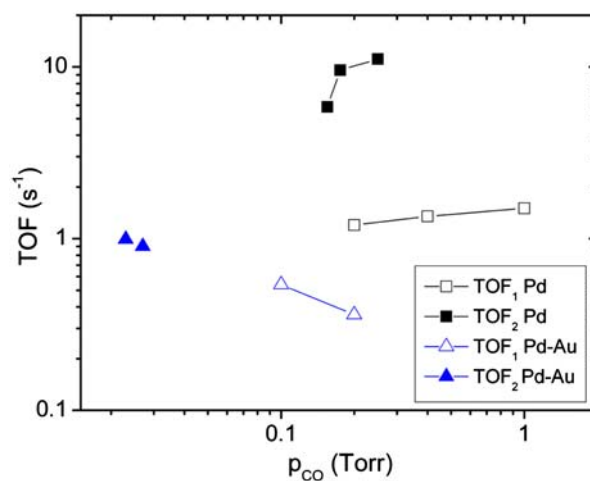


Figure 3. Turnover frequency of the first reaction regime (TOF₁) as a function of the CO initial pressure p_{CO}^0 (open symbols) and turnover frequency of the second reaction regime (TOF₂) as a function of the CO threshold pressure $p_{\text{CO}}^{\text{th}}$ (full symbols), for CO oxidation on Pd(111) (black squares) and Pd–Au(111) (blue triangles). $p_{\text{O}_2}^0 = 20$ Torr, $T = 160$ °C (steady state).

to exothermicity-induced CO desorption, as this would lead to an exponential increase of the reaction rate.

The addition of gold decreases the activity of Pd, *i.e.* both reaction rates (r_1 and r_2) are lower on Pd–Au(111) than on Pd(111). The ratio between $r_2(\text{Pd})$ and $r_2(\text{Pd–Au})$ (included in the 3–5 range, see Table 1) matches the ratio between the number of surface Pd atoms on Pd(111) and the one on the alloy (the Pd coverage in the top layer of Pd₇₀Au₃₀(111) is 0.25 [16]). Moreover, the CO threshold pressure ($p_{\text{CO}}^{\text{th}}$) is higher on Pd than on Pd–Au. We believe that this originates from a blocking effect of gold: the presence of Au decreases the probability of O₂ dissociation. As fewer adsorption sites are available on Pd–Au than on Pd, CO desorption is rate-limiting at lower CO pressures on the former surface. Consistently, the reaction rate on Pd–Au decreases as p_{CO} increases or as p_{O_2} decreases in the pressure range investigated here (figure 3 and Table 1). The same blocking effect has previously been observed for Au deposits on Pt surfaces [22, 23]. It may also explain the lower activity of Pd–Au/SiO₂ catalysts in CO oxidation with respect to Pd/SiO₂ [24].

We observe another important difference between Pd and Pd–Au. After reaction on the fresh surface, a second reaction run gives rise to an increase of the CO₂ production rate on Pd(111), whereas it has no significant effect on Pd₇₀Au₃₀(111). We ascribe this activation of Pd to the formation of a palladium oxide during the second regime of the first run (*i.e.* after the reaction light-off, when oxygen becomes the most abundant adspecies). The elevated oxygen pressures (above 10 Torr) favor oxide formation [25]. The Pd–O surfaces with rough structures [26, 27] exhibit higher activities than Pd surfaces due to the instability of the oxide (Mars–Van Krevelen mechanism) [27, 28]. Pd–Au(111) is less sensitive to oxidation than Pd(111).

Note that under our mild temperature conditions this palladium oxide phase is more probably a two-dimensional oxide than stoichiometric bulk PdO [29]. As such a surface oxide is unstable under UHV [30] and electron beams [31], *in situ* analysis by suitable techniques is required to check our hypothesis.

Finally, we ascribe the increase of the threshold CO pressure ($p_{\text{CO}}^{\text{th}}$) with the initial CO pressure (p_{CO}^{O}) (Figure 2) to CO-induced restructuring during the first reaction regime (where CO almost fully covers the surface). This pressure-dependent surface modification must increase the number of active sites and/or give rise to sites of increased activity (low-coordinated sites), as has been previously observed on Au(111) under elevated CO pressures [32].

5. Summary

The oxidation of carbon monoxide has been studied in static mode over Pd(111), Au(111) and Pd₇₀Au₃₀(111)

at temperatures below 160 °C, for total pressures in the 10–100 Torr range and a large O₂ excess. While no activity of the gold surface has been detected, Pd–Au(111) has been found to be less active than Pd(111) for CO oxidation.

On both surfaces, a sudden acceleration of the reaction rate occurs for a CO partial pressure threshold that depends on the surface, the partial pressures and the temperature. First, CO covers most of the surface, hampering oxygen adsorption. A reaction light-off occurs when the CO coverage becomes lower than a critical value, leading to a second kinetic regime which rate is limited by CO adsorption.

An increase in the reaction rate has also been observed upon evacuation of the reacted gases and introduction of a fresh reactant mixture in the sole case of Pd(111). The different behaviors of Pd and Pd–Au surfaces are ascribed to a gold-induced inhibition of O₂ adsorption and to the onset of a Mars–van Krevelen mechanism for CO oxidation upon palladium oxide formation.

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