

The CO-oxidation on Pd-rich surfaces of PdCu(110): hysteresis in reaction rates

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Abstract

The oxidation of carbon monoxide on PdCu(110) single crystal alloy surfaces was investigated. During temperature variations, at constant CO and O₂ pressures, regions of bistability could be detected by mass spectrometric reaction rate measurements, and a hysteresis was recorded. Initially, the top layer (TL) contained $\approx 100\%$ Pd atoms. After CO-oxidation experiments Cu/Pd ratio was increased up to ≈ 0.7 , as recorded by AES with surface region (SR) analysis of ≈ 4 layers. This increase was due to a chemisorption induced segregation of Cu atoms from the bulk into the three subsurface layers (3SSL), that lie beneath the TL. After prolonged CO-oxidation experiments, with CO pressures up to $\approx 10^{-3}$ mbar, the LEED pattern changed from a (1 \times 1) pattern, for the clean surface, to a *c*(2 \times 2) pattern. The CO-TDS measurements showed that after CO-oxidation measurements all the TDS maxima obtained shifted to lower temperatures. Observation of hysteresis with this alloy surface indicates that it may be possible to observe kinetic oscillations during this reaction.

Keywords: Carbon monoxide; Copper; Hysteresis; Oxidation; Palladium; Reaction rates; Surfaces

1. Introduction

In recent years the oscillatory behaviour of catalytic reactions has been the subject of considerable interest [1]. Such a chemical reaction that exhibits non-linear dynamics is the surface reaction of CO and O₂ on Pt group metals [2–4]. Depending on the controlling parameters partial pressure and flow rate of the CO (P_{CO}) and oxygen (P_{O_2}), as well as temperature, the rate of CO₂ formation can exhibit drastic oscillatory changes associated with the formation of dissipative structures [5].

Various microscopic techniques have been used to study the reaction mechanism involved in these oscillations. One of the most important is UV-photoemission electron microscopy (PEEM) [6] which has been used to study the surface reactions of CO and O₂ on Pd(110) [7]. The oscillatory CO-oxidation on Pt-surfaces has been imaged in situ, on an atomic scale, by field electron [8] and field ion microscopy [9].

In this communication the results of CO-oxidation experiments on an alloy are reported. These reaction studies are possible since the PdCu(110) single crystal alloy surface has been recently extensively characterized [10–13]. The hysteresis in the reaction rate of CO-oxidation on Pt group metals and of other oscillating reactions has

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always been observed. Several detailed investigations of the CO-oxidation on many Pt and Pd single crystals have shown a transition from a state of low reactivity (at low temperatures) to a state of high reactivity at higher temperatures, which were correlated to the transition from a CO rich phase to a CO poor phase and vice versa. Such a hysteresis was connected with reversible structural changes in the substrate, as in the case of Pt [14,15], and with a reversible loading of subsurface oxygen, oxide-type species as in the case of Pd [16].

We describe here, to the best of our knowledge, the first experimental observation of such a hysteresis phenomenon on an alloy surface.

2. Experimental

The ultrahigh vacuum (U.H.V.) system employed in these experiments has a base pressure of 8×10^{-11} mbar and was equipped with low electron energy diffraction (LEED), Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS) using a differentially pumped quadrupole mass spectrometer. The surface of the single crystal was cleaned in situ by Ar^+ ion bombardment. A series of sputtering and annealing cycles were carried out until the concentration of the sulphur and carbon contaminants was below the AES detection limit. Since the Auger signal of C (273 eV) overlaps with that of Pd (279 eV), the ratio of intensities of the 279 to 330 eV signals should have a minimum value

Table 1

AES, CO-TDS measurements and other related experimental conditions which were used to determine the percentages of Pd at the T1 and 3SSL before (i) and after subsequent sets of CO oxidation experiments (ii–iv). From AES: $I(\text{Pd } 180 \text{ eV})/I(\text{Pd } 330 \text{ eV}) = R_1$, $I(\text{Pd } 270 \text{ eV})/I(\text{Pd } 330 \text{ eV}) = R_2$

	Cu/Pd	SR	TL	3SSL	R_1	R_2
(i)	From AES and CO-TDS (Fig. 1a)	0.12 ± 0.02	Pd	Cu/Pd=0.16 or 14% Cu	0.05 ± 0.01	0.36
Pd-rich surface. fcc lattice in the surface region. LEED: (1×1) pattern.						
<i>CO-oxidation:</i>						
Hysteresis was obtained at pressures $\geq 10^{-6}$ mbar. The conditions for Fig. 2: $P_{\text{CO}} \approx 1 \times 10^{-5}$ and $P_{\text{O}_2} \approx 3 \times 10^{-5}$ mbar.						
Time of exposing the surface to the gases ≈ 50 h.						
LEED: weak $c(2 \times 2)$ pattern.						
CO-TDS: shifted to lower temperature (Fig. 1b).						
bcc lattice in the surface region.						
(ii)	From AES and CO-TDS	0.62 ± 0.05	Pd	Cu/Pd=1.0 or 51% Cu	0.21	0.30
Under the same experimental conditions as above, but after additional experimental time ≈ 15 h, a hysteresis similar to that in Fig. 2 was obtained.						
(iii)	From AES and CO-TDS (Fig. 1b)	0.60 ± 0.05	Pd	Cu/Pd=1.0 or 51% Cu	0.5	0.28
Experimental conditions: after ≈ 16 h at $P_{\text{O}_2} \approx 2 \times 10^{-4}$ mbar and P_{CO} between 1×10^{-4} and 8×10^{-4} mbar, a hysteresis similar to that in Fig. 2 was obtained. A lower reactivity rate was obtained (curve 2 of Fig. 3).						
LEED: $c(2 \times 2)$ pattern with very high background intensity.						
CO-TDS: completely changed (Fig. 1c).						
(iv)	From CO-TDS (Fig. 1c) and from AES		Pd	Assumption: as before, Cu/Pd ~ 1.0 or $\sim 50\%$ Cu	≈ 2	

(Table 1) in order to indicate the cleanliness of the surface. Moreover, it has been shown that CO TD spectra are very sensitive to small concentrations of carbon [17]. Using this fact in addition to following the CO and CO₂ production rate upon treating the surface with oxygen, enabled us to confirm the absence of C on the surface. Details of the equipment used, the methods of investigation and the sample cleaning procedure have been described previously [10–12].

The CO and oxygen gases were admitted to the chamber using U.H.V. Balzers leak valves. A home-built temperature controller was used to provide a linear heating rate for the crystal.

2.1. Surface preparation and characterization

The PdCu single crystal alloy used had a bulk Cu/Pd ratio of 1 and was prepared as a (110)-plane. It was treated by sputtering and annealing at temperatures below that of Cu segregation, i.e., ≈ 550 K. This produced a Cu/Pd surface composition (SR) of ≈ 0.1 , with a (1 \times 1) surface structure. Combination of CO-TDS, which was used for top layer characterization, and the SR of ≈ 4 layers depth, analyzed by AES, allowed the average ratio of Cu/Pd in the next three subsurface layers to be evaluated [10]. At the beginning of this investigation, for a Cu/Pd (SR) of ≈ 0.1 , the TL consisted of $\approx 100\%$ Pd, while the 3SSL contained up to 14% Cu atoms.

Co-oxidation experiments were performed over the Pd-rich surfaces. In order to operate such a smooth surface, the Cu atoms must be removed by following a careful procedure. Prior to the low temperature sputtering and annealing, mentioned above, further annealing of the alloy at ≈ 700 K was needed. The CO-TDS was developed as a reliable technique for surface characterization, allowing the determination of the degree of surface smoothness or the presence of high index planes in rough surfaces [10]. Fig. 1(a) presents the CO-TD spectra obtained from the alloy surface with Cu/Pd (SR) ≈ 0.1 . The main adsorption states appear at desorption temperatures of ≈ 250 and 400 K, with a slight shoulder at about 450 K,

previously referred to as β_2 , β_4 and β_5 , respectively [10]. The first maximum is characteristic of this alloy, while the other two are similar to that of CO desorbed from pure Pd(110) [10]. In the case of such a low Cu/Pd ratio, almost exclusively Pd atoms built up the crystal lattice in the SR, resulting in the appearance of a (1 \times 1) LEED pattern for the clean surface structure.

3. Results and discussion

The CO oxidation proceeds via a Langmuir–Hinshelwood (L–H) mechanism, where the reaction takes place between the adsorbed gases CO and oxygen:

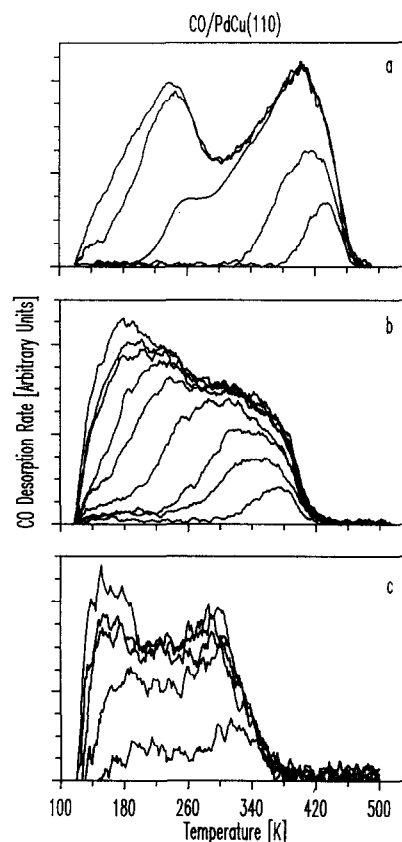


Fig. 1. The CO-TD spectra measured for a clean Pd-rich PdCu(110) surface is presented in (a). (b) and (c) present the spectra obtained after a series of CO-oxidation experiments. The experimental conditions are listed in Table 1. The CO coverage varied from 0.2 L up to 30 L where the saturation level was reached at ~ 10 L. The heating rate during the experiments was 5 K/s.

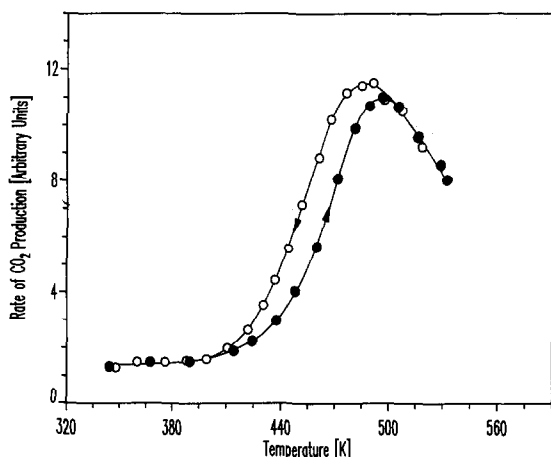
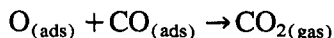
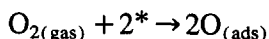
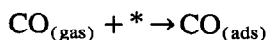


Fig. 2. The hysteresis obtained from measuring the rate of CO_2 production while heating (\bullet) up to 540 K and cooling (\circ) the PdCu(110) single crystal alloy. During these measurements the pressures of CO and O_2 were kept constant at $P_{\text{CO}} \approx 1 \times 10^{-5}$ mbar and $P_{\text{O}_2} \approx 3 \times 10^{-5}$ mbar.



(* = an empty surface site)

This mechanism is known to show a hysteresis at certain values of the controlling parameters and a range of bistability, in particular, at high oxygen/CO pressure ratios. This range of bistability was predicted mathematically by solving the corresponding differential equations [18].

CO oxidation on Pd(110) has been studied extensively. Phase diagrams were established, which show the existence of regions of monostability, bistability and oscillations for large pressure ranges (10^{-5} –1 Torr of oxygen) [19].

The PdCu(110) alloy under investigation here has a Pd-rich composition (TL \approx 100% Pd). It was of interest to study the influence of Cu atoms (especially the subsurface Cu) present in the SR on the Pd towards CO-oxidation.

Hysteresis, which was expected in connection with the L–H mechanism, was indeed observed on the PdCu(110) single crystal alloy. The details of AES and CO TDS measurements before and after the CO-oxidation experiments are given in Table 1.

Fig. 2. presents an example of such hysteresis measured at constant CO and O_2 pressures of $P_{\text{CO}} \approx 1 \times 10^{-5}$ mbar and $P_{\text{O}_2} \approx 3 \times 10^{-5}$ mbar. Such hysteresis was routinely obtained at operational pressures of CO and O_2 between 10^{-6} mbar and $\approx 10^{-3}$ mbar. The reaction experiments were performed by keeping two of the external control parameters constant (P_{CO} and P_{O_2}) and by varying the third parameter (temperature) in a step-wise manner. The pumping speed was held constant during the experiments. At each temperature a steady state was established before recording the reaction rate. A hysteresis for CO-oxidation on PdCu(110) was obtained. This result can be compared with earlier work [16] where a hysteresis was observed on Pd(110) under different experimental conditions, i.e., with constant P_{O_2} and temperature, and variable P_{CO} .

In Fig. 2 at low temperatures (< 400 K) the rate of CO_2 production was very low, because the surface was covered with CO, inhibiting oxygen adsorption. Increasing the temperature of the alloy led to an increase in the desorption rate of CO, thereby enabling oxygen to be adsorbed and thus increasing the rate of CO_2 production. Beyond ≈ 500 K the reaction rate started to decrease again. At these relatively high temperatures, the desorption rate of CO is very fast leading to a low steady state coverage of CO and consequently the CO-oxidation rate starts to decrease. Cooling the crystal leads to the appearance of the maximum in the reaction rate, but at a lower temperature than that for the maximum obtained while heating. Such a hysteresis in the reaction rate of CO-oxidation is well known and has been thoroughly investigated on many Pt and Pd single crystals [14–16,19,20].

It can be seen that, at a certain fixed temperature between 400 K and 500 K, two states with different reactivity towards the CO-oxidation exist; a higher reactive state (cooling branch in Fig. 2) and a lower reactive one (heating branch). Which one of the two states is formed, depends on the direction of scanning the temperature. Thus, this range between 400 K and 500 K is the range of bistability.

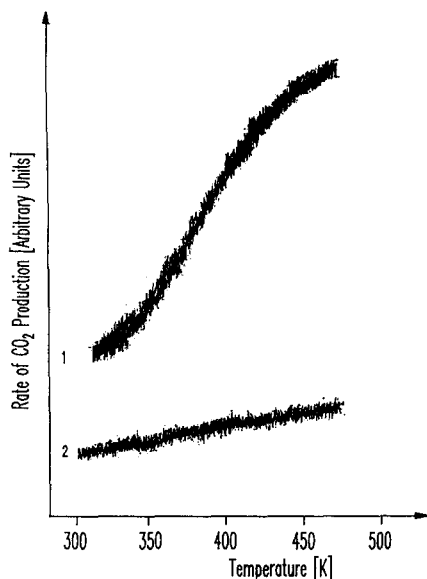


Fig. 3. The rate of CO₂ production from the PdCu(110) surface during the first CO-oxidation experiment is shown in curve 1, while curve 2 presents the lower reaction rate obtained after a few cycles of the oxidation reaction. These curves were obtained while heating the sample at constant pressures of $P_{\text{CO}} \approx 1 \times 10^{-4}$ mbar and $P_{\text{O}_2} \approx 2 \times 10^{-4}$ mbar.

A general conclusion about the CO-oxidation behaviour on the PdCu alloy, with Pd-rich SR, can be drawn from Fig. 3, where the CO₂ production rate is high at the beginning of the experiments (curve 1) and decreases with the reaction time (curve 2). The decrease in the CO₂ production rate, presented in Fig. 3, illustrates that after each CO-oxidation experiment less CO can be adsorbed on the surface. Such behaviour is the subject of current experiments. In the present communication we summarize results pertaining to composition and structural changes.

During the CO-oxidation experiments, the maximum temperature was below that at which the Cu atoms start to segregate. The increased value of Cu/Pd (SR) of ≈ 0.7 , which was recorded after the CO-oxidation experiments, required preparation temperatures (sputtering and annealing) of between 600 and 635 K [11]. However the maximum temperature in the CO oxidation was only 540 K (Fig. 2). Hence the increased Cu/Pd (SR) value could not be due simply to thermal segregation. It was separately shown in

the case of a TL of $\approx 100\%$ Pd, that the Cu/Pd (SR) ratio increased from 0.5 to 0.7 after a 15 min dose of CO at a pressure of 3×10^{-5} mbar at 415 K.

The shapes of the CO-TD spectra in Figs. 1a and 1b are already known [10]. After the CO-oxidation experiments, the CO-TD spectra in Fig. 1b revealed a disappearance of the Pd bridge-sites at the TL (the small shoulder at about 450 K disappeared). After prolonged CO-oxidation, the TD spectra shifted to lower temperatures (Figs. 1b, 1c). When $P_{\text{CO}} > 10^{-6}$ mbar, Cu atoms present in the bulk segregated mostly into the 3SSL.

The appearance of the new shoulder at 190 K in Fig. 1b, under the CO-oxidation process at high CO pressures, could be ascribed to the increased surface roughness, i.e., the occurrence of high index planes [10].

During the CO-oxidation experiments the LEED pattern changed from (1×1) to $c(2 \times 2)$. This change did not arise from the change in the Cu/Pd ratio; hence it was previously shown [11] that different surface compositions showed (1×1) and (1×2) LEED patterns only. It is believed that the $c(2 \times 2)$ structure could possibly arise from the same reason as the enhanced 180 eV Auger signal. This possible connection is under investigation. After CO-oxidation experiments the Pd Auger transition at 180 eV was enhanced, and this is shown in Table 1 as R_1 , the ratio of the intensity (I) of this 180 eV transition to that at 330 eV. In the same table the ratio of the intensities of the Pd transitions at 270 eV and 330 eV is given as R_2 . R_2 did not increase as a result of the CO-oxidation experiments, confirming that there was no carbon formation on the surface. Further investigations of these interesting phenomena, including the influence of Cu atoms in the top layer as well as in the surface region on the CO-oxidation, are in progress.

After the CO-oxidation experiments, the clean surface could be restored by sputtering and annealing. These again produced a CO-TDS similar to that shown in Fig. 1a, as well as a higher reactivity rate similar to that presented in Fig. 3a.

4. Conclusions

CO-oxidation experiments were carried out on the Pd-rich PdCu(110) surface of a single crystal alloy. Exposing the surface to the reaction at up to 540 K and at a total constant pressure of up to 9.5×10^{-4} mbar resulted in the following observations:

(i) It was possible to obtain a hysteresis in the CO₂ reaction rate when both partial pressures of CO and O₂ were held constant while varying the temperature stepwise. For the CO and oxygen pressures used in Fig. 2 the bistability range was between 400 K and 500 K.

(ii) The Cu/Pd (SR) ratio increased from ≈ 0.1 to ≈ 0.7 after a long reaction time (≈ 50 h).

(iii) The LEED pattern changed from (1×1) to $c(2 \times 2)$, with very high background intensity.

(iv) The increase in the number of subsurface Cu atoms did not prevent the occurrence of the hysteresis. However a large decrease in the reactivity was observed.

(v) After CO-oxidation experiments in the pressure range of 10^{-6} to 10^{-5} mbar, the CO-TD spectra showed a new desorption state at 190 K. This state was previously explained by surface roughness.

The observation of hysteresis, the shape of the bistability region and both operational pressure and temperature ranges together fulfill one of the requirements for obtaining kinetic oscillations on the surface of this PdCu(110) single crystal alloy (during reaction).

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References

- [1] G. Ertl, *Adv. Catal.*, 37 (1990) 213.
- [2] M. Ehsasi, O. Frank, J.H. Block and K. Christmann, *Chem. Phys. Lett.*, 165 (1990) 115.
- [3] M.P. Cox, G. Ertl and R. Imbihl, *Phys. Rev. Lett.*, 54 (1985) 1725.
- [4] M. Eiswirth, P. Moller, K. Wetzell, R. Imbihl and G. Ertl, *J. Chem. Phys.*, 90 (1989) 510.
- [5] M. Ehsasi, A. Karpowicz, M. Berdau, W. Engel, K. Christmann and J.H. Block, *Ultramicroscopy*, 49 (1993) 318.
- [6] W. Engel, M.E. Kordesch, H.H. Rotermund, S. Kubala and A. von Oertzen, *Ultramicroscopy*, 36 (1991) 148.
- [7] M. Berdau, M. Ehsasi, A. Karpowicz, W. Engel, K. Christmann and J.H. Block, *Vacuum*, in press (1994).
- [8] J.H. Block, M. Ehsasi and V. Gorodetskii, *Progr. Surf. Sci.*, 42 (1993) 143.
- [9] V. Gorodetskii, W. Drachsel and J.H. Block, *Catal. Lett.*, 19 (1993) 223.
- [10] M.S. Mousa, J. Loboda-Cackovic and J.H. Block, *Vacuum*, 46 (1995) 117.
- [11] J. Loboda-Cackovic, M.S. Mousa and J.H. Block, *Vacuum*, in press (1994).
- [12] M.S. Mousa, J. Loboda-Cackovic, S. Jaenicke and J.H. Block, *Surf. Sci.*, 307–309 (1994) 401.
- [13] J. Loboda-Cackovic and J.H. Block, to be published (1995).
- [14] R. Imbihl, M.P. Cox and G. Ertl, *J. Chem. Phys.*, 84 (1986) 3519.
- [15] M. Eiswirth and G. Ertl, *Surf. Sci.*, 177 (1986) 90.
- [16] S. Ladas, R. Imbihl and G. Ertl, *Surf. Sci.*, 219 (1989) 88.
- [17] J. Goschnick, M. Wolf, M. Grunze, W.N. Unertl, J.H. Block and J. Loboda-Cackovic, *Surf. Sci.*, 178 (1986) 831.
- [18] V.I. Bykov, V.I. Elochin and G.S. Yablonskii, *React. Catal. Lett.*, 4 (1976) 91.
- [19] M. Ehsasi, M. Berdeau, T. Rebitzki, K.P. Charle, K. Christmann and J.H. Block, *J. Chem. Phys.*, 98 (1993) 9177.
- [20] S. Ladas, R. Imbihl and G. Ertl, *Surf. Sci.*, 280 (1993) 14.