

## Kinetic Evidence for the Influence of Subsurface Oxygen on Palladium Surfaces Towards CO Oxidation at High Temperatures

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*Dedicated to Professor Dr. Gerhard Ertl*

**Abstract:** Transient state kinetics of the catalytic oxidation of CO with O<sub>2</sub> on Pd-surfaces has been measured under isothermal conditions by using a molecular beam approach. Systematic studies were carried out as a function of reaction temperature and CO+O<sub>2</sub> composition. With sufficient kinetic evidence, we have demonstrated the positive in-

fluence of subsurface oxygen towards CO-adsorption and oxidation to CO<sub>2</sub> at high temperatures (600–900 K) on Pd-surfaces, and the likely electronic

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nature of the surface changes with oxygen in the subsurface. These studies also provide a direct proof for CO-adsorption with a significantly reactive sticking coefficient at high temperatures on Pd-surfaces exhibiting a significant subsurface O-coverage.

### Introduction

The CO+O<sub>2</sub> reaction on Pd and other noble metal surfaces has been studied in detail for the last few decades.<sup>[1–7]</sup> All these studies consider the interaction between the surface adsorbed reactant species (CO and O) to explain the reaction details, including the Langmuir–Hinshelwood mechanism.<sup>[1–2]</sup> Nonetheless, recent reports on the oxygen interaction with Pd-surfaces indicate that the oxygen atoms diffuse into the subsurface/bulk of the Pd metal above 500 K.<sup>[8–16]</sup> However, the effect of subsurface oxygen atoms towards oxidation reactions has not been discussed until now, partly because of the complexity involved in characterisation of the species beneath the surface.

Oxygen chemisorption on any metal surface represents the first step towards the formation of metal oxides, which needs to be understood in order to explain any other associated phenomenon. Up to an oxygen coverage ( $\theta_{\text{O}}$ ) of 0.25 ML and below a temperature of 500 K, a (2×2) structure was observed on Pd(111) surfaces by low energy elec-

tron diffraction (LEED) and scanning tunnelling microscopy (STM) studies.<sup>[8–11]</sup> At temperatures above 500 K, and either at high O<sub>2</sub> pressure or with stronger oxidants, oxygen diffuses into the subsurface, giving rise to different surface structures.<sup>[9,10]</sup> These structural changes and the formation of palladium oxide (Pd<sub>x</sub>O<sub>y</sub>) are highly dependent on the oxygen pressure and substrate temperature. A metastable Pd<sub>5</sub>O<sub>4</sub> phase forms on Pd(111) surfaces either at relatively high O<sub>2</sub> partial pressures ( $>10^{-3}$  mbar) at 430 K, or upon prolonged exposure to oxygen at  $10^{-6}$  mbar between 500–600 K.<sup>[12]</sup> Upon heating, the metastable phase decomposes and small clusters of PdO appear. Bulk PdO forms above 650 K and then decomposes completely at 815 K.<sup>[12]</sup> Similarly, a strong kinetic hindrance to bulk oxide formation on Pd(100) surfaces at 675 K and ambient O<sub>2</sub> pressure was reported by Lundgren et al.<sup>[16]</sup> Indeed, in situ experiments are essential to observe and understand the oxygen diffusion phenomenon, since post-mortem experiments provide hardly any relevant information.<sup>[9,12,14]</sup> Such experiments are further complicated by the disappearance of oxygen as it diffuses into the subsurface, and very few spectroscopic details on this phenomenon are available.<sup>[12,14–16]</sup> Zemlyanov et al. demonstrated an instant dissociation of the metastable oxide phase using in situ XPS studies in the presence and absence of an oxygen atmosphere.<sup>[12]</sup> Also, the oxidation of Pd surfaces has been investigated theoretically and show that subsurface oxygen is just a precursor to surface oxidation.<sup>[16]</sup>

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Variations in the catalytic activity of oxidation reactions on supported Pd catalysts were reported, and generally these are attributed to the differences in activity between Pd and PdO.<sup>[17–20]</sup> Oscillations in catalytic activity have also been reported for Pd-catalyzed methane oxidation with a near stoichiometric CH<sub>4</sub>/O<sub>2</sub> ratio.<sup>[17–19]</sup> An interesting observation made by Engle and Ertl was that the rate of CO<sub>2</sub> production increases with increasing oxygen coverage at high temperatures on Pd(111), but not on Pt(111).<sup>[1–2]</sup> Further, Zheng and Altman showed that an ordered surface oxide is less active than chemisorbed oxygen on Pd(100) toward the oxidation of CO above 300 K.<sup>[10]</sup> However, Gabasch et al. found that the converse is true, and demonstrated that chemisorbed oxygen on Pd(111) surfaces is more reactive than any other forms, such as Pd<sub>5</sub>O<sub>4</sub> or deeply oxidized surfaces for CO oxidation.<sup>[12]</sup> Although oxygen solubility in Pd-metal is a well known phenomenon,<sup>[19]</sup> the nature of changes that occur in the presence of oxygen and a reductant, such as CO or H<sub>2</sub>, has not been explored, and the influence they have on the catalytic activity remains a subject of debate.<sup>[10–12]</sup>

In view of the above facts, it is important to understand the nature of palladium under reaction conditions to ascertain the catalytically active Pd-species. Interactions between O<sub>2</sub> and Pd have important implications on oxidation reactions, yet no detailed reports are available on the influence of subsurface oxygen on oxidation reactions. The present generation of automotive catalytic converters that are working under air-rich conditions, and in which Pd is increasingly used as an active ingredient,<sup>[17–21]</sup> underscores the need to understand this topic. Hence, we carried out CO oxidation reactions, with a mixed (CO+O<sub>2</sub>) molecular beam (MB), on Pd(111) and polycrystalline Pd surfaces under a variety of conditions (T=400–900 K, CO/O<sub>2</sub>=7:1 to 1:10). These studies provide direct proof for CO-adsorption with a significant reactive sticking coefficient (rs<sub>CO</sub>) at high temperatures

(> 500 K) on Pd-surfaces exhibiting a significant surface and subsurface O-coverage.

## Results and Discussion

Figure 1 shows the typical raw kinetic data measured under isothermal conditions. An effusive CO/O<sub>2</sub>=1:2 MB was directed onto a Pd(111) surface kept at 490 K and the partial

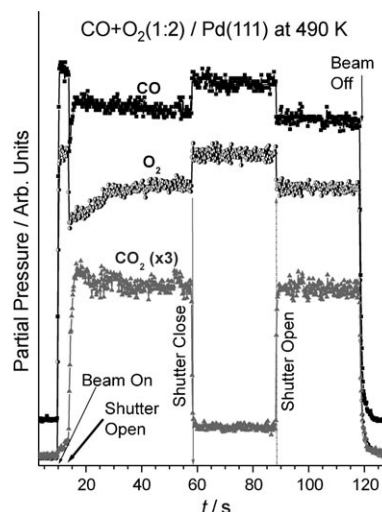


Figure 1. Typical raw kinetic data measured under isothermal condition is shown. An effusive CO/O<sub>2</sub>=1:2 molecular beam was directed onto a Pd(111) surface kept at 490 K and the relevant mass species (CO, O<sub>2</sub>, CO<sub>2</sub>) were followed as a function of time.

pressures of relevant mass species (CO, O<sub>2</sub>, CO<sub>2</sub>) were followed as a function of time. The CO+O<sub>2</sub> beam was turned on at t=10 s, and at this point, reactant molecules were scattered in the UHV chamber. Upon shutter opening at t=13 s, a decrease in the partial pressure of the reactants was observed along with an increase in the CO<sub>2</sub> partial pressure. The CO+O<sub>2</sub>/Pd(111) system was allowed to evolve until a steady-state (SS) was reached. In the SS, the MB was deliberately blocked (t=58–88 s) to measure the SS rate of the reaction. Our SS rate measurements are in good agreement to those already reported;<sup>[2,4–6]</sup> details about the SS kinetics will be discussed separately in another publication. The MB was turned off at a later time (t=112 s). Subsequent reactions were carried out after the surface was cleaned between any two reactions, especially for those experiments at high temperatures (≥ 600 K).

A systematic set of kinetic studies for the CO+O<sub>2</sub> reaction on Pd(111) was carried out as a function of surface temperature and CO/O<sub>2</sub> ratio by following the procedure described in the previous paragraph. The partial pressures of the different gases were then converted into parameters such as sticking coefficient, reaction rates, and coverage by following a calibration procedure described in an earlier publication.<sup>[13]</sup>

## Abstract in Tamil:

பல்லேடிய (Pd) வினைபூக்கி மேற்பரப்புகளில் கார்பன் மோனாக்சைடு (CO) ஆக்சிஜனேற்றத்தின் தொடக்க வினைவேகம், மூலக்கூறு கற்றைகளின் துணை கொண்டு மாறாவெப்பநிலைகளில் அளவிடப்பட்டன. வேதிவினை வெப்பநிலைகளை மாற்றியும், CO மற்றும் பிராண வாயு (O<sub>2</sub>) விகிதங்களை மாற்றியும் திட்டமிடப்பட்ட பயிற்சிகள் மூலம் சோதனைகள் மேற்கொள்ளப்பட்டன. உயர் வெப்பநிலைகளில் (600 - 900 K), உள்பரப்பு ஆக்சிஜன் அணுக்களால், CO மூலக்கூறுகள் Pd மேற்பரப்புகளில் கவரப்படுவதையும், கரியமில வாயு (CO<sub>2</sub>) வாக ஆக்சிஜனேற்றப் படுவதையும், சாதகமான முறையில் ஊக்குவிப்பதைப் போதுமான வினைவேக சோதனை சான்றுகள் மூலம் நிறுவ முடிகிறது. மட்டுமல்லாமல், பல்லேடிய மேற்பரப்பின் மின்னணு இயல்பை உள்பரப்பு ஆக்சிஜன் அணுக்கள் மாற்றுவதாக அனுமானிக்கப் படுகிறது. மேற்கூறப்பட்ட சோதனை முடிவுகள் உயர் வெப்பநிலைகளில், குறிப்பிடத்தக்க ஒட்டுகைமாறிலிகள் மற்றும் உள்பரப்பு ஆக்சிஜனைத் தன்னகத்தே கொண்ட பல்லேடிய மேற்பரப்புகள் CO மூலக்கூறுகளைக் கவர்கின்றன என்பதற்கு நேரடி சாட்சிகளாம்.

Figure 2 shows a set of kinetic data of the  $\text{CO} + \text{O}_2$  reaction at 750 K on a Pd(111) surface, with a  $\text{CO}/\text{O}_2$  ratio between 7:1 and 1:1. Upon removal of the shutter, a definite

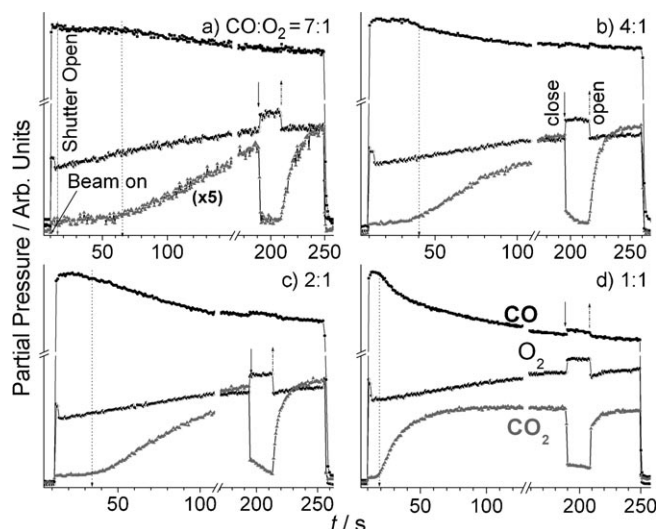


Figure 2. Temporal evolution of the partial pressure of CO,  $\text{O}_2$ , and  $\text{CO}_2$  during the  $\text{CO} + \text{O}_2$  reaction at 750 K on Pd(111) surfaces for different  $\text{CO}/\text{O}_2$  ratios. a) 7:1, b) 4:1, c) 2:1 and d) 1:1. Dotted arrows indicate the onset of simultaneous CO adsorption and  $\text{CO}_2$  desorption. Beam oscillation was carried out by closing the shutter at 190 s and opening at 210 s to measure the steady-state (SS) rate. Solid and dashed arrows indicate shutter closing and opening, respectively.

decrease in  $\text{O}_2$  partial pressure because of continuous adsorption was observed. This indicates a change in the nature of the Pd(111) surface, namely, from a clean-metal to an O-covered Pd(111) ( $\text{O}/\text{Pd}(111)$ ) surface, observed for all beam compositions; however, no direct CO uptake upon shutter removal was discernible. A gradual increase in direct  $\text{CO}_{\text{ads}}$  could be measured with CO-rich beams after a delay time ( $\Gamma$ ) of up to 50 s, and  $\Gamma$  decreases with an increasing  $\text{O}_2$ -content. An onset in  $\text{CO}_{\text{ads}}$  and  $\text{CO}_2$  production, observed simultaneously after the above delay, correlates well, which indicates that  $\text{CO}_{\text{ads}}$  occurs exclusively on  $\text{O}/\text{Pd}(111)$  under the above conditions. An estimate using the above data showed the surface  $\theta_{\text{O}}$  to be 0.20–0.40 ML on Pd(111), for 7:1 to 1:1 beams, before any  $\text{CO}_{\text{ads}}$  began and the  $\theta_{\text{O}}$  was well above the saturation  $\theta_{\text{O}}^{\text{[1]}}$ . This observation suggests that a significant amount of adsorbed oxygen had diffused into the subsurface. Despite a high  $\text{CO}$ -flux ( $F_{\text{CO}}$ ), onset of  $\text{CO}_{\text{ads}}$  and  $\text{CO}_2$  desorption only above the threshold  $\theta_{\text{O}}$ , asserts that subsurface oxygen might play a critical role. The phase diagram of palladium oxide formation<sup>[14]</sup> at a large range of pressure and temperature clearly suggests that there could be no surface  $\text{Pd}_x\text{O}_y$  formation under the experimental conditions employed in the present work. In the following studies, we demonstrate the diffusion of oxygen into the subsurface as well as the increase in the rate of  $\text{O}_2$  diffusion with increasing temperature, through a set of systematic experiments.

It should be noted that the  $\text{CO}/\text{O}_2$  partial pressure kept changing from the onset to higher times, not because of any change in flux, but because of the chamber flushing effect. No change in  $\text{CO}_2$  partial pressure at the SS (Figure 2d) asserts that the flux remains constant. However, there is a dynamic change in the  $\text{CO}/\text{O}_2$  ratio on the surface, until the reaction reaches the SS.

Independent CO adsorption,  $\text{O}_2$  adsorption (and CO titration) experiments were carried out to demonstrate that oxygen molecules diffuse into the Pd-subsurface as well as to highlight the significantly large oxygen sticking coefficient ( $s_{\text{O}_2}$ ) on a clean Pd(111) surface. Figure 3a shows CO ad-

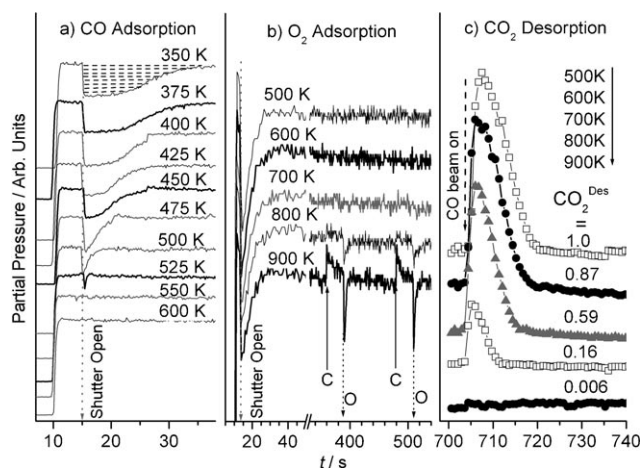


Figure 3. a) CO adsorption, and b)  $\text{O}_2$  adsorption on Pd(111) surfaces at different temperatures. c) CO titration carried out on the surface prepared in (b) to measure the surface  $\theta_{\text{O}}$ . Hatched area in panel a indicates the extent of CO-adsorption or  $\theta_{\text{CO}}$ .

sorption on Pd(111) surfaces between 350 and 600 K. A decrease in the partial pressure of CO, upon shutter opening, indicates its uptake on the surface (hatched area in Figure 3a) and this continues till the surface is saturated, then no further adsorption occurs. Notably, the directly measurable CO adsorption decreases with increasing temperature because of the increase in the rate of desorption and decrease in the CO sticking coefficient ( $s_{\text{CO}}$ ); hence no net CO adsorption was observed above 550 K on a clean Pd(111) surface, which is in good agreement with the literature reports.<sup>[1,2,4–6]</sup>  $\text{O}_2$  adsorption on Pd(111) surfaces measured between 500 and 900 K is shown in Figure 3b. The rate of  $\text{O}_2$  adsorption on a clean Pd(111) surfaces remains high at all temperatures studied. Unlike the systematic decrease observed in direct CO adsorption from 350 to 550 K, direct  $\text{O}_2$  adsorption continues above the oxygen desorption maximum (750–850 K)<sup>[9,10]</sup> at a rate comparable to that observed at low temperatures. Notably, a small amount of surface oxygen desorbs from the O-saturated surfaces at the time of shutter closing (denoted as C in Figure 3b), and then adsorbs at shutter opening at  $\geq 800$  K at a latter time (denoted as O). Indeed the above  $\text{O}_2$ -adsorption measurement at 900 K is in excellent agreement with the measurement made

by Leisenberger et al.<sup>[9]</sup> under similar conditions, and is attributed to the subsurface diffusion. This clearly suggests that there is subsurface diffusion of oxygen on Pd(111) surfaces. Further, the rate of oxygen desorption seems to be significantly lower compared to the rate of oxygen diffusion into the subsurface at  $\geq 800$  K. Oxygen saturated Pd(111) surfaces, prepared by oxygen dosing for 650 s at different temperatures (Figure 3b), were titrated with CO at 500 K to measure the surface  $\theta_{\text{O}}$  through  $\text{CO}_2$  desorption. The  $\text{CO}_2$  estimated in the above titration decreases with an increase in  $\text{O}_2$  adsorption temperature, and suggests a linear decrease in surface  $\theta_{\text{O}}$ . This decrease in  $\text{CO}_2$  yield at high temperatures may be attributed to an increasing oxygen subsurface diffusion. These observations also suggest that the oxygen saturated surfaces do not prevent CO-adsorption and subsequent  $\text{CO}_2$  production below  $\leq 800$  K; however the  $\text{CO}_2$  production depends on the  $\theta_{\text{O}}$  available on the surface, which decreases with increasing temperature.

Some relevant quantitative parameters calculated from the  $\text{CO} + \text{O}_2/\text{Pd}(111)$  data measured at different temperatures and different  $\text{CO}/\text{O}_2$  ratios are provided in Figure 4. It shows the dependence of delay time in  $\text{CO}_{\text{ads}}$  or  $\text{CO}_2$  desorption ( $\Gamma$ ) in seconds, initial  $s_{\text{O}_2}$  ( $s_{\text{O}_2}^0$ ),  $rs_{\text{CO}}$ , and reactive  $s$  for  $\text{O}_2$  ( $rs_{\text{O}_2}$ ) on  $\text{CO}/\text{O}_2$  ratio and temperature.  $\Gamma$  decreases systematically with a decrease in temperature when the  $\text{CO}/$

$\text{O}_2$  composition changes from 7:1 to 1:2, with no delay observed for  $\text{O}_2$ -rich ( $>1:4$ ) beams. Indeed an increasing  $\text{O}_2$ -content in the beam covers the Pd(111) surface with oxygen at a faster rate, and hence the decrease in the delay. Similarity in  $rs_{\text{O}_2}$  values at steady state and  $s_{\text{O}_2}^0$  for CO rich beams underlines that the rate of  $\text{O}_{2-\text{ads}}$  remains the same throughout the reaction (Figures 2 and 4b–d). Nonetheless, a decrease in  $rs_{\text{O}_2}$  values at SS compared to  $s_{\text{O}_2}^0$  for  $\text{O}_2$  rich beams suggests that the rate of  $\text{O}_{2-\text{ads}}$  decreases rapidly towards  $\text{O}_2$ -rich beams. These points suggest a significant diffusion of oxygen into the subsurface, irrespective of the beam composition. Another important observation is the  $rs_{\text{CO}}$  observed between 0.02 and 0.25 in the SS depending on the beam composition and temperature. CO-rich beam compositions ( $\text{CO}/\text{O}_2 = 7:1$  and  $4:1$ ) show low, but significant  $rs_{\text{CO}}$  values around 0.03; however, the  $rs_{\text{CO}}$  value increases up to 0.25 with increasing oxygen content in the beam and at decreasing temperature up to 500 K. Further, an appreciable  $rs_{\text{O}_2}$  and  $rs_{\text{CO}}$  observed up to 800 K at SS (in contrast to  $s_{\text{CO}}^0 \sim 0$  at  $\geq 600$  K on clean Pd(111)) highlights the importance of oxygen in the subsurface towards CO oxidation. These observations support the conclusion that CO adsorption occurs exclusively on the Pd-surfaces that exhibit a significant amount of subsurface oxygen coverage. It is also expected that the oxygen coverage in the subsurface changes the electronic nature of the Pd-surface to a slightly oxidized form or attributes cationic character because of oxygen in the subsurface.

Additional experiments were performed to gain more insight into the diffusion of oxygen into the subsurface and its influence on CO-oxidation. Figure 5a shows the  $\text{CO} + \text{O}_2$  reaction with  $\text{CO}/\text{O}_2 = 1:2$  beam at 750 K for 100 s, then the

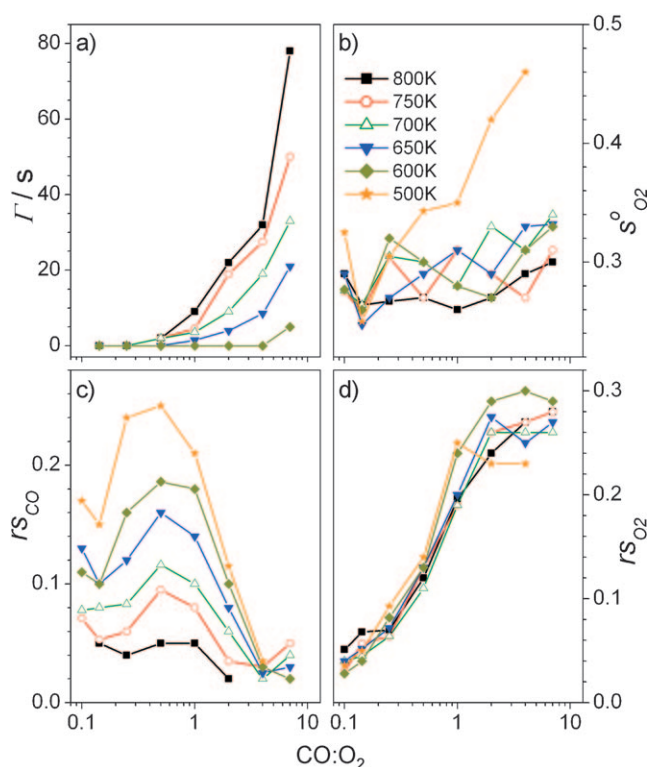


Figure 4. a) Delay ( $\Gamma$ ) in simultaneous CO adsorption and  $\text{CO}_2$  desorption measured is given for all  $\text{CO}/\text{O}_2$  ratios at different temperatures. b)  $s_{\text{O}_2}^0$  measured in the transient state, c)  $rs_{\text{CO}}$ , and d)  $rs_{\text{O}_2}$  measured under SS are plotted for all  $\text{CO}/\text{O}_2$  compositions and reactions temperatures. Note the large variation in  $rs_{\text{O}_2}$  compared to marginal changes in  $s_{\text{O}_2}^0$  from CO-rich to  $\text{O}_2$ -rich beam compositions.

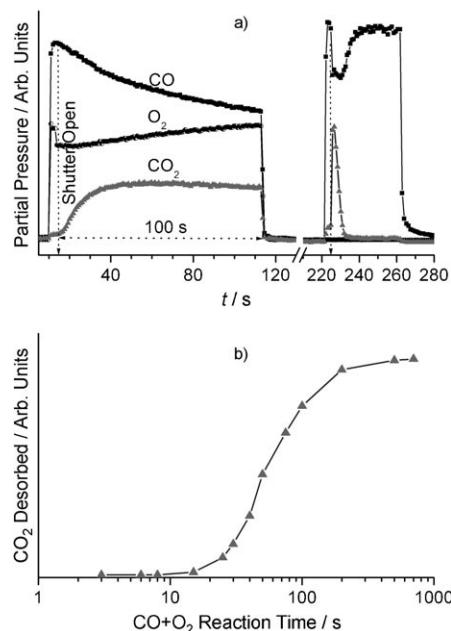


Figure 5. a)  $\text{CO} + \text{O}_2$  (1:2) reaction was measured on Pd(111) at 750 K for different periods of time, between 3 and 800 s, followed by CO titration at 500 K to measure the oxygen coverage. b) Quantity of  $\text{CO}_2$  desorbed is plotted versus the  $\text{CO} + \text{O}_2$  (1:2) exposure time.



reaction surface was titrated with a CO-beam to measure  $\theta_{\text{O}}$ . The same reaction was also measured as a function of CO+O<sub>2</sub> exposure time (up to 800 s) followed by CO-titration at 500 K. Similar measurements with CO-rich beams (7:1 and 1:1) did not yield any CO<sub>2</sub> during CO-titration, which indicates that the surface adsorbed oxygen had been consumed under these reaction conditions and that there is no build-up of any significant surface  $\theta_{\text{O}}$ . Figure 5b shows the quantity of CO<sub>2</sub> desorbed as a function of CO+O<sub>2</sub> exposure time. Up to a reaction time of 15 s, no measurable  $\theta_{\text{O}}$  was observed. However, an increase in  $\theta_{\text{O}}$  with increasing reaction time is observed and approaches the saturation level in the steady state, between 200 and 500 s. No observation of measurable  $\theta_{\text{O}}$  up to a reaction time of 15 s clearly indicates a preferential subsurface diffusion of oxygen, which later induces the surface reactivity. These results also suggest the necessity to populate the subsurface states with oxygen before the onset of reaction on the surface.

An O<sub>2</sub>-beam pulse followed by a CO-beam pulse applied to Pd(111) surfaces was carried out to further confirm the above conclusions. Figure 6 shows the pulsed oxygen dosing

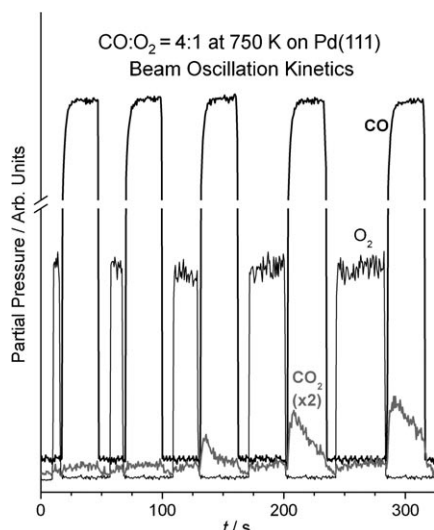


Figure 6. Pulsed oxygen dosing (thin black trace) for different periods of time followed by CO pulses (bold black trace) for 30 seconds and simultaneous CO<sub>2</sub> production (bold gray trace) on a Pd(111) surface with CO/O<sub>2</sub>=4:1 at 750 K.

(thin black trace) for increasing periods of time with intermediate CO pulses (bold black trace) for 30 seconds and simultaneous CO<sub>2</sub> production (bold gray trace) at 750 K on Pd(111) surface. CO and O<sub>2</sub> concentration corresponds to a ratio of 4:1. A five-way valve was employed to switch between the oxygen and CO beams. Oxygen pulsing time was increased gradually from 5 to 40 s. No CO<sub>2</sub> desorption was observed for the first two oxygen pulses investigated, namely for 5 and 10 s. However, a gradual increase in CO<sub>2</sub> production was observed with the longer oxygen pulse times investigated followed by CO-titration. Indeed, in another experiment (not shown), a continuous 25 s oxygen pulse too

did not produce any CO<sub>2</sub> upon CO-titration; however a subsequent oxygen pulse for 10 s, did produce CO<sub>2</sub> upon CO-titration. Indeed the sum of oxygen dosing time (35 s) after which CO<sub>2</sub> production starts is in agreement with the delay time given in Figure 4a for a 4:1 composition ( $\Gamma=28$  s). This provides support that the oxygen initially adsorbed diffuses into the subsurface thereby filling the subsurface states. It is only after attaining the sufficient subsurface oxygen coverage that CO<sub>2</sub> production starts from the surface. Also, the rate of O-diffusion into the subsurface seems to be much faster on clean metal surfaces rather than the reaction with CO, and hence no CO<sub>2</sub> production is observed in the initial stages. Any palladium oxide (Pd<sub>x</sub>O<sub>y</sub>) formation has been ruled out in the present case and is further supported by literature reports.<sup>[8–16]</sup> Indeed the phase diagram of Pd<sub>x</sub>O<sub>y</sub> formation at a wide temperature and pressure range reported by Ketteler et al.<sup>[14]</sup> clearly supports that there can be no surface oxide formation under the conditions employed in the experiments reported in the present work.

It is very likely that the defects on Pd(111) might be a source for O-diffusion into the subsurface and thus account for the delay in CO<sub>ads</sub> and CO<sub>2</sub> production (Figures 2 and 4a). To test this, the CO+O<sub>2</sub> reaction was measured on a polycrystalline Pd-metal surface and the representative results are shown in Figure 7 with CO/O<sub>2</sub>=4:1 at 700 K, and CO/O<sub>2</sub>=2:1 at 700 K. A similar beam flux was employed as that on Pd(111). No delay in CO<sub>2</sub> production was observed at reaction temperatures less than 700 K. It is also noted that the steady state was reached much quicker on polycrystalline Pd than on Pd(111) (compare Figure 2b–c). Although no delay in CO<sub>ads</sub> was observed, the onset of CO<sub>2</sub> desorption was delayed as in Pd (111), but occurred sooner on poly-Pd than Pd (111) under comparable conditions. This supports

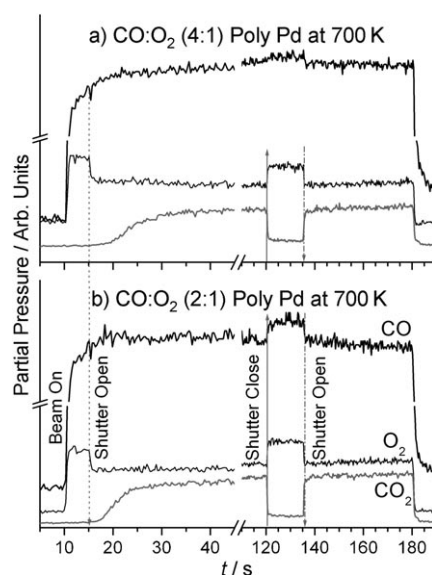


Figure 7. Representative examples of CO+O<sub>2</sub> reactions carried out on polycrystalline Pd surfaces with a) CO/O<sub>2</sub> = 4:1 at 700 K, and b) CO/O<sub>2</sub> = 2:1 at 700 K.

the conclusion derived from the Pd(111) investigation and supports that active  $\text{CO}_{\text{ads}}$  towards  $\text{CO}_2$  production, begins only after the subsurface has been occupied with a threshold coverage of O-atoms. Qualitatively, a similar trend in  $\Gamma$  was observed on polycrystalline Pd as well as Pd(111) surfaces, but to a lesser extent, highlighting the significant role of surface defects in O-diffusion into the subsurface. This demonstrates that the present findings are not structure sensitive and thus inherent to all Pd-surfaces. It also underscores the relevance of the above findings to Pd nanoparticles with a large defect density,<sup>[22,23]</sup> especially below 10 nm, and hence the role of subsurface diffusion. Our results on polycrystalline Pd-surfaces are in qualitative agreement with those of Epling et al.,<sup>[24]</sup> which suggests that the adsorbed oxygen diffuses into the subsurface and can then migrate to the surface by reductive treatment with CO or hydrogen.

## Conclusion

The influence of subsurface oxygen coverage on Pd-surfaces towards CO adsorption and its oxidation to  $\text{CO}_2$  at high temperatures was studied by molecular beam methods. Molecular beam studies with a  $\text{CO} + \text{O}_2$  mixture provide a direct proof for CO-adsorption with a significant  $r_{\text{SCO}}$  above 500 K on Pd-surfaces containing significant surface and subsurface oxygen coverage. Arising from the time required to populate the subsurface with oxygen atoms, there is an initial delay observed both in CO-adsorption as well as  $\text{CO}_2$  production, with CO-rich beams. Subsurface O-coverage influences the CO-adsorption capacity and the  $r_{\text{SCO}}$  observed varies between 0.02 and 0.25 depending on the temperature and  $\text{CO}/\text{O}_2$  composition. A similar observation on polycrystalline Pd-surfaces suggests the defects on the surface increase the O-diffusion into the subsurface. It is expected that the electronic nature of the Pd surface changes to a mildly oxidized state with significant subsurface oxygen coverage that is favorably oxidized at high temperatures. It would be worth exploring this phenomenon through structural and spectroscopic means to identify the mechanism. In general, revisiting oxidation reactions at high temperatures is an effort worth making. Detailed results on the same system are to be published later.

## Experimental Section

Experiments reported were performed using a molecular beam instrument (MBI).<sup>[25–27]</sup> Full details of our MBI experimental set-up have already been reported.<sup>[13,27]</sup> Experiments reported were performed in a MBI using the principle of an extension of the King and Wells collimated beam method.<sup>[25]</sup> All molecular beam experiments reported here were performed using a homemade 12 L capacity stainless steel ultra-high vacuum (UHV) chamber evacuated with a turbo-molecular drag pump to a base pressure of  $2 \times 10^{-10}$  Torr. This system is equipped with a quadrupole mass spectrometer for the detection of all the relevant gas-phase species of the reaction, a sputtering ion gun for cleaning the sample and a MB doser for beam generation. The QMS is placed out of the line-of-sight to avoid any angular effect that might arise from the single crystal.

MB doser assembly, aimed directly at the crystal surface, is connected to a gas manifold unit and the beam flux ( $F$ ) is set both by filling the gas-manifold unit to a specified pressure and by fixing the precision leak valve to a predetermined position.  $F_{\text{O}_2+\text{CO}} = 0.16 \text{ ML s}^{-1}$  is the total flux of the  $\text{O}_2 + \text{CO}$  mixture for any desired composition that was used in all the experiments reported here, unless otherwise specified. A movable stainless steel shutter is placed between the Pd-surface and the doser to block or unblock the beam when required. A five-way valve connected between the beam doser and gas-manifolds enables performance of beam-oscillation experiments with up to three different beam compositions.

Blank experiments (such as independent oxygen and CO adsorption at different temperatures while following all relevant mass species) were measured to confirm that there was no background contribution, such as production of  $\text{CO}_2$  or  $\text{H}_2\text{O}$ . This is to confirm that there is no surface cleaning of adsorbed components, especially adsorbed oxygen, occurring during the course of the experiments reported.

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