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Kinetic modeling of the CO oxidation reaction on supported metal clusters

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Abstract. The CO oxidation on Pd is generally considered to be structure insensitive and is not expected to depend on the size of the Pd particles. However, several size effects have already been evidenced for this reaction. Near the temperature where the steady-state reaction rate is maximum, the reactivity per Pd surface atom (turnover number (TON)) increases for small particles. At low temperature, in transient molecular beam experiments, a second peak of CO_2 appears after the CO beam is closed, while the oxygen is still supplied to the sample. This peak shifts, and its shape changes with temperature and oxygen pressure. This peak is explained by the presence of CO strongly bound to the particle edges. This strongly bound CO reacts well after the CO adsorbed on the facets has desorbed. A kinetic model is presented which explains the evolution of this peak with temperature and oxygen pressure.

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1 Introduction

The study of the reactivity of metal clusters is of key importance in understanding heterogeneous catalysis. CO oxidation has been extensively studied on supported Pd clusters, which are used as model catalysts [1–11]. The Langmuir–Hinshelwood mechanism was definitely established (at least at low pressure) on extended Pd surfaces from the work of Ertl's group [12]. This reaction is generally considered to be structure insensitive [13], although some recent measurements have shown sizable increases of reactivity for open [14] and stepped Pd surfaces [15]. Boudart [16] has shown that the rate of a structure-insensitive reaction is independent of cluster size. A first apparent size dependence has been observed [1] and finally explained by an increase of the concentration of CO on the Pd particles by the capture of CO molecules physisorbed on the alumina support [3, 5]. The same effect has been also observed for mica, silica, and MgO supports [2, 7, 9]. Xu and Goodman [6] have found that the reaction rate is constant with cluster size. However, Xu *et al.* experiments were made at a high pressure (2×10^3 Pa); this leads to a high CO coverage, for which the reaction is truly structure insensitive [17]. From our recent molecular beam measurements (at low pressure, i.e., $<1\times10^{-4}$ Pa) on Pd clusters supported on MgO(100), it turns out that after correction for the effect of the capture of CO adsorbed on the support, the reaction rate, near the temperature where the steady-state reaction rate reaches a maximum, is size dependent [9]. Transient experiments have shown a new phenomenon: Below 230 °C, a second peak of CO_2 was observed after the CO beam was closed (the isotropic oxygen pressure was kept constant) [11]. In this paper, we present additional data on the evolution of the second production of CO_2 as a function of sample temperature and oxygen pressure. A kinetic model explaining the origin of this phenomenon is also presented. This model predicts qualitatively the evolution of the second peak.

2 Experimental procedures

The experiments were performed in a UHV chamber with a base pressure of 3×10^{-8} Pa. The system was equipped with facilities for UHV cleavage and preparation of the MgO(100) supports: an LN_2-cooled Knudsen cell for Pd evaporation, an Auger electron spectrometer, and a supersonic molecular beam source (for CO) associated with a differentially pumped mass spectrometer for reactive scattering measurements (MBRS) [18]. The equivalent pressure in the CO molecular beam at the sample surface was 4.5×10^{-5} Pa. Oxygen was introduced isotropically through a standard UHV leak valve. The Pd clusters were epitaxially grown between 80 and 400 °C on the *in situ*-cleaved, or air-cleaved and *in situ*-cleaned, MgO crystals by the condensation of a beam of Pd (1×10^{13} atoms cm^{-2}s^{-1}). After reaction experi-

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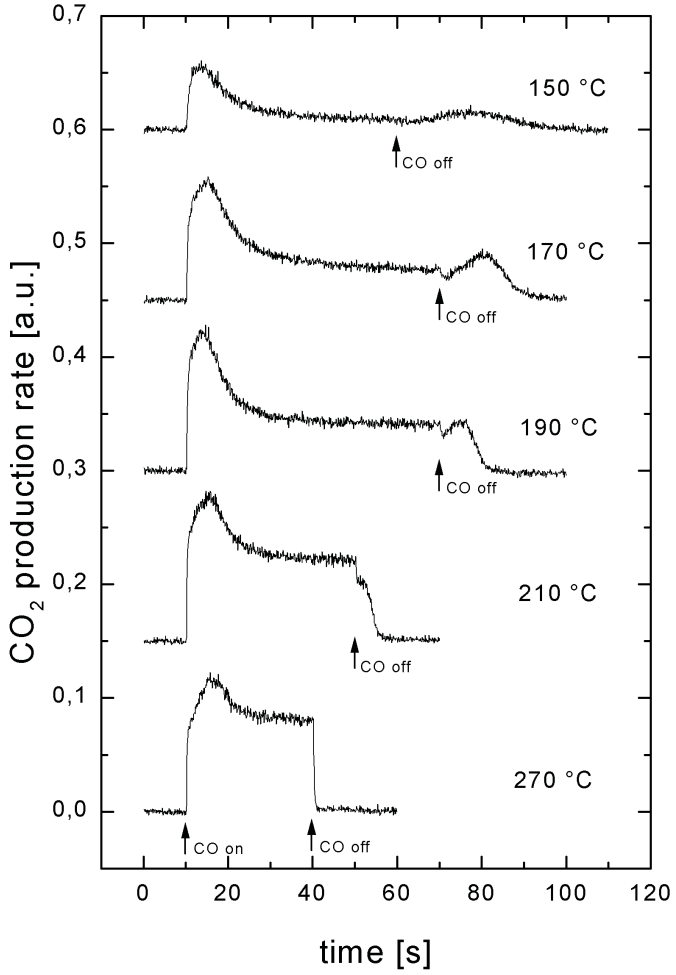

Fig. 1. CO_2 transients on 4 nm Pd particles supported on MgO(100) as a function of the sample temperature. The isotropic oxygen pressure is 5×10^{-8} Torr, and the equivalent pressure in the CO beam is 3.4×10^{-7} Torr.

ments, the samples were observed by TEM (JEOL 2000 FX). From the micrographies, the size distribution was measured. The shape of the particles is dependent on the growth conditions, as has been shown previously by various TEM techniques [17, 19]. For the experimental results presented in this paper, the particles have the shape of a truncated half-octahedron and a mean size of 4 nm.

3 Experimental results

After deposition of the Pd particles, a constant pressure of oxygen ($P_{O_2} = 6.6$ or 13.3×10^{-6} Pa) was maintained and a single pulse of CO was directed to the sample. The CO and CO_2 pulses re-emitted from the sample surface in the normal direction were simultaneously recorded by the mass spectrometer. Subsequent CO incident pulses gave the same results.

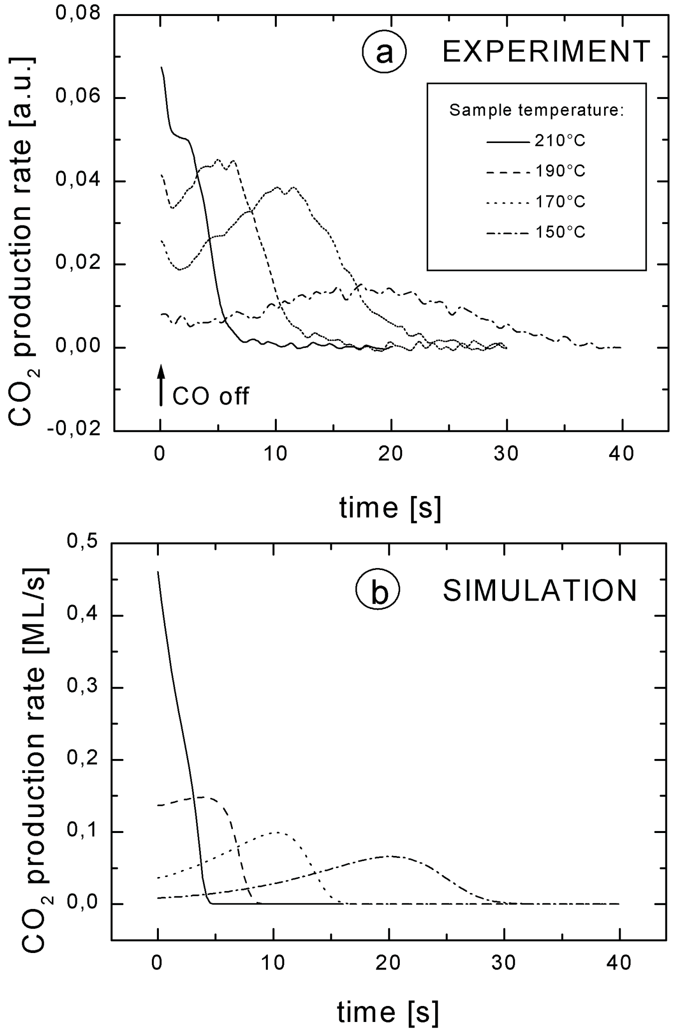

Fig. 2. Evolution of the second peak of CO_2 as a function of the sample temperature: (a) experiment, $P_{O_2} = 5 \times 10^{-8}$ Torr; (b) calculation, $P_{O_2} = 1 \times 10^{-6}$ Torr, same temperatures as in (a).

Figure 1 shows the evolution of the CO_2 pulses for various sample temperatures. At 270 °C (the maximum of reactivity is obtained between 240 and 250 °C) the signal shows a transient burst that slowly decreases towards the steady-state value. When the beam is closed, the production of CO_2 falls rapidly to zero. The same behaviour is observed down to 230 °C. Below 230 °C, when the CO beam is turned off, the reaction rate decreases and increases again, forming a second pulse of CO_2. The maximum of this second peak is shifted to longer times and becomes flatter when the temperature decreases. In previous measurements [11], we had observed the same evolution, and we showed that the relative area of the second peak increased when cluster size decreased. Figure 2a shows closely the evolution of the second peak with temperature. At constant temperature, the second peak of CO_2 follows qualitatively the same evolution when the oxygen pressure decreases, as seen in Fig. 3a.

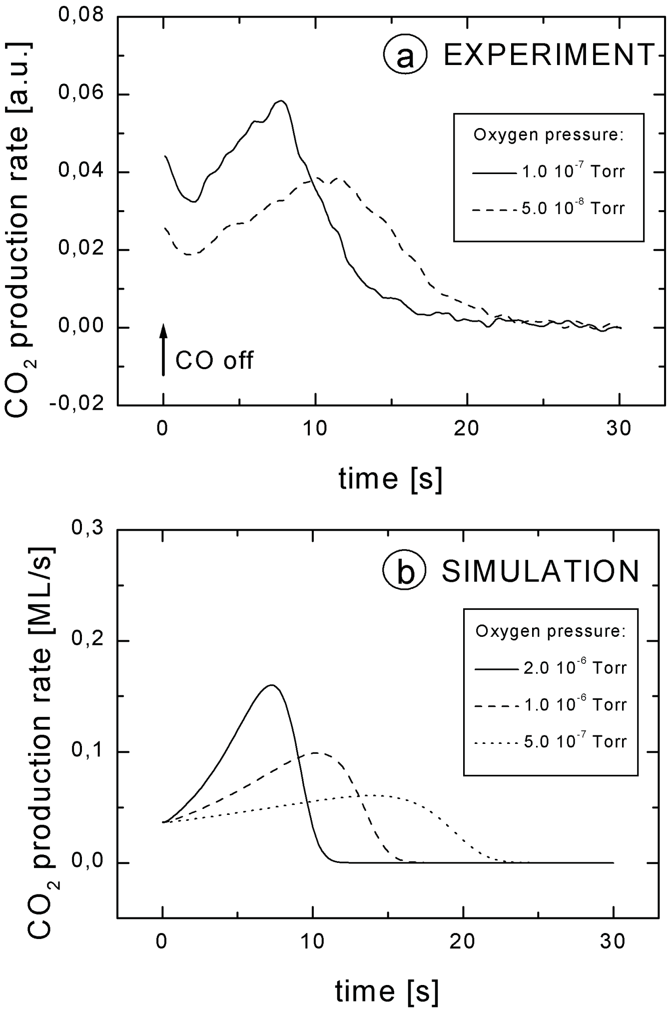

Fig. 3. Evolution of the second peak of CO_2 as a function of oxygen pressure at 170 °C: (a) experiment; (b) calculation.

4 Kinetic model

Experiments on the CO oxidation on supported Pd particles have shown that under transient conditions (pulsed CO beam, constant isotropic oxygen pressure), a second peak of CO_2 appears after the closing of the CO beam. This peak shifts towards longer delays and is smashed when the temperature or the oxygen pressure decreases. Such a peak could be expected on extended surfaces, at low temperature when the CO coverage is close to saturation and the sticking coefficient of oxygen is practically zero, as has already been observed on Pt(110) [20]. However, several differences appear in the present case. First, at 150 °C, the desorption of CO becomes negligible after 4 s, during the reaction, while the maximum of the peak occurs around 20 s and vanishes near 40 s. This means that some CO is still present on the particles when normal CO adsorbed on the facets is desorbed. The second difference is that the coverage of this strongly bound CO, measured from the area of the CO_2 peak, depends strongly on particle size. It increases from 0.02 for 14 nm particles to 0.2 for 2.8 nm particles. The only way to solve this problem is to assume that CO molecules are trapped on some special sites and react with adsorbed oxygen after closing the CO beam. In fact, in previous work we have shown that at low coverage (≈ 0.01 ML), the adsorption energy of CO increases strongly for small Pd clusters below 5 nm [21]. This effect has been explained by a higher binding energy of CO on low coordinated Pd atoms, namely, edge and corner atoms [17]. Following this idea, it becomes possible to explain the origin of the second peak. At steady state (before closing of the CO beam), below 230 °C, CO completely saturates the edges, and no reaction occurs on these sites. The CO coverage on cluster facets (normal sites) is far from saturation, and reaction occurs with adsorbed oxygen. After the closing of the CO beam, CO still adsorbed on the facets rapidly desorbs or reacts with oxygen. However, CO adsorbed on the edges can diffuse towards a facet (this barrier has to be high) and then diffuse across the facet and rapidly react with adsorbed oxygen. When empty sites are present on the edges, oxygen can be adsorbed there, and now the reaction can take place on these sites; thus the total reaction rate increases, but it will soon turn to zero because of the lack of adsorbed CO.

In summary, to explain the origin and the shape of the second peak of CO_2, it is necessary to have a source of strongly bound CO (the edges), a large barrier between these sites and the normal sites (facets), and a second channel for reaction which increases the reaction rate (volcano shape of the peak). From this scheme, we propose a simple mechanism, represented by the following elementary reactions:

$$\mathrm{CO^e + s^f \rightarrow CO^f + s^e} \qquad (1)$$

$$\mathrm{CO^f + O^f \rightarrow CO_2 + 2s^f} \qquad (2)$$

$$\mathrm{O_2 + s^e + s^f \rightarrow O^e + O^f} \qquad (3)$$

$$\mathrm{CO^e + O^e \rightarrow CO_2 + 2s^e} \;. \qquad (4)$$

The symbols e and f design the edge sites and the facet sites respectively, and s means a free site. Equation (3) means that when an oxygen molecule dissociates on an edge, one atom adsorbs on the edge and the second one adsorbs on the neighbouring facet. This choice has been made because the total coverage on the edges is always large compared to the total coverage on the facets. In this model, the desorption of CO and the diffusion of CO from a facet to an edge are neglected, because the reaction on the facets is much faster. In addition, the adsorption of oxygen on the facets is not considered a limiting step. This set of elementary reactions can be represented by the two following coupled differential equations:

$$\mathrm{d}\theta^{\mathrm{e}}_{\mathrm{CO}}/\mathrm{d}t = -k_1\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{f}}_{\mathrm{s}} - k_4\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{e}}_{\mathrm{O}} \qquad (5)$$

$$\mathrm{d}\theta^{\mathrm{e}}_{\mathrm{O}}/\mathrm{d}t = k_3 p_{\mathrm{O_2}}\theta^{\mathrm{e}}_{\mathrm{s}}\theta^{\mathrm{f}}_{\mathrm{s}} - k_4\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{e}}_{\mathrm{O}} \qquad (6)$$

$$v_{\mathrm{CO_2}} = k_2\theta^{\mathrm{f}}_{\mathrm{CO}}\theta^{\mathrm{f}}_{\mathrm{O}} + k_4\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{e}}_{\mathrm{O}} \;. \qquad (7)$$

The k_i are the rate constants for the elementary i reactions (see (1)–(4)). The θ represent the coverages and $p_{\mathrm{O_2}}$ the oxygen pressure.

We take the following initial conditions:

$$\theta^{\mathrm{e}}_{\mathrm{CO}}(t=0)=1 \tag{8}$$

$$\theta^{\mathrm{e}}_{\mathrm{O}}(t=0)=0 \tag{9}$$

and we assume that the maximum value of the total coverage of the adsorbed species is one. In addition, we make the hypothesis that the oxygen coverage on the facets is nearly constant and equal to 0.25, like on extended Pd(111) surfaces. Furthermore, we assume that the reaction on the facets is much faster than the diffusion from the edges to the facets. This means $k_2 \gg k_1$, or, in other words, the edge to facet diffusion is the limiting step for the reaction on the facets. Then we have:

$$k_2\theta^{\mathrm{f}}_{\mathrm{CO}}\theta^{\mathrm{f}}_{\mathrm{O}} \approx k_1\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{f}}_{\mathrm{s}}\,. \tag{10}$$

The total reaction rate becomes:

$$v_{\mathrm{CO}_2} \approx k_1\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{f}}_{\mathrm{s}} + k_4\theta^{\mathrm{e}}_{\mathrm{CO}}\theta^{\mathrm{e}}_{\mathrm{O}} = -\,\mathrm{d}\theta^{\mathrm{e}}_{\mathrm{CO}}/\,\mathrm{d}t\,. \tag{11}$$

The rate constants are:

$$k_1 = \nu_1\exp(-E_1/kT_{\mathrm{s}}) \tag{12}$$

$$k_3 = s_{\mathrm{O}_2}/N_0(2\pi m_{\mathrm{O}_2}kT_{\mathrm{O}_2})^{1/2} \tag{13}$$

$$k_4 = \nu_4\exp(-E_4/kT_{\mathrm{s}}) \tag{14}$$

where ν_1 and E_1 are the frequency factor and the energy barrier for a CO molecule to diffuse from an edge to a facet. ν_4 and E_4 are the frequency factor and the energy barrier for the Langmuir–Hinshelwood reaction on edges. s_{O_2}, m_{O_2}, and T_{O_2} are the sticking coefficient on edges, the molecular weight, and the temperature of a gas phase oxygen molecule, respectively. N_0 is the density of surface sites, taken to be equal to the density of surface atoms on Pd(111), which is $1.53\times10^{15}\,\mathrm{cm}^{-2}$. $T_{\mathrm{O}_2} = 300\,\mathrm{K}$.

We have solved numerically the system of coupled differential equations (5, 6, 10). In order to limit the fit procedure we have taken $\nu_1=\nu_2=1\times10^{12}\,\mathrm{s}^{-1}$ and $s_{\mathrm{O}_2}=1$.

Figure 2b shows the best fit between the model and the experiment for the variation, with temperature, of the second CO_2 peak. The model can reproduce at least qualitatively the evolution observed experimentally. Figure 3b shows also a qualitative agreement of the evolution with the oxygen pressure. However, it is noteworthy that the best agreement is obtained for a higher oxygen pressure than those measured in the experiments. This difference is certainly due to the simplicity of the model. Nevertheless, it does not seem useful to refine the kinetic model by the introduction of unknown parameters. Our aim is only to present a qualitative explanation of the second peak. As the evolution with temperature is rather well described by the model, one can look closely at the energy parameters obtained through this fit. The barrier for the reaction, on the edges, is 23 kcal/mol. On Pd single crystals this barrier is around 25 kcal/mol, at low coverage, and decreases down to 14 kcal/mol at high coverage [12,13]. On the edges, the coverage is high (at least at the beginning of the peak), but one expects that the reaction is more difficult than on a flat surface; then the derived value seems reasonable. More intriguing is the value of the diffusion barrier between an edge and a facet. We obtain 27 kcal/mol, which seems, at first sight, a large value. Indeed, it is large compared to those measured for the diffusion of CO on Pt or Pd surfaces, which are between 4 and 12 kcal/mol. However, we have to consider that if the CO molecules adsorbed on the edges are more strongly bound than on the facets, then the barrier between the two sites must increase. To get an estimate of the height of the barrier, we take 30 kcal/mol for the adsorption energy on the facets and 10 kcal/mol for the diffusion energy on the facets. From the measurements of the adsorption energy of CO, at low coverage on small Pd clusters, the adsorption energy on the edges must be larger than or equal to 40 kcal/mol, and thus the barrier height between the edge and the facet adsorption sites must be higher than or equal to 20 kcal/mol (in addition, the existence of a Schwoebel effect [22] on the edge would further increase this barrier), which is on the order of what is deduced from the fit between the experimental results and the kinetic model.

5 Conclusion

In this paper, we have presented new experimental results which confirm the presence of a second peak of CO_2 in the transient CO oxidation measurements on small Pd clusters. This peak, which appears several seconds after the CO beam is closed, reaches its maximum later when the temperature or the oxygen pressure decreases. This second peak is explained by the presence of CO molecules strongly bound to the cluster edges (and possibly to other defects on the particle surface) which constitute a reservoir of CO that reacts slowly with adsorbed oxygen, i.e., long after all the CO adsorbed on the cluster facets has desorbed. A kinetic model gives a good qualitative agreement of the evolution of the second peak with surface temperature and oxygen pressure. This agreement is obtained for a value of the diffusion barrier from an edge site to a facet site that is rather high: 27 kcal/mol. However, this barrier height is realistic if we take into account that the adsorption energy on the particle edges is larger than 40 kcal/mol.

The present results show again that the CO oxidation reaction on small particles is more complicated than on extended surfaces. At steady state, near the maximum of reactivity (around 500 K) the reaction rate on the small particles is larger than on extended surfaces [9], because the CO coverage on the edges is much higher than on the facets, but is still below saturation. At lower temperature, CO saturates the edges; then mainly the facets are active for the CO oxidation, and the reaction rate is equal (or even smaller) than on extended surfaces [9]. The size effects observed for this reaction (and also for the CO adsorption [17]) are due to the presence of strong adsorption sites for CO on the edges of the Pd clusters.

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