On faceting instability of Pt (110) under catalytic oxidation of adsorbed CO

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Short Communication

On faceting instability of Pt (110) under catalytic oxidation of adsorbed CO

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Résumé. — La face (110) du platine, soumise à l'oxydation catalytique $CO + \frac{1}{2}O_2 \rightarrow CO_2$, se déforme en microfacettes sous certaines conditions de pression et de température [1-4]. Nous suggérons que cette transformation est assistée mécaniquement par la réaction elle-même. On donne une évaluation des différentes contributions à l'énergie de surface et du temps caractéristique de la transformation morphologique.

Abstract. — The microfaceting, under catalytic oxidation of carbon monoxide, of the (110) surface of platinum is discussed from the point of view that Pt mass transport, as involved in the process, should be energetically assisted by the reaction itself. We give an evaluation of the relative contributions to the relevant surface energy, and of the time required to complete the morphological transformation.

1. The problem.

Catalytic oxidation of carbon monoxide on various faces [(100), (111) and (110)] of crystalline platinum, has been studied experimentally for a long time: not only the conditions for an optimization of catalytic activity, but also — and in relationship to the latter — structural changes including periodic oscillations of the Belusov-Zhabotinskii type, and microfaceting. These properties have been recently described in detail in [1-3] and in references therein.

In this note, we address specifically the problem of microfaceting, under reaction conditions, of the (110) Pt surface into orientations belonging to the [001] zone — principally the (340) and (430) orientations. This profile has been characterized by careful LEED experiments [1]. It is a regular, symmetric "sawtooth" profile, obtained at temperatures $\approx 450 - 500$ K under CO

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and O_2 pressures of order 10^{-4} torr. The spatial period is about 150 Å (75 lattice units) along the $[1\bar{1}0]$ direction. The duration of the morphological transformation, at these temperatures, is on the order of a few hundred seconds [4, 2]. Upon interruption of gas flow, the system "reorders" to the initial (110) orientation.

Underlying these morphological-change properties, is the CO-induced surface phase transformation (SPT): above CO coverages of 20 % (in the absence of oxygen and therefore of reaction), the 1 × 2 "missing-row" reconstruction of the Pt (110) surface is lifted and replaced by patches of the 1 × 1 non-reconstructed structure. This involves correlated, surface transport of platinum atoms along the [001] and $[1\bar{1}0]$ directions (for a detailed description, see Ref. [3]). Under reaction conditions, on the so-called low-rate branch where CO adsorption dominates, the basic tiling of the (110) surface will remain with the 1 × 1 structure. The question is: what is the driving force for the (340-430) "faceting"? In the experimental work of reference [1] and in the simulation of reference [2], it is assumed that this is closely associated to CO-coverage fluctuations and to the corresponding SPT transformation (this mechanism appears to be at work indeed in the surface-layer structural periodic oscillation regime).

Here, we add the idea that the energy of the catalytic oxidation reaction itself, and not only the continuous removal and readsorption of the gaseous species, should also play a key role. The argument is that microfaceting involves much more extensive correlated Pt mass transport than single surface-layer transformations. In the next section, we give a simplified evaluation of the surface free energy corresponding to the sawtooth profile. We conjecture that this configuration is energetically favored in the considered conditions of dominant CO adsorption, but that it is separated from the initial flat (110) configuration by an energy barrier $B \gg k_BT$. In section 3 we suggest a possible scheme for reaction-assisted shaping of the profile, including a nucleation-and-growth channel for (340) and (430) microdomains. Concluding remarks are given in section 4.

2. (340-430) vs. (110) profiles under CO coverage.

The non-reconstructed 1 × 1 structure on CO-covered (110) Pt surface corresponds, then, to an energy minimum in structural-configuration space. This, however, is certainly not the only minimum, and is not even necessarily an absolute minimum. The results in references [1-3] and in the literature quoted therein lead us to expect the following. The (340) and (430) orientations — among other orientations of the [001] zone as described in [1] in terms of sequences of (110) 1 × 1 terraces and (100) steps — are strongly stabilized by substantial CO coverages, once they have been formed under oxidation-reaction conditions. The adsorption mechanism for this stabilization is not clearly identified at the molecular level (no more than it is for the pure orientation (110)). The experimental fact is that the reaction itself is efficiently inhibited at substantial CO partial pressures [1, 2]. One can then surmise that CO adsorbs preferentially on superficial or "bridge" sites [2], whereas oxygen prefers deeper sites. As a result, a possible scheme for stabilization of (340)-like orientations, under CO coverage, is depicted in figure 1. The large-density stepping would be "locked" by chemisorbed CO molecules rigidly correlating one edge site, A, to a terrace site A'.

We expect therefore that the (340) orientation (or, symmetrically, (430)) corresponds in configurational space to a rather deep minimum. The fact that the (340, 430) profile is irreversibly selected under reaction conditions, makes us believe that this minimum is lower than the former one (110): see figure 2. We shall come back to a qualitative discussion of the configurational barrier B. At the moment, let us consider the energy difference $\Delta E = E_{110} - E_{340}$.

We recall that we are considering CO-covered, 1 × 1 surfaces; a bare platinum surface would
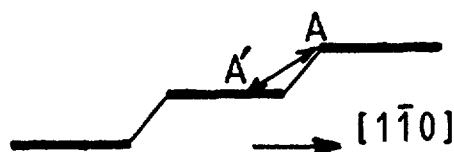
Fig. 1. — (340) surface under CO coverage (schematic). Thick segment: three 1×1 (110) terraces; thin segment: one (100) step; arrow: CO "bridging".
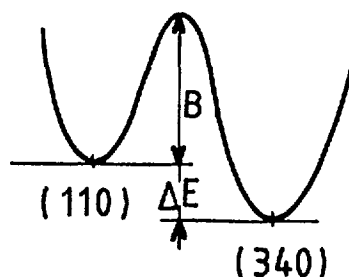

Fig. 2. — Configurational double well.

certainly be more stable in the (110), 1×2 reconstructed, configuration. Indeed, at high enough temperature, the system undergoes thermal reordering [4, 1, 2] and eventually returns to this configuration after interruption of CO gas flow [4].

The discussion of ΔE is complicated by the fact that the (340) minimum in figure 2 corresponds, not to a uniform orientation, but to a symmetrical "sawtooth" profile:... (340), (430), .. , along $[1\bar{1}0]$, with period $\lambda \simeq 75$ lattice units [1] (see Fig. 3). E_{340} is the corresponding surface free energy, and has the following structure, per unit length along the "groove" direction [001] and per period λ along $[1\bar{1}0]$:

$$E_{340} = \frac{\lambda}{\cos \varphi}\alpha_{340} + E_{\mathrm{el}} + E_{\mathrm{cusp}} \tag{1}$$

where $\alpha_{340} = \alpha_{430}$ is the (covered-) surface energy of a uniform (340), or (430), facet; E_{el} is the elastic energy associated with the deformation field due to the sawtooth cusping; and E_{cusp} is the intrinsic energy of a cusp-anticusp pair. The latter is given in order of magnitude by [5, 6]:

$$E_{\mathrm{cusp}} \approx \alpha_{340} \, \xi, \tag{2}$$

ξ being a microscopic length of order a few atomic distances. On the other hand, we evaluate E_{el} from a result obtained by Marchenko [7] in a different context (equilibrium shape problem):

$$E_{\mathrm{el}} = -\frac{1 - \sigma^2}{\pi Y}F^2 \ln\frac{\lambda}{\pi a}, \tag{3}$$

where a is an atomic length, σ and Y are the Poisson coefficient and the Young modulus of Pt crystal, and the force density F (Fig. 3), distributed along $[1\bar{1}0]$, is here given by:

$$F = 2\beta\sin \varphi. \tag{4}$$

β is the tangential, surface stress [8, 6] on (340) or (430), and involves both α_{340} and its derivatives with respect to strain. In order of magnitude: $\beta \approx \alpha_{340}$. Strictly, equations (3) and (4) imply: (i) isotropic elasticity, and (ii) small angles, $\varphi \ll 1$. Neither condition is satisfied here. But it is clear anyway that — due to the largeness of λ/ξ, and of Y/F (an inverse length) — equation (1) is largely dominated by the first term. In other words, $\Delta E = E_{110} - E_{340}$ (Fig. 2) is dominated by the difference in nominal surface energies, more precisely by: $\alpha_{110} - \alpha_{340}(\cos \varphi)^{-1}$ A plausible order of magnitude for this difference could be $\gtrsim 0.1$ eV per unit (110) cell (CO-covered).
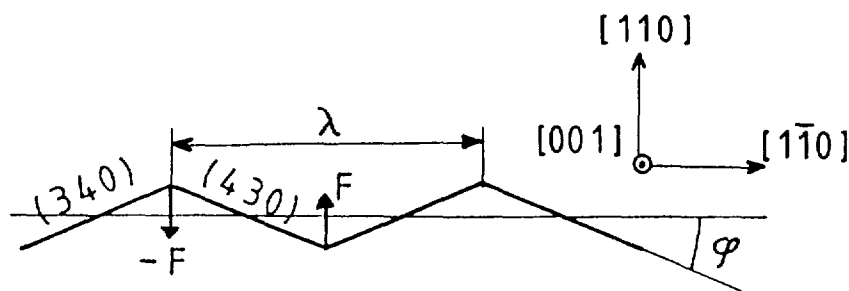

Fig. 3. — Sawtooth profile and force-density F distribution.

3. Reaction-assisted shaping of the sawtooth profile.

In spite of this conclusion, the (340-430) profile cannot be considered as an equilibrium morphology, and figure 2 cannot be reduced to part of a polar Wulff diagram (α vs. orientation). The original workers [1, 2, 4] actually identify this morphology with a stationary "dissipative structure" based on the $1 \times 2 \rightarrow 1 \times 1$ SPT transformation. A few remarks are in order. First, the period λ of the pattern is much smaller indeed than would be predicted by thermodynamics [7]. Second, this period (≈ 150 Å) is remarkably close to the characteristic length of the 1×1 patches along $[1\bar{1}0]$ (see Ref. [3] and Sect. 1 above). Finally, Pt mass transport under reaction conditions seems to proceed by correlated transport, along $[1\bar{1}0]$, of [001] rows, whereas the simple SPT, triggered by CO coverage, proceeds mainly by correlated motion, along [001], of $[1\bar{1}0]$ rows [3]. These points lead us to suggest that, in the relevant part of the (p, T) "phase diagram" [1] — that is, the low-reaction rate region with predominant CO adsorption:

1) the initial patches on (110)-1×1 [3] provide a blueprint for the 340-430 sawtooth pattern;
2) the shaping of this pattern is mechanically assisted by the reaction itself, which helps overcome the configurational barrier B (Fig. 2).

The argument is schematically depicted in figure 4.

i) Oxygen adsorbs preferentially at the edges of the 1×1 patching. The catalytic reaction starts there, excavating a few Pt atoms (chains along [001], shaded area).

ii) This proceeds in time up to a rms roughness $\simeq 3$ layers [1] (presumably, it would be energetically too expensive to dig out deeper Pt atoms. Note: the rms roughness is quite comparable (2.6 monolayers [1]), on the high-reaction rate, disordered branch). Simultaneously, the grooves tend to smoothen in the [001] direction, due to tension forces.
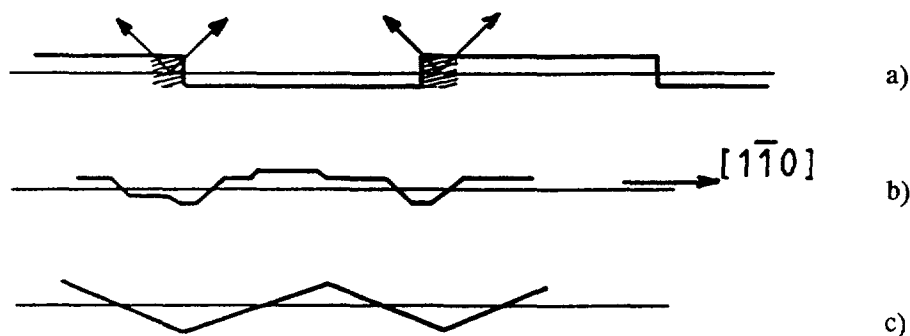
Fig. 4. — Progressive shaping of the (340-430) pattern (see text, first part of Sect. 3).

iii) Finally, the stationary, regular profile is reached after an exposure time t^* of several minutes, typically [4, 2]. Note that the periodic, symmetric sawtooth pattern is the one that ensures minimum platinum mass transport.

Clearly, this is a very qualitative scenario. However, from the energy scales quoted in reference [3], we expect the barrier B to be on the order of $0.5 - 0.7$ eV (≈ 15 kcal/mole). The nominal energy liberated by the oxidation reaction is $\simeq 70$ kcal/CO_2 mole [9]. Most of this leaves out as kinetic energy of carbon dioxide. Since the mass of a platinum atom is 4.5 times the mass of a CO_2 molecule, mechanical balance of energy and momentum tells us that 20 %, at most, of the available energy could be conveyed to a Pt atom, i.e. about 15 kcal/mole again. Of course, most of the accessible final states will involve collective vibration of the whole metallic substrate. Nonetheless, we see that the "scraping" process shown in figure 4a and b, does work: jumping over barrier B (Fig. 2) is hardly thermally activable, but can be mechanically assisted by the catalytic reaction itself.

We emphasize that very little is known about the stereochemistry of adsorption, as well as of catalysis: preferential sites (for CO and for O_2), preferential bond orientations, preferential take-off directions, etc. Above, we have used the total recombination energy of the CO_2 molecule. The latter might however leave essentially normally to the substrate, or leave in a highly excited rotational-vibrational state (CO_2^*, predissociation); in both cases the available energy would then be much less. This seems to be the case for the CO-covered microfaceted profile: once it has been shaped by the reaction, this shape does not change any more. It might even, contrary to a genuine dissipative structure, remain stationary under pure CO exposure. This sort of morphological "passivation" has of course nothing to do with the actual catalytic rate: the latter, in fact, increases on the faceted surface [4, 1, 2].

Microfaceting is specifically associated with the low (initial) reaction-rate branch with predominant CO coverage. It seems natural to infer that the disordered, excavated structure depicted in figure 4b has time, then, to organize into a number of (340) critical "nuclei" through Pt atom diffusion: see figure 5. These nuclei will then grow by step flow and finally coalesce into the final, regular profile after a time t^*. Let us discuss the order of magnitude of t^*. Building on the original worker's results [1, 2], we consider the problem in one dimension only ($// [1\bar{1}0]$), assuming long regular grooves parallel to [001]. Let c be the expansion velocity of a typical (340) domain, and
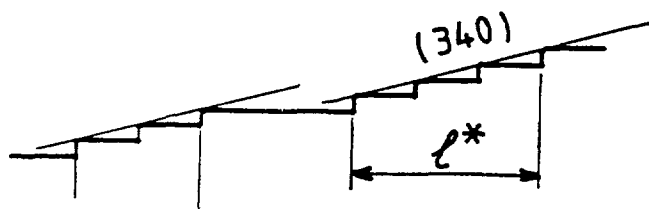
$$J = \frac{W}{\tau}, \tag{5}$$

Fig. 5. — Nucleation and growth of (340) microdomains.

the birth rate of (340) nuclei per unit length along $[1\bar{1}0]$. The natural time scale τ is the reaction-cycle duration, $\tau \approx 0.1$ s [2, 4]; under the working conditions, this is longer than the time scale for substrate changes [2]. For the linear probability density, we take:

$$W = \frac{1}{a}\exp\; -\frac{E_c}{T}, \tag{6}$$

with $a = 2$ Å an atomic length, and $E_c = 0.4$ eV an effective nucleation energy somewhat smaller than B since the process is reaction-assisted. Thus: $J \approx 5 \times 10^{-4}$ s^{-1} Å^{-1} at $T = 500$ K. At time t, the length covered by (340) domains is:

$$\ell(t) = \frac{\lambda}{2} J \int_0^t dt'(t-t')c \approx \frac{\lambda}{2} J c t^2. \tag{7}$$

Faceting is over when $\ell = \dfrac{\lambda}{2}$, that is, at time:

$$t^* = \left(\frac{1}{Jc}\right)^{1/2} \tag{8}$$

The characteristic domain size then being:

$$\ell^* = ct^* = \left(\frac{c}{J}\right)^{1/2} \tag{9}$$

Assume there are about five domains per half period $\left(\dfrac{\lambda}{2} = 75\ \text{Å}\right)$: $\ell^* = 15$ Å. This leaves us with a time $t^* = (J\ell^*)^{-1} = 130$ s, which can be compared to the experimental time [4, 2]. Of course, small changes in E_c could easily improve the result, but this order-of-magnitude argument is too rough anyway to make such refinements meaningful. Our aim was only to call attention to the relevance of two energy scales in the problem: the configurational barrier B and the mechanical energy initially available from the reaction itself, both on the order of half an electron volt.

4. Concluding remarks.

As already mentioned, and as emphasized in references [4, 2, 1], the formation of the micro-faceted profile on Pt (110) results in enhanced catalytic efficiency, associated primarily with better sticking properties at step sites. This kind of causal loop is of course of considerable practical interest. It was foreseen seventy years ago by Langmuir [10] who noted that, under catalytic CO oxidation, a platinum filament "was undergoing a progressive change in the direction of becoming a better catalyst", and that "there is good evidence that the effect is caused by changes in the structure of the surface itself, brought about by the reaction".

This improved catalytic activity is not, however, the "character" that is "selected" in the course of the process. Rather it is, as we view it, a consequence of the selection of a particular pattern, the CO-covered "340-430" profile, which lowers the surface energy. The shaping of this pattern requires initial mechanical activation to ensure Pt mass transport over several-layers thicknesses. This activation is provided, kinetically, by the reaction itself. Were it not for this "scraping" effect, such major structural changes could probably not be achieved in times of a few minutes only. Although the latter conclusion seems unescapable, many of the speculations in section 3 might gain support, or denial, from a better knowledge of the stereochemistry of adsorption and catalysis. As for characterization of the sawtooth profile, little seems to have to be added to the detailed LEED results of reference [1]. This concludes to the regularity of the array of microfacets over more than 2000 Å. Both periodicity and coherence length (and changes thereof depending on (p, T) conditions) might be probed, with great accuracy and truly *in-situ*, by grazing-angle X-ray scattering. This technique would also yield precise characterization (e.g. as a function of time) of the rms roughness of the (110) surface, either disordered or faceted.

Acknowledgements.

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