Catalytic oxidation of CO on a curved Pt(111) surface: simultaneous ignition at all facets through a transient CO-O complex

Fernando Garcia-Martinez,[†] Carlos García-Fernández,[†] Juan Pablo Simonovis,[‡]
Adrian Hunt,[‡] Andrew Walter,[‡] Iradwikanari Waluyo,[‡] Florian Bertram,[¶] Lindsay
R. Merte,[¶] Mikhail Shipilin,[¶] Sebastian Pfaff,[¶] Sara Blomberg,[§] Johan
Zetterberg,[¶] Johan Gustafson,[¶] Edvin Lundgren,[¶] Daniel Sánchez-Portal,[†]
Frederik Schiller,[†] and J. Enrique Ortega^{*,†,||,⊥}

[†]*Centro de Física de Materiales CSIC/UPV-EHU-Materials Physics Center, Manuel
Lardizabal 5, 20018-San Sebastian, Spain*

[‡]*National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973,
USA*

[¶]*Department of Physics, Lund University, Lund 221 000, Sweden*

[§]*Department of Chemical Engineering, Lund University, Lund 221 000, Sweden*

^{||}*Departamento Física Aplicada I, Universidad del País Vasco, 20018-San Sebastian, Spain*

[⊥]*Donostia International Physics Centre, Paseo Manuel de Lardizabal 4, 20018-San
Sebastian, Spain*

E-mail: enrique.ortega@ehu.es

Abstract

The catalytic oxidation of carbon monoxide (CO) on transition metals, such as platinum (Pt), is commonly viewed as a sharp transition from the CO-inhibited surface to the active metal, covered with oxygen (O). However, we find that minor amounts of O are present in the CO-poisoned layer that explain why, surprisingly, CO desorbs at stepped and flat Pt crystal planes at once, irrespectively of the reaction conditions. Using near-ambient pressure X-ray photoemission and a curved Pt(111) crystal we probe the chemical composition at surfaces with variable step density during the CO oxidation reaction. The systematic analysis of carbon and oxygen core levels across the curved crystal reveals that, right before light-off, subsurface O builds up within (111) terraces. This is key to trigger the simultaneous ignition of the catalytic reaction at different Pt surfaces, as indicated by ab-initio theory: a CO-Pt-O complex is formed that equals the CO chemisorption energy at terraces and steps, leading to the abrupt desorption of poisoning CO from all crystal facets at the same temperature.

Introduction

The catalytic oxidation of CO by Pt-group metals has enormous technological, industrial and environmental relevance.¹⁻⁴ Pt itself is of the utmost importance as a catalyst for car exhaust cleaning or for the water gas shift reaction,^{5,6} whereas Pt crystal surfaces are model systems for investigating the catalytic CO oxidation at the atomic scale.⁷⁻¹² In the last four decades many researchers have studied the separate, sequential and simultaneous interaction of CO¹³⁻²³ and oxygen²⁴⁻³⁵ with Pt crystal surfaces under High or Ultra-High Vacuum (HV or UHV) conditions. All such works have provided a good description of fundamental steps in the reaction, such as O₂ dissociation,⁸ CO and O chemisorption,^{13-15,21,27,28} and CO-O interaction.^{11,36} As a result, a widely accepted picture for the catalytic process emerged: at a critical temperature, and in the presence of O₂ and CO gas, there is an abrupt transition from a low-activity phase (so-called poisoned stage),^{37,38} in which a chemisorbed CO (Chem-CO) layer prevents the dissociative adsorption of O₂ and blocks the reaction, to the Langmuir-

Hinshelwood (LH) active stage, where the CO coating is substituted by a relatively open chemisorbed oxygen (Chem-O) layer, which allows CO to coadsorb and immediately react to produce CO₂.³⁹

At a much higher concentration of reactants, the CO oxidation on Pt has been shown to be more complex than previously thought. Recent experiments undertaken at near-ambient or ambient pressure conditions (NAP or AP) have demonstrated the existence of other surface species, particularly during the active stage, which depend on the rate of reactants and their effective transport to and from the surface. NAP experiments show that the Chem-O layer may precede or/and coexist with surface Pt oxides that are catalytically active.^{40–45} In the absence of oxides, the LH process remains the main reaction mechanism in most metal surfaces,^{46–50} but in their presence, the oxidation of CO can occur by direct oxygen capture from the metal oxide.^{41,43,44,51} Nevertheless, Pt oxides exhibit poor thermal stability around characteristic ignition temperatures and in the presence of CO as a reducing agent,⁵² explaining the discrepancies about their CO oxidation capability compared to the Chem-O phase,^{40,44,47,53} or their apparent absence in some experiments,⁵⁰ even in high O₂ excess.^{48,54}

The complexity is maximum when we consider low-symmetry crystal planes, that is, vicinal surfaces with terrace and step sites of different atomic coordination. Vicinal planes are of major importance, since they strictly span most of the surface in spherical nanoparticles. Early HV and UHV experiments found a higher activation energy at steps compared to terraces.^{37,55–59} However, the high oxygen dissociation probability at steps may be ineffective due to an equally low CO oxidation rate, making it *a priori* unclear whether steps are beneficial for the catalytic efficiency of the surface.⁵⁵ Only a few experiments have been done on vicinal surfaces at millibar pressures, which prove the presence of structural instabilities^{42,60} and volatile oxides,⁵² pointing to diverse reaction mechanisms and structural/chemical interplay. The role of steps can be better rationalized through a simultaneous analysis of different surface planes, e.g., using cylindrical crystals. This was first demonstrated in HV experiments by Hopster *et al.*,⁵⁵ and at the range of reaction oscillations (10^{−4} mbar) by

Sander *et al.*⁶¹ At millibar pressures, though, only a curved Pd(111) surface has been examined.^{62,63} Here Planar Laser Induced Fluorescence (PLIF) experiments proved different ignition temperatures at the A- and B-type stepped sides of the sample,⁶² whereas Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS), performed under stationary temperature and pressure, showed a smoothly varying distribution of poisoning and active species across the same curved surface.⁶³

Here we combine PLIF and NAP-XPS to investigate the CO oxidation reaction at vicinal Pt(111) surfaces in the millibar regime, using the same curved sample design [c-Pt(111), see Figure 1a] as for the Pd experiment.^{62,63} In contrast to the clear structure-dependence of Pd, we find that the catalytic activation of Pt occurs in all vicinal planes simultaneously, irrespectively of the reaction parameters. The systematic analysis of chemical species across the entire curved surface provides the clues for this surprising behavior. As the surface CO concentration decreases when approaching ignition, minor amounts of oxygen build up at both steps and (111) terraces. First-principles theory indicates that the latter is forming a CO-Pt-O complex that binds CO molecules to terraces strongly, leveling its adsorption energy to that of low-coordinated steps, and explaining why CO abruptly desorbs at the same temperature along the different crystal facets that make up the curved Pt surface.

Simultaneous ignition at all vicinal planes

In the PLIF and NAP-XPS experiments shown in Figure 1b and c we exposed the sample to different pressure, CO:O₂ ratio, and flux (6 mbar, 1:1, and 4 mL/s in PLIF; 1 mbar, 1:6, <0.1 mL/s in NAP-XPS), and both techniques prove a parallel ignition at all points on the curved surface. PLIF images in Figure 1b correspond to two snapshots below and above the reaction ignition acquired during a fast (3 K/min) heating cycle of the sample, whereas the PLIF signal in the bottom panel corresponds to the integrated intensity measured at the densely stepped A- and B-edges of the sample as a function of the temperature. The CO₂ fluorescence is abruptly lit at T=580.0 K over the whole surface, in clear contrast with the

Figure 1: Simultaneous ignition of the catalytic CO oxidation on a curved Pt surface. (a) Sketch of the c-Pt(111) curved crystal sample featuring A-type and B-type vicinal surfaces, from the (111) direction (sample center) up to the (335) and (553) planes (sample edges), respectively. (b) Top-middle, two-dimensional snapshots of Planar Laser Induced Fluorescence (PLIF) of CO_2 for a 6 mbar, $\text{CO}:\text{O}_2$ 1:1 mixture in front of the c-Pt(111) surface right before (575 K) and after (590 K) light-off, illustrating the simultaneous ignition of the CO oxidation at all vicinal planes. Bottom, CO_2 PLIF signal measured at the stepped A- and B-edges of the sample (integrated intensity inside boxes shown in top panels) as a function of the temperature, marking the ignition at ~ 580 K. (c) O 1s (left) and C 1s (right) photoemission intensity images measured at three different points on the c-Pt(111) sample exposed to ~ 1 mbar, $\text{CO}:\text{O}_2$ 1:6 during a heating cycle. The vanishing of Chem-CO and the emergence of the oxygen-related species mark the abrupt ignition of the reaction, occurring at ~ 565 K in the three crystal planes simultaneously.

strong A-B anisotropy imaged for the analogous c-Pd(111) surface.⁶² In the NAP-XPS plot of Figure 1c the temperature is step-wise increased (5 K steps, at an effective rate of ~ 0.1 K/min), and the C 1s and O 1s spectra are successively acquired at the center [(111) plane], and the two A- and B-type stepped edges of the sample during each heating step. Poisoning Chem-CO vanishes and oxygen-related active species (Chem-O and oxides) emerge in an abrupt way in all flat and stepped crystal planes at $T=562.5$ K, contrasting again with the inhomogeneous ignition observed in NAP-XPS experiments performed on c-Pd(111).⁶³ In

both PLIF and NAP-XPS one also finds that changing rate/flux of reactants, and sample heating rates, the ignition temperature varies [see Supplementary Information (SI) [Figs. S1 and S2](#)], but the simultaneous character of the reaction ignition across the curved c-Pt(111) surface is not affected.

Evolution of the CO poisoning layer before light-off

Carbon monoxide binds to Pt step edges stronger than at (111) terraces.^{66,67} Therefore, the simultaneous quenching of the whole CO signal shown in [Figure 1c](#) is unexpected, since a significant portion of CO chemisorbed on step atoms should remain at the surface when terraces become CO-free. In [Figure 2](#) we carefully probe the variable composition of the Chem-CO poisoning layer when the sample is exposed to 1 mbar, 1:6 CO:O₂. Photoemission intensity images in [Figure 2a](#) show the C 1s map across the curved surface acquired (left) after CO saturation at 300 K in UHV (10 L dose), and in NAP far from (350 K, center) and close to (550 K, right) the reaction ignition at 565 K. In panel [Figure 2b](#) we show individual C 1s spectra corresponding to the center and the stepped edges of the sample, together with a line-fit analysis using four XPS lines at slightly variable energy for terrace lines (<50 meV),⁶⁸ namely Terrace-Top (T_T , 287.6 eV) and Terrace-Bridge (T_B , 286.9 eV), and fixed energy for Step-Top (S_T , 286.2 eV) and Step-Bridge (S_B , 285.7 eV) (see Materials and Methods for fitting details). At 300 K in UHV, CO saturation leads to the $c(4 \times 2)$ structure in the (111) surface, yielding a coverage of 0.5 monolayer (ML) CO equally adsorbed at T_B and T_T sites.^{11,21} In the vicinal (223) and (553) planes one additionally detects step-chemisorbed S_T and S_B species (see sketch in the inset), as well as a small decrease in total coverage as compared to the (111) plane, as expected.^{64,67,68} The same four Chem-CO species are found in NAP-XPS experiments, but the terrace/step and the terrace bridge/top ratios are notably lower. In particular we note that the S_T emission in NAP-XPS remains almost constant up to 550 K, reflecting the fact that, when approaching the ignition of the reaction, CO stays anchored to steps while terraces become partially emptied.

Figure 2: Chem-CO species prior to ignition. (a) C 1s intensity maps across the c-Pt(111) sample exposed to (left) 10 L CO dose at 300 K in UHV (spectra acquired at 100 K), and in the NAP regime (1 mbar, CO:O₂ 1:6) at 350 K (center) and 550 K (right). (b) Spectra extracted from the scans in (a) at the (223), (111) and (553) planes on the surface. Line-fitting to NAP spectra is consistently performed with UHV data (see Materials and Methods). T_T , T_B , S_T and S_B stand for emission from CO molecules respectively adsorbed in Terrace-Top, Terrace-Bridge, Step-Top, and Step-Bridge sites, sketched inside the right hand panel. (d) Step ($S_T + S_B$, top), Terrace ($T_T + T_B$, middle) and total (Step + Top, bottom) CO coverage across the curved surface as determined from line-fitting to all spectra in (a). A minor contribution from T_T vibrational states was also considered (gray).⁶⁴ Straight lines for Terrace and Step panels are fits to the data assuming a simple CO adsorption model with steps having a finite width W_s .⁶⁵ The breaks in the slope in NAP are explained by adsorption-induced step-doubling occurring at critical α_C (see the text).

The temperature-dependent CO coverage at steps and terraces can be evaluated across the entire set of vicinal planes from a line-fit analysis to all spectra in [Figure 2a](#). After converting the peak area into CO coverage by normalizing to 0.5 ML the (111)-UHV spectrum, we obtain the step-CO (S_T+S_B), terrace-CO (T_T+T_B) and total-CO coverage variation over the curved surface, shown in [Figure 2c](#). The step-CO coverage increases linearly from the sample center toward the stepped edges at the same rate in the three cases, proving that, close to ignition in NAP, steps remain CO-saturated at all vicinal planes. Assuming 50% filling of atomic step sites upon CO saturation,⁶⁷ the linear fit to the data renders the effective lateral extension (width W_S) of the steps for A-type ($W_S^A=3.65 \text{ \AA} \approx 1.5$ atom rows) and B-type ($W_S^B=2.66 \text{ \AA} \approx 1.1$ atom rows) steps,⁶⁵ suggesting that understep regions (0.7 and 0.3 atom rows in A- in B-steps, respectively) are largely depleted of CO. A finite width W of the step automatically leads to the reduction of the total (111)-terrace area as a function of α , which in turn explains the steady terrace-CO coverage decrease shown in the central panel of [Figure 2c](#). In UHV at 300 K, the terrace-CO coverage decreases linearly away from the (111) center, as expected on simple grounds, that is, for a constant terrace-CO density at all vicinal angles.⁶⁵ In contrast, the terrace-CO in NAP, particularly at 550 K, exhibits changes in the decreasing rate at $\alpha_c > -9^\circ$ and $\alpha_c > 7^\circ$ in the B- and the A-side of the crystal, respectively, which are also mirrored in the Total-CO-coverage curve of the bottom panel. Assuming again constant CO density at terraces, this sudden reduction of the slope at α_c in [Figure 2c](#) can be explained by an effective increase of the terrace size at fixed α . As we shall see below, this occurs when the vicinal surface undergoes a step-doubling transition.

CO-Pt-O complex in the (111) plane

Although steps remain CO-saturated near ignition, [Figure 2d](#) demonstrates that the CO coverage at terraces decreases from 0.50 ML at 300 K to ~ 0.3 ML at 350 K, and to ~ 0.2 ML at 550 K. This has great importance, because a more open CO layer allows O_2 molecules to impinge, dissociate and, eventually, react with CO or Pt. However, small amounts of

Figure 3: Presence of a terrace oxygen before light-off. (a) O 1s and C 1s spectra at the (111) surface exposed to 1 mbar, CO:O₂ 1:7 in a slow heating cycle (0.25 K/min, 2.5 K steps), describing three different stages of the CO oxidation reaction: far from ignition (poisoned, 350 K), right below (transient, 560 K), and immediately after (active, 570 K). The C 1s spectra reflects the partial desorption of Chem-CO at 560 K, and its complete removal after surface activation at 570 K. In the O 1s panel for the transient stage the spectrum of the 350 K poisoned phase appears overlaid (red dotted line). Differences between both cannot be attributed to Chem-CO desorption alone, but to the presence of a “Transient-O” peak at ~532.1 eV. (b) Top, evolution of the O 1s/C 1s intensity ratio before light-off. The sharp increase near ignition is attributed to the Transient-O species in (a). Bottom, temperature variation of the O 1s intensity for each surface species around the ignition, as deduced from line-fit analysis to individual spectra. (c) From left to right, model structures for the poisoned (Chem-CO), transient (CO-Pt-O complex), and active (only Chem-O) stages.

oxygen in the poisoned phase may pass unnoticed in photoemission spectra, due to the very prominent O 1s emission from CO. In Figure 3 we carefully examine the parallel evolution of C 1s and O 1s spectra during a slow activation process (0.25 K/min, 2.5 K steps) for a

1 mbar, CO:O₂ 1:7 mixture in the (111) plane. The spectra in [Figure 3a](#) illustrate three different temperature steps of the reaction, that is, far from the ignition (350 K), right before (560 K) and immediately after (570 K). Data at 350 K and 560 K nominally belong to the same CO-poisoned phase, but they look markedly different. Upon heating, the C 1s shows a significant intensity reduction, but no shifts in energy or changes in shape, in contrast to the O 1s line, which appears significantly altered. In top of [Figure 3b](#) we represent the evolution of the total O 1s/C 1s intensity ratio during the thermal activation of the reaction. It appears to slowly increase up to 555 K, but it clearly overshoots near the ignition temperature. Both, the spectral changes in the O 1s line and the increasing O 1s/C 1s ratio can be explained assuming the presence of an extra O 1s contribution from a carbon-free species (Transient-O species). In order to determine the energy and intensity of such “Transient-O” line, we perform the joint, consistent fit of the O 1s and C 1s regions, including an extra fixed-energy, Transient-O peak that forces both the T_T^{C1s}/T_T^{O1s} and T_B^{C1s}/T_B^{O1s} intensity ratios to remain constant (see details in Materials and Methods). Under such constraints, a prominent Transient-O peak emerges at ~ 532.1 eV (see [Figure 3a](#)). Following the same three-peak fitting protocol for the entire ignition process, the temperature dependence of the resulting O 1s lines is depicted in the bottom panel of [Figure 3b](#). It shows a smooth decrease of Chem-CO and, mirroring the O 1s/C 1s curve on top, the rapid build-up of the Transient-O emission near the light-off.

Transient states during the CO ignition on Pt surfaces have been postulated before,^{46,69} but always related to the instability of the oxygen-rich active stage (Ref. 52, see also the analysis of the active stage in the present experiment in Figs. S7 and S8). The present transient state, though, is Chem-CO-rich (~ 0.2 ML), it exhibits low catalytic activity and is thermally stable. Regarding the Transient-O species, its O 1s level at around 532.1 eV indicates oxygen atoms in a radically different environment compared to the hollow-adsorbed Chem-O of the active stage, whose O 1s peak appears below 530 eV (see [Figure 3](#) and Ref. 30). In order to understand the chemical nature of such transient layer we turn to Density

Functional Theory (DFT), and examine the stability of different CO-Pt-O complexes on the Pt(111) plane. The results of the theoretical analysis are shown in [Table 1](#) (see calculation details and structures in the SI and [Fig. S4](#)). To agree with NAP-XPS experiments, we consider stable (lowest energy per atom in [Table 1](#)) combinations of CO and O, with the O 1s energy of the CO molecule close to the T_T line at 532.7 eV, and the O 1s energy of the Transient-O around 532.1 eV. With increasing temperature, T_B CO desorbs before T_T , leading to a (2×2) structure in the (111) plane.²¹ This reduces the exploration to periodic 0.25 ML CO structures, that is, (2×2) CO adsorbed atop Pt surface atoms, combined with two distinct oxygen species inside the unit cell, namely, surface O and subsurface O. As listed in [Table 1](#), the CO-Pt(111) system with the oxygen atom at hollow fcc sites (0.25 ML) is the most stable configuration, but its O 1s binding energy (530.3 eV) discards it as potential candidate for the transient state. When considering subsurface oxygen adsorption below the hcp surface site,^{70,71} we immediately find two stable surface-CO/subsurface-O complexes which fulfill these two requirements. The most stable one is shown in [Figure 3c](#) and corresponds to a geometry where the subsurface oxygen and the CO adsorbed molecule share one Pt surface atom. Note that this configuration breaks the normal orientation of the C-O bond and lifts the Pt atom underneath, mimicking the adsorption geometry of the CO molecule at the step edge. Moreover, the adsorption energy for the CO molecule in the CO-Pt-O complex increases by about 0.3 eV with respect to that in the bare (2×2) CO layer, roughly equaling the adsorption energy difference between terraces and steps sites on Pt(111) vicinal surfaces ($\Delta E \sim 0.3 - 0.4\text{eV}$),⁷² and hence explaining the simultaneous desorption of CO in the whole curved surface at the ignition point. Buckling at the topmost Pt plane is the key ingredient. In fact, in the CO-O_{sub}* configuration, surface CO and subsurface oxygen are not coordinated to the same Pt surface atom, resulting in a less stable system, with minor disruption of the (111) surface plane ([Fig S4-e](#)), and lower chemisorption energy for CO. Doubling the subsurface oxygen coverage (0.5 ML) in such CO-O_{sub} causes buckling of the topmost Pt plane ([Fig S4-f](#)), increases the CO adsorption energy, and levels again the

Table 1: DFT calculations of CO-O structures. Total energy per atom, O 1s core-level energies for CO and oxygen species and CO adsorption energy variation determined for a number of CO-O pure and mixed structures on Pt(111). The 0.25/0.25 ML surface-CO/subsurface-O appears sketched in the middle panel of [Figure 3c](#). All the structures are shown in [Fig. S4](#) of the SI.

Structure	ML	site	Total E [eV]	E_O^{O1s} [eV]	E_{CO}^{O1s} [eV]	ΔE_{ad}^{CO} [eV]
CO	0.25/0.00	top	-6.05		532.7	0
CO-O _{fcc}	0.25/0.25	hollow-fcc	-6.05	530.3	532.8	+0.10
CO-O _{sub}	0.25/0.25	tetra	-6.00	531.3	532.8	-0.31
CO-O _{sub} *	0.25/0.25	tetra	-5.97	532.1	532.9	+0.22
CO-2O _{sub}	0.25/0.50	tetra	-5.96	531.0	532.8	-0.48

CO chemisorption energy of terraces to that of steps.

Transient-O and step doubling at vicinal planes

The existence of Transient-O species away from the (111) surface is examined in [Figure 4a](#), where we compare O 1s spectra far (350 K) and close (550 K) from the ignition (at 565 K) in different crystal planes. Experiments are undertaken with a 1 mbar, CO:O₂ 1:6 mixture at the A-side of the crystal, while data for the B-side and spectra acquired under different reaction conditions are shown in [Fig. S5](#) of the SI. The temperature-dependent changes in energy and shape of the main peak reveal the presence of Transient-O in (111) terraces. Such changes are significant at the (111) center and progressively disappear toward the (557) surface, as expected for any terrace-like feature. The quantitative evaluation of the O 1s peak away from the (111) surface becomes more complex, due to the growing contribution of step CO (S_T). In reality, T_T and S_T peaks lie very close to one another (see [Fig. S6](#) and Ref. 67), and hence we consider a single ($T_T + S_T$) line to perform a line fit analysis similar to that of [Figure 3c](#) (see Materials and Methods). From left to right, we consistently obtain two terrace-like (decreasing intensity) T_B and Transient-O peaks, and the step-like (growing intensity) ($T_T + S_T$) peak, as well as a chemisorbed oxygen feature (labeled DS-O in the insets) emerging at 529.6 eV. The DS-O peak is also a step-like feature (it grows as a

Figure 4: Terrace and step oxygen in the transient stage. (a) O 1s spectra at 350 K and 550 K across the A-side of the c-Pt(111) surface exposed to a (1 mbar, CO:O₂ 1:6) mixture. 550 K spectra have been fitted with four different lines [($T_T + S_T$), Transient-O, T_B and DS-O] at fixed binding energy (see Materials and Methods). (b) Intensity (area under peak) for the Transient-O and the DS-O lines deduced from the fit to the spectra in panel (a). The dotted line marks the same α_c angle of Figure 2c. (c) Pictorial description of the different surface chemical species detected in NAP during the CO oxidation reaction on Pt(335), far from (350 K), close to (550 K), and immediately after the ignition. Step-doubling occurs prior to light-off, leading to one extra row of terrace atoms at the expenses of one corner-atom row. The Step-O signature detected in the active stage (see Fig.S8) is assigned to the lowest binding energy species theoretically discussed in Ref. 73.

function of α), but different to the oxygen chemisorbed at steps in the active stage (at 528.9 eV, see Figs. S7 and S8). Both Transient-O and DS-O intensities are plotted as a function of α in Figure 4b, where they neatly exhibit their terrace-like and step-like nature, respectively. The orange dotted line in this figure marks the α_c transition discussed in the terrace-CO

coverage curve of [Figure 2c](#). Within the limits set by the fitting uncertainties (error bars), the critical α_c is coincident with the growing onset of the DS-O species, but also with a change in the attenuation rate of the terrace-like Transient-O. Such coincidence strongly suggests that both [Figure 2c](#) and [Figure 4b](#) curves mirror the same structural transition.

Step-doubling induced by minor doses of oxygen has been reported at vicinal planes in a variety of transition metals in UHV.^{74–77} It is also observed in the active stage during the CO oxidation reaction in nearly-stoichiometric mixtures.⁶⁰ As we sketch in [Figure 4c](#), we postulate a step-doubling transition in A-type vicinals during the transient stage prior to light-off, caused by oxygen bound to bridge positions in the two-atom-wide (100) nanofacet (labeled Double Step O, DS-O). In fact, oxygen binds with similar energy to hollow and bridge sites in (111) and (100) terraces, respectively,⁷⁸ and hence the same O 1s energy (529.6 eV) should be expected. Note that step doubling leads to one extra atom-row in terraces (light orange in the sketch) every two steps, at the expenses of one corner atom row (blue). This fine increase in the number of terrace sites per surface area explains the subtle changes of slope observed in Terrace-CO curves of [Figure 2c](#), which in turn show their potential to prove structural changes in vicinal surfaces through CO titration of terrace and surface sites. [Figure 2c](#) curves also indicate step-doubling for B-type vicinals, for which no DS-O signal is detected ([Figure 2b](#)). Although the increase in the oxygen ratio of the mixture may force the appearance of a tiny DS-O 1s signal in B-type surfaces (see [Fig. S6](#)), we cannot discard that step-doubling in that case is triggered by CO.⁷⁹

Summary

In summary, the transition from the CO-poisoned to the O-active stage in the oxidation of CO at all Pt surfaces vicinal to the (111) plane occurs simultaneously, through a transient phase characterized by small amounts of oxygen mixed with the CO poisoning layer. A joint DFT/NAP-XPS theory/experiment analysis points to the formation of a surface-CO/Pt/subsurface-O complex at (111) terraces that binds the CO molecule to atop Pt

terrace sites strongly, leading to almost equivalent CO chemisorption energy at terraces and steps, and hence to a similar CO desorption temperature. Varying the reaction conditions and the annealing rates changes the ignition temperature and the composition of the active phase, but it does not alter the simultaneous ignition process at all Pt crystal planes.

Acknowledgement

We acknowledge financial support from the Spanish Ministry of Economy (Grants MAT-2016-78293-C6, MAT-2017-88374-P), the Basque Government (Grant IT-1255-19), the Knut and Alice Wallenberg foundation (DNR KAW 2015.0058 "Atomistic Design of new Catalysts") and the Swedish Research Council (DNR 349-2011-6491 "Catalysis on the atomic scale"). This research used resources of the 23-ID-2 (IOS) beamline of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704.

Supporting Information Available

The supplementary information file contains:

Materials and Methods

Supplementary information and discussion on the composition of the active stage

Supplementary Figures S1-S8

Supplementary information and data are provided to illustrate the variability of the ignition temperature as a function of the reactant concentration and flux, as determined in NAP-XPS (Fig. S1) and PLIF (Fig. S2), the transition to the active/poisoned stage measured in heating/cooling-off cycles (Fig. S3), all the structures calculated in DFT to assess the CO-Pt-O complex of the transient stage (Fig. S4), O 1s intensity maps in UHV and in NAP at two temperatures below ignition (Fig. S5), XPS spectra at two temperatures below ignition and at different reaction conditions for A- and B-type surfaces (Fig. S6), O 1s intensity maps for the surface exposed to 10 L O₂ (UHV) and in the active stage in NAP at different reaction conditions, together with the corresponding plots of Chem-O and oxide intensity as a function α (Fig. S7), and spectra and fitting lines at selected planes in order to illustrate the variety of active oxygen species depending on the reaction conditions and step density (Fig. S8).

Materials and Methods

The Pt curved sample [c-Pt(111)] is sketched in the center of Fig.1a of the main text. The cylindrical section design is analogous to the one used by Sander *et al.*,⁶¹ being advantageous over the full-cylinder concept,⁵⁵ due to its compatibility with standard sample holders used in Ultra High Vacuum (UHV) setups. Since the cylinder axis is parallel to the $[1\bar{1}0]$ direction, and the sample center is the (111) surface, vicinal surfaces with increasing density of close-packed steps with $\{100\}$ (A-type) and $\{111\}$ (B-type) microfacets are found as one moves away from the center. As also depicted in Fig. 1a of the main text, a total vicinal angle range $\Delta\alpha = \pm 15^\circ$ is spanned, that is, one can probe all close-packed vicinal orientations from the (111) surface to crystal planes beyond the (335) and (553) at sample edges. The curved surface is prepared in vacuum following the standard procedure applied to regular crystals, namely sputtering (Ar^+ , 1 keV), annealing (1000 K), O_2 -annealing (2×10^{-7} mbar O_2) cycles and short flashes to 1100 K. This procedure leads to a carbon-free surface exhibiting a sharp low energy electron diffraction pattern across the whole sample.⁶⁸

Planar Laser Induced Fluorescence (PLIF) experiments were performed in a gas mixture of 4 mLn/min each of CO and O_2 , and 92 mLn/min of the carrier gas Ar, at a total pressure of 150 mbar. Individual mass flow controllers (Bronkhorst EL-FLOW) were used to regulate the gas flow, and the gas pressure in the reactor was regulated and monitored using a pressure controller (Bronkhorst EL-PRESS). The gas composition in the reactor was measured by a quadrupole mass spectrometer (MS, Pfeiffer, QME 220) connected to the outlet. The temperature was measured with a type D thermocouple attached to the back of the sample. During the experiments, the temperature was ramped at a rate of 0.05 K/s from 470 K to 600 K. To probe the CO_2 in the gas mixture, a laser setup was used, where a Nd:YAG source pumps an infrared optical parametric oscillator (IR-OPO, GWU, versaScan-L 1064), generating a laser beam at $2.7 \mu\text{m}$. The latter, shaped as a thin sheet, was used to excite the CO_2 molecule through the transition $(0000) \rightarrow (1001)$, approximately $300 \mu\text{m}$ above the sample surface. The resulting CO_2 relaxation fluorescence at $\sim 4.3 \mu\text{m}$ was detected using a

IR camera (Santa Barbara Focal Plane, SBF LP134), featuring an internal interference filter to suppress the strong thermal background. The resulting CO₂ images were acquired with an update frequency of 10 Hz, but for better statistics "snapshots" shown in Fig. 1 of the main text and Fig. S2 are the resulting average over 50 frames. A more detailed description of the PLIF technique can be found in Ref. 80, whereas the setup is described in detail in Ref. 81.

High-resolution UHV-XPS experiments were performed at beamline I311 at MaxII in Lund, Sweden.⁸² To ensure the highest surface sensitivity, the photon energy was set to 650 and 400 eV, to measure the O1s and C1s core-level regions. The gases were dosed at 300 K, but the UHV-XPS spectra were acquired with the sample temperature kept at 80 K.

NAP-XPS experiments were carried out at beamline 23-ID-2 (IOS) in the National Synchrotron Light Source II (NSLS-II, Brookhaven, New York), which has been described elsewhere.⁸³ XPS spectra were acquired using a SPECS Phoibos 150 NAP analyzer, and tuning the photon energy to 650 eV for the O1s and 650 or 450 eV for the C 1s. Experiments were performed at normal emission geometry, using p-polarized light (50° incidence with respect to surface normal), which resulted in an effective spot size 16 μm (vertical) x 70 μm (horizontal) on the sample. In NAP experiments the sample temperature was measured using a K-type thermocouple spot-welded to a Ta foil placed between the sample and the heater (BN filament), and the pressure was recorded with a hot cathode ion gauge, at the low range < 10⁻⁵ mbar, and a capacitance manometer at the high range > 10⁻⁵ mbar. A second run of experiments were performed with a Pt filament as a heater, which caused the early ignition of the CO-O₂ mixture, leading to a large increase in CO₂ pressure, and to the decrease of the CO pressure near the Pt surface. This lowered the ignition temperature at the Pt crystal surface (see Fig. S1) and eliminated the hysteresis of the process in a heating/cooling cycle (see Fig. S3). The composition of the gas was continuously tracked using a Residual Gas Analyzer (RGA) placed in the second differential pumping stage of the analyzer. CO (research purity, 99.999%) and O₂ (ultrahigh purity 99.98%) were purchased from Matheson

and were introduced into the chamber using high precision variable leak valves.

Line fitting was done using separate Doniac-Sunjic profiles⁸⁴ convoluted with a Gaussian for the surface species in the spectra (markedly asymmetric for the C 1s, and very symmetric for the O 1s^{11,21,22}), while the gas-phase lines were fitted using a Gaussian-Lorentzian mixed profile. The asymmetry was kept constant with the temperature but the width was allowed to change. A Shirley-type background was subtracted to the spectra.⁸⁵ We combined both CasaXPS⁸⁶ and Igor Pro⁸⁷ packages for data analysis.

To determine the CO coverage of terraces and steps during the poisoned stage at different temperatures (Fig. 2 of the main text), we used the 10 L CO spectra acquired in UHV as reference. At 300 K in UHV the 10 L dose is sufficient to reach the CO saturation in the (111) surface, at which the $c(4 \times 2)$ structure develops, yielding a coverage of 0.5 ML CO, with 0.25 ML T_T and 0.25 ML T_B . Therefore, following Kinne *et al.*,²¹ we applied a correction factor to the T_B intensity so as to normalize both T_T and T_B peak areas to 0.25 ML CO coverage each. The same intensity-to-coverage factor is applied to the step-related S_T and S_B peaks. For the NAP spectra, we assume the same step saturation coverage in both UHV and NAP experiments at 350 K at the (335) surface.

To extract the Transient-O peak contribution to the O 1s line in Fig.3 of the main text, we perform a consistent line fitting of C 1s and O 1s spectra. It is based in the fact that the O 1s/C 1s intensity ratio from surface Chem-CO must remain constant at any temperature, and therefore, the change in the total O 1s/C 1s intensity of Fig.3c in the main text must be explained by another carbon-free oxygen-related species in the O 1s spectra. First, we fit the C 1s spectra at the (111) surface, which only contains the emission from carbon species, that is, CO adsorbed in top and bridge sites. This determines the intensity curves of both as a function of temperature. Assuming zero Transient-O at the lowest temperature, we fit the O 1s peak with only two (top and bridge) lines, and hence determine the C 1s-to-O 1s intensity conversion factor for CO bridge and top peaks. Afterwards, we input the C 1s intensity for bridge and top CO at each temperature, multiplied by the C 1s-to-O 1s

intensity conversion factor, and introduce a Transient-O peak to achieve a good fit. Since the C 1s bridge and top peaks do not shift in energy as a function of temperature, we also assume fixed binding energies for the corresponding O 1s bridge and top lines.

The quantitative evaluation of the Transient-O peak done in Fig. 4 of the main text is carried out by direct line fitting of the O 1s spectrum at 550K, assuming four different lines at fixed energies, namely, (T_T+S_T) at 532.7 eV, Transient-O at 532.1 eV, T_B at 530.9 eV and Double-step-O (DS-O) at 529.6 eV. Therefore, we do not consider separate emission lines for step and terrace. In fact, as observed in the C 1s spectrum, CO should also exhibit a separate emission from step-top and step-bridge sites in O 1s. However, since the step-top emission is shifted by just ~ 0.2 eV to lower binding energy with respect to the terrace-top line,⁶⁷ both will significantly overlap at a stepped surface. Empirically we observe tiny differences between stepped and (111) surfaces, as shown in the central panel of Fig. S5, where we overlay the 350K-NAP spectra for the (111) and the (223) surfaces. The presence of step-top emission barely affects the main peak in the O 1s spectrum, which remains essentially unchanged when shifting from the (111) to the (223) surface, with only a slight intensity enhancement also observed in the UHV image. The same comparison performed with the 550 K spectra reveals a shift to high binding energy from the (111) to the (223) surface. This can only be explained assuming the prominent presence of the Transient-O peak at 532.1 eV in the (111) surface, which is partially suppressed in the (223) surface. On the other hand, the four-line approach is also supported by the consistency of the fitting results, also shown in the bottom graph of Fig. S5. Here we represent the intensity evolution as a function of α for the four species, revealing a consistent terrace-like (intensity decrease away from the sample center) behavior for Transient-O and Bridge-CO, and step-like (intensity increase) for the DS-O peak. For the Top-CO, the fit reveals step-like behavior up to a certain angle, indicating the increasing contribution of CO-saturated steps, while beyond that angle the Top-CO intensity remains constant.

Periodic DFT calculations were performed using the Vienna *ab-initio* package⁸⁸ within

the spin-polarized generalized gradient approximation and the Perdew-Burke-Ernzerhof exchange correlation functional (GGA-PBE).⁸⁹ We employed Projector augmented wave (PAW) pseudopotential from the VASP database,⁹⁰ with a plane wave cutoff of 400 eV. The orbital occupancies were defined using a first-order Methfessel-Paxton scheme, with smearing width $\sigma = 0.2$ eV. Self-consistent field convergence was considered sufficient for a total energy difference of less than 10^{-4} eV between iterations, and the structures optimized until the atomic forces were smaller than 0.01 eV/Å. The theoretical lattice constant of the cubic Pt bulk structure was set to 3.968 Å, exceeding in 1.2% the experimental value of 3.92 Å. The corresponding (111) surface was then modeled using a six-layer slab with a (2×2) surface unit cell, and a Γ -point centered (4×4×1) Monkhorst-Pack mesh. Approximately 12 Å of vacuum was introduced in the surface normal direction to separate repeating slabs. During geometry optimization adsorbed atoms and the top three Pt layers were permitted to fully relax, while the lowermost three atomic layers were fixed at its bulk position. The adsorption energy was computed following the equation $E = [E_{pt,bare} + E_{mol} - E_{surf,mol}]$, where $E_{pt,bare}$ is the energy of the bare Pt(111) slab, E_{mol} is the energy of the isolated triplet O₂ molecule, and $E_{surf,mol}$ is the energy of the Pt(111) slab with the CO molecule adsorbed. Finally, to appropriately account for core-level energies, we have computed the binding energy of the atop CO molecule on a (2×2) Pt(111) surface (0.25 ML) as reference system, fixing all our theoretical core level energy calculations with respect to the CO-O1s experimental value of 532.7 eV.

Chemical composition of the active stage

The passage from the transient to the most active stage is defined by the fast quenching of Chem-CO features in C 1s spectra, and the abrupt emergence of the oxygen-related doublet in the O 1s region (see Fig. 3 in the main text). However, in contrast to the robustly defined poisoned/transient stage, the chemical composition of the active plane in NAP exhibits larger sensitivity to the local crystal plane, and a strong variability with respect to reaction

parameters. This can be qualitatively deduced from the selected scans shown in Fig. S5, where we compare the UHV O 1s spectra for the c-Pt(111) surface exposed to O₂ at 300 K (10 L dose, left panel), with NAP scans acquired immediately after light-off, but under different reaction conditions. In all cases, the spectrum is defined by the Chem-O emission from terraces and steps at the low binding energy side (below the 530.5 eV dotted line), together with a broader peak at higher binding energies (above 530.5 eV), assigned to various Pt oxides at the surface region.⁹¹

All individual spectra extracted from the image plots in Fig. S5 have been fitted using different core-level lines. As a way of example, in Fig. S6 we show XPS spectra at different points on the curved crystals for the UHV experiments and in NAP under the different reaction conditions. The peak at 529.6 eV (O_{terr}, blue) corresponds to chemisorbed atomic O on (111) terraces,³⁰ whereas the 528.9 eV feature (O_{step}, light blue) is assigned to chemisorbed atomic O at steps, as expected from its lower binding energy/coordination.⁹² Such binding energy/coordination trend is similar to that of chemisorbed CO on Pt(111) terraces and steps.⁶⁸ As for the oxides/suboxides, the peak at 531.4 eV (dark green, "Oxide") is assigned to Pt oxide at (111) terraces, and the peak at 530.7 eV (light green, "Surf-O") to oxide at steps, since it grows with the step density. A peak of similar energy has been reported before in stepped surfaces.^{41,91,93} In UHV, the resolution is higher, allowing to visualize extra peaks. The peak at 530.3 eV (violet, PtO₂) is assigned to PtO₂,^{94,95} whereas the one at 533.6 eV (orange, PtO_x) could be attributed to a more oxidized Pt species, or to physisorbed O₂.⁹⁶ The peak at ~528 eV is compatible with oxygen adsorbed at defects,⁵² and in fact remains small and constant over the entire curved surface. Nonetheless, the presence of CO condensation at LN₂ temperature is not discarded in UHV experiments. At such temperature, CO does not react with oxygen, and hence its O 1s signal could be significant in the corresponding spectra.¹¹

The results for the line-fitting, that is, the peak areas appear as data points in the lower panels of Fig. S5, where "Chem-O" is the sum of O_{Terr} and O_{Step} and "Oxide" is the

contribution of Surf-O, Oxide in NAP, and Surf-O, Oxide and PtO in UHV. We note that the α -dependent distribution of hollow-adsorbed Chem-O is relatively robust with respect to the reaction parameters, particularly as compared to the variability of the suboxides. In UHV Chem-O and oxides equally accumulate at the stepped edges of the crystal, and at the B-side (likely caused by the impinging light beam³³), and the same is observed in NAP, independently of the reaction parameters (temperature, ratio). In contrast, the Pt surface oxidation, which is significantly enhanced with respect to the UHV case, can be either minimum or maximum at the (111) center, and appear larger or smaller at the B-side with respect to the A-side, as one changes reaction conditions. Such an apparent random behavior is likely reflecting the oxide instability (reducibility) in the presence of CO,⁵² which, on the grounds of Fig. 4, is dependent on both, the reaction parameters and the step-density.

Figure S1: Ignition temperature variation and gas phase analysis. **a** Ignition (filled circles, T_i) and cooling (open circles, T_c) temperature as determined from the CO desorption in XPS, and as a function of the O_2/CO ratio in three different experimental runs. Data in red correspond to experiments of the main text, where a boron nitride filament was used for sample annealing, while black data are experiments undertaken with a Pt heating filament and a thermo-element attached to a different part of the sample. The Pt filament ignites the gas mixture ~ 50 K below the actual activation of the sample, leading to a significant build-up of $CO_{2(g)}$ in front of the surface, and hence to mass-transfer constraints. The pressure ratio is the direct readout from the Residual Gas Analyzer (RGA) immediately before the curved surface activation (cooling). **b** CO and CO_2 gas phase signal in the RGA (left scale, lines) and the NAP-XPS spectrum (area under the peak, right scale, filled dots) measured during a heating cycle (~ 1 mbar, $CO:O_2$ 1:6, ~ 0.1 K/min) in the (111) plane of the c-Pt(111) surface (see also Fig. 1c in the main text).

Figure S2: Variability of the transition temperature as a function of the $\text{CO}:\text{O}_2$ ratio and flow geometry, as determined in PLIF. Variation of the ignition temperature (3 K/min heating rate) for the CO oxidation reaction on the c-Pt(111) sample by varying the flow and rate of reactants, as observed in PLIF. Experiments are performed in a gas mixture of 4 mLn/min each of CO and O_2 , and 92 mLn/min of the carrier gas Ar, at a total pressure of 150 mbar. **(a)** 1:1 ratio of $\text{O}_2:\text{CO}$ with normal flow: gas inlet at one side of the chamber, and outlet located under the sample holder. Ignition temperature at 580 K (see also Fig. 1b in the main text). **(b)** 1:1 ratio of $\text{O}_2:\text{CO}$ with stagnation flow: gas flowing from a tube directly above the surface, and outlet located under the sample holder. Ignition temperature at 593 K. **(c)** 1:4 ratio of $\text{O}_2:\text{CO}$ with stagnation flow geometry of the setup. Ignition temperature at 565 K.

Figure S3: O_2 :CO ratio variation and hysteresis during heating/cooling cycles.

Temperature evolution of the O 1s and C 1s spectra during heating (red vertical scale) and cooling-off (blue vertical scale) cycles of the active stage of the CO oxidation reaction sequentially measured at the indicated points of the c-Pt(111) sample under different reaction conditions, namely in **a** 1 mbar, CO:O₂ 1:4 and heating rate of 0.25 K/min, and **b** 0.5 mbar, CO:O₂ 1:1 and heating rate of 0.30 K/min. In **a** we observe simultaneous ignition and cooling-off processes, each occurring at a different temperature (580 K and 510 K, respectively). However, there is also an abrupt increase in the O₂/CO concentration in the active stage, due to the large CO₂ build-up in the chamber. In **b** the presence of a Pt filament heater leads to an early ignition (CO₂ build-up) of the reaction away from the sample, resulting in a high oxygen concentration, which accelerates the combustion of graphitic C ~284.4 eV from the surface and, more important, allows a more stable CO:O₂ ratio of 1:5-1:6 during surface activation. Such stability of the CO:O concentration leads to a much reduced (525 K-530 K) hysteresis in the ignition/cooling-off of the catalytic reaction on the sample.

Figure S4: Side view of the different CO-Pt-O complexes calculated in DFT. a CO molecule adsorbed atop Pt surface atoms for a (2×2), 0.25 ML coverage. **b** Chemisorbed oxygen on a Pt(111) fcc-hollow site for a (2×2), 0.25 ML coverage. **c** Combined adsorption of CO molecules on top (0.25 ML) and oxygen atom in the hollow fcc sites (0.25 ML). **d** Optimized structure for the chemisorbed CO molecule (0.25 ML) and subsurface oxygen below the hcp surface site (0.25 ML), sharing a Pt surface atom. **e** Optimized structure for the chemisorbed CO molecule (0.25 ML) and subsurface oxygen below the hcp surface site (0.25 ML). **f** Optimized structure for the chemisorbed CO molecule (0.25 ML) and 2 subsurface oxygen atoms below the hcp surface site (0.50 ML).

Figure S5: Presence of DS-O at B-type vicinals. O 1s spectra at the (223) and (553) planes measured at (1 mbar, CO:O₂ 1:4) (top) and (1 mbar, CO:O₂ 1:6) (bottom), and at different temperatures (350 and 550 K for top panels, and 520 and 560 K for bottom panels). At lower O₂ concentration, the DS-O species is found only in the A-type (223) surface, where it grows bigger in a more oxidizing gas mixture. In B-type (553) surface, the DS-O signal is absent in the low-oxidizing mixture.

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Figure S6: O 1s α -scan of the CO-covered surface. O 1s intensity maps across the c-Pt(111) sample exposed to (top-left) 10 L CO₂ at 300 K in UHV (spectra acquired at 100 K), and in NAP during the poisoned stage under (1 mbar, CO:O₂ 1:6) at 350 K (top-right) and 550 K (bottom-left). T_T , T_B and S_T stand for emission from CO molecules respectively adsorbed in Terrace-Top, Terrace-Bridge and Step-Top, respectively. The presence of a separate S_T emission line that overlaps the T_T line manifests in the intensity enhancement at stepped edges, although T_T and S_T peaks can hardly be resolved, due to their similar binding energy.⁶⁷ This in fact is obvious when overlaying the (111) and the (223) spectra at 350 K, as done in the inset of the top-right panel. Note that superimposing spectra at 550 K reveals an apparent shift to higher binding energy [from (111) to (223)], which can only be explained by the sizeable presence of Transient-O in the (111) case. In the bottom-right panel we show the intensity evolution of the four different peaks used to fit individual spectra at 550 K, shown in the bottom-left panel. Data are discussed in Fig. 4 of the main text.

Figure S7: Variability of the active stage depending on the reaction conditions. O 1s intensity maps across the c-Pt(111) sample exposed to (left) 10 L O₂ 300 K, (center) 1 mbar CO: O₂ 1:4 at 600 K and (right) 0.5 mbar CO: O₂ 1:2 at 580 K. The vertical line at 530.2 eV mark the difference between chemisorbed phases and oxides.

Figure S8: Line fitting of the active stage at different vicinal angles. Selected O 1s fitted spectra at (553) (top panels), (111)(middle panels) and (223)(bottom panels) planes on the c-Pt(111) sample exposed to (left panels) 10 L O₂ 300 K, (center panels) 1 mbar CO: O₂ 1:4 at 600 K and (right panels) 0.5 mbar CO: O₂ 1:1.5 at 580 K.

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