

One-Dimensional PtO₂ at Pt Steps: Formation and Reaction with CO

J. G. Wang,¹ W. X. Li,^{1,*} M. Borg,² J. Gustafson,² A. Mikkelsen,² T. M. Pedersen,¹ E. Lundgren,² J. Weissenrieder,²
J. Klikovits,³ M. Schmid,³ B. Hammer,¹ and J. N. Andersen²

¹*Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*

²*Department of Synchrotron Radiation Research, Lund University, Box 118, S-221 00, Sweden*

³*Institut für Allgemeine Physik, Technische Universität Wien, A-1040 Wien, Austria*

(Received 5 August 2005; published 15 December 2005)

Using core-level spectroscopy and density functional theory we show that a one-dimensional (1D) PtO₂ oxide structure forms at the steps of the Pt(332) surface after O₂ exposure. The 1D oxide is found to be stable in an oxygen pressure range, where bulk oxides are only metastable, and is therefore argued to be a precursor to the Pt oxidation. As an example of the consequences of such a precursor exclusively present at the steps, we investigate the reaction of CO with oxygen covered Pt(332). Albeit more strongly bound, the oxidic oxygen is found to react more easily with CO than oxygen chemisorbed on the Pt terraces.

DOI: [10.1103/PhysRevLett.95.256102](https://doi.org/10.1103/PhysRevLett.95.256102)

PACS numbers: 68.47.De, 68.43.Bc, 68.43.Fg, 82.65.+r

Steps are inevitably present on the surface of nanoscale particles commonly used in heterogeneous catalysis. The adsorption of, and reactions amongst, molecules are often very different at steps than on the flat parts of the particle surfaces. The steps may therefore profoundly influence the catalytic properties of the surfaces, which has indeed been demonstrated for, e.g., NO/Ru [1], N₂/Ru [2], and O₂/Pt [3]. The altered adsorption and reaction behavior is often ascribed to the fact that the lower coordination number at a step modifies the electronic structure in its vicinity and that the molecules may adsorb in new geometrical configurations at steps [4]. However, in addition to these effects, the steps may also be significantly modified by one or more of the reactant molecules through local compound formation occurring as an integral part of the reaction. Such compound formation may be expected to occur more easily at steps because of the larger freedom for geometrical rearrangements there than on flat parts of the surface.

The possibility of compound formation is of particular relevance in oxidation reactions, since typical catalyst materials all have a high propensity for oxide formation [5]. It was recently shown that the active phase of Ru in oxidation reactions is that of a thin bulk oxide [6], and for late-transition and noble metal elements such as Rh [7], Pd [8], and Ag [9], surface oxides have been proposed as the active phases.

In the present Letter we give experimental and theoretical evidence that for the stepped Pt(332) surface, oxide formation also takes place even at relatively moderate oxygen pressures. The oxide found, however, only occurs in the form of one-dimensional (1D) Pt-oxide stripes along the steps. These oxide stripes turn out to be a key ingredient in understanding CO oxidation on this stepped surface. We demonstrate, using core-level spectroscopy (CLS), that adsorbates at steps and on the terraces of such stepped surfaces may lead to different core-level binding energies. Detailed information on the adsorption sites is extracted from these core-level binding energy fingerprints via com-

parison to density functional theory (DFT) calculations. The Letter is organized as follows. First, the O adsorption site is identified comparing measured Pt 4f_{7/2} and O 1s CLS and DFT results. Then, the C 1s CLS is introduced as a probe to (step vs terrace) adsorption sites of CO and, finally, the C 1s CLS is used to monitor the sequence of oxygen removal over Pt(332) during annealing after low-temperature CO exposure.

The experiments were performed at beam line I311 at MAX-lab, Lund, Sweden [10]. The Pt crystals were cleaned by Ar⁺ sputtering, annealing in O₂, and final annealing in vacuum at 1200 K in order to remove residual oxygen. The sample cleanliness was checked by monitoring the Pt 4f_{7/2}, C 1s, and O 1s core-level regions. The sample temperature was measured by Chromel-Alumel thermocouples spot welded to the crystals. Surface ordering was checked by low-energy electron diffraction showing well-ordered surfaces.

The slab based DFT calculations were done using the DACAPO package [11] with ultrasoft pseudopotentials, plane waves (E_{cut} = 25 Ry) **k**-point mesh, the revised Perdew, Burke, Ernzerhof (RPBE) exchange-correlation functional [12], and the calculated Pt lattice constant of 4.02 Å. For Pt(332) we used a (2 × 1) super cell [cf. Figs. 1(b) and 1(c)] with four (111) Pt layers, two of which were relaxed together with the adsorbates. Core-level shifts were calculated using pseudopotentials with core holes [13].

The Pt(332) surface is composed of six atomic rows wide (111) terraces and a (111) type step. Hence core-level photoemission spectra for Pt(332) and Pt(111) are expected to be very similar. In Fig. 1(a) we present the Pt 4f_{7/2} core spectra obtained after saturation of the two surfaces with O as achieved by a $p \approx 10^{-6}$ Torr O₂ exposure for 500 s at 310 K. Indeed, both spectra contain a bulk component (dashed line) at 70.90 eV, a component at ~70.5 eV (“clean”) from surface Pt atoms not coordinat-

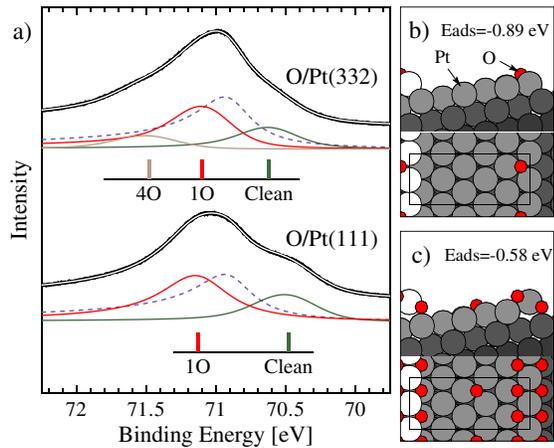


FIG. 1 (color online). (a) Pt $4f_{7/2}$ core-level spectra for O/Pt(332) and O/Pt(111) after saturation with oxygen at 310 K. In the decompositions, the dashed blue line is bulk. (b)–(c) Calculated equilibrium structures and average adsorption potential energy at (b) low and (c) high O coverage.

ing to any O [14], and a component at ~ 71.1 eV (“1O”) from Pt atoms coordinating to one chemisorbed O [15]. Interestingly, the spectrum for O/Pt(332) further contains a high-energy component (“4O”) not present in the spectrum for O/Pt(111). Below, we assign this peak to step Pt bonded to four O.

In the case of the O $1s$ spectra (not shown) only a single peak is found for either surface, the peak being shifted slightly from 529.75 for Pt(111) to 529.55 eV for Pt(332). Comparing the intensities, we find, however, a saturation value which is about 1.7 times higher on Pt(332) than on Pt(111). On the Pt(111) surface, the saturation structure is known to be 0.25 monolayers [ML, 1 ML equals the number of Pt atoms in one (111) layer] [16] meaning that the saturation coverage on Pt(332) becomes about 0.42 111 ML [where the designation 111 ML refers to the density of Pt in the (111) surface].

Returning to the $4f_{7/2}$ spectra, Fig. 1(a), we note that the finding of an intense clean component on O/Pt(332) indicates that a significant part of the terrace Pt atoms do not form bonds to any O atoms. This excludes the formation of any high-coverage O structure on the terraces. Instead we conclude that the 0.42 111 ML O coverage is achieved via the formation of a high-coverage O structure along the Pt steps.

In order to obtain a structural model of this O structure on Pt(332), we performed an extensive search using DFT. The characterization of low-coverage O structures on stepped Pt with DFT has been done by Feibelman *et al.* [17], who found every second step edge, fcc site occupied with O. For the Pt(332) surface such a structure corresponds to an O coverage of 0.09 111 ML [Fig. 1(b)]. This coverage is considerably smaller than what was determined in our O $1s$ CLS, and we have consequently searched for structures having higher oxygen coverages.

Based on the calculated chemisorption energies we constructed the surface free energy diagram to determine which structures would form as a function of the oxygen chemical potential. The only other stable structure found is the one depicted in Fig. 1(c). The structure has an O coverage of 0.46 111 ML, with four out of five oxygen atoms bonding to the step Pt. Every step Pt is fourfold coordinated to O (hence the designation 4O above), and the step can thus be described as a repeated 1D PtO_2 unit, an oxide stripe.

The high-coverage structure [Fig. 1(c)] is preferred for oxygen chemical potentials, μ_{O} , in the range $-0.50 \text{ eV} < \mu_{\text{O}} < -0.41 \text{ eV}$, where the lower bound corresponds to the switch to the low-coverage structure [Fig. 1(b)] and the upper bound to the onset of bulk oxide formation. At 310 K the μ_{O} range translates to the oxygen pressure range, $5 \times 10^{-5} \text{ Torr} < p_{\text{O}_2} < 8 \times 10^{-2} \text{ Torr}$. Given the calculational (several orders of magnitude for pressures) and experimental ($\sim 10\%$ for absolute coverages) uncertainties, we consider the calculation of a high oxygen coverage (0.46 111 ML) structure in this pressure range to be consistent with the experimental findings under our exposure conditions. We note that the slightly lower experimental coverage might also be due to difficulties in reaching saturation caused by the oxygen adsorption being an activated, dissociative process. In addition, we also find good agreement for calculated and experimental O $1s$ and Pt $4f$ CLS. Compared to O/Pt(111), we calculate three different O $1s$ shifts for O/Pt(332): -0.25 and -0.23 eV for the upper and lower O at the step, and $+0.09$ eV for the terrace O. The measured ~ 0.2 eV lower O $1s$ binding energy on Pt(332) than on Pt(111) is thus consistent with most O on Pt(332) being Pt step bonded. For Pt $4f$ [Fig. 1(a)], using clean terrace Pt as the reference, we calculate shifts of $+0.51$ and $+0.81$ eV for the terrace Pt bonding to one O, and the Pt within the PtO_2 stripe. These numbers are in excellent agreement with the measured values of $+0.5 \pm 0.07$ and $+0.85 \pm 0.07$ eV for 1O and 4O, respectively. Finally, the structure in Fig. 1(c) is also consistent with the experimental finding of a significant intensity for the clean component in Fig. 1(a).

In order to elucidate the electronic structure of the PtO_2 stripe, we performed a Wannier orbital [18] population analysis. An isolated PtO_2 stripe was realized by removing all Pt from Fig. 1(c) except for the step Pt. Subsequently, the supercell size was adjusted so that the stripe assumed its equilibrium length per PtO_2 unit in the direction of the stripe. This stripe, surrounded by vacuum, showed electronic charge transfer from Pt to O of approximately $0.8e^-$ per O atom. When the PtO_2 stripe is supported on a metal surface, the charge transfer increases. Pt(332) is too large for our analysis code, but for the very similar PtO_2 structure, recently identified on Pt(110)-(1 \times 2) [19], we find about $1.3e^-$ transferred to every O. With the significant charge transfer involved, we consider the PtO_2 to be largely ionically bound.

Comparing the calculated stability of the 1D-PtO₂ oxide to competing high oxygen coverage structures on other vicinal Pt(111) surfaces with (111) steps, we generally find that a 1D oxide is preferred over chemisorption phases at oxygen chemical potentials down to ~ -0.5 eV, which is below the threshold for bulk PtO₂ formation, $\mu_{\text{O}} = -0.41$ eV. Thus, the 1D oxide may serve as a precursor for bulk oxide growth on Pt surfaces, that contain steps and kinks. Considering Pt nanoparticles in catalysis, their steps and edges must hence be expected to undergo 1D oxidation above $\mu_{\text{O}} \sim -0.5$ eV. At 300, 400, and 500 K this corresponds to pressures of $p_{\text{O}_2} > 7 \times 10^{-9}$, 6×10^{-4} , and 1 bar. Under operating conditions, such nanoparticles may therefore appear as enchainned in a 1D-oxide network, much like an automobile tire mounted with snow chains.

As an example of the influence of these oxide stripes on surface reactions, we studied the CO oxidation reaction on Pt. First, this was done by predosing O₂ at 310 K to form the 1D oxide and then exposing the surface to CO for a given time at a given temperature, after which the sample was immediately cooled down to 100 K to prevent further reaction. The amount of atomic O removed was then determined from the decrease of the atomic O 1s component in a way similar to that used recently by, e.g., Kinne *et al.* [20,21]. From this we find, in agreement with earlier results for Pt(111) [20], that CO oxidation on Pt(111) is negligible below ~ 270 K, whereas for Pt(332) the temperature has to be lower than 220 K in order to quench the reaction. For temperatures where CO oxidation occurs on both surfaces we find, for the same O precoverage on both surfaces, that more atomic O is removed from Pt(332) than from Pt(111). At 273 K, a CO exposure of 5×10^{-9} Torr for 100 s to an O precoverage of 0.25 ¹¹¹ML leads to a relative reduction of the atomic O coverage by 25% on Pt(332), but only by 10% on Pt(111).

Having established a higher reactivity of the Pt(332) surface, we then used the C 1s level from adsorbed CO to derive information on the structure of the oxidized surface before and after reduction by CO. This is possible because CO molecules adsorbed at steps give rise to a specific C 1s component. Figure 2(a) shows measured C 1s CLS for CO saturation on Pt(332) and Pt(111). For CO/Pt(111) we find the 2 C 1s components, which have been assigned to CO molecules in on-top (286.7 ± 0.05) and bridge (286.0 ± 0.05) sites [15]. For CO/Pt(332) we find, however, 3 C 1s components at binding energies of 286.60, 286.27, and 285.93 eV. Comparing with the (111) spectra, two of these can be assigned to terrace bonded CO molecules, whereas the component at 286.27 eV must be due to CO adsorbed at the steps. Comparison to calculated CLS [Fig. 2(b)] confirm this interpretation and additionally demonstrates that the CO molecules at the steps adsorb in on-top positions as also suggested by the calculated adsorption potential energies at CO saturation [Figs. 2(c) and 2(d)].

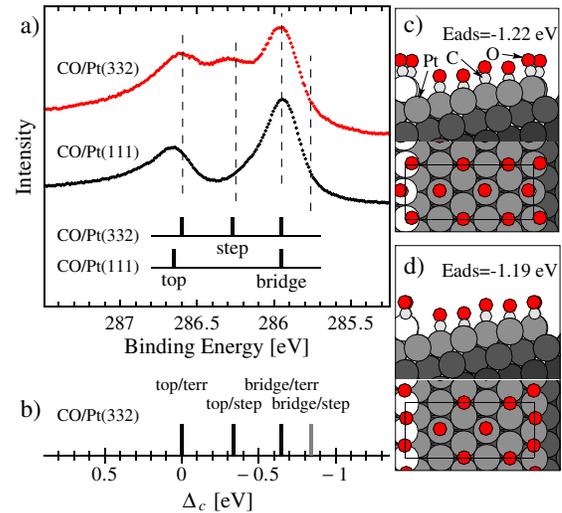


FIG. 2 (color online). (a) C 1s spectra for CO/Pt(332) compared to CO/Pt(111) showing an additional signal for step bonded CO. (b) Calculated C 1s shifts and (c)–(d) structures and average adsorption potential energies per CO for CO/Pt(332). The dashed lines in (a) are based on the calculated shifts.

Using the C 1s as a CO “adsorption site fingerprint” we find that CO preferentially adsorb at steps on the O-free Pt(332) surface; $\sim 70\%$ of the CO molecules are at the steps after a 0.5 Langmuir (L , $1 L = 10^{-6}$ Torr s) CO exposure at 220 K. Preadsorbing O changes this site preference strongly; after a similar CO exposure at 220 K—where no reaction occurs—the amount of step-adsorbed CO is found to decrease roughly linearly with O precoverage from the value for the O-free surface to zero for O-saturation coverage even though the total amount of adsorbed CO decreases by only 15% at the highest O precoverage. This behavior suggests that the intensity of the step-C 1s component can be used to monitor what fraction of the Pt steps have not turned into the 1D oxide. In other words, it facilitates selective “titration” of the steps before and after reduction with CO.

Figure 3 shows the evolution at 247 K of the C 1s intensity following a 0.5 L CO exposure at 220 K of Pt(332) with an O precoverage of 0.25 ¹¹¹ML. The total C 1s intensity decreases with time as part of the CO oxidizes and desorbs as CO₂. The splitting of the C 1s intensity into separate contributions from terrace and step bonded CO clearly demonstrates that the reaction causes a fast decrease of the terrace CO component and at the same time an increase of the step CO component. Even after about 30% of the CO is removed (as measured by the total C 1s and/or O 1s intensity decrease), the step component is more intense than before the reaction. The observed C 1s behavior strongly suggests that it is preferentially the oxygen atoms within the 1D Pt-oxide stripes which are reacted away in the reduction process thereby causing an increase

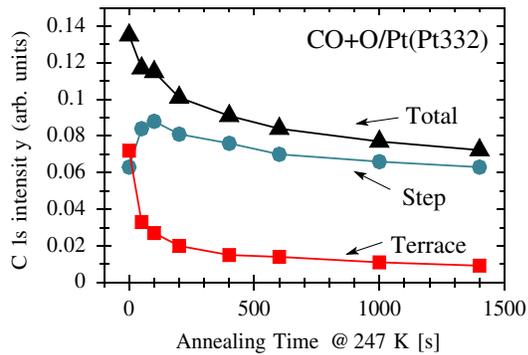


FIG. 3 (color online). The development of the C 1s intensity as a function of annealing time at 247 K after a 0.25 ^{111}ML O/Pt(332) surface is exposed to 0.5 L CO at 220 K. The total intensity (triangles) is decomposed into terrace bonded CO (squares) and step bonded CO (circles).

of the fraction of O-free steps and thus also of the intensity of the step-C 1s component

Preferential oxygen removal from the oxide stripes is further supported by our DFT calculations. A CO molecule bonding to the terrace at the foot of the PtO_2 covered step encounters a 0.60 eV energy barrier for forming CO_2 with an oxygen atom extracted from the bottom O row in the PtO_2 stripe. For CO reacting with an oxygen atom in a local $p(2 \times 2)$ -(O,CO) structure on the terrace of Pt(332) the barrier is higher, 0.71 eV, i.e., comparable to that reported in the similar O and CO coadsorption structure on Pt(111), 0.74 eV [22]. The calculated lower barrier for oxidizing CO from oxidic O, as compared to chemisorbed O, explains the lower onset in temperature of the reaction at Pt(332) compared to Pt(111), since oxidic O is present on the stepped surface only. The lower barrier must originate from a more favorable transition state being possible at the step, since we do not see the O bond strength in the oxide as the reason for the lower barrier: Extracting a single O atom from the PtO_2 covered step costs 0.77 eV [23], whereas removing a single terrace bonded O costs only 0.54 eV.

In conclusion, we have shown that on Pt(332) a 1D PtO_2 oxide forms at the steps under conditions where bulk oxidation is not yet preferred. Since, for a test reaction of $\text{CO} + \text{O}$, the 1D oxide is found to be highly active, our results suggest that compound formation at defect sites may be an important mechanism happening on catalyst particles and that such compounds may be important for the activity of the particles.

This work was financially supported by the Swedish Research Council, the Danish Research Council, Dansk Center for Scientific Computing, the EC Contract No. NMP3-CT-2003-505670 (NANO2), and the Austrian Fonds zur Förderung der Wissenschaftlichen Forschung. Support by the MAX-lab staff is gratefully acknowledged.

*Present address: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

- [1] T. Zambelli, J. Winterlin, J. Trost, and G. Ertl, *Science* **273**, 1688 (1996).
- [2] S. Dahl, A. Logadottir, R.C. Egeberg, J.H. Larsen, I. Chorkendorff, E. Törnqvist, and J.K. Nørskov, *Phys. Rev. Lett.* **83**, 1814 (1999).
- [3] P. Gambardella, Z. Sljivancanin, B. Hammer, M. Blanc, K. Kuhnke, and K. Kern, *Phys. Rev. Lett.* **87**, 056103 (2001).
- [4] B. Hammer, O.H. Nielsen, and J.K. Nørskov, *Catal. Lett.* **46**, 31 (1997).
- [5] V.E. Henrich and P.A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, England, 1996).
- [6] H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, and G. Ertl, *Science* **287**, 1474 (2000).
- [7] M. Todorova, W.X. Li, M.V. Ganduglia-Pirovano, C. Stampf, K. Reuter, and M. Scheffler, *Phys. Rev. Lett.* **89**, 096103 (2002).
- [8] B.L.M. Hendriksen and J.W.M. Frenken, *Surf. Sci.* **552**, 229 (2004).
- [9] C.I. Carlisle, D.A. King, M.L. Bocquet, J. Cerdá, and P. Sautet, *Phys. Rev. Lett.* **84**, 3899 (2000).
- [10] R. Nyholm, J.N. Andersen, U. Johansson, B.N. Jensen, and I. Lindau, *Nucl. Instrum. Methods Phys. Res., Sect. A* **467**, 520 (2001).
- [11] <http://www.camp.dtu.dk/campos>.
- [12] B. Hammer, L.B. Hansen, and J.K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
- [13] M. Birgersson, C.O. Almbladh, M. Borg, and J.N. Andersen, *Phys. Rev. B* **67**, 045402 (2003).
- [14] The slight shift in the clean surface Pt component from O/Pt(111) to O/Pt(332) may be understood in terms of a contraction of the stepped terraces. A similar behavior is observed for the clean surfaces.
- [15] O. Björnehalm, A. Nilsson, H. Tillborg, P. Bennich, A. Sandell, B. Hernnäs, C. Puglia, and N. Mårtensson, *Surf. Sci.* **315**, L983 (1994).
- [16] J.L. Gland and V.N. Korchak, *Surf. Sci.* **75**, 733 (1978).
- [17] P.J. Feibelman, S. Esch, and T. Michely, *Phys. Rev. Lett.* **77**, 2257 (1996).
- [18] K.S. Thygesen, L.B. Hansen, and K.W. Jacobsen, *Phys. Rev. Lett.* **94**, 026405 (2005).
- [19] W.X. Li, L. Österlund, E.K. Vestergaard, R.T. Vang, J. Matthiesen, T.M. Pedersen, E. Lægsgaard, B. Hammer, and F. Besenbacher, *Phys. Rev. Lett.* **93**, 146104 (2004).
- [20] M. Kinne, T. Fuhrman, J.F. Zhu, C.M. Whelan, R. Denecke, and H.P. Steinrück, *J. Chem. Phys.* **120**, 7113 (2004).
- [21] The CO O 1s binding energies all exceed 531 eV and thus do not interfere with the atomic O 1s.
- [22] W.X. Li and B. Hammer, *Chem. Phys. Lett.* **409**, 1 (2005).
- [23] Removing *all* oxidic oxygen atoms costs an *average* energy of 0.60 eV.