Supplementary Information for

In situ X-ray Probing Reveals Fingerprints of Surface Platinum Oxide[†]

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Details of FEFF8 calculations

All chemisorbed adlayers were constructed on the (flat) surface of a hemispherical ($R = 10$ Å) 188 atom Pt/Rh(111) cluster comprising a single pseudomorphic monolayer of Pt. The unit cells of these hypothetical structures with adsorption sites, Pt–O bond distances, and references to experimentally observed corresponding structures on pure Pt(111)[1–3] are shown in Table S1. The Pt-Rh interlayer spacing, Δz_{PtRh}, was set to the bulk Rh value, $\Delta z_{RhRh} = 2.196$ Å. While it is likely that the platinum overlayer undergoes adsorbate- or strain-induced relaxation, we have neglected these effects in our structure models. However, in an effort to quantify the uncertainty introduced by employing unrelaxed structures, we built one Pt/Rh(111) cluster where the Pt overlayer was expanded outwards by 0.215 Å, such that the per-atom-volume of the topmost Pt/Rh bilayer, $V_{Pt/Rh(111)} = \sqrt{3}z_{PtRh}d_{Rh}^2/2$, where the Pt–Pt nearest-neighbor distance is reduced to $d_{Rh} = 2.689$ Å, would be equal to that of bulk Pt, namely $V_{Pt} = d_{Pt}^3/\sqrt{2} = 15.1$Å^3 with $d_{Pt} = 2.775$ Å. We find that vertical relaxation does not significantly affect the width and intensity of the white line, but merely causes features more than ~ 10 eV above the absorption edge to shift in energy.

The "SCF" radius for all calculations using the Pt/Rh(111) cluster was set to $r_{SCF} = 7.5$ Å, a value chosen so as to include at least one surface unit cell for all structure models. The "FMS" radius (r_{FMS}) must be set large enough in order not to neglect important scattering paths. The convergence of the XANES simulations with respect to the choice of r_{FMS} was therefore carefully checked for the adsorbate-free Pt/Rh(111) cluster; a value of 9.0 Å was found to be sufficient.

Furthermore, we carefully assessed the assignment of potential indices *"ipot"* in the Pt/Rh(111) clusters. To better represent the extended surface of a large single-crystal using a finite cluster we assigned identical potential indices to Pt atoms that would be symmetry-equivalent if the cluster were extended to an infinite slab. Rh atoms were assigned only two potential indices; one for the topmost Rh layer and one for Rh in all other layers. The resulting spectrum for clean Pt/Rh(111) does not discernibly differ from a more complex calculation where all five layers of the Pt/Rh(111) cluster were given different potential indices.

Since all of the inequivalent Pt atoms of the surface unit cell contribute to the spectrum, we took the weighted average of their individual spectra, each of which was computed with the Pt absorber as close as possible to the center of the cluster.

For the platinum oxides PtO, Na$_x$Pt$_3$O$_4$ ($x = 0, 1$) and α-PtO$_2$ we obtained the unit cell parameters[4–7] listed in Table S2 from the Inorganic Crystal Structure Database (ICSD, http://icsd.fiz-karlsruhe.de) and constructed large spherical clusters of radius 9 Å with the absorbing Pt atom at the center. The "SCF" radius was set to 7.5 Å, a value that includes typically ~ 10 coordination shells around the absorbing atom. Extending r_{SCF} beyond 7.5 Å did not appreciably change the computed spectra. An FMS radius of 9.0 Å was sufficient to ensure convergence of the multiple-scattering calculations.

References

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Table S1 Surface unit cells, Pt–O bond distances ($d_{Pt–O}$) and adsorption sites for scaled model structures. References refer to experimentally observed analogous structures on Pt(111).

Model structure	Surface unit cell	O adsorption site	$d_{Pt–O}$(Å)	Ref.
OH-H$_2$O/Pt/Rh(111)	$c(3 \times 3)$	on top	2.23 (Pt–OH$_2$) 2.11 (Pt–OH)	[1]
O/Pt/Rh(111) ($\theta_O = 0.25$ ML)	$p(2 \times 2)$	*fcc* hollow	1.99	[2]
O/Pt/Rh(111) ($\theta_O = 0.50$ ML)	$p(2 \times 1)$	*fcc* hollow	1.99	[3]

Table S2 Unit cell parameters used to construct spherical clusters of bulk oxides.

Model structure	Unit cell parameters	Spacegroup	Ref.
PtO	$a = b = 3.04$Å; $c = 5.34$Å; $\alpha = \beta = \gamma = 90°$	*P42/mmc*	[4]
NaPt$_3$O$_4$	$a = b = c = 5.6868$Å; $\alpha = \beta = \gamma = 90°$	*Pm-3n*	[5]
Pt$_3$O$_4$	$a = b = c = 5.585$Å; $\alpha = \beta = \gamma = 90°$	*Pm-3n*	[6]
α-PtO$_2$	$a = b = 3.1$Å; $c = 4.161$Å; $\alpha = \beta = 90°$;$\gamma = 120°$	*P-3m1*	[7]