Supporting Information

Interplaying Coordination and Ligand Effects on Near-Surface Alloys of Pt to Break or Make Adsorption-Energy Scaling Relations

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S1. Computational methods and tabulated energies

The DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP).\cite{1} To represent ion-electron interactions, we used the projector augmented-wave (PAW) method.\cite{2} The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used to calculate the total energies.\cite{3} The near-surface alloys (NSAs) were modeled as a 4-metal layer slab in which the second layer was filled with a guest atom (3d elements from V to Zn, 4d elements from Nb to Cd, 5d elements from Ta to Hg), while the rest of the surface was occupied by Pt (see section S4). The top two layers were allowed to relax, while the others were kept fixed at the optimized bulk positions of Pt, for which we found a converged lattice constant of 3.98 Å. The separation between periodical images in the vertical axis was larger than 14 Å, which suffices to avoid spurious electrostatic interactions between them.

The relaxations were computed using a plane-wave cutoff of 450 eV and an electronic temperature of 0.2 eV, and all energies were extrapolated to 0 K. The conjugate gradient method was employed to minimize the maximum forces on the atoms, until the maximal force was below 0.05 eV Å\(^{-1}\). To sample the k-space we used Monkhorst-Pack grids\cite{4} of (6×7×1) and (4×5×1) for the (2×2) (111) and (3×1) (331) slabs, respectively. The free molecules (CO, CO\(_2\), H\(_2\)O and H\(_2\)) were modelled in cubic boxes of 15 Å × 15 Å × 15 Å with an electronic temperature of 0.001 eV and sampling only the Γ-point in k-space.

The free energies were approximated as: \(G \approx E_{\text{DFT}} + ZP\text{E} - TS + E_{\text{solv}}\), where \(E_{\text{DFT}}\) is the total energy calculated with DFT; \(ZP\text{E}\) is the zero-point energy obtained from DFT-based vibrational analyses within the harmonic oscillator approximation; \(TS\) are the entropy corrections for the free molecules taken at \(T = 298.15\) K, and those for the adsorbates were neglected, as a first
approximation; and $E_{solv}$ are the water-adsorbate stabilization effects, the values of which for *CO and *OH were extracted from previous studies (see Table S1).\[^{5,6}\] Water was simulated as a gas, but its energetics are provided in the liquid phase, which is made by means of an entropy correction.\[^{6,7}\] To calculate the free energy of proton-electron pairs, the computational hydrogen electrode was used.\[^{7}\] This allowed us to describe such complicated energetics in solution in terms of that of H$_2$ in the gas phase. All the energetic corrections and free energies of adsorption in this study are shown in Tables S1, S2 and S3.

**Table S1.** Corrections needed to assess the free energies of the molecules and adsorbates in this study. The ZPEs of *OH and *CO appear in Tables S2-S4.

| Species    | ZPE [eV] | TS [eV] | $E_{solv}$ [eV] |
|------------|----------|---------|----------------|
| CO(g)      | 0.13     | 0.61    | 0.00           |
| CO$_2$(g)  | 0.31     | 0.66    | 0.00           |
| H$_2$(g)   | 0.28     | 0.40    | 0.00           |
| H$_2$O(l)  | 0.58     | 0.67    | 0.00           |
| *OH        | –        | 0.00    | -0.58          |
| *CO        | –        | 0.00    | -0.10          |

**Table S2.** Zero-point energies and free energies of adsorption of *CO and *OH on the (111) facet of Pt NSAs.

| Alloy  | ZPE$_{CO}$ [eV] | ZPE$_{OH}$ [eV] | $\Delta G_{CO}$ [eV] | $\Delta G_{OH}$ [eV] |
|--------|-----------------|-----------------|----------------------|----------------------|
| Pt-V   | 0.20            | 0.33            | -0.15                | 0.61                 |
| Pt-Cr  | 0.21            | 0.33            | -0.20                | 0.42                 |
| Pt-Mn  | 0.21            | 0.33            | -0.52                | 0.30                 |
| Pt-Fe  | 0.21            | 0.33            | -0.67                | 0.52                 |
| Pt-Co  | 0.21            | 0.33            | -0.57                | 0.75                 |
| Pt-Ni  | 0.21            | 0.33            | -0.57                | 0.80                 |
| Pt-Cu  | 0.21            | 0.33            | -0.35                | 1.04                 |
| Pt-Zn  | 0.20            | 0.32            | -0.13                | 1.20                 |
| Pt-Nb  | 0.20            | 0.32            | -0.11                | 0.70                 |
Table S3. Zero-point energies and free energies of adsorption of *CO and *OH on the (331) facet of Pt NSAs.

| Alloy  | ZPECO [eV] | ZPEOH [eV] | ΔGCO [eV] | ΔGOH [eV] |
|--------|------------|------------|-----------|-----------|
| Pt-V   | 0.20       | 0.35       | -0.46     | 0.96      |
| Pt-Cr  | 0.20       | 0.32       | -0.67     | 0.68      |
| Pt-Mn  | 0.21       | 0.31       | -0.89     | 0.57      |
| Pt-Fe  | 0.21       | 0.34       | -1.01     | 0.41      |
| Pt-Co  | 0.21       | 0.33       | -1.05     | 0.42      |
| Pt-Ni  | 0.21       | 0.33       | -1.04     | 0.37      |
| Pt-Cu  | 0.21       | 0.33       | -0.91     | 0.49      |
| Pt-Zn  | 0.20       | 0.33       | -0.88     | 0.56      |
| Pt-Nb  | 0.20       | 0.32       | -0.43     | 0.83      |
| Pt-Mo  | 0.20       | 0.34       | -0.58     | 0.71      |
| Pt-Tc  | 0.21       | 0.31       | -0.82     | 0.65      |
| Pt-Ru  | 0.21       | 0.32       | -0.99     | 0.52      |
| Pt-Rh  | 0.21       | 0.34       | -1.11     | 0.35      |
| Pt-Pd  | 0.21       | 0.34       | -1.11     | 0.33      |
| Pt-Ag  | 0.21       | 0.34       | -0.86     | 0.55      |
| Pt-Cd  | 0.21       | 0.33       | -0.88     | 0.53      |
| Pt-Ta  | 0.20       | 0.32       | -0.43     | 0.84      |
| Pt-W   | 0.20       | 0.34       | -0.55     | 0.72      |
| Pt-Re  | 0.21       | 0.31       | -0.81     | 0.64      |
| Pt-Os  | 0.21       | 0.34       | -0.99     | 0.38      |
|       |   |   |   |   |
|-------|---|---|---|---|
| **Pt-Ir** | 0.21 | 0.33 | -1.17 | 0.30 |
| **Pt-Pt**  | 0.21 | 0.34 | -1.20 | 0.29 |
| **Pt-Au**  | 0.21 | 0.34 | -0.99 | 0.44 |
| **Pt-Hg**  | 0.21 | 0.34 | -0.87 | 0.60 |

**S2. Adsorption Configuration of *OH**

In Figure S1 we show different views of *OH adsorbed on the two different surfaces considered.

**Figure S1.** Adsorption configuration of *OH on near-surface alloys. (a) and (b) correspond to the top and side views of a (111) near-surface alloy, while (c) and (d) correspond to a (331) near-surface alloy. *OH is adsorbed atop in all cases. Grey spheres represent Pt, cyan is used for the guest atom in the subsurface layer, white for H and red for O.
S3. Lewis Diagrams

The 8 and 18-electron rule can be used to predict the most stable alloy configuration for a given adsorbate.\textsuperscript{[8]} To identify these alloys, Lewis diagrams were constructed. The idea is to apply the 8-electron rule to the adsorbate, and the 18-electron rule to the surface. Following this procedure, Figure S2 is generated.

![Lewis Diagram](image)

**Figure S2.** Most stable alloy configuration for *CO and *OH adsorption on NSAs of Pt(111). For *CO, the alloys that resemble the electronic structure of noble gases correspond to those where the guest atom has 8 valence electrons (Fe, Ru, Os). For *OH, the optimal configuration is found when the guest atom possesses 7 valence electrons (Mn, Tc, Re). The symbols indicate shared pairs of electrons (lines), lone pairs (dots) and dative bonds (arrows). The Lewis diagrams were made based on reference.\textsuperscript{[8]}

S4. Results for Pt(100) NSAs

The calculations were made as described in section S1 with (2×2) 4-layer-thick slabs and a k-point sampling of (6×6×1). Again, the mismatch of the minima causes the non-scalability of *OH and *CO (Figure S3A-B). Interestingly, when the data for the three facets ((111), (100) and (331)) are plotted altogether a scaling line seems to contain most of the points (see the ellipse in Figure S3C) and there is also a region of departed data. The adsorption energies and ZPEs appear in Table S4.
Figure S3. Trends in the adsorption energies of (A) *OH and (B) *CO on the (100) facet of NSAs of Pt and transition metals as a function of the number of outer electrons ($N$) of the guest atom. C) Adsorption energies of *OH plotted versus those of *CO for the (111), (100) and (331) facets of NSAs. The ellipse is drawn as a guide to the eye.
Table S4. Zero-point energies and free energies of adsorption of *CO and *OH on the (100) facet of Pt NSAs.

| Alloy | ZPE$_{CO}$ [eV] | ZPE$_{OH}$ [eV] | ΔG$_{CO}$ [eV] | ΔG$_{OH}$ [eV] |
|-------|----------------|----------------|---------------|---------------|
| Pt-V  | 0.19           | 0.33           | -0.26         | 0.56          |
| Pt-Cr | 0.19           | 0.33           | -0.42         | 0.25          |
| Pt-Mn | 0.20           | 0.33           | -0.65         | 0.30          |
| Pt-Fe | 0.20           | 0.33           | -0.71         | 0.54          |
| Pt-Co | 0.20           | 0.33           | -0.65         | 0.64          |
| Pt-Ni | 0.20           | 0.33           | -0.77         | 0.61          |
| Pt-Cu | 0.20           | 0.33           | -0.84         | 0.54          |
| Pt-Zn | 0.19           | 0.32           | -0.53         | 0.86          |
| Pt-Nb | 0.20           | 0.32           | -0.48         | 0.29          |
| Pt-Mo | 0.19           | 0.33           | -0.45         | 0.31          |
| Pt-Tc | 0.20           | 0.33           | -0.57         | 0.42          |
| Pt-Ru | 0.20           | 0.33           | -0.77         | 0.57          |
| Pt-Rh | 0.21           | 0.33           | -0.86         | 0.61          |
| Pt-Pd | 0.21           | 0.33           | -1.00         | 0.54          |
| Pt-Ag | 0.20           | 0.33           | -0.88         | 0.57          |
| Pt-Cd | 0.20           | 0.32           | -0.57         | 0.85          |
| Pt-Ta | 0.19           | 0.32           | -0.47         | 0.27          |
| Pt-W  | 0.19           | 0.33           | -0.47         | 0.28          |
| Pt-Re | 0.20           | 0.34           | -0.52         | 0.35          |
| Pt-Os | 0.20           | 0.33           | -0.82         | 0.46          |
| Pt-Ir | 0.21           | 0.33           | -0.92         | 0.58          |
| Pt- Pt | 0.21           | 0.33           | -1.05         | 0.56          |
| Pt-Au | 0.21           | 0.34           | -1.04         | 0.48          |
| Pt-Hg | 0.20           | 0.34           | -0.78         | 0.74          |

S5. Direct coordinates
| Surface(331) | Direct |
|-------------|--------|
| 0.0048657475908 0.154674672842 0.046362573206 | T T T |
| 0.302149347599 0.460189498867 0.472123978569 | T T T |
| 0.712149578402 0.208232154657 0.0672123978569 | T T T |
| 0.081720546570 0.790504136602 0.094369374016 | T T T |
| 0.502670447446 0.862587459032 0.862587459032 | T T T |
| 0.012538450628 0.260546798709 0.094369374016 | T T T |
| 0.104610226739 0.120973659671 0.120973659671 | T T T |

| Surface(331) | Non-Direct |
|-------------|-----------|
| 0.0048657475908 0.154674672842 0.046362573206 | F F F |
| 0.302149347599 0.460189498867 0.472123978569 | F F F |
| 0.712149578402 0.208232154657 0.0672123978569 | F F F |
| 0.081720546570 0.790504136602 0.094369374016 | F F F |
| 0.502670447446 0.862587459032 0.862587459032 | F F F |
| 0.012538450628 0.260546798709 0.094369374016 | F F F |
| 0.104610226739 0.120973659671 0.120973659671 | F F F |

**JH CO**

Surface(331) | Direct |
|-------------|--------|
| 0.094846382462 0.059840584096 0.029572998735 | T T T |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |

Surface(331) | Non-Direct |
|-------------|-----------|
| 0.094846382462 0.059840584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |
| 0.004674082636 0.088040584096 0.029572998735 | F F F |

**BO CO**

Surface(331) | Direct |
|-------------|--------|
| 0.0000000000 0.0000000000 0.0000000000 | T T T |
| 0.0000000000 0.0000000000 0.0000000000 | T T T |
| 0.0000000000 0.0000000000 0.0000000000 | T T T |
| 0.0000000000 0.0000000000 0.0000000000 | T T T |
| 0.0000000000 0.0000000000 0.0000000000 | T T T |

Surface(331) | Non-Direct |
|-------------|-----------|
| 0.0000000000 0.0000000000 0.0000000000 | F F F |
| 0.0000000000 0.0000000000 0.0000000000 | F F F |
| 0.0000000000 0.0000000000 0.0000000000 | F F F |
| 0.0000000000 0.0000000000 0.0000000000 | F F F |
| 0.0000000000 0.0000000000 0.0000000000 | F F F |
| Pt   | Pd   | O    | C    |
|------|------|------|------|
| 0.8435280000000000 | 0.0000000000000000 | 0.0000000000000000 |
| 0.7563925875758819 | 0.5337653477582628 | 0.8612075690220415 |
| 0.7209457575478701 | 0.5703925875758819 | 0.7384399846763818 |
| 0.7238697575478701 | 0.5703925875758819 | 0.6916875690220415 |

**Surface535 (1) layer**

| Pt   | Pd   | O    | C    |
|------|------|------|------|
| 0.4208388181166238 | 0.5252701581292878 | 0.8531255846078096 |
| 0.7563925875758819 | 0.5337653477582628 | 0.8612075690220415 |

**Surface344 (1) layer**

| Pt   | Pd   | O    | C    |
|------|------|------|------|
| 0.4185280000000000 | 0.0000000000000000 | 0.0000000000000000 |
| 0.7563925875758819 | 0.5337653477582628 | 0.8612075690220415 |
| Surface(331) | 0.8245598770580713 | 0.9473734883136515 | 0.5986079999999987 | F F F |
|-------------|---------------------|---------------------|---------------------|------|
| 0.6140323445533795 | 0.6842082932855078 | 0.6715879999999999 | F F F |
| 0.9473680488809180 | 0.6842082932855078 | 0.6715879999999999 | F F F |
| 0.8570578403459634 | 0.1400891540123491 | 0.8113352918660527 | T T T |
| 0.6315772348318589 | 0.7894776349564054 | 0.9649129391594045 | F F F |
| 0.7819166096248769 | 0.6822558527215253 | 0.9335353917808318 | T T T |
| 0.0917569473501132 | 0.5408259463554139 | 0.4912241727305329 | F F F |
| 0.2807627133442757 | 0.6842082932855078 | 0.6715879999999999 | F F F |
| 0.8421020476 | | | |
| 0.0526319511190820 | 0.3157917067144922 | 0.6350959999999972 | F F F |
| 0.0188779956787407 | 0.0558631495838539 | T T T |
| 0.0020700577288985 | | |
| 0.4545706357998820 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.6132307206876829 | 0.5237666840957147 | 0.5237666840957147 | T T T |
| 0.3013204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.0513204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.6132307206876829 | 0.5237666840957147 | 0.5237666840957147 | T T T |
| 0.3013204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.0513204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.6132307206876829 | 0.5237666840957147 | 0.5237666840957147 | T T T |
| 0.3013204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.0513204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.6132307206876829 | 0.5237666840957147 | 0.5237666840957147 | T T T |
| 0.3013204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
| 0.0513204521926871 | 0.6132307206876829 | 0.5237666840957147 | T T T |
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