Electronic Supplementary Information:
Automated Detection and Characterization of Surface Restructuring Events in Bimetallic Catalysts

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1 vdW-DFT benchmark of bulk properties

![Figure S1: Lattice constant of (a) Ag and (b) Pd, calculated from DFT using the PBE functional and different vdW corrections/functionals. Experimental values are indicated by black lines.](image)

We test bulk properties of Ag and Pd using the PBE functional\textsuperscript{11} with pair-wise vdW corrections (PBE-D3;\textsuperscript{2} PBE-TS;\textsuperscript{3} PBE-dD\textsuperscript{4,5} ) as well as nonlocal self-consistent vdW functionals (vdW-DF correlation\textsuperscript{6,7} with optB86b, optB88, or optPBE exchange;\textsuperscript{8,9} the original vdW-DF formulation using rPBE exchange;\textsuperscript{6} vdW-DF2 formulation using rPW86 exchange\textsuperscript{10}). We use the experimental benchmark reported by Csonka et al.\textsuperscript{11} with zero-point anharmonic expansion subtracted for lattice constant and zero-point vibrational energy added for cohesive energy. We verify that optPBE-vdW is in good agreement with the experimental values, within 0.1 Å and 0.2 eV error for lattice constant (Fig. S\textsuperscript{1}) and cohesive energy (Fig. S\textsuperscript{2}), respectively. The choice of optPBE-vdW is further motivated by its performance on adsorption energy, discussed in Sec. 10.

For Pd-Ag interaction, we calculate solvation energy of a single Pd atom in bulk Ag:

\[
E_{sol} = \frac{1}{N}(E_{Pd/Ag} - N_{Ag}\mu_{Ag}^{bulk} - N_{Pd}\mu_{Pd}^{bulk}).
\] (1)
Figure S2: Cohesive energy of (a) Ag and (b) Pd, calculated from DFT using the PBE functional and different vdW corrections/functionals. Experimental values are indicated by black lines.

Figure S3: Magnitude of solvation energy of a single Pd atom in bulk Ag, calculated from DFT using the PBE functional and different vdW corrections/functionals.

Here, $N = N_{\text{Ag}} + N_{\text{Pd}}$ is the number of atoms in the alloy unit cell, and $\mu^{\text{bulk}}$ is the chemical potential of an atom in its pure bulk phase. We use a $2 \times 2 \times 2$ supercell of the FCC Bravais...
lattice, corresponding to 12.5 at. % Pd. The Brillouin zone is sampled using a Γ-centered $9 \times 9 \times 9$ $k$-point grid. We find that all functionals considered give small negative values ($\approx -30$ meV) for the solvation energy (Fig. S3), in agreement with the experimental value of $-17$ meV for the mixing enthalpy of a solid alloy with 20 at. % Pd measured at 600 K.$^{12}$
2 Adatom diffusion at step edges of close-packed surface from DFT

Homoepitaxial adatom diffusion on Ag close-packed surfaces has been studied extensively in the computational literature in the context of island growth, most frequently employing molecular mechanics,\textsuperscript{5} MD,\textsuperscript{19} KMC,\textsuperscript{19} and genetic algorithm,\textsuperscript{18} majority of them based on EAM or SMA-TB potentials. Although elementary homoepitaxial adatom diffusion involving a small number of atoms in the surface layer has been mapped out thoroughly with empirical potentials (e.g.\textsuperscript{29}), more accurate characterization at the DFT level remains scarce.\textsuperscript{24,51–53} Furthermore, to our best knowledge, no computational or experimental study has been reported on heteroepitaxial adatom diffusion of Pd on Ag close-packed surfaces, of much interest to the growth of bimetallic catalysts (e.g. Pd/Ag\textsuperscript{54}). We therefore perform a systematic DFT study of adatom diffusion at step edges of close-packed Ag surface, comparing the energetics of Ag/Ag versus Pd/Ag.

Simple, linear atomic trajectories involving only one or two surface atoms are optimized via the CI-NEB method\textsuperscript{55,56} using 3 intermediate images generated by linear interpolation, where the total forces, given as the sum of the spring force along the chain and the true force orthogonal to the chain, are converged to 0.05 eV/Å. Table S1\textsuperscript{1} describes the computational set-up of the slab models of close-packed Ag surface considered for adatom diffusion at step edges. Due to the localized nature of the events and larger computational cost associated with \textit{ab initio} CI-NEB calculations, we use slab models with one less row of close-packed terrace (CPT) than the ones used in our MD simulations (Table 1 of the main text).

Table S1: Computational set-up of Ag slab models considered for adatom diffusion at step edges of close-packed surface.

<table>
<thead>
<tr>
<th>Facet</th>
<th>Features</th>
<th>Unit cell</th>
<th>Number of layers</th>
<th>k-point grid</th>
</tr>
</thead>
<tbody>
<tr>
<td>(211) 3-row CPT with A-step edge</td>
<td>3×4</td>
<td>4 (bottom 1 fixed)</td>
<td>8×5×1</td>
<td></td>
</tr>
<tr>
<td>(331) 3-row CPT with B-step edge</td>
<td>6×4</td>
<td>4 (bottom 1 fixed)</td>
<td>4×5×1</td>
<td></td>
</tr>
</tbody>
</table>
Table S2: Ag or Pd adatom diffusion barriers at A- or B-step edges of Ag surface, calculated from DFT: (a) simple diffusion; (b) 2D evaporation; (c) step descent; (d) vacancy insertion. $E_{ES}$ refers to the Ehrlich-Schwoebel barrier\cite{ref1,ref2} associated with step descent. Available experimental values for Ag/Ag are noted in the footnote.

<table>
<thead>
<tr>
<th></th>
<th>Ag$_{(ads)}$</th>
<th>Pd$_{(ads)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-step</td>
<td>B-step</td>
</tr>
<tr>
<td>(a)</td>
<td>Terrace diffusion$^a$</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Corner diffusion</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Edge diffusion$^b$</td>
<td>0.21</td>
</tr>
<tr>
<td>(b)</td>
<td>2D evaporation$^c$</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>2D evaporation (kink)</td>
<td>0.48</td>
</tr>
<tr>
<td>(c)</td>
<td>Hopping descent</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>Exchange descent</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>$E_{ES}^d$</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Exchange descent (kink)</td>
<td>0.26</td>
</tr>
<tr>
<td>(d)</td>
<td>Kink insertion (lower edge)</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Kink insertion (upper edge)</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>Vacancy insertion (upper edge)</td>
<td>0.39</td>
</tr>
</tbody>
</table>

$^a$ Exp.: 0.05-0.18 (Lü et al\cite{ref3} and Refs. therein)
$^b$ Exp.: 0.30 (B-step)\cite{ref4}
$^c$ Exp.: 0.71±0.03\cite{ref5}
$^d$ Exp.: 0.13±0.04\cite{ref6}
Figure S4: Calculated activation energy $E_a$ (forward and reverse) versus the corresponding cost in coordination number ($\Delta CN_a$) of Ag or Pd adatom and/or auxiliary Ag atom in motion for all diffusion events at step edges of Ag close-packed surface as listed in Table S2.
We consider 4 main classes of events, as outlined in Table S2. We benchmark our calculations with available experimental values for Ag/Ag measured in scanning tunneling microscopy (STM) experiments of island growth/decay. We note that the experimental values are effective quantities, meaning they do not necessarily correspond to specific microscopic processes, unless stated otherwise.

First, simple diffusion only involves one adatom [Table S2(a)]. Terrace diffusion of both Ag and Pd adatom are facile, with energy barriers of only 51 and 31 meV, respectively. The diffusion occurs between FCC and HCP hollow sites via bridge site, with negligible energy difference between the two types of site. The low Ag/Ag value is in good agreement with the experimental values typically reported in the range of 50-100 meV (See Lü et al. and Refs. therein). Corner diffusion is similarly facile, involving diffusion from a corner site to an edge site. The energy barrier involving A-step is lower than the one involving B-step, in good agreement with previously reported corner diffusion anisotropy (CDA), where singly-bonded adatom at the corner of a hexagonal island can more easily access A-step than B-step. Edges provide the most stable adsorption site for adatoms in terms of coordination. We find that diffusion along edges are sufficiently facile (< 0.5 eV), and our value of 0.29 eV at B-step is in good agreement with the experimental value of 0.30 eV at B-step. The facile edge diffusion, combined with CDA, has been attributed for the growth of islands orthogonal to A-step with elongated B-step edges.

Second, 2D evaporation refers to detachment of an edge atom [Table S2(b)]. We find that the detachment process involves an edge atom to first dangle at the corner site of its neighboring edge atom, after which it becomes detached completely as an isolated adatom. The corner site acts as an intermediate state, which is the reason our energy barriers for Ag/Ag (0.55-0.65 eV) are slightly lower than the experimental value of 0.71 eV. The process is more facile for an atom at a kink site with a neighboring vacancy. Due to the already low starting coordination number of the kink atom, the resulting smaller coordination loss allows the energy barriers to be lower by around 0.2 eV. For both cases, Pd atom experiences
energy barriers that are higher than those of Ag atom by around 0.3 eV. Due to the higher surface energy of Pd than Ag, Pd experiences larger energetic cost from a given coordination loss compared to Ag.

Third, step descent involves an adatom moving over a step edge, from upper edge to lower edge [Table S2(c)]. Exchange descent is discussed in detail in the main text (Class 1). We find that there is a negligible difference between hopping descent at A-step and B-step, in agreement with previous computational characterizations (e.g.\textsuperscript{29}). Hopping descent, incurring coordination loss of the usual type, has higher energy barriers for Pd adatom that Ag adatom by around 0.3 eV, similar to the case of 2D evaporation. The situation is reversed for exchange descent, however, due to the stronger thermodynamic driving force for Pd to be incorporated into the edge. Furthermore, exchange descent at B-step is expected to dominate over that at A-step, not only because of the lower value of $E_{ES}$, but also due to the aforementioned CDA that promotes elongated B-steps.

Fourth, vacancy insertion of an adatom occurs via displacement of an auxiliary Ag atom [Table S2(d)]. All energy barriers shown are lower than 0.5 eV, suggesting feasibility of the processes at room temperature. Insertion into kink sites can occur from either the upper edge as an isolated adatom, or the lower edge as an adatom at the edge site. We find the former to be more facile, which is attributed to the stronger thermodynamic driving force for an isolated adatom to be incorporated into the edge. In particular, the kink insertion barrier for Pd adatom at upper A-step edge is zero, similar to the case of exchange descent at B-step.

Lastly, we show that coordination loss acts as the primary descriptor for all of our calculated energy barriers. From Fig. S1, there exists an approximately linear relationship between activation energies and coordination loss associated with the said activation, defined as the cost in coordination number going from initial to transition state. This linearity is consistent with the terrace-step-kink model\textsuperscript{62,63} where surface energetics is described in terms of coordination number of surface atoms. In general, Pd adatom tends to experience
higher energy barrier than Ag adatom for a given process, as seen from the larger slope, with exceptions for processes such as exchange descent and insertion with strong thermodynamic driving force.
3 Pd-Ag direct exchange on close-packed terrace from DFT

Here, we present preliminary DFT calculations of Pd-Ag direct exchange processes on close-packed terrace, using the PBE functional\textsuperscript{11} We find that PBE and optPBE-vdW\textsuperscript{6,8} give identical direct exchange barrier on Ag(111) [Table 6(b), Pd\textsubscript{(ads)} of the main text], consistent with similar performance of the two functionals on bulk Ag properties as described in Sec. 1. Due to the relatively straightforward nature of direct exchange trajectories, suitable transition state estimates are optimized via the dimer method\textsuperscript{64} (See Computational Details Section) rather than the more computationally demanding CI-NEB method. Table S3 describes the computational set-up of the slab models of close-packed Ag surface considered for Pd-Ag direct exchange.

Table S3: Computational set-up of Ag slab models considered for Pd-Ag direct exchange.

<table>
<thead>
<tr>
<th>Facet</th>
<th>Features</th>
<th>Unit cell</th>
<th>Number of layers</th>
<th>k-point grid</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>Close-packed terrace (CPT)</td>
<td>4×4</td>
<td>4 (bottom 1 fixed)</td>
<td>5×5×1</td>
</tr>
<tr>
<td>(533)</td>
<td>4-row CPT with A-step edge</td>
<td>4×4</td>
<td>4 (bottom 1 fixed)</td>
<td>5×5×1</td>
</tr>
</tbody>
</table>

We first consider sequential Pd insertion into close-packed terrace. As shown in Table S4(a-d), all forward energy barriers are in the range of 0.8-1.0 eV. The presence of auxiliary Ag adatoms has a negligible effect. Direct exchange at lower edge remains similarly strained [Table S4(f)]. Direct exchange at upper edge has a slightly lower energy barrier [Table S4(e)] due to the enhanced ability of edge atoms to accommodate distortion, but still too high to be feasible (> 0.5 eV). In our MD simulation, we find that the presence of an edge vacancy significantly facilitates direct exchange [Table 6(d-e) of the main text]. These results further highlight the difficulties associated with brute-force exploration of atomic trajectories and the need for an automated, unbiased approach, even for simple processes such as direct exchange.
Table S4: Pd-Ag direct exchange on close-packed terrace with (a) zero, (b) one, or (c–d) two auxiliary Ag adatoms after sequential Pd insertion, and at (e) upper edge or (f) lower edge, with step edge indicated by black line. Exchange pairs are indicated with an asterisk. Case (a) is identical to Table 6(a); Pd/Ag of the main text. The structures and the energy level diagram are fully optimized by DFT. Activation energies ($E_a$) are noted in eV.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Transition state</th>
<th>Final state</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td><img src="image1.png" alt="Initial state" /></td>
<td><img src="image2.png" alt="Transition state" /></td>
<td><img src="image3.png" alt="Final state" /></td>
</tr>
<tr>
<td>(b)</td>
<td><img src="image4.png" alt="Initial state" /></td>
<td><img src="image5.png" alt="Transition state" /></td>
<td><img src="image6.png" alt="Final state" /></td>
</tr>
<tr>
<td>(c)</td>
<td><img src="image7.png" alt="Initial state" /></td>
<td><img src="image8.png" alt="Transition state" /></td>
<td><img src="image9.png" alt="Final state" /></td>
</tr>
<tr>
<td>(d)</td>
<td><img src="image10.png" alt="Initial state" /></td>
<td><img src="image11.png" alt="Transition state" /></td>
<td><img src="image12.png" alt="Final state" /></td>
</tr>
<tr>
<td>(e)</td>
<td><img src="image13.png" alt="Initial state" /></td>
<td><img src="image14.png" alt="Transition state" /></td>
<td><img src="image15.png" alt="Final state" /></td>
</tr>
<tr>
<td>(f)</td>
<td><img src="image16.png" alt="Initial state" /></td>
<td><img src="image17.png" alt="Transition state" /></td>
<td><img src="image18.png" alt="Final state" /></td>
</tr>
</tbody>
</table>

Legend:
- Green: Pd to be inserted
- Red: Ag to be exchanged by Pd
- Pink: Auxiliary Ag adatom
- Gray: Intragrain Ag
4 EAM potential energetics

We test Pd-Ag-H ternary EAM potential developed by Hale et al.\textsuperscript{65} for surface energetics, using our DFT energetics as a benchmark. We perform static calculations using Ag(211) surface as described in Table S\textsuperscript{1}. We first test the stability of Pd dopant \textit{in vacuo}. As shown in Fig. S\textsuperscript{5} the EAM potential is in qualitative agreement with DFT: Pd prefers to reside in subsurface sites. However, the energy penalty of Pd at surface sites relative to subsurface sites is approximately doubled by the EAM potential, demonstrating that DFT refinement is needed for quantitative accuracy.
Figure S6: Three H adsorption sites considered on Ag(211): (a) upper bridge site; (b) upper hollow site; (c) step bridge site.

Table S5: Relative energy of H adsorption sites on Ag(211) calculated with DFT versus EAM potential. The energies are relative to each other only within a given method.

<table>
<thead>
<tr>
<th></th>
<th>Upper bridge</th>
<th>Upper hollow</th>
<th>Step bridge</th>
<th>Step hollow</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>0.00</td>
<td>0.00</td>
<td>0.23</td>
<td>Unstable</td>
</tr>
<tr>
<td>EAM</td>
<td>Unstable</td>
<td>0.44</td>
<td>Unstable</td>
<td>0.00</td>
</tr>
</tbody>
</table>

We also test H adsorption on Ag(211) (Fig. 6). As shown in Table 5, the stability hierarchy is reversed by the EAM potential, predicting four-fold A-step hollow site to be the most stable solely based on coordination number of the H atom. In our DFT calculation, the step hollow site is unstable, relaxing the H atom to the upper bridge site. We therefore preclude H atom from all of our MD simulations.
5 Adatom diffusion on close-packed terrace from MD

Figure S7: Plots of ensemble-averaged mean-squared displacement (MSD) (Å²) of Ag adatom on Ag(111) on linear scales over simulation time of 20 ns at 300-1200 K: (a) total MSD; (b) $z$-component of MSD. Vertical lines in (a) indicate simulation half-time.

We simulate adatom self-diffusion on Ag(111) at 300-1200 K. We use a 12×12 unit cell with 10 layers, freezing the bottom-most layer at 0 K (velocities and forces set to zero) to prevent it from acting as a surface. We take the second half of 20 ns simulation as a linear diffusive regime, where the mean-squared displacement (MSD) behaves linearly as a function of time. As shown in Fig. S7(a), linear surface diffusion is maintained up to 700 K (blue). Starting at 800 K, interlayer exchange starts to dominate (red), evidenced by the onset of nonzero $z$-component of MSD in Fig. S7(b).
Table S6: Diffusion coefficient ($D$) of adatom self-diffusion on Ag(111) at 300-700 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$D$ ($\text{Å}^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>$8.67 \times 10^{10}$</td>
</tr>
<tr>
<td>400 K</td>
<td>$1.73 \times 10^{11}$</td>
</tr>
<tr>
<td>500 K</td>
<td>$3.51 \times 10^{11}$</td>
</tr>
<tr>
<td>600 K</td>
<td>$3.89 \times 10^{11}$</td>
</tr>
<tr>
<td>700 K</td>
<td>$6.30 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Figure S8: Arrhenius plot of adatom self-diffusion on Ag(111) at 300-700 K.

Diffusion coefficient (Table S6) is defined as

$$D = \lim_{t \to \infty} \frac{\langle [r(t) - r(0)]^2 \rangle}{2dt},$$

where $r$ is the adatom position, time zero is set to the beginning of linear diffusive regime, and $d$ is the dimensionality of the system. The MSD is ensemble-averaged over 60 different simulations to ensure sufficient noise reduction. Temperature dependence of the diffusion coefficient shows an Arrhenius behavior (Fig. S8),

$$\ln(D) = \ln(D_0) - \frac{E_a}{k_B T},$$

from which the corresponding activation energy ($E_a$) and diffusion prefactor ($D_0$) are obtained as 88 meV and $2.44 \times 10^{12}$ $\text{ Å}^2$/s, respectively. See Computational Details Section for further discussions.
Figure S9: Plots of ensemble-averaged mean-squared displacement (MSD) ($\text{Å}^2$) of Pd adatom on Ag(111) on linear scales over simulation time of 20 ns at 300-1200 K: (a) total MSD; (b) $z$-component of MSD. Vertical lines in (a) indicate simulation half-time.

We also simulate Pd adatom diffusion on Ag(111). As shown in Fig. S9(a), planar diffusion is stable only up to 400 K (blue), above which interlayer exchange starts to dominate (red). In fact, Pd is already in the surface layer after equilibration starting at 700 K, as seen in Fig. S9(b), with further migration into the subsurface layer starting at 1000 K.
Simulation temperature and unit cell size

(a)  $T = 1100 \text{ K}$

(b)  $T = 1200 \text{ K}$

Figure S10: Initial and final snapshot of 20 ns simulation of Ag/Ag(111) at (a) 1100 K and (b) 1200 K. Only the top 3 layers are shown. Atoms are colored permanently according to their initial $z$-coordinate.

We test simulation temperature in the range 300-1200 K. As shown in Fig. S10, sufficient amount of interlayer restructuring is achieved in Ag(111) within a 20 ns period starting at 1100 K. Although 1200 K promotes restructuring across all top 3 layers, it is too close to the melting point of Ag (1235 K\textsuperscript{[46]}. See main text for further justifications.
We also test unit cell size to determine the extent of periodic boundary effect on the observed restructuring events. We find that no new classes of events are introduced in a 12×12 unit cell of Ag(111), compared to a 4×4 unit cell, suggesting that most relevant events are spatially localized (Fig. S11).
7 Simulation statistics

Here, we present restructuring event statistics for the 3 different surfaces considered (Table 1 of the main text): close-packed terrace (Fig. S12); A-step (Fig. S13); B-step (Fig. S14). The absolute event frequencies are not expected to be physically accurate due to the empirical nature of the EAM potential, but qualitatively reasonable enough for the purposes of event discovery. See main text for discussion of the event classes.

Figure S12: Summary of event statistics on Ag(111) (close-packed terrace).
Figure S13: Summary of event statistics on Ag(533) (A-step).
Figure S14: Summary of event statistics on Ag(221) (B-step).
8 Step doubling phenomenon

Table S7: Step formation energies of single step, double step, and double stair for A-step and B-step, calculated from DFT.

<table>
<thead>
<tr>
<th>(eV)</th>
<th>Single step</th>
<th>Double step</th>
<th>Double stair</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-step</td>
<td><img src="A-step_single_step.png" alt="Image" /></td>
<td>3.517</td>
<td>3.519</td>
</tr>
<tr>
<td>B-step</td>
<td><img src="B-step_single_step.png" alt="Image" /></td>
<td>3.496</td>
<td>3.499</td>
</tr>
</tbody>
</table>

We note that the primitive unit cell of B-step Ag(221) requires double the number of atoms compared to that of A-step Ag(533), due to the doubled periodicity of B-step edge packing. As such, we witness significant amount of step doubling in our simulation of Ag(221), which is prohibited in Ag(533) by construction due to its periodic constraint. To determine the stability of such structures, we calculate step formation energies for single step, double step, and double stair using DFT (Table S7):

\[
E_t = \frac{1}{N}(E_{\text{step}} - N\mu_{\text{bulk}}).
\]

Here, \(N\) is the number of atoms in the unit cell, and \(\mu_{\text{bulk}}\) is the chemical potential of a Ag atom in the bulk phase. We find that the three types of steps are degenerate in energy, with B-step thermodynamically more stable than A-step by 21 meV. Our energetics is consistent with our observation of step doubling primarily in the form of double stair.
9 Imaginary frequencies of representative transition states

Table S 8: Imaginary frequencies of the transition states of representative restructuring processes, calculated from DFT. Ag/Ag and Pd/Ag refer to the green atom being Ag or Pd, respectively.

<table>
<thead>
<tr>
<th>Event</th>
<th>Ag/Ag</th>
<th>Pd/Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange descent at A-step</td>
<td>33</td>
<td>36</td>
</tr>
<tr>
<td>Table 2(a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exchange descent at B-step</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>Table 2(b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacancy insertion at B-step</td>
<td>41</td>
<td>44</td>
</tr>
<tr>
<td>Table 4(e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct exchange at A-step</td>
<td>34</td>
<td>31</td>
</tr>
<tr>
<td>Table 6(b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interlayer exchange at A-step; part 1</td>
<td>49</td>
<td>42</td>
</tr>
<tr>
<td>Table 7(b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interlayer exchange at A-step; part 2</td>
<td>36</td>
<td>22</td>
</tr>
<tr>
<td>Table 7(c)</td>
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<td></td>
</tr>
</tbody>
</table>
Segregation thermodynamics in the presence of adsorbates

We first test adsorption energy ($E_{\text{ads}}$), defined as the change in energy as the system goes from an isolated slab and a gas phase species to a combined system interacting as the species adsorbed on the slab. For H$_2$ dissociative adsorption, we choose $\frac{1}{2}$H$_2$ stoichiometry:

$$E_{\text{ads}} = E_{\text{H(ads)/slab}} - E_{\text{slab}} - \frac{1}{2}E_{\text{H}_2(\text{g})}. \quad (5)$$

We use the experimental benchmark for Pd(111) with zero-point energy change subtracted using the PBE functional, as reported by Wellendorff et al.$^{67}$ Gas phase species are optimized in a 14×15×16 cell at the Γ-point. We use a 2×2 unit cell of (111) surface, corresponding

Figure S15: Pd/Ag segregation with H$_2$ adsorption at the A-step. The energies are calculated from DFT, with relatively more favorable values indicated in blue over red.
Figure S16: Pd/Ag segregation with CO adsorption at the A-step. The energies are calculated from DFT, with relatively more favorable values indicated in blue over red.

to 1/4 ML coverage. Adsorbates are placed at the FCC hollow site. The Brillouin zone is sampled using a \( \Gamma \)-centered \( 9 \times 9 \times 1 \) \( k \)-point grid. The slab consists of 6 layers, with the bottom 3 layers fixed at bulk positions to mimic bulk properties.

We find that optPBE-vdW gives the adsorption energy of \(-0.43 \) and \(-1.94 \) \( \text{eV} \) for \( \text{H}_2 \) and \( \text{CO} \), respectively. Although good agreement is achieved with the experimental value of \(-0.47 \) \( \text{eV} \) for \( \text{H}_2 \) adsorption (constant up to 1/2 ML\[^{63}\]), significant overbinding is observed for \( \text{CO} \) compared to the experimental value of \(-1.49 \) \( \text{eV} \). Least negative value is obtained with optPBE-vdW among the "opt-vdW" functionals considered. Ongoing work is testing additional methods to address this issue without sacrificing the performance on the bulk properties described in Sec. 1. Our benchmark is consistent with the one reported by
Gautier et al.\textsuperscript{69} for Pt(111). For now, we use optPBE-vdW for DFT calculations involving adsorbates as well.

Our preliminary results show that Pd segregation energy ($E_{\text{seg}}$) at Ag step edge, an otherwise endothermic quantity \textit{in vacuo} (+0.39 eV), becomes close to zero (−0.02 eV) in the presence of adsorbed H (Fig. S15). In other words, surface and subsurface Pd become nearly degenerate in energy at Ag step edge. However, there is a large energetic cost of dissociatively adsorbing H\textsubscript{2} at Ag step edge in the first place (+0.47 eV), unless it happens at another surface Pd site (+0.06 eV) that is either metastable or stabilized by other coadsorbates to begin with.

On the other hand, more strongly bound adsorbates such as CO (Fig. S16) do not experience this problem, as it binds to Ag with sufficient strength (−0.40 eV at Ag step edge). The corresponding segregation energy also becomes much more negative (−0.52 eV), thereby providing a stronger thermodynamic driving force compared to H.
References


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