A Comprehensive Search for Stable Pt–Pd Nanoalloy Configurations and Their Use as Tunable Catalysts

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Abstract
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Keywords
Materials Science and Engineering, First-principles, Cluster expansion, Nanoalloy, Hydrogen adsorption, Od, Pt, Hydrogen evolution, Catalysis

Disciplines
Condensed Matter Physics | Materials Science and Engineering | Physical Chemistry

Comments
A Comprehensive Search for Stable Pt–Pd Nanoalloy Configurations and Their Use as Tunable Catalysts

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Supporting Information

ABSTRACT: Using density-functional theory, we predict stable alloy configurations (ground states) for a 1 nm Pt–Pd cuboctahedral nanoparticle across the entire composition range and demonstrate their use as tunable alloy catalysts via hydrogen-adsorption studies. Unlike previous works, we use simulated annealing with a cluster expansion Hamiltonian to perform a rapid and comprehensive search that encompasses both high and low-symmetry configurations. The ground states show Pt(core)–Pd(shell) type configurations across all compositions but with specific Pd patterns. For catalysis studies at room temperatures, the ground states are more realistic structural models than the commonly assumed random alloy configurations. Using the ground states, we reveal that the hydrogen adsorption energy increases (decreases) monotonically with at. % Pt for the (111) hollow (100) bridge adsorption site. Such trends are useful for designing tunable Pd–Pt nanocatalysts for the hydrogen evolution reaction.

KEYWORDS: First-principles, cluster expansion, nanoalloy, hydrogen adsorption, Pd, Pt, hydrogen evolution reaction, catalysis

Bimetallic nanoparticles (nanoalloys) have found use in a number of applications, including catalysis.1 Although the properties of nanoalloy are highly affected by the configurations (atomic arrangements) that exist, it is di–”nanoalloys because di–”bulk phase as well. Bulk alloys that mix may not do so invarious con–”gurations (ground states) for a 1 nm Pt–Pd cuboctahedral nanoparticle across the entire composition range and demonstrate their use as tunable alloy catalysts via hydrogen-adsorption studies. Unlike previous works, we use simulated annealing with a cluster expansion Hamiltonian to perform a rapid and comprehensive search that encompasses both high and low-symmetry configurations. The ground states show Pt(core)–Pd(shell) type configurations across all compositions but with specific Pd patterns. For catalysis studies at room temperatures, the ground states are more realistic structural models than the commonly assumed random alloy configurations. Using the ground states, we reveal that the hydrogen adsorption energy increases (decreases) monotonically with at. % Pt for the (111) hollow (100) bridge adsorption site. Such trends are useful for designing tunable Pd–Pt nanocatalysts for the hydrogen evolution reaction.

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adsorption energies, we further speculate how the addition of Pd to Pt would improve the catalytic activity for the hydrogen evolution reaction (HER).\textsuperscript{20,21} Our calculations show that the activity in 1 nm-sized Pt NPs is lower than that of Pt surface due to size effect,\textsuperscript{22,23} and the addition of Pd improves the catalytic activity by appropriately tuning $E_{\text{ad}}$. Although one ideally desires a temperature—composition—coverage phase diagram, where coverage effects may potentially alter local atomic arrangements, limited H-adsorption cannot change the trends predicted here, as discussed.

**Computational Model and Approach.** For FCC metals or alloys, commonly observed FCC-derived NP shapes include the truncated octahedron and cuboctahedron\textsuperscript{1,24} and possibly the icosahedron in the free-standing case. For $\sim 1$ nm-size Pt NPs, although amorphous clusters\textsuperscript{25} are preferred, H-adsorption has been shown to stabilize the cuboctahedron NP by removing the shear instability of $\{100\}$ facets.\textsuperscript{26} In addition, cuboctahedral Pt−Pd nanoalloys with diameters between 1 and 5 nm (with Pd segregated to the outer shell) have been observed experimentally for particles prepared via colloidal synthesis\textsuperscript{2,3,27} and via laser vaporization techniques.\textsuperscript{28,29}

Figure 1. DFT formation energies of Pd−Pt nanoalloy configurations versus at. % Pt. Energies are bounded from below by a ground state hull (red line) that connects ground state energies (circles). DFT energies from each search iteration are labeled: 1st (filled squares), 2nd (∗), 3rd (+), and 4th (filled circles). Also shown are the CE formation energies of the random solutions (dashed line) and energy differences (diamonds) between each ground state and its corresponding random solution at fixed stoichiometry, i.e., NP ordering energy.

As such, we use a 55-atom cuboctahedron ($\sim 1$ nm in diameter) as the model for the nanoalloy with each atomic site being occupied by either a Pd or Pt atom. Energies of nanoalloy configurations are computed using density functional theory (DFT)\textsuperscript{30,31} to obtain reliable relative energies. DFT calculations were done using Vienna ab initio simulation package (VASP)\textsuperscript{32,33} within a projected augmented wave (PAW) basis\textsuperscript{34} based on the generalized-gradient approximation (GGA) using the PW91\textsuperscript{35} exchange-correlation functional (revised PBE functional\textsuperscript{36} for H adsorption).

Using calculated DFT formation energies as the learning set, we construct a CE Hamiltonian for the Pd−Pt cuboctahedron. The Hamiltonian is a linear expansion in terms of atomistic cluster correlations, and with appropriate truncation, one only needs a small set of clusters to accurately reproduce the alloy configuration DFT energies. Because only atomistic interactions are present, the CE enables rapid evaluation of millions of configurations, sufficient to address reliably alloy thermodynamics, and has been applied extensively to bulk alloys\textsuperscript{11,12,37–50} and recently nanoalloys.\textsuperscript{15,51,52} An iterative procedure combining CE with simulated annealing is used for searching low-energy configurations; a high proportion of low-energy configurations are obtained in subsequent iterations. A lowest-energy hull is constructed, and it serves as the lower energy bound of the nanoalloy configurational energies. Configurations on the hull are ground states. States close to the hull are relatively more stable (low-energy excitations of the ground states) and are thus more likely to be observed in experiments at low temperatures. Formation energies of random alloy solutions are calculated using the CE Hamiltonian (see the Supporting Information), and the energy differences between the ground states and their corresponding random alloy solutions are a measure of their relative stability.

We illustrate in Figure 2 selected ground states and near-ground states, showing site-specific occupation at different compositions. Importantly, the ground states exhibit Pt(core)−Pd(shell) properties across all compositions. This implies that Pt(core)−Pd(shell) nanoalloys (of ca. 1 nm) are energetically favored and indeed, the perfect core−shell structure, GS\textsubscript{13}, has the lowest formation energy. The preference for Pt in the core can be attributed to its higher cohesive energy than Pd while having almost the same atomic radius.\textsuperscript{4}

For Pt-rich compositions, one observes that the initial preferred segregation site for Pd is at the surface edge. These sites are populated with Pd (see GS\textsubscript{7−54}) on two of the $\{100\}$ facets before face-center sites are populated (GS\textsubscript{41,43}). At Pd-rich compositions, Pt first occupies the central core site (GS\textsubscript{1}) followed by the second inner shell (GS\textsubscript{2−13}), and the formation energy decreases monotonically with each addition of Pd, clearly showing Pt’s preference for core sites. When Pt atoms are added beyond GS\textsubscript{13}, Pt starts to occupy the surface edge sites (GS\textsubscript{14−19}), and the formation energy increases.

Segregation Profile Versus (100) Semi-Infinite Surface. The 55-atom cuboctahedron consists of mainly $\{100\}$ facets. To show the effect of nanosize on alloy segregation, we compare the nanoalloy ground states with those obtained from a (100) semi-infinite surface modeled as a four-layer slab (see the Supporting Information). As shown in Figure 3, segregation of
Figure 2. Selected ground states ($G_{Sn}$) and near ground state ($NG_{Sn}$) configurations for the Pd–Pt 55-atom cuboctahedron, where $n$ is the number of Pt (gray) atoms, consisting of 8 {111} facets, 6 {100} facets, and 24 edges. The perfect core–shell structure, $G_{S13}$, has all 13 (42) core (shell) atomic sites occupied by Pt (Pd). For high-symmetry configurations (Pd, Pt, $G_{S1}$, and $G_{S13}$), the symmetry-distinct adsorption sites are illustrated using a Pt cluster, with {111} hollow sites (d and e), {100} hollow site (c), bridge sites (a, b, and f), and atop sites (g, h, and i). Lower-symmetry configurations such as $G_{S15}$ contain additional unique adsorption sites.

Figure 3. Selected ground states for the (100) Pd–Pt semi-infinite surface. Exchange of atoms is allowed for the top two layers, the bottom two layers (not shown) are occupied by Pt (see the Supporting Information). The configurations are labeled according to at. % Pt of the top two layers.
Table 1. Single H-Adsorption Energies (eV) on Various Sites for Pure Pt and Pd Surfaces and Selected Nanoalloys Calculated via DFT Using a Revisied PBE Functional\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th>hollow (fcc)</th>
<th>hollow (hcp)</th>
<th>hollow (square)</th>
<th>bridge</th>
<th>atop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd (111)</td>
<td>−0.38</td>
<td>−0.34</td>
<td>N.A.</td>
<td>U</td>
<td>0.12</td>
</tr>
<tr>
<td>Pd (100)</td>
<td>N.A.</td>
<td>N.A.</td>
<td>−0.33</td>
<td>U</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd (nano)</td>
<td>−0.41 (e)</td>
<td>−0.42 (d)</td>
<td>−0.22 (c)</td>
<td>U (b)</td>
<td>0.12 (g)</td>
</tr>
<tr>
<td>Pt (111)</td>
<td>−0.32</td>
<td>−0.27</td>
<td>N.A.</td>
<td>U</td>
<td>−0.32</td>
</tr>
<tr>
<td>Pt (100)</td>
<td>N.A.</td>
<td>N.A.</td>
<td>−0.09</td>
<td>U (b)</td>
<td>−0.31</td>
</tr>
<tr>
<td>Pt (nano)</td>
<td>−0.15 (e)</td>
<td>−0.21 (d)</td>
<td>(c)</td>
<td>U (c)</td>
<td>−0.46</td>
</tr>
<tr>
<td>GS\textsubscript{13}</td>
<td>−0.36 (e)</td>
<td>−0.37 (d)</td>
<td>−0.30 (c)</td>
<td>−0.44 (b)</td>
<td>0.14 (g)</td>
</tr>
<tr>
<td>GS\textsubscript{45}</td>
<td>−0.23 (e)</td>
<td>−0.19 (d)</td>
<td>U (c)</td>
<td>−0.50 (g)</td>
<td>0.15 (g)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} For NPs, adsorption energies are followed by location indices shown in Figure 2. \textsuperscript{b} Sites labeled “U” are unstable, and the H relaxes to an adjacent stable site of lower \( E_{\text{ads}} \).

Pd (Pt) to the surface (subsurface) layers is also preferred. The ground state at x\textsubscript{Pt} = 0.5, whose top (subsurface) layer is fully occupied by Pd (Pt), has the lowest formation energy (see Figure S3). The specific ordering pattern on the (100) surface, however, differs. In particular, Pd atoms exhibit a zigzag chain at x\textsubscript{Pd} = 0.75 (Figure 3) and a dimer arrangement at higher Pt concentration of x\textsubscript{Pt} = 0.875 (Figure S4), which are not observed in the nanoalloy case.

Nanoalloy Ground States Versus Random Alloys. Here, we justify the use of Pt(core)–Pd(shell) ground states (rather than random alloy states\textsuperscript{19}) as catalytic models at room temperatures. From Figure 1, the energy of the perfect core–shell structure (GS\textsubscript{13}) is 47 meV below that of the random alloy (ordering energy). As an estimate, observations of random states will become significant around 550 K at nearby compositions. Likewise, observations will be core–shell like between 0.1 < x\textsubscript{Pt} < 0.85 at room temperatures (300 K), since the ground states are at least 26 meV more stable than random solutions in this range. Furthermore, the nearest-neighbor coordination numbers of the core–shell ground states are closer to experimental values than those obtained for random solutions (see Table S3).

Hydrogen Adsorption on Surfaces versus Nanoparticles. Before showing how Pd–Pt compositions affect hydrogen adsorption, we do a systematic evaluation of H adsorption on Pt and Pd cuboctahedron. In addition to their common occurrence in experiments, the cuboctahedron structure of Pt is also stabilized by adsorption of atomic H.\textsuperscript{56} Adsorption energies are calculated via

\[
E_{\text{ads}} = E_{M-m\text{H}} - E_M - \frac{m}{2} E_{\text{H}_2}
\]

\( E_{M-m\text{H}} \) is the DFT energy of the nanocluster (or surface) with \( m \) adsorbed H atoms; \( E_M \) and \( E_{\text{H}_2} \) are the DFT energies of the bare nanocluster (or surface) and H\textsubscript{2} molecule. A more negative \( E_{\text{ads}} \) implies stronger adsorption.

Table 1 compares the adsorption of a single H atom (\( n = 1 \)) on various NP adsorption sites. To elucidate the size effect, we compare the results with those from semi-infinite surfaces. The H coverage on the NP corresponds to 1/42 monolayer (ML), while that of the surfaces corresponds to a 0.25 ML; \( E_{\text{ads}} \) of the surface may be lowered by ca. 0.03 eV when the results are extrapolated to 1/42 ML.\textsuperscript{53}

In general, H binds more strongly to Pd (Pt) on \{111\} \{(100)\} surfaces/facets. For Pt NP, adsorption at \{100\} bridge sites is most energetically favored, while that of \{111\} hollow site (hcp and fcc) is least favored. In contrast, a Pd NP shows stronger adsorption on \{111\} hollow sites than on the \{100\} bridge sites; adsorption on atop sites is highly unfavorable. Surfaces and NPs of the same metal display similar preferences for adsorption facets and sites, although the adsorption energies are altered due to the size effect. Interestingly, different facets on Pd and Pt are impacted differently. Adsorption strength on Pt NP \{100\} bridge site is enhanced over that of the (100) surface, while adsorption on \{111\} hollow sites is weakened compared to \{111\} surface. The reverse effect is seen for Pd, where adsorption on NP \{111\} hollow \{(100) bridge\} site is stronger (weaker) than those of semi-infinite surfaces.

\textbf{H-Adsorption on Nanoalloy Ground States}. Table 1 clearly shows that Pd NP adsorbs \textit{H} more strongly (weakly) at bridge (\{111\} hollow) sites than Pd NP. Similar systematic evaluations are also shown for GS\textsubscript{13} and GS\textsubscript{45} and in most cases, the adsorption energies lie between that of Pd and Pt cases. As a simple indicator of how alloying affects adsorption properties,\textsuperscript{19} we calculate the mean \( E_{\text{ads}} \) of multiple H atoms adsorbed symmetrically on each facet for each unique adsorption site of interest in the selected ground states; for example, we adsorb one H atom on one of the bridge sites “a” on all six \{100\} facets (see Figure S6 of the Supporting Information). Mean adsorption energies are obtained using (2). The results in Figure 4 show that the adsorption energies on bridge sites and \{111\} hollow sites follow opposing trends. Bridge sites are most stable for compositions above ca. 15% Pt, while \{111\} hollow sites are most stable below 15% Pt. At Pd-rich compositions, adsorption energies at bridge sites are lower by ca. 0.4 eV compared to hollow sites, and this energy difference changes in a quadratic manner with composition. At Pd-rich compositions, \{111\} hollow sites are more stable by ca. 0.1 eV (compared to bridge sites), and the energy difference changes linearly with composition. This implies that adsorption characteristics are more sensitive to composition changes for Pt-rich alloys. The continuous change in adsorption energies demonstrates the possibility of tuning catalytic properties via alloying.

\textbf{H-Adsorption Effect on Segregation}. To show how H-adsorption affects segregation in nanoalloys, we compare the relative stability of configurations at x\textsubscript{Pt} = 29/55, before and after H-adsorption at various sites and H-coverage in Figure 5. We note that Pt (Pd) prefers the core (shell) for the bare nanoalloy and H adsorbs more strongly to Pt at the bridge site (see Table 1) and may thus induce Pt segregation to the surface. For all configurations, the \( E_{\text{ads}} \) is calculated using (2).
compensated by the stronger binding to Pt by a large number of sensitive to segregation; all energies are within 0.07 eV of one stable case. Speciﬁcally, bridge sites (pure Pd, and Pt. Best-show an opposite trend.

Figure 5. Mean $E_{ad}$ of nine configurations at $\eta_0 = 29/55$ (generated during the CE ground state search) for different ML of H at selected adsorption sites (see Figures 2 and S6 and S7). Configurations are ranked according to their stability (measured by $E_i$) before H-adsorption ($GS_{29}$ is thus ranked 1 = most stable), and the number of surface Pt are in parentheses. The top four configurations have pure Pt cores but different atomic ordering on the shell.

with $E_M$ being the energy of bare $GS_{29}$, hence $E_{ad}$ measures the relative stability of configurations with adsorbed H. Figure 5 shows that, at low-H coverage, configurations with the same number of Pt (Pd) at the core (shell) have comparable stability (or $E_{ad}$). In contrast, configurations with more Pt in the shell could result in $E_{ad}$ being 0.4 eV higher than that of the most stable case. Specific atomic arrangement on the shell affects stability to a lesser extent than if Pt atoms were segregated to the surface, which is also reﬂected in the CE (compare the single-point and multibody effective cluster interactions (ECI) in Table S1 of the Supporting Information). Thus low-coverage H-adsorption does not change the segregation behavior as the energy cost for Pt segregation to the shell is large. However, at high coverage (0.5 ML and beyond), $E_{ad}$ are no longer sensitive to segregation; all energies are within 0.07 eV of one another. The energy cost to move Pt to the shell is now compensated by the stronger binding to Pt by a large number of H atoms at the bridge sites. Importantly, the $E_{ad}$ of $GS_{29}$ differs from the most stable case by at most 0.06 eV in all instances. Thus, errors incurred (using ground states of bare nanoalloy in adsorption calculations) are small enough not to alter the trend in Figure 4, which we can safely use to discuss the catalytic activity of HER below.

Effect on Hydrogen Evolution Reaction. To show how the adsorption trends would affect the catalysis of HER, $(1/2)\text{H}_2 + \text{H}^+ + e^- \rightarrow \text{H}_2$, we utilize the model by Nørskov et al. which predicts the catalytic activity of HER electrodes via the adsorption free energies of $H$. For transition-metal surfaces, the free energy of adsorption is approximately $\Delta G_{ad}^\text{H} = E_{ad} + (0.04 + 0.20) eV$ (see the Supporting Information). Good HER electrocatalysts have values close to the optimal value of $\Delta G_{ad}^\text{H} = 0$ or $E_{ad} = -0.24 \text{ eV}$. Between the boundaries of $E_{ad} = -(0.24 \pm 0.08) \text{ eV}$ in Figure 4, the adsorption site is expected to be more active than the hollow site of Pt (111) surface (our benchmark). Considering bridge sites and {111} hollow sites of Pt cuboctahedron, the adsorption at bridge (hollow) site is too strong (weak); Pt cuboctahedron is likely to be less catalytically active than Pt (111). Adding Pt, the H adsorption energies on the {111} and {100} facets are tuned continuously. At ca. 0.3 Pd, the H adsorption energy at {111} hollow site falls within the boundaries, and the activity of this facet is comparable to that of Pt (111). However, the bridge sites remain blocked by H atoms. A further increase in activity is expected beyond ca. 0.6 Pd, when the H adsorption energy at bridge sites also falls within the boundaries. Now both {111} and {100} facets are more active than Pt (111). The effective adsorption coverage considered for the NP are between 0.14 and 0.19 ML (see Figure S6), which are close to that of the surface at 0.25 ML. For more accurate predictions, adsorption energies at equilibrium H coverage are required.

Conclusions. Using ﬁrst-principles-based cluster expansion method together with simulated annealing, we conducted a comprehensive search for ground states of a 55-atom Pd–Pt cuboctahedral nanoalloy. The ground states exhibit Pt(core)–Pd(shell) structure across all compositions, agreeing with experimental ﬁndings. We calculated the hydrogen-adsorption properties of the ground states, showing that the energy trends versus Pd–Pt composition depend on adsorption site. In particular, adsorption energies on {111} hollow sites and {100} bridge sites exhibit opposing trends. We demonstrated the possibility of tuning NP catalyst behavior via alloying for the hydrogen-evolution reaction.

Associated Content

Supporting Information
Computational details, ﬁgures and table showing effective cluster interactions, comparison of predicted conﬁgurations with experiment, segregation on (100) surface, ﬁgures showing adsorption of multiple H atoms, and deﬁnition of adsorption free energy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing ﬁnancial interest.

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