Computational Design of Alloy-Core@Shell Metal Nanoparticle Catalysts

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Supporting Information

ABSTRACT: The alloy-core@shell nanoparticle structure combines the advantages of a robust noble-metal shell and a tunable alloy-core composition. In this study we demonstrate a set of linear correlations between the binding of adsorbates to the shell and the alloy-core composition, which are general across a range of nanoparticle compositions, size, and adsorbate molecules. This systematic tunability allows for a simple approach to the design of such catalysts. Calculations of candidate structures for the hydrogen evolution reaction predict a high activity for the PtRu@Pd structure, in good agreement with what has been reported previously. Calculations of alloy-core@Pt 140-atom nanoparticles reveal new candidate structures for CO oxidation at high temperature, including Au$_{0.65}$Pd$_{0.35}@$Pt and Au$_{0.73}$Pd$_{0.27}@$Pt, which are predicted to have reaction rates 200 times higher than that of Pt(111).

KEYWORDS: alloy-core/shell, nanoparticles, binding energy, catalyst design, hydrogen evolution, CO oxidation

1. INTRODUCTION

A promising geometry for new nanoparticle catalysis has a homogeneous noble-metal shell around a random alloy core of tunable composition. The noble shell protects the particle core during the catalytic processes, and the alloy-core composition allows for fine tuning of the catalytic properties. Alloy-core@shell nanoparticles can be synthesized by covering a random-alloy nanoparticle with the thin layer of the shell metal. There are two common synthetic techniques for this. The first is acid leaching of the non-noble-metal component in the shell and thermal treatment to form a noble-metal skin. Examples of this include Pt$_x$M for M = Fe, Ni, Co. These bimetallic alloys covered with a Pt-skin, that were synthesized by Stamenkovic and co-workers, exhibited an improved oxygen reduction reaction (ORR) activity versus conventional Pt catalysts. Second, under potential deposition (UPD) can be used to form a homogeneous monolayer shell on the core via careful potential control. Recent work in Adzic’s group and ours, demonstrated successful synthesis of PdAu@Pt nanoparticles by Cu UPD on a PdAu core with subsequent galvanic exchange of the Cu with Pt.

Previous work shows that there is a nearly linear correlation between the O binding energy on alloy-core@shell nanoparticles and the alloy-core composition. In this paper, we demonstrate that this linear correlation extends to many different adsorbates, and holds for geometries ranging from small nanoparticles to single crystal surfaces.

In this study, adsorbate binding energies were calculated with density functional theory (DFT), as implemented in the Vienna ab initio simulation package. Core electrons were described using the projector augmented wave method. Kohn–Sham single-electron wave functions were expanded in a plane wave basis with a kinetic energy cutoff of 300 eV to describe the valence electrons. The generalized gradient approximation

Received: August 11, 2014
Revised: December 9, 2014

DOI: 10.1021/cs501776b
ACS Catal. 2015, 5, 655−660
using the revised Perdew–Burke–Ernzerhof functional was chosen to evaluate the exchange-correlation energy. Spin polarization was tested and was used when necessary. All atoms in the nanoparticle were allowed to relax; geometries were considered optimized when the force on each atom was less than 0.01 eV/Å.

Linear correlations between alloy-core compositions and the binding energy of adsorbates A (A = O, C, H, N, S, CO, NO) were examined. Two geometries were studied, a nanoparticle containing 140 atoms and a face-centered-cubic (FCC) single-crystal (111) surface with a Pt monolayer skin covering a Pd/Au random alloy, as illustrated in Figure 1. The nanoparticles were modeled as FCC crystallites in the shape of a truncated octahedron (denoted as NP140) with 44 core and 96 shell atoms. A cubic box of side length 26 Å was used to contain the particle with a vacuum gap of 11 Å in all directions to avoid interactions from periodic images. A Γ-point sampling of the Brillouin zone was used for the isolated particles. Convergence was checked by increasing the energy cutoff to 400 eV and the k-point mesh sampling to 2×2×2; the oxygen binding energy on a Pt 140-atom nanoparticle was found to change by only 1 meV (<0.1%). For each configuration, an adsorbate atom or molecule was bound to the center of each (111) facet, giving eight adsorbates in total. The binding energy Eb of adsorbate A was calculated by averaging over these eight sites as

$$Eb = \frac{1}{8}(E_{\text{NP+8A}} - E_{\text{NP}} - 8E_A)$$

where $E_{\text{NP+8A}}$ is the energy of the particle with eight bound adsorbates A, $E_{\text{NP}}$ is the energy of the bare particle, and $E_A$ is the reference energy of the adsorbate, A.

Single-crystal surfaces were modeled with five-layer (3×3) slabs, to simulate the (111) facets of large nanoparticles. The bottom four layers consisted of a PdAu random alloy, and the topmost layer contained monometallic Pt. A surface of this size and a vacuum gap of at least 12 Å between slabs was used to isolate the adsorbates from their periodic images. A (4×4×1) Monkhorst–Pack k-point mesh was used to sample the Brillouin zone. In all calculations, the bottom two layers of the slab were held frozen in their lattice positions. For each configuration, the binding energy of adsorbate A on the nine different FCC hollow sites are calculated as

$$Eb = E_{\text{slab+A}} - E_{\text{slab}} - E_A$$

For both the NP140 and slab models, binding of O, C, H, N, S, and NO was studied on the FCC-hollow sites of the (111) facet, while CO was bound to on-top sites. Details about the reference energies of the adsorbates, $E_A$, are given in the Supporting Information. CO adsorption energies are corrected on the basis of the CO stretching frequency as proposed by Mason. Ten different random-alloy configurations were generated to calculate the average binding energy for each core composition, giving a total of 80 binding sites for the nanoparticle and 90 sites for the slab model, contributing to the average. Although the number of random configurations considered is less than the total possible number, our sampling is sufficient for capturing trends in binding energies (see Figure SI. Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Linear Binding Energy Correlation. Trends in the binding energy of the seven adsorbates were calculated as a function of composition in a Pd/Au subsurface alloy, covered with a monolayer of Pt. As demonstrated by Nørskov et al., there is a good scaling relationship between a single atomic adsorbate and its hydrides with the same binding geometry, e.g. O vs OH, C vs CH₃, and N vs NH₂. Accordingly, the seven adsorbates were chosen to cover most of the key reactant motifs of interest for heterogeneous catalysis related to energy. Figure 2 shows the average binding energy of the adsorbates on the PdAu@Pt NP140 and slab geometries with Pd ratios x = 0, 0.25, 0.5, 0.75 and 1.0, in the random alloy core. The standard deviation of the binding energy distribution is indicated by the error bars. The linear relationship between the binding energy and core composition is a result of the linear correlation between alloy-core compositions and the binding energy of adsorbates A, $E_A$, is given in the Supporting Information. CO adsorption energies are corrected on the basis of the CO stretching frequency as proposed by Mason. Ten different random-alloy configurations were generated to calculate the average binding energy for each core composition, giving a total of 80 binding sites for the nanoparticle and 90 sites for the slab model, contributing to the average. Although the number of random configurations considered is less than the total possible number, our sampling is sufficient for capturing trends in binding energies (see Figure SI. Supporting Information).
Similar linear correlation trends between the core composition and the d-band center of the shell was observed previously for the PdCu@Pd system. In that work, it was shown that strain and charge redistribution are two major factors affecting the d-band of the nanoparticle shell. In the PdCu@Pd system, the two effects had a similar influence on the d-band center, but in general their relative weight will depend upon the specific metals. In the PdAu@Pt system, for example, the d-band center shift is dominated by strain effects. Charge redistribution is much more important in the PdIr@Pt system, where the adsorbate binding to the single-core@shell structure gives rise to advantages over single-core@shell structures. In other words, by calculating adsorbate binding energy for the PdCu@Pd system, we are able to explore the parameter space of alloy cores connected by any two structures with the same shell metal.

Following the theoretical framework of Nørskov et al., the Sabatier rate of a reaction \( r(v) \) is constructed as a function of the reactivity descriptors \( \{E_b\} \), where \( v = \{E_b^1, E_b^2, ..., E_b^n\} \) is the descriptor vector and \( E_b \) is the binding energy of key adsorbate. For the alloy-core@shell structures \( X_i Y_{1-x}@Z \), the descriptor vector at an intermediate alloy-core composition \( x \) can be estimated from a linear interpolation between the two single-core@shell structures as

\[
v(x) = x v_{X@Z} + (1 - x) v_{Y@Z}
\]

where \( v_{X@Z} \) and \( v_{Y@Z} \) are the descriptor vectors of \( X@Z \) and \( Y@Z \), respectively. The Sabatier rate is then expressed as a function of alloy-core composition \( x \), and the extremum of the reaction rate of \( X_i Y_{1-x}@Z \) is achieved where

\[
\frac{\partial x}{\partial x} = \frac{\partial r}{\partial v} \frac{\partial v}{\partial x} = \nabla \cdot (v_{X@Z} - v_{Y@Z}) = 0
\]

In principle, the extremum composition can be obtained analytically by solving eq 5, where the gradient of the rate is normal to the vector connecting the two single-core@shell compositions. In a special case where the dimension of the descriptor vector is 1, e.g. the ORR and HER, where the catalytic activity of the reaction can be described by the binding energy \( E_b \) of a single adsorbate, \( E_b \) eq 5 can be simplified as

\[
V = (dr)/(dE_b) = 0.\text{ If the reaction rate reaches its extremum at } E_b^* \text{, where } (dr)/(dE_b) = 0, \text{ then the composition } x^* \text{ with the extreme rate is}
\]

\[
x^* = \frac{E_b^* - E_b_{Y@Z}}{E_b_{X@Z} - E_b_{Y@Z}}
\]

To have \( x^* \in [0, 1] \), the condition \( (E_b - E_b_{X@Z})/(E_b^* - E_b_{Y@Z}) < 0 \) must be satisfied. In other words, \( X@Z \) and \( Y@Z \) must be on different sides of the volcano peak.

The above optimization scheme works on the basis of linear binding energy correlations for alloy-core@shell nanoparticles, as well as models that correlate binding with the catalytic activity. There are a couple of approximations in this approach which should be highlighted. First, in binding energy calculations the random alloy-core compositions were held fixed. Thus, effects of large geometric deformations due to variations of composition are not considered in our model. Structural rearrangements and alloy-core segregation may cause deviations from the linear correlations presented. Second, the BEP relations and Sabatier analysis are essential to obtain the correlation of descriptors and activity. Uncertainties in either approximation will affect the accuracy of this optimization scheme.

### Table 1. Free Energy of Adsorption for Hydrogen \( \Delta G_H \) (eV) on a Variety of Pd- and Pt-Shelled Slabs

<table>
<thead>
<tr>
<th>structure</th>
<th>core metal</th>
<th>Pd</th>
<th>Pt</th>
<th>Ir</th>
<th>Rh</th>
<th>Ru</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-shell</td>
<td>Au</td>
<td>−0.25</td>
<td>−0.18</td>
<td>0.10</td>
<td>0.11</td>
<td>0.17</td>
<td>0.25</td>
</tr>
<tr>
<td>Pt-shell</td>
<td>Ag</td>
<td>−0.22</td>
<td>−0.05</td>
<td>0.22</td>
<td>0.24</td>
<td>0.33</td>
<td>0.41</td>
</tr>
</tbody>
</table>

657  DOI:10.1021/cs501176b
ACS Catal. 2015, 5, 655−660
3.3. Hydrogen Evolution Reaction. The HER is the cathode reaction in water electrolysis, where hydrogen is produced from proton reduction. It was first proposed by Parsons that the free energy of hydrogen adsorption $\Delta G_{H2}$ is a good reaction descriptor of the HER, and the optimal activity is near $\Delta G_{H2} = 0.0$ eV. With well-defined approximations for the zero-point energy and entropy, the free energy of hydrogen adsorption on different surfaces can be calculated as $\Delta G_{H2} = E_{B_H} + 0.24$ eV, where $E_{B_H}$ is the binding energy of hydrogen atom on the surface. Since this 0.24 eV shift is constant for different surfaces, the alloy-core composition optimization strategy of eq 6 is applicable to the HER. Table 1 gives the free energy of adsorption for hydrogen on a variety of single-core@Pd-shelled and Pt-shelled slabs. For both Pd- and Pt-shelled slabs, the free energy of adsorption is negative when the core is Au, Ag, Pd, or Pt, and it is positive with cores of Ir, Rh, Ru, and Cu. In order to satisfy the ratio of X in the alloy core is

<table>
<thead>
<tr>
<th>metal Y</th>
<th>metal X</th>
<th>Pd-shell</th>
<th>Pt-shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>0.71</td>
<td>0.69</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>0.64</td>
<td>0.55</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.33</td>
<td>0.19</td>
</tr>
<tr>
<td>Rh</td>
<td>0.69</td>
<td>0.67</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td>0.53</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31</td>
<td>0.17</td>
</tr>
<tr>
<td>Ru</td>
<td>0.60</td>
<td>0.56</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>0.45</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu</td>
<td>0.50</td>
<td>0.47</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>0.40</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>0.11</td>
</tr>
</tbody>
</table>

3.4. CO Oxidation. CO oxidation has been widely studied as a model catalytic reaction on a wide variety of systems, such as metal surfaces, clusters, and supported metal clusters. There are two primary reaction mechanisms involved: (1) the dissociative mechanism (R1–R4), consisting of O$_2$ dissociation and subsequent association with CO to form CO$_2$, and (2) the associative mechanism (R5), which is active when the pressure of O$_2$ is high enough and the O$_2$ molecules can oxidize CO directly without dissociation. \[ \text{CO} + * \leftrightarrow \text{CO}^* \] (R1)
\[ \text{O}_2 + * \leftrightarrow \text{O}_2^* \] (R2)
\[ \text{O}_2^* + * \leftrightarrow 2\text{O}^* \] (R3)
\[ \text{CO}^* + \text{O}_2^* \leftrightarrow \text{CO}_2 + 2* \] (R4)
\[ \text{CO}^* + \text{O}_2^* \leftrightarrow \text{CO}_2 + \text{O}^* + * \] (R5)

On the basis of these mechanisms (R1–R5), Falsig et al. built a volcano plot of the Sabatier rate over a closed-packed metal surface as a function of the O and CO binding energies, $E_b(O)$ and $E_b(CO)$. In this work, we calculated $E_b(O)$ and $E_b(CO)$ for several single-core@Pt-shell NP140 and explored potential alloy-core@shell structures for CO oxidation on the basis of Falsig’s Sabatier rate model. In Figure 4 we reproduce Falsig’s contour plot of relative Sabatier activity for CO oxidation $\log_{10}(r/r_{Pt})$ as a function of $E_b(O) - E_b(Pt)$ and $E_b(CO) - E_b(Pt)[CO]$. The contours are reproduced from the model in Falsig’s work. Of the pure metal slabs (black circles) Pt emerges as the best catalyst. Several single-core@Pt-shell particles also have high activity (blue triangles), with Pd$_{Au_{0.08}}$@Pt NP140 (green points) passing close to the volcano peak.

A quick way to understand how the alloy-core particles can be tuned is to draw a line connecting any two different single-core@Pt-shell NP140 species on the contour plot. If the line intersects a region of high activity, a promising catalytic material can be achieved by alloying the elements of the end point particles in the core. As illustrated in Figure 4, a line between the Au@Pt and Pd@Pt particles passes near the volcano peak. The green scatter points between Au@Pt and Pd@Pt represents Pd$_{Au_{0.08}}$@Pt NP140, with x = 0.25, 0.50, and 0.75. The distribution of $E_b(O)$ and $E_b(CO)$ due to the different alloy cores and binding sites sampled is indicated by the error bars. Several other core element combinations also have the potential to reach the highly active region; a selection is presented in Figure 5. In each cell of the table, the fraction on top is the optimal ratio $x^*$ of metal X in the alloy core, and the blue number in brackets shows the relative rate at this optimal alloy-core composition, which is also the highest activity this X$_y$Y$_{1-y}$@Pt-shell NP140 can attain. If $x^* = 0$, Y@Pt NP140 has the best performance for X$_y$Y$_{1-y}$@Pt and alloying X in the core will not improve the reactivity, while $x^* = 100\%$ indicates that X@Pt is the most reactive composition.

Highlighting one example, the CO oxidation activity of Ag and Au-core@Pt-shell particles can be enhanced by alloying other transition metals into the core. As shown in Figure 5, the CO oxidation rates of alloy-core@Pt NP140 with core compositions $Au_{0.08}$Cu$_{0.10}$, $Au_{0.71}$Ir$_{0.27}$, $Au_{0.65}$Pd$_{0.35}$, $Au_{0.72}$Rh$_{0.28}$, $Au_{0.74}$Ru$_{0.22}$, $Au_{0.75}$Pt$_{0.27}$ and $Ag_{0.59}$Pt$_{0.41}$ are 2 orders of magnitude faster than the rate of CO oxidation on the
Figure 6 shows the calculated segregation energy of Pt shell nanoparticles with and without adsorbates (O, C, H, N, S, CO, and NO). The insets indicate the preferred structures according to the sign of the segregation energy (adsorbates are not shown).

4. CONCLUSIONS

We have shown general linear correlations between the adsorbate binding energy to the shell of an alloy-core@shell nanoparticle and the composition of the core. This relationship allows for interpolation of the properties of single-core@shell particles and an approach for tuning the catalytic activity of the particle. Application to the HER and COox reactions reveals a series of promising catalysts. A previously reported Pt$_{0.5}$Ru$_{0.5}$@Pd for HER has been identified by this approach; many other predictions have not yet been tested. While our demonstration is only for the HER and COox reactions, this method of tuning catalytic activity provides a general framework for computational optimization of alloy-core@shell nanoparticles for other reactions of interest.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501176b.

Details about the reference energy for the adsorbates, the number of samples in each random alloy core composition, the linear binding trends of individual adsorbate, a comparison of factors influencing the PdAu@Pt and PdIr@Pt d-band of the Pt shell, and a stability analysis of Pd-shell NP140 (PDF)
ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences (Contract No. DE-FG02-13ER16428). Computing time was provided by the National Energy Research Scientific Computing Center and the Texas Advanced Computing Center at the University of Texas at Austin.

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