Effects of Surface–Subsurface Bond-Energy Variations on Equilibrium Compositional Structures Evaluated for Pt–Ir Nanoparticles

Hagar Tigger, Leonid Rubinovich, and Micha Polak*

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

ABSTRACT: The compositional structures of equilibrated Pt–Ir 923-atom cuboctahedron nanoparticles (NPs) are predicted by employing the recently introduced approach for deriving DFT-based coordination dependence of bond-energy variations (CBEVs) combined with the highly efficient statistical-mechanical free-energy concentration expansion method (FCEM). The roles played by preferential strengthening of intrasurface and surface–subsurface bonds in site-specific segregation are elucidated. While CBEV effects enhance Pt surface segregation to all NP surface sites, the driving force obtained for certain (111) sites exceeds the (100) values, in contrast to the simple bond-breaking model. Moreover, the CBEV induces Ir segregation to subsurface sites except the NP subvertexes. Computation of the complete temperature dependence of the compositional structure for low Pt content NPs indicates the occurrence of several smoothly varying atomic exchange processes between surface sites, which are reflected as distinct Schottky-type peaks in the configurational heat-capacity curve. Preliminary results, computed for high Pt content NPs, having onion-like structure at low temperatures, reveal a sharp intracore separation-like phase transition.

1. INTRODUCTION

Chemical and physical properties of alloy nanoparticles (NPs) differ considerably from the corresponding bulk alloys. The variations are related to their reduced size and the resultant geometrical and compositional structures, especially of the outer surface shell constituting a large portion of the matter in small and medium-size NPs.1–4 Studies of site-specific compositions in alloy NPs are motivated mainly by their direct relevance to technology-related applications in heterogeneous catalysis, magnetic media, etc.5 In particular, Pt–Ir nanoparticles, such as studied in this work, are used as catalysts in hydrogenolysis reactions, in oxygen reduction reactions,6 and in fuel cells.7,8

Limitations of current experimental characterization techniques make theoretical-computational modeling nearly the only means for acquiring the NP full atomic-scale compositional information. Here we implement a new approach introduced in our recent study of the equilibrated system of atom exchanging Pt–Pd cuboctahedron (CO) NPs.9 It is capable of coping with medium-size alloy NPs due to a combination of the highly efficient (and transparent) statistical-mechanical free-energy concentration expansion method (FCEM)10 and coordination-dependent bond energetics (CBEV) based on DFT data.11 Quite unexpected CBEV-induced Pt segregation at certain sites of the (111) faces was revealed9 and confirmed most recently by direct DFT computations12 and by Monte Carlo (MC) simulations in conjunction with the modified embedded-atom method (MEAM).13 Moreover, CBEV/FCEM computations of near-surface compositional profiles for Pt0.25Rh0.75(111) were found to be in very good agreement with reported medium energy ion scattering (MEIS) experimental data.14 Their accuracy is further proven by the close similarity to predictions based on the cluster expansion technique in conjunction with DFT.15,16

In the present study, the CBEV/FCEM approach is used for modeling the low-temperature compositional structures of Pt–Ir 923-atom CO NPs and their variations with temperature. Depending on size, the fcc-based CO is one of several possible stable (or metastable) transition-metal NP shapes.3,17–19 The first study of Pt–Ir NPs used the simplistic bond order simulation (BOS) empirical model to predict 201-atom truncated-octahedron compositional structures by means of coordination-dependent constituent site energies.20 The embedded atom method (EAM) was used to predict composition profiles for Pt–Ir(111) and Ir(100) thin films.21 Recently, DFT calculations (0 K) for Pt–Ir(111) thin films22 and for 55-atom CO NPs,23 both containing a single alloying atom, were reported. Here, we apply the CBEV/FCEM approach to cope with a more practical NP size (923 atoms), which is presently unfeasible by DFT, and with the roles of the overall composition and temperature.

After addressing briefly the methodology, computed results for low-temperature compositional structures of low-Pt content NPs are presented, followed by their temperature dependence.
and the corresponding configurational heat capacity. A brief description of preliminary results concerning notable intracore separation-like phase transitions in high-Pt content NPs concludes the article. The predicted phenomena are discussed mainly in terms of preferential strengthening of elemental intrasurface and surface–subsurface bonds having reduced coordinations.

2. METHODOLOGY

The coordination dependence of surface bond-energy variations, introduced by the CBEV method, is extracted from DFT derived pure metal surface-energy anisotropies. It is based on the following expression for the surface energy,

\[ E_s = \sum_m y_m = \sum_m \frac{1}{2} \left( \sum_{n \neq m} \delta w_n \right) \]

which includes contributions of the simple “bond-breaking model”, \( \delta w_n \), and of strengthening of the remaining bonds, \( \delta w_{mn} \) (\( y_m \) denotes the \( m \)-site contribution to \( E_s \)). 

Since all subsurface sites in a CO NP are fully coordinated (\( \Delta Z_{sub} = 0 \)), the reduced coordination of surface sites alone affects both intrasurface and surface–subsurface bond energy and compositional variations (a two-layer model). The bond-energy variations derived for both Pt and Ir exhibit the expected general tendency to increase for lower coordinations (Figure 1). The clear differences between the \( \delta w_{mn} \) curves obtained for the two metals can affect the alloy NP near-surface compositional structure, as discussed in Section 3.

It should be noted that the bulk energy (per atom, \( E_b = 6w_b \)) was obtained using experimental cohesive energies corrected for the free-atom s–d promotion and spin-polarization energies, as introduced recently.

\[ E_b = E_{coh} - E_{pro} - E_{SP} \]

The reason for the correction is the need to use the free-atom bulk-like excited state as the reference energy (\( E = 0 \)) to \( E_{coh} \) instead of the ground-state energy of the free atom relaxed in cohesion measurement experiments. The correction can be quite appreciable in the case of transition metals like Pt and Ir (Table 1), but what matters more in the present context is the change in the energy difference between the two metals, \( \Delta E_b = 0.66 \) vs \( \Delta E_{coh} = 1.10 \) eV, namely, a 40% reduction from the cohesive energy difference. Using the uncorrected \( E_{coh} \) values as input can significantly modify the results as described below, and as we demonstrated before for Pt–Rh 55-atom CO NPs it can even cause an erroneous segregation reversal.

The separation (demixing) tendency in Pt–Ir alloys can be characterized by the effective heteroatomic interaction

\[ V = \frac{1}{2} \left( w_{Pt}^{Pt}\!\!\!\!\!\!\!\!\!/w_{Ir}\!\!\!\!\!\!\!\!\!\!/w_{Ir}\!\!\!\!\!\!\!\!\!\!/w_{Pt}^{Ir} \right) \]

which is quite small (−23 meV derived from DFT-computed zero-temperature formation enthalpy) as compared to the individual bond energies. Hence, possible coordination-dependent variations in \( V \) are neglected. Likewise, since Pt and Ir have rather similar atomic radii, with only about 2% difference, possible atomic size mismatch effects are not expected to modify surface segregation in this alloy and hence are neglected too. It can be noted that although the derived \( V \) relates to 0 K (and correspondingly does not include entropic contributions) its substitution in the FCEM yields a bulk separation critical temperature (−1600 K), which is in quite good agreement with the Pt–Ir experimental phase diagram. This apparent weak dependence of \( V \) on temperature, related to lattice vibration induced thermal decrease of bond energies, is indeed expected to affect \( V \) only slightly well below the melting temperature (e.g., at the 365 K transition in Pt_{47}Ir_{53} CO NPs) described in section 3.2. It can be evaluated by the heat capacity Debye model of a crystalline solid or by using experimental heat capacity data. Implementing the latter gives for both Pt and Ir bulk bond weakening of less than 2% at 500 K (the surface free enthalpy change, depending on alterations of both bulk and surface bonds, amounts to 6%).

Furthermore, since homoatomic and heteroatomic bond energies enter eq 3 with opposite signs, their slight variations with temperature should be partially canceled.

The FCEM takes into account short-range order as well as configurational entropy contributions related to different arrangements of constituent atoms on the CO sites. It is highly efficient due to the use of: (i) explicit analytical expression for the free energy and (ii) concentric central-symmetric “shells” (comprising of equivalently coordinated atomic sites) that reduce significantly the number of the independent concentration variables to be determined. In the

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**Figure 1.** Coordination dependence of surface–subsurface (“inter”) and intrasurface (“intra”) bond-energy variations for elemental Pt and Ir as extracted from DFT-reported surface energies. The sum \( \Delta Z_1 + \Delta Z_2 \) denotes the total number of the 1–2 pair missing bonds. Some representative site pairs are indicated.

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**Table 1. Getting Correct Energies (eV)**

<table>
<thead>
<tr>
<th>energy</th>
<th>Ir</th>
<th>Pt</th>
<th>( \Delta E_{coh/b} )</th>
<th>( \Delta E_{coh/b}/E_{coh/b} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{coh} )</td>
<td>6.94</td>
<td>5.84</td>
<td>1.10</td>
<td>1.19</td>
</tr>
<tr>
<td>( E_{pro} )</td>
<td>~0</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{SP} )</td>
<td>1</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_b )</td>
<td>7.94</td>
<td>7.28</td>
<td>0.66</td>
<td>1.09</td>
</tr>
</tbody>
</table>

*Experimental cohesive energies according to Kittel (DFT computations gave 7.46 eV for Ir and 5.88 eV for Pt).*
case of the 923-atom CO NP, it amounts to 36 variables that are obtained by minimization of the free energy using the MATLAB computation package. The procedure of constrained minimization (using the “fmincon” function) is quite straightforward at high temperatures due to dominant, relatively smooth entropy contributions and to the proximity of the minimum to a random atomic distribution. At lower temperatures, a complex energetics-related landscape can result in sharp changes in shell concentrations (“phase transitions”), and therefore a genetic algorithm function of the global optimization toolbox was employed to verify the general position of the global minimum. A subsequent run of “fmincon” as a hybrid function finally specified the accurate position of the minimum, namely, yielding the real equilibrium site concentrations. Additionally, to accurately localize positions of possible phase transitions, quite small temperature steps (<10 K) were used, and a given temperature was approached by both heating and cooling. Substitution of the computed sets of site concentrations in the FCEM expression for the free energy provides temperature-dependent thermodynamic properties, including the NP configurational heat capacity.

3. RESULTS AND DISCUSSION

Generally, the present computations predict Pt segregation to the NP surface, similarly to the tendency reported by previous studies of this alloy system.4,20–23 The above-discussed diminished difference between the correct elemental bulk energies, as compared to the experimental cohesive-energy difference, should give lower Pt surface segregation levels, while, as discussed below, CBEV effects are expected to enhance them.

3.1. Low-Temperature Surface Compositional Structures. CBEV/FCEM computations for increasing overall Pt concentrations predict a distinct sequence of “magic” compositional structures (having shells fully occupied by a certain element), as shown in Figure 2. This sequence of site-specific segregation in the Pt–Ir NPs can be qualitatively comprehended in terms of the difference between the corresponding pure element m-site contributions to $E_i$ (eq 1),

$$
\Delta_{Pt-Ir}^{m} = E_{m-Ir}^{Pt} - E_{m-Ir}^{Ir} = \gamma_{m-Ir}^{Pt} - \gamma_{m-Ir}^{Ir} \quad (4)
$$

It constitutes an approximate segregation driving force that can govern the corresponding surface and subsurface compositional structures. Assuming dominance of the bond breaking term, Pt with lower $\gamma_{m-Ir}^{Ir}$ (1.21 vs 1.32 eV for Ir, in accordance with $\Delta E_k$ in Table 1) is expected to be the segregating element in this alloy, with preference to lower coordinated sites (having larger $\Delta Z_m$). This trend should be further enhanced since Pt intrasurface bonds are found to strengthen more than the Ir bonds ($\Delta\delta W_{m-ml}$, Figure 1). It is instructive to compare these CBEV-induced surface segregation modifications in Pt–Ir with those we reported for Pt–Pd NPs.7 In both cases, Pt intrasurface bonds strengthen more than the second element bonding. However, the relative bulk bond energies of the constituents (“bond-breaking model”) induce opposite surface segregation tendencies in Pt–Ir (Pt segregates) vs Pt–Pd (Pd segregates) since Pt bulk bond energy is weaker compared to Ir, but stronger as compared to Pd. While in the former case both bond breaking and CBEV effects operate concurrently, in Pt–Pd the two factors oppose each other, leading even to segregation reversal from Pd to Pt at certain surface sites.9

![Figure 2. CBEV/FCEM computed four magic-number surface compositional structures of low Pt content Pt–Ir 923-atom CO NPs at 1 K. (The numeration follows the distance from the CO center.)](image-url)
core starts to be populated, resulting in an onion-like/multishell Pt/Ir/Pt structure (Pt 417Ir506, shown later in Figure 5). Addition of 12 Pt atoms results in Pt429Ir494 having both the CO-55 core and subvertex populated by Pt. The same Pt population sequence involving subvertexes occurs for the CO-147 and CO-309 cores. The latter Pt683Ir240 compositional structure consists of a pure Pt surface, Ir-rich subsurface, and pure Pt inner core (Figure 3). This oscillatory segregation profile, overriding the Pt−Ir demixing tendency, is fully compatible with the Pt−Ir CBEV effect, namely, the extra strengthening of Ir surface−subsurface bonds compared to Pt (except the vertex−subvertex bond, Figure 1). Qualitatively, subsurface oscillations were obtained also for Pt−Ir thin films, but the further extension of the oscillations to underlying layers, in spite of the demixing tendency of this alloy, is questionable.

Nanoalloy subsurface segregation of the more cohesive element has been predicted previously in several works. In particular, using semiempirical many-body potentials derived within the SMA-TB model, three-shell onion-like bimetallic NP structures were predicted for Ni−Ag, Cu−Ag, and Pd−Ag systems. Unlike in the present alloy composed of close atomic-size elements, the origin of the subsurface segregation was attributed to efficient relaxation of surface atoms surrounding the underlying impurity. Furthermore, using simulations with the embedded atom potential revealed for Co−Ag 201-atom truncated-CO small numbers of Co atoms grouped at subsurface sites at low temperatures, attributed to competition between strain and Co binding.34

### 3.2. NP Thermal Variations. Low Pt Content

For NPs with overall composition for which Pt segregation to the outer surface in incomplete (<362 Pt atoms, e.g., Figure 2), equilibration at nonzero temperatures can result in a multitude of intrasurface atomic exchange processes, accompanied by minor exchange involving surface−subsurface and deeper sites at higher temperatures (Pt desegregation), as exemplified for Pt132Ir791 CO in Figure 4a. At T < 200 K, atomic exchange starts most prominently between the Pt-populated edge sites #35 and the Ir-populated corners of (111) (site #32) having, due to the CBEV effects, the closest segregation driving forces (Table 2). Correspondingly, the configurational heat-capacity curve exhibits a low-temperature peak (~200 K, Figure 4b). At higher temperatures (above ~500 K), additional atomic exchange processes are predicted to occur at the surface. In particular, the curve of site #32 reaches a maximum since Pt atoms start moving to other face sites. Moreover, Pt atoms move from vertex and edge to such sites (Figure 4a). These processes are reflected in the broader second peak of the configurational heat capacity (at ~700 K, Figure 4b). The even broader high-temperature peak (~3300 K) reflects Pt

<table>
<thead>
<tr>
<th>site type</th>
<th>(100) border (27,28,31)</th>
<th>(111) corner (32)</th>
<th>edge (35)</th>
<th>edge (33–34)</th>
<th>vertex (36)</th>
</tr>
</thead>
<tbody>
<tr>
<td>∆Z</td>
<td>4</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>△Pt−Ir(γ_m) = (γ_m^Pt − γ_m^Ir)</td>
<td>−0.58 to −0.59</td>
<td>−0.66</td>
<td>−0.72</td>
<td>−0.76</td>
<td>−0.78</td>
</tr>
</tbody>
</table>

Figure 3. Multishell compositional structure of Pt683Ir240 comprising a pure Pt surface, Ir-rich subsurface, and pure Pt CO-309 inner core (1 K).

Figure 4. (a) Pt132Ir791 CO site concentrations as a function of temperature (site numbering as in Figure 2). (b) The corresponding configurational heat-capacity curve, which exhibits Schottky-type peaks due to atomic-exchange processes between the indicated sites, was computed with the concentrations of all 923 sites as input.
desegregation from the surface to the subsurface (subvertex site #23 is populated first due to the CBEV effect) and to the inner core, leading ultimately to a homogeneous distribution (namely, a “solid solution”) corresponding to the nominal composition. Obviously, the predicted temperature-dependent processes are limited by the NP’s melting point (MP), which typically is lower than the corresponding bulk value. A simple formula based on the effective-medium approximation gives 2318 K for Pt$_{132}$Ir$_{93}$ compared to 2690 K of bulk Pt$_{313}$Ir$_{237}$ (both marked in Figure 4b). Hence, most of the processes described above are in the temperature range of the solid NP.

High Pt Content. Entirely different temperature-dependent phenomena can be anticipated for NPs with relatively high Pt content, like those having multishell onion-like structures at low temperatures. In addition to the inner core, the surface of such NPs is fully occupied by segregated Pt atoms, so that atomic exchange between surface sites is excluded. We have chosen to study in detail Pt$_{132}$Ir$_{93}$ with a 55-CO inner core (Figure 5). Exchange of Pt atoms between the vertexes of the inner core (#4, having the lowest Pt coordination) and the NP subvertexes (#23) begins at very low temperatures, and up to ~160 K it reaches almost 70%. Then, a more gradual exchange commences mainly from the #3 and #2 core sites (having higher Pt coordination) to the 147-CO (100) sites (#5), the subedge (e.g., #22), and marginally to other sites of the Ir intermediate layer in the onion-like structure. This “site-by-site” sequential disintegration of the inner core is followed by a very sharp compositional change at 365 K involving all these sites, particularly the CO 13 Pt atoms (sites #1 and #0), which are fully replaced by Ir atoms (Figure 5). The distinct transition should be reflected in a very sharp heat capacity peak, as compared to the above low-Pt content case (Figure 4b). This rather remarkable phenomenon, namely, the transition from the low-temperature Pt inner core to a structure comprised of small Pt-rich near-surface subclusters, is compatible with the CBEV effect favoring occupation of subsurface vertexes by Pt (Figures 1 and 3) and with the separation tendency in this alloy. Full thermodynamic analysis of these preliminary results concerning intracore separation-like phase transitions is underway. Furthermore, NP size and overall composition effects on the transition temperature will be explored to construct the corresponding “nanophase diagrams”.

Finally, the importance of using corrected elemental cohesive energies as correct bulk energies was verified by comparing the corresponding results. Thus, the uncorrected cohesive energies (characterized by a larger difference and ratio, see Table 1) give somewhat higher Pt surface segregation levels. However, the increase is quite small for $T < 1000$ K since the surface is almost fully Pt populated in both cases. On the other hand, effects on CBEV and correspondingly on the nanoparticle core compositional structure are more significant. For example, in the case of Pt$_{111}$Ir$_{500}$, the employment of uncorrected cohesive energies results in the abrupt dissolution of the low-temperature Pt core at 725 K, as compared to the transition at 365 K obtained when using correct bulk energies as input (Figure 5). In the former case, a nearly random core solid solution is formed since the temperature is too high for stable Pt-rich small subclusters.

4. CONCLUSIONS

Due to its distinct transparency, modeling of alloy nanoparticle compositional structures based on the CBEV/FCEM method can provide physical insight into atomic-scale phenomena relevant to the performance of heterogeneous catalysts, for example. In particular, computations done in this work for a system of Pt–Ir 923-atom cuboctahedrons reveal the following CBEV-induced effects:

(i) enhancement of Pt segregation to all surface sites;  
(ii) segregation driving force for certain (111) sites that is larger than the (100) values, in contrast to the simple bond-breaking model;  
(iii) Ir segregation to subsurface sites except the NP subvertexes.

Furthermore, the high efficiency of the method enables us to handle the complete temperature dependence of the medium-size NP compositional structure, indicating several smoothly varying atomic exchange processes between surface sites for low Pt content. In comparison, for high Pt content NPs, a separation-like nanophase transition between the Pt-core of an onion-like structure and small Pt-rich near-surface subclusters is predicted for the first time. Surface and subsurface bond energy relative variations derived for the two elements are found to play a distinct role in most of these phenomena.

![Figure 5. Top: Variations with temperature in the inner core and subsurface site concentrations computed for the Pt$_{132}$Ir$_{93}$ CO NPs. Bottom: 3D schematics and (111) cross sections of the two compositional structures (“nanophases”) involved in the transition: left, onion-like structure; right, near-surface Pt-rich subclusters, surrounding the Ir core.](image-url)
The authors declare no competing financial interest.

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