

The Onion-Ring Structure for Pd–Pt Bimetallic Clusters

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The onion-ring structure is validated in the Pd–Pt bimetallic clusters of total atom numbers 147 and 309 through the Monte Carlo method by using the second-moment approximation of the tight-binding (TB-SMA) potentials, which is conceived in predicting the possible structures of the bimetallic clusters by He et al. [*J. Am. Chem. Soc.* **2003**, *125*, 11034] and Hwang et al. [*J. Am. Chem. Soc.* **2005**, *127*, 11140]. In the onion-ring structure, Pd atoms and Pt atoms occupy alternate layers of the clusters. The formation of the onion-ring structure can be associated with the fact that the single Pt impurity is favorable to stay in the subsurface layer and the central part of bimetallic clusters.

The activity and selectivity of a pure metal catalyst can be improved by adding the second metallic component.^{1–5} This behavior may due to an ensemble and/or a ligand effect.⁶ An important system in catalysis research is the Pd–Pt bimetallic catalyst. As is well-known, Pd–Pt bimetallic catalysts exhibit high activities in the hydrogenation of aromatics,^{7–9} wet oxidation of the reactive dyes,¹⁰ hydrodechlorination of dichlorodifluoromethane,¹¹ hydrogenative ring-opening reaction,¹² and combustion of methane.¹³ In addition, the Pd–Pt system is of the high sulfur tolerance, excellent stability, and good quality.^{14,15} More interestingly, Pd–Pt bimetallic clusters with well-defined and controllable properties show greater activity than the pure Pd clusters.^{6,16} Due to the wide applications of Pd–Pt systems mentioned above, it is of great interest to study the structures of the Pd–Pt bimetallic clusters.

Detailed structural information of bimetallic clusters is of importance for the understanding of their catalytic activity and selectivity. The core–shell structures, i.e., the B–A structure, where the A atoms occupy the core and the B atoms lie in the shell, were found in bimetallic clusters theoretically^{17–20} and in experiment.^{21–23} In addition, three-shell onion-like structures (A–B–A) were predicted,^{24–26} in which the A atoms are enriched in the outer and third atomic shells, while the B atoms are in the second atomic shell. Interestingly, a novel structure of onion-ring morphology is assumed on the basis of alternate layering of two metals in considering the possible structures of the bimetallic clusters, as shown by He et al.²⁷ Similarly, Hwang et al.²⁸ also indicated that if A and B atoms could occupy alternate layers of the bimetallic clusters, an onion-ring structure is possible. However, the onion-ring structure still needs to be validated by both theoretical and experimental efforts.

In this letter, we report that the novel onion-ring structure was found in Pd–Pt bimetallic clusters by using Monte Carlo simulation. In the resulting structure, Pd atoms and Pt atoms occupy alternate layers of the clusters, thus forming the onion-

ring morphology; for example, the Pd–Pt–Pd–Pt–Pd onion-ring structure for the 309-atom Pd–Pt bimetallic clusters, i.e., the surface layer, the third layer (from surface to center), and the center of the bimetallic clusters are occupied by the Pd atoms, while the subsurface layer and the fourth layer of the bimetallic clusters are filled with the Pt atoms.

The second-moment approximation of the tight-binding (TB-SMA) model²⁹ was adopted to describe the interaction between the cluster atoms. The parameters for pure elements (Pd–Pd and Pt–Pt) were developed by Cleri and Rosato.²⁹ In addition, the Pd–Pt potential parameters were derived by taking averages of the Pd–Pd and Pt–Pt parameters, which were employed for the theoretical study of Pd–Pt bimetallic clusters with satisfactory results.^{30,31}

In this work, the semi-grand-canonical ensemble Monte Carlo (SEMI-GCMC) simulations were performed. Simulations and our programming details can be found in the literature^{32–35} and our previous work.³⁶ Within this method, the total number of atoms ($N = N_{\text{Pt}} + N_{\text{Pd}}$), temperature (T), and chemical potential difference ($\Delta\mu = \mu_{\text{Pt}} - \mu_{\text{Pd}}$) between the two species were fixed. N_{Pt} and N_{Pd} were allowed to vary in our algorithm. The chemical composition at a given temperature was therefore obtained by performing the SEMI-GCMC simulation at a fixed value of the chemical potential difference $\Delta\mu$ between the two species in a cluster. In our MC simulations, 20 000 steps were run for each atom. The first 10 000 steps per atom were used to reach the equilibrium, where the fluctuation of the total energy of the system was less than 0.2%, and the last 10 000 steps per atom were required for an average of the structural properties. The details of the simulation can also be found in our previous work.³⁶ In this work, the chemical potential difference ($\Delta\mu = \mu_{\text{Pt}} - \mu_{\text{Pd}}$) is fixed at $\Delta\mu = 1.9$. The simulation temperature ranges between 100 and 500 K. The Pd–Pt bimetallic clusters of interest contain 147 and 309 atoms with the icosahedral and decahedral structures, respectively.

Snapshots of 147-atom and 309-atom Pd–Pt icosahedral clusters at 100, 300, and 500 K are shown in Figure 1. It is

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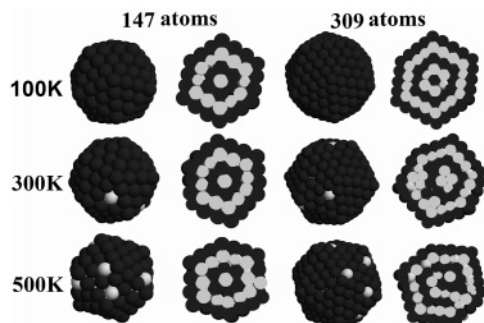


Figure 1. Snapshots of 147-atom and 309-atom Pd–Pt icosahedral clusters when $T = 100$, 300, and 500 K (dark gray atoms, Pd; light gray atoms, Pt).

found in Figure 1 that the onion-ring structure is obtained for the 147-atom and 309-atom Pd–Pt icosahedral clusters at 100, 300, and 500 K, in which the layers of clusters are alternately occupied by Pd atoms and Pt atoms. In addition, the surface layers of all the clusters are filled with Pd atoms, corresponding to their surface segregation. Aiming at understanding the structure in detail, we calculated the reduced pair correlation functions of 147-atom and 309-atom Pd–Pt icosahedral clusters, $g_{\text{cm}}^*(r)$. We define $g_{\text{cm}}(r)$ as the pair correlation function around the center of mass for the bimetallic clusters, and if $g_{\text{cm}}^*(r) = g_{\text{cm}}(r)/(V/N^2)$, then the reduced pair correlation function $g_{\text{cm}}^*(r)$ is given by $g_{\text{cm}}^*(r) = \langle \sum_{i=1}^n \delta(\vec{r}_i - \vec{r}_{\text{cm}} - r) \rangle$, where n is the number of atoms counted and \vec{r}_{cm} is the coordinates of the center of mass at each MC step. The reduced pair correlation function was calculated from the block ensemble average after equilibrium, in which a block contains 10 000 configurations.

It is found in Figure 1 that the 147-atom Pd–Pt icosahedral clusters possess the Pd–Pt–Pd–Pt onion-ring structure at 100, 300, and 500 K, in which the surface layer and the third layer of the clusters are occupied by Pd atoms, while the subsurface layer and center of clusters are filled with Pt atoms. The results indicate that the 147-atom Pd–Pt icosahedral clusters possess the onion-ring structure even at higher temperatures. The Pd–Pt–Pd–Pt onion-ring structure can be well-understood by investigating the reduced pair correlation function curves of the 147-atom Pd–Pt icosahedral clusters at 100 and 300 K, respectively (see Figure 2a,c). Obviously, as shown in Figure 2a, the Pd atoms occupy the surface layer and the third layer, while the Pt atoms are in the subsurface layer and the center of the cluster, forming the Pd–Pt–Pd–Pt onion-ring structure at 100 K. Similarly, the reduced pair correlation function curve indicates that the 147-atom Pd–Pt icosahedral cluster possesses the Pd–Pt–Pd–Pt onion-ring structure at 300 K (see Figure 2c).

For the 309-atom Pd–Pt icosahedral clusters, the Pd–Pt–Pd–Pt onion-ring structure is found at 100 K (see Figure 1), which is validated in the reduced pair correlation functions of the 309-atom Pd–Pt icosahedral cluster at 100 K (see Figure 2b). It is found in Figure 2b that the surface layer, the third layer, and the center of the cluster are occupied by the Pd atoms, while the subsurface layer and the fourth layer of the cluster are filled with the Pt atoms, thus forming the Pd–Pt–Pd–Pt–Pd onion-ring structure at 100 K. In contrast, at 300 and 500 K, the Pd–Pt–Pd–Pt onion-ring structure is found for the 309-atom Pd–Pt icosahedral clusters (see Figures 1 and 2d). The structure differences of the 309-atom Pd–Pt icosahedral clusters at 100, 300, and 500 K may due to the probabilities of site occupancies of Pd and Pt atoms in the area of the central atom, in particular.

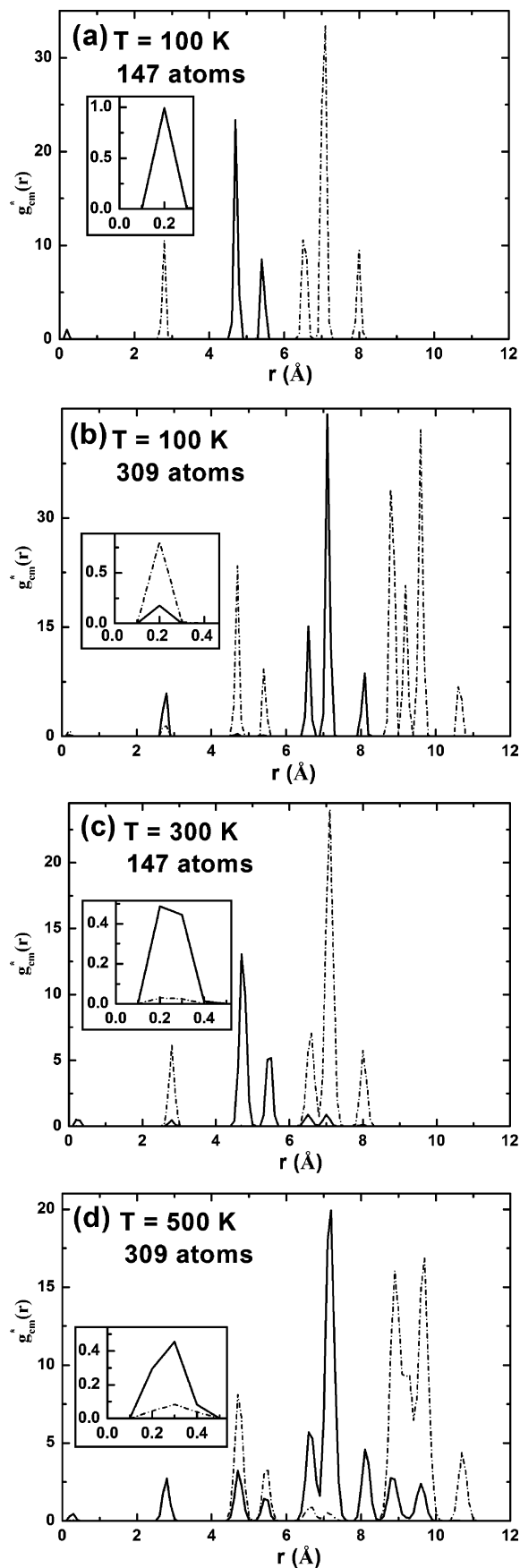


Figure 2. The reduced pair correlation functions (Pd, short dash–dot line; Pt, solid line) of Pd–Pt icosahedral clusters. (a) 147-atom at 100 K. (b) 309-atom at 100 K. (c) 147-atom at 300 K. (d) 309-atom at 500 K.

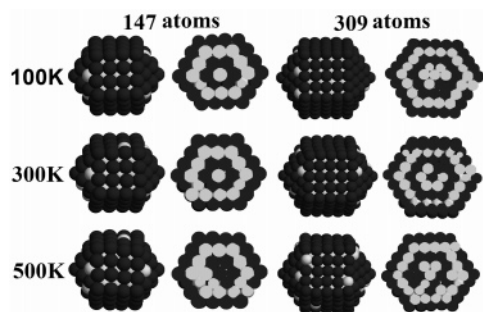


Figure 3. Snapshots of 147-atom and 309-atom Pd–Pt decahedral clusters when $T = 100, 300,$ and 500 K (dark gray atoms, Pd; light gray atoms, Pt).

In Figure 3, we present the snapshots of 147-atom and 309-atom Pd–Pt decahedral clusters at 100, 300, and 500 K. It suggests in Figure 3 that the 147-atom decahedral clusters possess the Pd–Pt–Pd–Pt onion-ring structure at 100 and 300 K and the Pd–Pt–Pd onion-ring structure at 500 K. Also, the Pd–Pt–Pd–Pt onion-ring structure is obtained for the 309-atom decahedral clusters at 100, 300, and 500 K (see Figure 3). Obviously, the decahedral clusters can also possess the onion-ring structure, but the structure is imperfect compared with that of the icosahedral clusters.

To understand the formation of the onion-ring structure for the icosahedral clusters and decahedral clusters, we calculated the impurity solution energy^{24,37} of one impurity atom Pt in the Pd clusters of N atoms, ΔE_{imp} , as follows.

$$\Delta E_{\text{imp}} = E(\text{Pd}_{N-1}\text{Pt}) - E(\text{Pd}_N) + \frac{1}{N}[E(\text{Pd}_N) - E(\text{Pt}_N)] \quad (1)$$

where $E(\text{Pd}_{N-1}\text{Pt})$, $E(\text{Pd}_N)$, and $E(\text{Pt}_N)$ are the total energies of mixed and pure clusters with N atoms. The impurity solution energy represents the energetic stability of the clusters³⁷ and was used to explain the formation of the three-shell onion-like structure for the bimetallic clusters very successfully.²⁴ Here, we calculated the impurity solution energies of the single impurity Pt placed in all the energetically inequivalent sites, whose numbers are 7, 11, 17, and 32 for four different clusters, including the 147-atom icosahedral, 309-atom icosahedral, 147-atom decahedral, and 309-atom decahedral clusters at 100 K. The shift impurity solution energy ΔE_{imp}^* is defined by $\Delta E_{\text{imp}}^* = \Delta E_{\text{imp}} - \Delta E_{\text{imp}}^{\text{center}}$, where $\Delta E_{\text{imp}}^{\text{center}}$ is the impurity solution energy for an impurity placed in the cluster sites which are closest to the geometrical center. Note that the central impurities are of $\Delta E_{\text{imp}}^* = 0$. Figure 4 shows the shift impurity solution energies ΔE_{imp}^* of one impurity atom Pt in the Pd clusters of 147 and 309 atoms with the icosahedral and decahedral structures, respectively. As is found from Figure 4, the shift impurity solution energies, ΔE_{imp}^* , in the surface layer are much higher than that in the interior sites, which means that the single Pt impurity prefers to be located in the interior sites, not in the surface layer. Moreover, the shift impurity solution energies, ΔE_{imp}^* , of the sites in the center and the subsurface layer are much lower than those of the other sites, which means that the single Pt impurity stays favorably in the center and the subsurface layer (see Figure 4). For the 147-atom icosahedral clusters, the sites of the center and the subsurface layer are favorable for the single Pt impurity, compared with the sites of the surface layer and the third layer, thus forming the Pd–Pt–Pd–Pt onion-ring structure (see Figure 4a). Furthermore, the behavior of 147-atom decahedral clusters is similar (see Figure 4c). For the 309-atom icosahedral clusters, the single Pt impurity

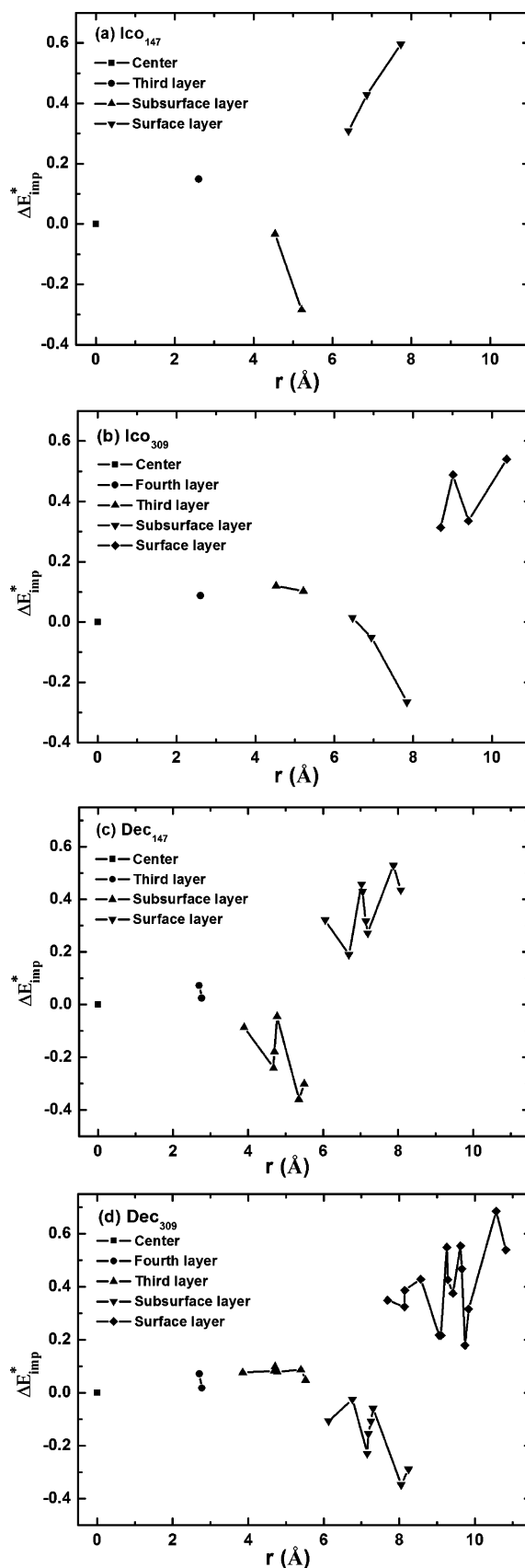


Figure 4. Impurity solution energies, ΔE_{imp}^* (eV), of one impurity Pt in the inequivalent sites of Pd clusters as a function of r (Å), which is the distance of the impurity from the geometrical center of the clusters at 100 K. (a) Icosahedral clusters with the size of 147 atoms (Ico_{147}). (b) Icosahedral clusters with the size of 309 atoms (Ico_{309}). (c) Decahedral clusters with the size of 147 atoms (Dec_{147}). (d) Decahedral clusters with the size of 309 atoms (Dec_{309}).

prefers to sit in the central part and the subsurface layer, rather than in the surface and the third layer. Therefore, the 309-atom icosahedral clusters are associated with the Pd–Pt–Pd–Pt onion-ring structure (see Figure 4b). Similar results are also found for the 309-atom decahedral clusters (see Figure 4d). However, the shift impurity solution energies, ΔE_{imp}^* , are close to each other in the sites of the center and the fourth layer, so that the 309-atom icosahedral and decahedral clusters may also possess the Pd–Pt–Pd–Pt–Pd onion-ring structure.

In summary, the novel onion-ring structure is validated by using Monte Carlo simulation, based on the second-moment approximation of the tight-binding (TB-SMA) potentials. The Pd–Pt–Pd–Pt onion-ring structure is observed for the 147-atom Pd–Pt bimetallic clusters with icosahedral structure at different temperatures. Furthermore, the 147-atom decahedral clusters are associated with the Pd–Pt–Pd–Pt onion-ring structure at 100 and 300 K and the Pd–Pt–Pd onion-ring structure at 500 K. In addition, the 309-atom Pd–Pt icosahedral bimetallic clusters possess the Pd–Pt–Pd–Pt–Pd onion-ring structure at 100 K and the Pd–Pt–Pd–Pt onion-ring structure at 300 and 500 K. Besides, only the Pd–Pt–Pd–Pt onion-ring structure is found for the 309-atom Pd–Pt decahedral bimetallic clusters at different temperatures. The impurity solution energies, ΔE_{imp} , of one impurity atom Pt in the Pd clusters are calculated to explain the formation of the onion-ring structure. The single Pt impurity prefers to stay in the sites with the lower impurity solution energies, thus forming the novel onion-ring bimetallic clusters. Our results indicate that it is possible to obtain the onion-ring bimetallic clusters by controlling the atomic ordering. Note that, since only the icosahedral and decahedral structures are considered here, it seems that more favorable structures for the Pd–Pt bimetallic clusters could be found in future work.

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