2P107

Understanding segregation behavior and electronic structures in 55 and 147-atom bimetallic TcPt and RePt nanoclusters: a first-principles study

○Jing Lu[1], Kazuya Ishimura [2], Shigeyoshi Sakaki[*,1]
[1] *Fukui Institute for Fundamental Chemistry (FIFC), Kyoto University, Takano-Nishihiraki-cho 34-4, Sakyou-ku, Kyoto 606-8103, Japan*
[2] *Institutes for Molecular Science (IMS), Okazaki 444-8585, Japan*

[Abstract] The segregation behavior and electronic property of 38, 55, 147-atom bimetallic Pt-Tc and Pt-Re clusters with Pt-shell are systematically explored using density functional theory. The calculated results indicate that $Pt_{32}M_6$ and $Pt_{42}M_{13}$ (M = Tc and Re) clusters do not have core-shell structure. Only in 147-atom Pt-Re cluster, $Re_{55}@Pt_{92}$ with core-shell structure is stable. Thus, size of cluster is one of the most important factors for taking core-shell structure. The cohesive energy, interaction energy, geometric feature, distortion energy, and charge transfer are discussed to explain the segregation behavior of these clusters.

[Introduction]
Bimetallic alloyed clusters/particles with core-shell structure have been utilized in a number of important areas, ranging from catalysis to optoelectronic and magnetic applications. Recently, bimetallic alloyed clusters/particles with core-shell structure such as Pt-Ti, Pt-Fe, Pt-Co, Pt-Ni, Pt-Cu, Pt-Ru, and Pt-Pd have been experimentally and theoretically reported as good candidate for electrode catalyst of fuel cell.[1] Cohesive energy, relative atomic size, and segregation energy are often discussed as the determining factors for taking core-shell structure. In general, metals with larger cohesive/surface energy tend to be in the core to provide the greater binding energy. Small atoms tend to occupy the more sterically confined core, because the core undergoes compression. For an A-B bimetallic nanocluster, the segregation behavior depends on the balance of these factors above as well as preparation method and experimental conditions. In this work, we wish to report systematical study to explain if core-shell structure is stable in these combinations and factors determining core-shell structure of bimetallic Pt-Tc and Pt-Re clusters and their electronic properties.

[Methods]
DFT calculations were performed using the VASP by implementing the generalized gradient approximation (GGA) with exchange-correlation functional Perdew-Burke-Ernzerhof (PBE). 1×1×1 k-point was sampled by the Monkhorst-Pack grid method for the optimized calculations due to the high computational cost when the spin polarity is included. The clusters were placed in the center of a large enough supercell to ensure sufficient separation (≈ 10 Å) between periodic images. The convergence criteria for total energies and forces were set to 1.0×10^{-4} eV and 0.01 eV/Å, (EDIFF = 0.0001, EDIFFG = -0.01), respectively. The single point calculations with B3LYP, B3PW91, and PBE0 functionals were performed using SMASH program.[2] The NBO charge analysis was calculated using Gaussian09 package with PBE0 functional.

[Results and Discussion]

In 38-atom cluster, the segregation energies (SEs) are -1.16 eV and -1.21 eV for the octahedral (O_h) $Pt_{32}Tc_6$ and $Pt_{32}Re_6$, respectively, as shown in Fig.1, where the negative SE indicates that core-shell structure $M_6@Pt_{32}$ with Pt_{32} shell is not stable. The stability decreases in the order of $Pt_{32}M_5M^{center}$ > $M_6@Pt_{32}$ > $Pt_{32}M_5M^{corner}$. In 55-atom clusters, the SE for $Pt_{42}Tc_{13}$ (O_h) is -1.18 eV. However, the SE for $Pt_{42}Re_{13}$ (O_h) (-0.32 eV) is larger (less negative) than that for $Pt_{42}Tc_{13}$ (O_h). Also, icosahedral (I_h) $Pt_{42}Re_{13}$ has a larger SE than $Pt_{42}Tc_{13}$ (I_h). In $Pt_{92}Tc_{55}$ (I_h), the most stable isomer is $Pt^{core2}Tc_{54}Pt_{91}Tc^{edge}$ (I_h) with the doublet state and the next stable isomer is $Pt^{core2}Tc_{54}Pt_{91}Tc^{center}$($I_h$) with the doublet state, indicating that a core-shell structure is not stable in $Tc_{55}Pt_{92}$ (I_h). In $Pt_{92}Re_{55}$ (I_h), however, a core-shell structure is the most stable. These results suggest that the core-shell structure is sensitive to the size and SE increases (becomes less negative) with increase in size of cluster.

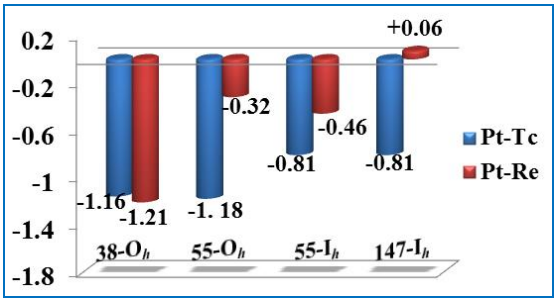

Fig. 1. Segregation energies (in eV) for the Pt_mM_n (M = Tc and Re, m+n=38, 55, 147) clusters.

The other factors influencing core-shell structure such as cohesive energy, interaction energy, distortion energy, and geometric features are also investigated. The cohesive energy increases in the order of Pt < Tc < Re, suggesting that Tc and Re may take core position. The cohesive energy of M_n cluster increases with the increase in size. This is one reason why a core-shell structure with Pt shell becomes stable with the increase in size.

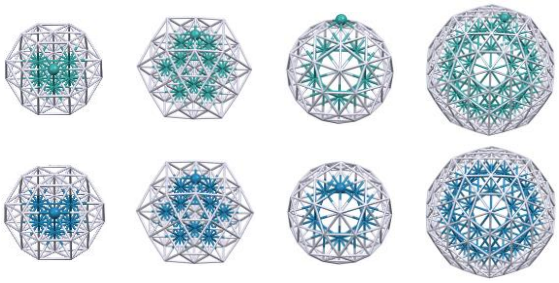

Fig. 2. The stable isomers for the Pt_mTc_n (up) and Pt_mRe_n (down) (m+n = 38, 55, 147) clusters.

The distortion energies of Tc_6 (O_h), Tc_{13} (O_h), and Tc_{55} (I_h) are 0.84 eV, 0.59 eV, and 1.79 eV, respectively, and those of Re_6 (O_h), Re_{13} (O_h), and Re_{55} (I_h) are 1.28 eV, 0.74 eV, and 5.00 eV, respectively. The distortion energy of Tc_n is smaller than that of Re_n, though Re has a greater tendency to have core-shell structure than Tc. In other words, distortion energy of M_n core is not an important factor for taking core-shell structure.

The distortion energy of Pt_m (O_h) shell is position (+1.00 eV) only in $Tc_{13}@Pt_{42}$ (O_h), but negative in all other cases examined here. The distortion energy of Pt shell is not parallel to the SE, suggesting that the Pt_m shell distortion is not an important factor.

The interaction energy between M_n core and Pt_m shell decreases as the size increases from 38 to 55 and 147. Also, the bond distance between Tc/Re in the core and Pt in the center position is shorter by 0.23/0.22 Å, 0.17/0.17 Å, and 0.08/0.11 Å in $M_6@Pt_{32}$ (O_h), $M_{13}@Pt_{42}$ (O_h), and $M_{55}@Pt_{92}$ (I_h), respectively, than in Pt_{38} (O_h), Pt_{55} (O_h), and Pt_{147} (I_h). These results indicate that the stronger interaction between core and shell is one important factor for taking core-shell structure. The NBO charge analysis shows that charge transfer occurs from Pt shell to M core, which is conducive to the stability of core-shell structure. The detailed discussions about the factors for taking core-shell structure of 147-atom Pt-Tc and Pt-Re will be shown in the poster.

[References]

[1] R. Ferrando, J. Jellinek, R. L. Johnston, *Chem. Rev.* **108**, 845 (2008).

[2] K. Ishimura, *SMASH-2.1.0*, *http://smash-qc.sourceforge.net/*.