Alloy nano-cluster surface phenomena modeled using DFT-based coordination-dependent bond-energy variations

Micha Polak and Leonid Rubinovich
Department of Chemistry, Ben-Gurion University, Beer-Sheva 84105, Israel
mpolak@bgu.ac.il

In model computations of site-specific compositions and thermodynamic properties of Pt-Pd and Rh-Pd cuboctahedron nanoclusters, we use a new procedure for deriving the underlying interatomic energetics, based on a search for a functional dependence of surface-induced bond energy variations on the corresponding pair coordinations. In particular, polynomial functions were fitted to DFT data reported recently for energies of six surfaces, (111), (100), (110), (311), (331) and (210) [1], and of small pure Pt, Pd and Rh clusters. The elemental energy variations were incorporated in the statistical-mechanical "free-energy concentration expansion method" (FCEM [2]), employed before using semi-empirical energetics [3].

While all alloy clusters exhibit Pd segregation to specific surface sites, certain segregation profiles for Pt-Pd and Rh-Pd differ considerably (Fig.1). For example, Pt-Pd and Rh-Pd exhibit maximal Pd enrichment and depletion, respectively, in the 2-nd layer. These unique profiles originate from particular variations in elemental bonding between the 1-st and 2-nd layers.

Further computations reveal for Rh-Pd intra-cluster (surface/core) and inter-cluster separation involving “magic number” Pd segregated structures exhibiting various types of "demixed" order. At higher temperatures atomic exchange among surface sites as well as surface-core desegregation processes are reflected in distinct configurational heat capacity peaks of the Schottky type, at temperatures and magnitudes depending on the cluster overall-composition, shape and size (Fig. 2). In case of the Pt-Pd clusters, the predicted structures do not exhibit distinct surface/core separation, primarily due to the interplay between surface-modified bond strengths of the two constituents and their mixing tendency. Using the highly efficient FCEM enables to explore also compositional structures and properties of Rh-Pt-Pd ternary nano-clusters.

References:

[1] I. Galanakis et al., Surf. Sci. **511** (2002) 1.
[2] M. Polak and L. Rubinovich, Surf. Sci. Rep. **38** (2000) 127.
[3] M. Polak and L. Rubinovich, Phys. Rev. B **71** (2005) 125426; L. Rubinovich at al., Phys. Rev. B **74** (2006) 035405.

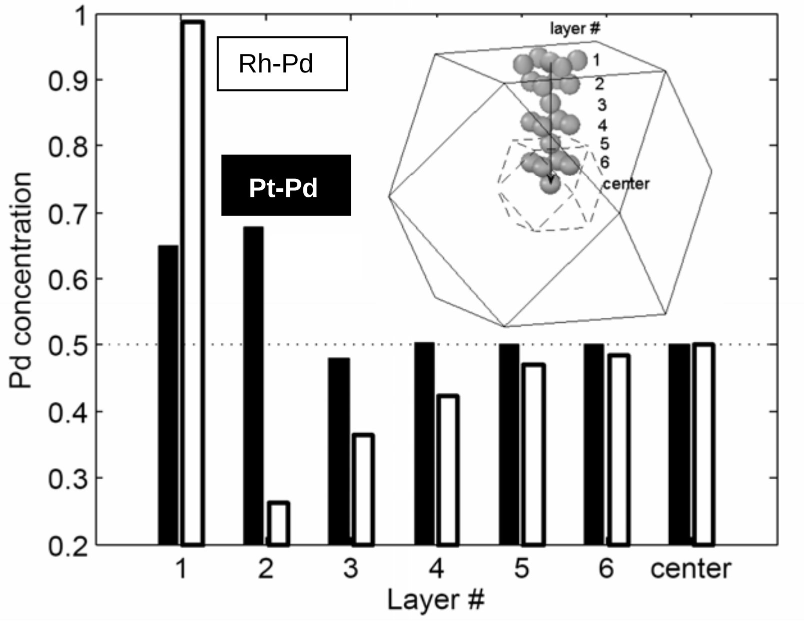

Fig.1. Pd segregation profiles computed for the (100) face of the 923-atom alloy cuboctahedron clusters (1500 K). Inset: schematics showing the pertinent profile layers.

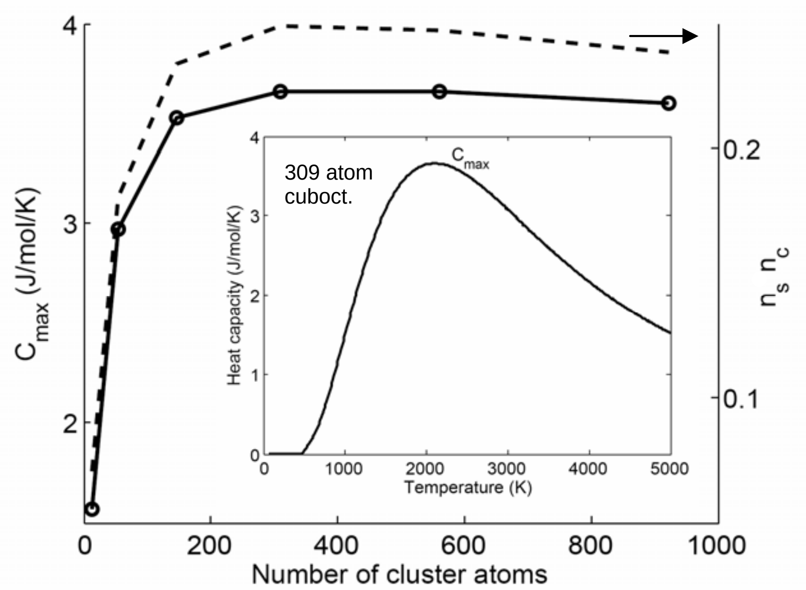

Fig.2. Nanocluster size effects: the heat capacity maximal value computed for 13 to 923-atom cuboctahedron Rh-Pd clusters having pure Pd surface and Rh core at low temperatures. Dashed line: the product of surface and core site fractions, representing the number of surface-core desegregation excitations. Inset: characteristic Schottky-type desegregation contribution to the cluster heat capacity.