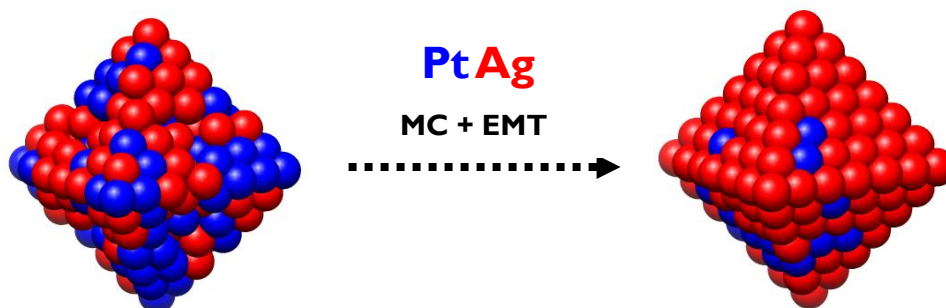


Monte Carlo simulations of alloy segregation in PtAg octahedral nanoparticles

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Abstract

Simulations were carried out to investigate phase segregation of insoluble alloy nanoparticles (NPs) such as PtAg. The distributions of Pt and Ag within a ~ 24 Å (231 atom) cluster were varied using the Monte Carlo method with effective medium theory potentials to model atomic interactions at 1073 K. The radial distribution functions and radial atom fraction profiles for Pt and Ag atoms showed that Ag prefers to segregate onto the PtAg nanoparticle surface for Ag compositions between 5-50 atom%. The presence of surface Ag at a majority of highly unsaturated octahedral edge sites would have a profound effect on catalytic selectivity, particularly at high temperatures. These findings are in agreement with previous characterization and catalytic testing of Pt₉₁Ag₇ octahedral nanoparticles for partial C₂H₂ hydrogenation.



Introduction

It has long been established that the reactivity of transition metal heterogeneous catalysts is determined by the arrangement and composition of its surface atoms. Modifications of these surfaces by alloying have been shown to improve reactivity, increase stability, and reduce the amount of costly precious metals (e.g., Pt). However, there is a lack of understanding about how alloying changes the arrangement and composition of surface atoms under different conditions, particularly during catalytic reactions on nanoparticles (NPs). NPs are known to have properties (e.g., lower melting points) that are distinct from their bulk counterparts, which can play critical roles during the formation of alloys. In particular, depending on the temperature, atmosphere, and miscibility of the alloy components, surfaces can become enriched in a particular element; these surface-enriched components will have the most influence on overall catalytic reactivity. It is thus desirable to understand and anticipate how particular alloys surface segregate.

In this project, the normalized radial probability profiles and distribution functions of PtAg octahedral NPs were simulated using the Monte Carlo method with effective medium theory potentials. The Monte Carlo (MC) method has been previously utilized to study phase segregation in bimetallic alloys [1], and Effective Medium Theory (EMT) potentials have been implemented for a variety of metallic systems (e.g., Pt, Ag, Cu, Pt, Au, Al, Ni) [2,3] whose material properties agree well with calculations. Recently, it was shown that sub-monolayer quantities of Ag at the surface of Pt octahedral nanoparticles enhance reactivity for partial C₂H₂ hydrogenation at elevated temperatures (T > 100 °C) [4]. This study aims to validate reasons for enhanced reactivity of PtAg octahedral nanoparticles (i.e., due to sub-monolayer surface Ag doping) by analyzing their surface segregation behavior at elevated temperatures.

Theory and Experiment

Simulations of atomic interactions within semi-crystalline alloys have been carried out for over 30 years. In one of the earliest developments [1], MC was applied by considering simply the change in potential energy due to interaction energies of nearest and next-nearest neighboring A and B atoms; in this framework, only the number of neighbors and sublimation energies of A and B were used in the calculations. A favorable interaction energy between A and B atoms would produce a homogeneously mixed alloy, while an unfavorable interaction resulted in phase separation. Nearly 2 decades later, the Effective Medium Theory was applied using the same MC method in a semi-empirical manner to produce structural and energetic calculations that were in much better agreement with experimental results [3].

The semi-empirical nature of the effective medium theory is derived from equation parameterization such that electron densities, cohesive energies, shear moduli, and lattice constants are in good agreement with experimental values. Equation parameters are generated by first calculating the energy of an atom, A or B, in a reference system referred to as the "effective medium". In most cases, particularly for highly conducting metallic systems, the effective medium is a homogeneous electron gas with a density equal to the average electron density around the atom in a system of interest (e.g., FCC crystal with 12 nearest neighbors). If the energy calculated in the effective medium is a good approximation, then the energy of the atom in the real system can be solved using perturbation methods. The full treatment of this concept is given in [3]:

$$E = \sum_i E_{c,i}(s_i) + \Delta E_{AS}(i) + \Delta E_{1el}, \quad E_{c,i}(s_i) = E_o f[\lambda(s_i - s_o)], \quad f[x] = (1 + x) \exp(-x)$$

$$s_i = s_o - \frac{1}{\beta \eta_2} \log\left(\frac{\sigma_{1,i}}{12}\right), \quad \sigma_{1,i} = \sum_{j \neq i} \exp[-\eta_2(r_{ij} - \beta s_o)], \quad \Delta E_{AS}(i) = \frac{1}{2} \left[\sum_{j \neq i} V(r_{ij}) - 12V(\beta s_i) \right],$$

$$V(r_{ij}) = -V_o \exp[-\kappa \left(\frac{r_{ij}}{\beta} - s_o \right)], \quad B = \frac{-E_o \lambda^2}{12\pi s_o}, \quad C_{44} = \frac{s V_o \kappa \delta}{8\pi s_o}, \quad \delta = \beta \eta_2 - \kappa$$

Table 1: List of EMT Parameters

EMT	E_0	S_0	V_0	η_2	κ	λ	n_0
Parameters	(eV)	(bohr)	(eV)	(bohr ⁻¹)	(bohr ⁻¹)	(bohr ⁻¹)	(bohr ⁻³)
Ag	-2.96	3.01	2.132	1.652	2.79	1.892	0.00547
Pt	-5.85	2.9	4.067	1.812	3.145	2.192	0.00802

E is the total energy, $E_{c,i}(s_i)$ is the cohesive energy, $\Delta E_{AS}(i)$ is the atomic-sphere correction, and ΔE_{1el} is the one-electron correction, which has a functional form similar to $\Delta E_{AS}(i)$. The relevant EMT parameters for the remaining equations are given in Table 1, where S_0 is the lattice constant, E_0 is the negative cohesive energy, λ is derived from the bulk modulus B , and $V_0\delta$ is determined from the shear modulus C_{44} . A ratio of V_0/δ is chosen such that calculated heats of formation and heats of solution are in reasonable agreement with measured experimental values.

Simulations of octahedral PtAg NPs were carried out using standard MC swaps of Ag and Pt atoms positions and energy calculations from EMT potentials. PtAg alloy clusters (331 and 670 atoms) were generated by placing Ag atoms (red) randomly within an FCC Pt (blue) octahedron NP (Fig. 1a,b). A quasi-Newton energy minimization was first carried out prior to MC stepping such that the forces on all atoms, calculated using EMT, are less than 1 eV/bohr. MC steps were then carried out, which involved calculating initial potential energy using EMT, randomly selecting both an Ag and a Pt atom, swapping the 2 atomic positions, and calculating a new potential energy using quasi-Newton minimization and EMT. Detailed balance was satisfied using the Metropolis criterion, which accepted or rejected Ag-Pt atom swaps according to Boltzmann statistics at $T = 1073$ and 573 K. This process was carried out for 3-6X (MC sweeps) the number of Ag atoms (12, 46, 60, and 116) to reach a stable energy configuration (Fig. 1,c) while Pdb files were written for animation (Caption 1). Afterwards, additional MC moves were carried to record statistics for radial distributions of Pt and Ag atoms within the cluster. Histograms were computed every MC sweep, and the calculated results are plots of atom fraction profiles (Fig. 2) and normalized radial distribution profiles (Fig. 3).

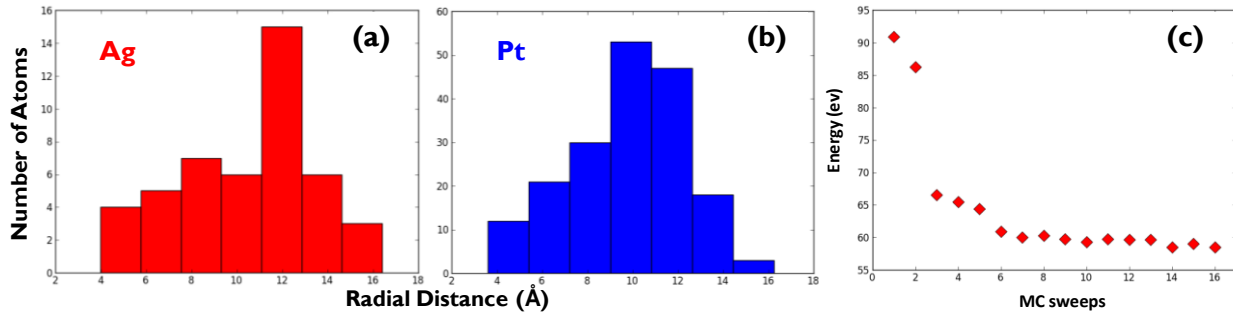


Figure 1. Histograms showing random initial positions of (a) Ag and (b) Pt atoms within an octahedral FCC cluster. (c) Energy stabilization as a function of MC sweeps.

Results and Conclusions

All simulations (i.e., 231 atom cluster with 5, 20, and 50% Ag atoms (Fig. 3); 630 atom cluster with 9% Ag atoms (Fig. 4)) resulted in Ag segregation at and near the surface of the octahedral NPs. For a 231 atom cluster with 5-50 Ag atom%, the atom fractions of Ag as a function of radial distance are highest for distances $> 6 \text{ \AA}$ ($\sim 43\%$ of the maximum distance, 14 \AA); by comparison, Pt fractions peak around $6-8 \text{ \AA}$ and drop off quickly afterwards (Fig. 3a-c). Clearly, Ag atom distributions are shifted to higher radial distances compared to Pt. These trends are further verified for a 670 atom cluster with 9 Ag atom% (Fig. 4a); Ag atom fractions are highest for distances $> 10 \text{ \AA}$, while Pt atom fractions drop-off after $\sim 12 \text{ \AA}$. This result is further emphasized by calculating a fractional or relative radial distribution function for Ag (Fig. 4b) and Pt (Fig. 4c) (i.e., $g_{\text{Ag}}(r) + g_{\text{Pt}}(r) = g(r)$). Ag atoms have a very small $g_{\text{Ag}}(r)$ before peaking around $\sim 12 \text{ \AA}$, while $g_{\text{Pt}}(0-23 \text{ \AA})$ for Pt atoms remain larger than the bulk $g_{\text{Pt}}(24 \text{ \AA})$ (It should be noted that $g(r)$ values are discrete and could actually drop below 1 at intermediate r values).

In conclusion, the MC method in combination with EMT potentials is an effective way to investigate the surface enrichment of PtAg alloy nanoparticles. Results of simulations were consistent with the notion that Ag is enriched at the NP surface. Moreover, Ag tended to occupy high energy corner and edge sites of the NP, which would have a dramatic effect on the catalytic reactivity. These observations are in good agreement with previous experimental results for C_2H_2 hydrogenation on $\sim 7 \text{ nm}$ octahedral NPs with sub-monolayer quantities of Ag.

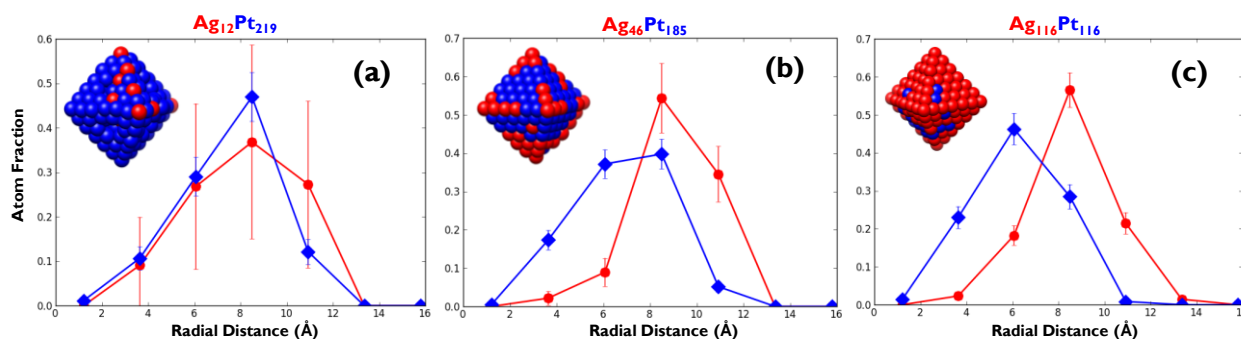


Figure 2. Ag and Pt atom fraction profiles for (a) $\text{Ag}_{12}\text{Pt}_{219}$, (b) $\text{Ag}_{46}\text{Pt}_{185}$, and (c) $\text{Ag}_{116}\text{Pt}_{116}$. Averages and errors are calculated by recording radial histograms at each MC sweep (3-6 total).

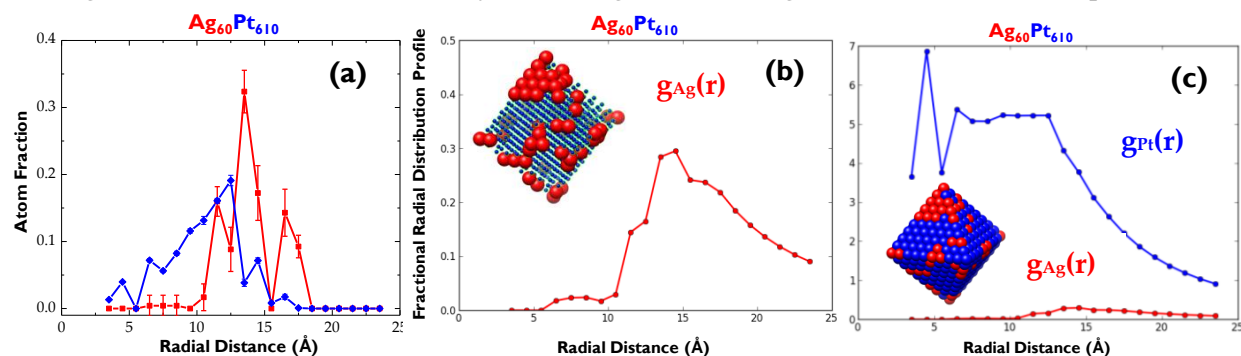


Figure 3. Ag and Pt atom fraction profiles for (a) $\text{Ag}_{60}\text{Pt}_{610}$ after 6 MC sweeps, and resulting fractional (relative) radial distribution profiles for (b) Ag ($g_{\text{Ag}}(r)$) and (c) Pt ($g_{\text{Pt}}(r)$) atoms.

References

- 1) V. Sundaram *et al.*, *Surf. Sci.* 52, 569 (1975)
- 2) J. Nørskov *et al.* *Surf. Sci.* 283, 277 (1993)
- 3) J. Nørskov *et al.* *Surf. Sci.* 366, 394 (1996)
- 4) L. C. Jones, Z. Buras, M. J. Gordon, *J. Phys. Chem. C*, Accepted
- 5) All packages included were from Atomic Simulation Environment (see attached files):
S. R. Bahn and K. W. Jacobsen, [An object-oriented scripting interface to a legacy electronic structure code](#), *Comput. Sci. Eng.*, Vol. 4, 56-66, 2002

Movie Caption

An MC + EMT simulation of Pt₁₁₆Ag₁₁₆ @ 1073 K, starting from an initially energy minimized random PtAg configuration, and proceeding through 3 MC sweeps. At each MC swap, energy minimizations are carried out to calculate the probability of the swap subject to the Metropolis criterion. The enrichment of Ag atoms (red) at the surface of the octahedral nanoparticle is evident and consistent with previous experimental observations.