

Fuel Chemistry Division Invited Paper
Spring ACS Meeting April 5-10, 1992, San Francisco, CA
last revision: January 9, 1992

COMPUTATIONAL APPROACH TO THE PREDICTION OF BIMETALLIC CLUSTERS

PREPRINTS OF THE FUEL CHEMISTRY DIVISION, ACS

Liqiu Yang, Todd J. Raeker, Ann M. Schoeb, Xi Wu,
Terry King and Andrew E. DePristo
Ames Laboratory, USDOE
Iowa State University, Ames, IA 50011

Keywords

structure of bimetallics; corrected effective medium theory; partial bond energies

Abstract

The catalytic properties of bimetallic clusters will be influenced by the detailed structure of the cluster surface. Enrichment of one metal at the surface is one feature of obvious importance. Other, less obvious, features are preferential population of edge and corner binding sites on the surface and micromixing that influences ensemble size on the surface planes.

We review the range of methods developed to treat this problem, from the computationally demanding corrected effective medium (CEM) theory (a semi-empirical density functional based method) to the computationally simple method of partial bond energies. Parametrization of the latter is shown to be feasible using the former.

Comparisons of theoretical predictions with experimental data will be made for heats of formation in selected alloys and for surface segregation behavior in $\text{Rh}_{0.9}\text{Pt}_{0.1}(111)$. Detailed results on the shape, site composition and surface micromixing will be shown for selected systems chosen from $\text{Rh}_x\text{Pd}_{1-x}$, $\text{Ni}_x\text{Pd}_{1-x}$, and $\text{Rh}_x\text{Ni}_{1-x}$, $\text{Rh}_x\text{Pt}_{1-x}$ and $\text{Pt}_x\text{Cu}_{1-x}$ with $x=[0,1]$ for sizes between 200 and 1200 total atoms.

Introduction

The prediction of structure and energies of bimetallic clusters in the range of 200-2000 atoms provides an important technological problem for fundamental descriptions of metal-metal bonding. These systems are relevant to the performance of bimetallic catalysts¹ and also small enough to be treated by reasonably accurate theoretical density functional theory methods.²⁻⁴ They are also large enough to be treatable by empirical bonding models.⁵⁻⁷ Thus, such systems can provide an excellent testing ground for theoretical methods as well as demonstrate the utility of new theoretical methods in conjunction with rapidly advancing computer technology.

Theory

A hierarchy of theories have been used to describe bimetallics. We give a brief overview of each here. The reader interested in more details should consult the references, especially ref.(2d) for CEM, ref.(2c) for MD/MC-CEM and ref.(4) for construction of embedding functions in either theory. Applications to bimetallic

surfaces can be found in ref.(3). For the method of partial bond energies, the reader should consult refs.(5-7) for an overview.

For a set of N-atoms, $\{A_i, i=1, \dots, N\}$, the CEM theory utilizes the following equations to calculate the interaction energy:

$$\Delta E(\{A_i\}) = \sum_{i=1}^N \Delta E_{LMTO}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V_c(i, j) + \Delta G(\{A_i\}) \quad (1)$$

$$n_i = \frac{1}{2Z_i} \sum_{j=1}^N \int n(\vec{r} - \vec{R}_i) n(\vec{r} - \vec{R}_j) d\vec{r} \quad (2)$$

$n(\vec{r} - \vec{R}_i)$ is the unpolarized atomic electron density distribution (from Hartree-Fock calculations) while Z_i and \vec{R}_i are the atomic number and nuclear position, respectively. This equation is valid under the assumption that the total system electron density can be approximated as the superposition of atomic electron densities.

The first term is the sum of the embedding energy for each atom, *each term of which is solely a function of the average electron density environment of that particular type of atom*. The subscript 'LMTO' indicates that these are provided by forcing the CEM method to duplicate the results of self-consistent Linearized Muffin Tin Orbital density functional calculations on the cohesive energy of the homogeneous bulk solid at lattice constants from 30% expansion to 10% contraction.^{4a} Since these embedding energies are a major component of the system interaction energy, it is important to determine them accurately and this procedure does so, at least for coordinations approaching that of the bulk. For very low coordinations, it is necessary to supplement the LMTO calculated values with experimental data from the diatomic binding curve.^{4b}

The second term consists of pairwise additive coulombic energies. $V_c(i, j)$ is the sum of electron-electron, electron-nuclear and nuclear-nuclear coulomb interactions between atoms A_i and A_j . These are determined from the electron densities of each atom and are not adjustable.

The last term, ΔG , is the difference in kinetic-exchange-correlation energies of the N-atom and atom-in-jellium systems. It is a true many body term which is extremely time consuming computationally since it involves computation of a three dimensional multicenter integral of complicated functions of both the electron density and its gradient with respect to electronic coordinates.

To lower the computational effort, a simpler theory has been developed with acronym MD/MC-CEM since it is fast enough to use in direct MD and MC simulations of large systems. In this method, the ΔG term is approximated as a function of n_i and incorporated into new effective embedding terms. This yields the working equation as:

$$\Delta E(\{A_i\}) = \sum_{i=1}^N \Delta F_{LMTO}(A_i; n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N V_c(i, j) \quad (3)$$

The effective embedding functions, ΔF_{LMTO} are determined again from LMTO calculations on the homogeneous bulk system.

The above two methods involve continuous change in interaction energies with separations between atoms. Neither is pairwise additive, and thus describes the delocalized bonding in metals. The CEM method can be derived from the fundamental density functional theory under the assumption of additive atomic densities. The MD/MC-CEM method is more empirical, depending upon a rather uncontrolled approximation to the kinetic-exchange-correlation energy difference energy. This method is very similar to the EAM method which simply postulates a form like Eq.(3) and replaces all terms by empirical forms. (e.g. Morse potentials or shielded coulomb like terms for the two body interactions).^{8,9} The EAM approach also utilizes the density at the nucleus of atom A_i instead of the average in Eq.(2), to identify a jellium density.

We have also utilized a much simpler formulation than either CEM theory. This calculates the energy of an atom by counting the bond energies with each of its nearest neighbors, adjusting the strength of each bond according to the number of neighbors. This is the method of partial bond energies and leads to the working equation for a system of one atom type:

$$\Delta E ([A_i]) = \sum N_i \epsilon (A_i ; N_i) \quad (4)$$

where $\epsilon(A_i; N_i)$ is the bond energy of atom A_i with N_i nearest neighbors. This equation must be supplemented with the interchange energy when there are different types of atoms.⁵ Note that bond lengths are not required in the application of this method because the interatomic potential is a function of coordination rather than distance. However, this approach does require the assumption that the metal particle maintains a fixed lattice type during the simulation. In the results reported below the simulations are fixed in an fcc lattice.

The connection between these methods is that the CEM theory can be used to provide the partial bond energies by using selected calculations on various metal surfaces and metal vacancy formation.¹⁰

Results and Discussion

First, consider the Rh_xPt_{1-x} system. The surface energies (in J/m^2) predicted by CEM (MD/MC-CEM) are 2.37 (2.73), 2.52(2.88) and 2.71 (3.12) for Rh(111), Rh(100), Rh(110), respectively.^{4a} Experimental data on surface free energies of polycrystalline samples¹¹ at the metal's melting point and at 298 K can be used to extrapolate to 0 K with the result being 2.94 J/m^2 . The agreement is excellent as it is for other fcc metals.^{4a} The CEM predictions of the alloy formation energy are -2.4, -2.2 and -1.7 kJ/mole for $x=0.75$, 0.5 and 0.25 respectively. Since Pt and Rh alloy even at low temperatures, this small negative alloy formation energy is very reasonable. The MD/MC-CEM method predicts 42.0, 53.3 and 39.1 kJ/mole, respectively, and is thus inaccurate for this system. Indeed, we have found that MD/MC-CEM is inaccurate for all mixtures of Ir, Pt and Au with all other metals, except Ir,Pt and Au.

Using CEM calculations of the various Pt and Rh systems yields the partial bond energies shown in Fig.(1). For comparison, partial bond energies using a quadratic fit to limited experimental data are also shown. The agreement is quite good except at very low coordinations where the previous approach involves extrapolation.

Predictions of the surface fraction of Rh in Rh_xPt_{1-x} bimetallics cluster with 201 total atoms is shown in Fig.(2) based upon Monte-Carlo simulations at 973 K. These

are calculated using the partial bond energies assuming that the cluster retains a fcc lattice arrangement of atoms. Even though these simulations allow the structure of the particle to deviate from the initial cubo-octahedral shape, no such morphology change occurs due to the thermodynamic stability of that arrangement. The one point from the CEM results is also shown. Since the latter allows for continuous deformation of all atomic positions, it provides confidence that the use of the partial bond energy/Monte-Carlo simulation with an fcc lattice is adequate for this system.

Next, consider the Rh_xPd_{1-x} system. The surface energies (in J/m^2) predicted by CEM (MD/MC-CEM) are 1.63 (1.89), 1.74(2.00) and 1.87 (2.18) for Pd(111), Pd(100), Pd(110), respectively.^{4a} Experimental data on surface free energies of polycrystalline samples¹¹ at the metal's melting point and at 298 K can be used to extrapolate to 0 K with the result being $2.17 J/m^2$. The agreement is again excellent. The CEM predictions of the alloy formation energy are 1.5, 1.9 and 1.5 kJ/mole for $x=0.75$, 0.5 and 0.25 respectively. The experimental value¹² at 1575 K is 10 kJ/mole with the difference from 0 K easily made up by variation in heat capacity. The MD/MC-CEM method predicts 2.2, 2.9 and 2.2 kJ/mole, respectively, and is thus quite acceptably accurate.

Results for 201 and 1289 atom clusters are shown in Figs.(3) and (4), respectively. The clusters exhibit increased enrichment of Pd on the surface and a substantial favoring of edge-corner sites at the surface. Thus Pd atoms occupy low coordination sites on the surface. There is only a slight temperature dependence of the enrichment between 600 K and 1000 K.

In the Ni_xPd_{1-x} and Rh_xNi_{1-x} clusters (not shown), the metal segregating to the surface is Pd for the former and Ni for the latter. From these and other systems, a few general statements can be made: 1/ the metal with the smallest surface energy segregates to the lowest coordination sites first, then to other low coordination sites; 2/ an increase in temperature drives the mixing and thus decreases the degree of segregation; and, 3/ as the size of the cluster increases, the surface-segregating metal populates the entire surface at lower total concentration.

Experimental verification of these predictions is problematic. Only surface composition measurements have been attempted leaving site population and micromixing properties to speculation. The standard surface science tools such as Auger electron spectroscopy (AES) are not feasible due to the very nature of the particles. In addition, traditional methods of estimating surface composition using selective chemisorption are known to significantly perturb these bimetallic systems.⁵ In certain simple systems a combination of 1H NMR and hydrogen chemisorption have indicated the predictions give reasonable results.¹³ We can apply the predictions to low-index plane simulations that are more easily verified experimentally, however. The fcc(111) surface of $Rh_{0.9}Pt_{0.1}$ was simulated with the partial bond energy/Monte Carlo method in the same manner as the 201 atom particle discussed above yielding the results in Fig.(5). Recently, Fisher and co-workers have used AES and ion scattering spectroscopy to determine that the surface composition of this system is $\approx 70\%$ Rh in the 1200 K temperature range,¹⁴ which is in good agreement with our predictions.

Acknowledgement

This work was supported by the Advanced Industrial Concepts Division of the U.S. Department of Energy through the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under Contract No. W-7405-Eng-82. The more extensive CEM calculations were performed on the nCUBE 2 hypercube at two different sites: 1) the Scalable Computing Laboratory, Ames Laboratory; 2) the Massively Parallel Computational Research Laboratory, Sandia National Laboratory at Albuquerque.

References

1. J. H. Sinfelt, Bimetallic Catalysts: Discoveries, Concepts and Applications, John Wiley & Sons, (1983).
2. a) J. D. Kress and A. E. DePristo, *J. Chem. Phys.* **88**, 2596 (1988);
b) J. D. Kress, M. S. Stave and A. E. DePristo, *J. Phys. Chem.* **93**, 1556 (1989);
c) M. S. Stave, D. E. Sanders, T. J. Raeker and A. E. DePristo, *J. Chem. Phys.* **93**, 4413 (1990);
d) T. J. Raeker and A.E. DePristo, *Int. Rev. Phys. Chem.* **10**, 1 (1991).
3. a) T. J. Raeker, D. E. Sanders and A. E. DePristo, *J. Vac. Sci. Tech.* **A8**, 3531 (1990);
b) T. J. Raeker and A. E. DePristo, *Surf. Sci.* **248**, 134 (1991);
c) T. J. Raeker and A. E. DePristo, "Alloy formation energetics and dynamics in the Ni/Cu(100) and Ni/Cu(111) systems," *J. Vac. Sci. Tech.* **A** (in press, 11/91).
4. a) S. B. Sinnott, M. S. Stave, T. J. Raeker and A. E. DePristo, *Phys. Rev. B* **44**, 8927 (1991);
b) D. E. Sanders, D. M. Halstead and A. E. DePristo, "Metal/metal homo-epitaxy on FCC(111) and FCC(001) surfaces: deposition and scattering from small islands," *J. Vac. Sci. Tech.* **A** (in press, 12/91).
5. T. S. King, "Bond Breaking and Chemical Thermodynamic Models of Surface Segregation," in Surface Segregation Phenomena, eds. P. A. Dowben and A. Miller, CRC Press (1990).
6. X. Wu, S. Bhatia and T. S. King, "Characterization of Small Metal Particles," *J. Vac. Sci. Tech.* **A** (in press).
7. J. K. Strohl and T. S. King, *J. Catal.* **118**, 53 (1989).
8. C. L. Liu, J. M. Cohen, J. B. Adams and A. F. Voter, *Surf. Sci.* **253**,334 (1991).
9. a) M. S. Daw and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1984);
b) S. M. Foiles, M. I. Baskes and M. S. Daw, *Phys. Rev. B* **33**, 7983 (1986);
c) T. Ning, Q. Yu and Y. Ye, *Surf. Sci.* **206**, L857 (1988);
d) M. S. Daw, *Phys. Rev. B* **39**, 7441 (1989).
10. T. J. Raeker, L. Yang, A. M. Schoeb, X. Wu, T. S. King and A. E. DePristo, (to be submitted).
11. L. Z. Mezey and J. Giber, *Jap. J. App. Phys.* **21**, 1569 (1982).
12. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys (American Society for Metals, Metals Park, OH, 1973).
13. X. Wu, B. C. Gerstein and T. S. King, *J. Catal.* **121**, 271 (1990).
14. a) G. B. Fisher and C. L. DiMaggio, *Surf. Sci.* (submitted);
b) D. D. Beck, C. L. DiMaggio and G. B. Fisher (personal communication).

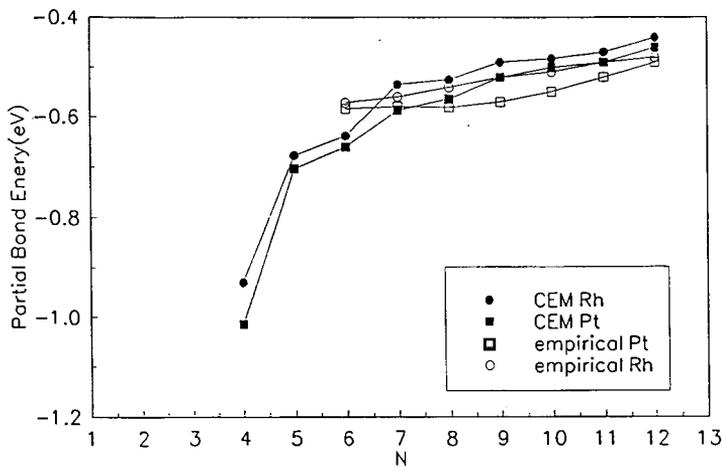


Fig. 1 Partial bond energies for Pt and Rh as determined from CEM calculations and also from previous work using a quadratic form (in N) fit to surface energies.

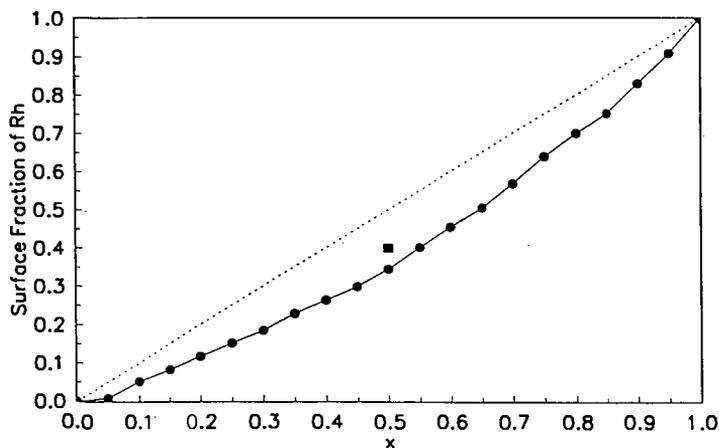


Fig. 2 Surface fraction of Rh in $\text{Rh}_x\text{Pt}_{1-x}$ clusters with 201 total atoms as predicted by the partial bond energy model at 973 K. A single point for $x=0.5$ (■) is shown based upon a full CEM simulation at 600 K. The dotted line separates enrichment (above) and depletion (below) regions.

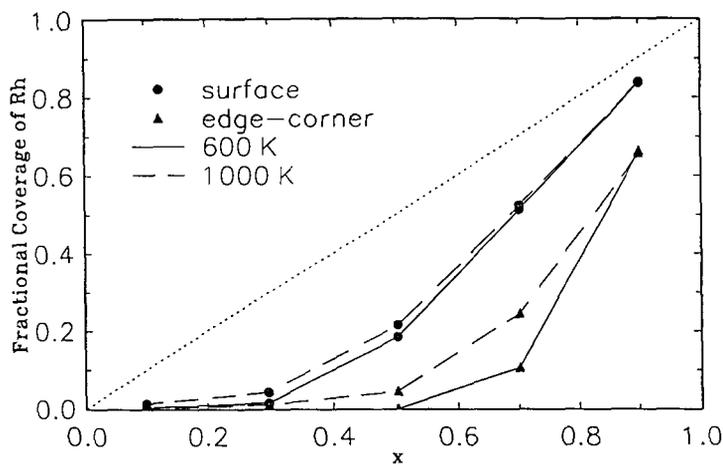


Fig. 3 Fractional coverage of Rh at surface and edge-corner sites in $\text{Rh}_x\text{Pd}_{1-x}$ clusters with 201 total atoms as predicted by the MD/MC-CEM model.

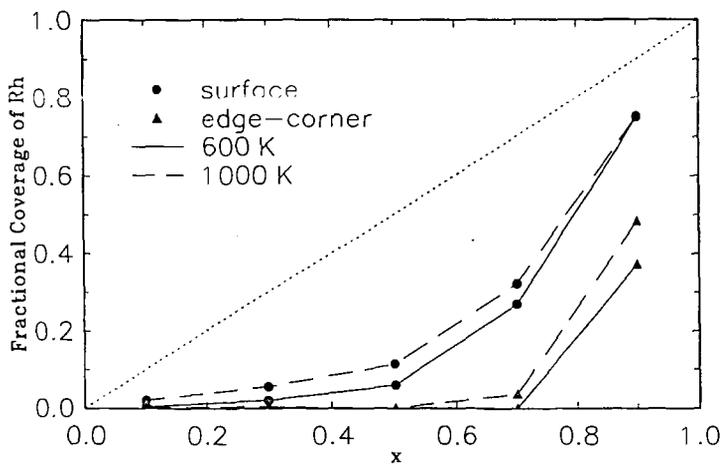


Fig. 4 Same as Fig.(3) but for 1289 total atoms.

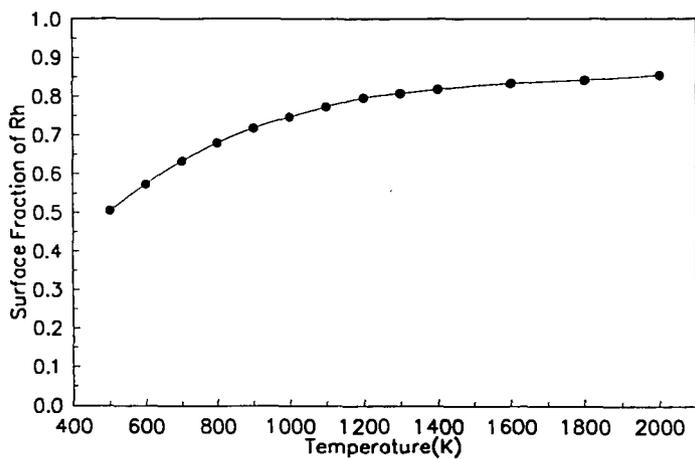


Fig. 5 Surface fraction of Rh in $\text{Rh}_{0.9}\text{Pt}_{0.1}$ (111) as predicted by the partial bond energy model.