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First-principles Study of PdAu Segregation with CO Coverage

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ABSTRACT

Alloying has been one of the strategies to develop alternatives to Pt based CO oxidation catalyst. PdAu bimetallic alloy has recently been shown to have better reactivity and thermal stability toward CO oxidation for diesel engine applications as compared to pure metal catalysts. The key factor for low temperature light off in diesel engine catalysis is reactivity of alloy catalysts under CO environment, which in turn depends on the alloy surface composition and morphology. We explored the segregation processes in bimetallic Pd-Au alloy using first-principles calculations, assisted by a Monte-Carlo (MC) scheme that combines an improved Embedded Atom Method (EAM) and an atomistic treatment for adsorbed CO molecules for searching low energy states. Our simulation results show that PdAu surface changes from Au-rich to Pd-rich with increase in CO coverage up to 0.75 ML, beyond which additional CO adsorption is no longer favorable. A quantitative relationship between CO coverage and Pd concentrations on the surface is also revealed.

INTRODUCTION

Bimetallic alloys have been widely used in electrochemistry and surface catalysis. A higher reactivity can be achieved by optimizing the additional engineering flexibility in bimetallic systems which are not readily accessible in pure metal catalysts. PdAu bimetallic alloy has recently attracted much interest due to their potential applications in aromatics hydrogenation and CO oxidation [1,2]. These alloys also show good stability towards sintering and oxidation. To understand their physical and chemical properties, many density function theory (DFT) calculations have been carried out to study catalytic performance of PdAu alloys. However, most of the studies focus on well ordered bulk phase PdAu alloy and under low CO coverage conditions [3,4]. A systematic investigation of CO adsorption patterns on PdAu and the adsorbate-induced segregation of PdAu is still lacking.

In order to gain insight into the CO adsorption processes and effects of CO molecules on PdAu bimetallic alloy segregation, we have performed DFT calculations and Monte-Carlo (MC) simulations to search for the ground states of PdAu alloy under different CO coverage conditions. Based on the simulation results, Pd concentration in the top layer gradually increases with CO coverage and reaches a monolayer at CO saturation coverage of 0.69 ML. The surface segregated Pd atoms come from either sub-surface layer or from deeper layers depending on the CO coverage. A quantitative relation between CO concentration and Pd surface concentration is observed.

COMPUTATIONAL METHODS

The DFT calculations were done using the Vienna Ab-initio Simulation Package (VASP) [5], where Kohn-Sham single-electron wavefunctions are expanded by a series of plane waves. The interactions between ions and valence electrons are described using the projected augmented wave (PAW) method with an energy cut off of 400 eV, at which the CO binding energies are converged to a few meV. We used the revised Perdew–Burke–Erzernhof functional (RPBE) functional, which produces good agreement with experimental adsorption energy values for a number of molecules on transition metal surfaces [6]. The CO binding energies were calculated as the difference in total energy between the optimized PdAu-CO complex and the sum of the energies of the optimized bare surface and gas phase CO molecules:

$$\Delta E = E_{total} - (E_{slab} + nE_{CO})$$

In order to probe complex CO equilibrium adsorption configurations at different CO coverages and adsorbate-induced segregation in PdAu alloy, we used a $(2\sqrt{3} \times 4)$ unit cell with 16 atoms per layer. The metal slab consists of four layers, with the bottom layer of the slab fixed in its crystallographic positions and the other atoms free to relax in all directions [7,8]. A $4 \times 4 \times 1$ k-point mesh was used to sample the Brillouin zone. A vacuum layer thickness of approximately 15 Å has been introduced to eliminate any image interactions. We consider the geometry fully relaxed when the force on each atom is less than 0.03 eV/Å.

Due to the complex nature of PdAu alloy morphology with CO adsorption and diffusion on the surface, we complement our DFT simulations with classical MC simulations to quickly search over the large configuration space. The total energy of the system in the MC simulations is a sum of energy of surface adsorbates and energy of the alloy substrate. Parameters for calculation of the CO adsorption energies were obtained from a set of DFT calculations that takes into account the effect of both local environment and lateral interactions. The energy of the metal substrate is calculated using an accurate Embedded Atom Method (EAM) potential that were shown to reproduce well PdAu alloy segregation energies. The parameterization of the EAM potential includes 33 unique configurations of PdAu slab with different composition ratios and the details can be found in Ref. [9]. For MC simulation of a $(2\sqrt{3} \times 4)$ unit cell, there are 96 binding sites for adsorbates; 16 atop, 16 fcc, 16 hcp sites, and 48 bridge sites. Except for the atoms in the bottom layer fixed at 1:1 composition ratio, other metal atoms in the slab are free to exchange with each other. To efficiently explore the configuration space of CO adsorption and locate the global minimum, we carried out MC simulations with the Metropolis algorithm [10] and a simulated annealing protocol [11]. The MC simulations used periodic boundary conditions and were run for ten million steps. Within each MC steps, ten trial steps of metal swapping and CO diffusion on the surface are carried out, respectively. The lowest lying energy states are recorded and verified with DFT calculations. Below, we discuss the ground states properties of PdAu alloy under different CO coverage.

RESULTS AND DISCUSSION

Zero Coverage Limit CO Adsorption on PdAu Alloy Surface

We first studied the adsorption properties of CO molecules under zero coverage limit conditions. Figure 1 shows different types of possible adsorption sites for CO on a PdAu(111) alloy surface. Besides the adsorption energy difference due to binding sites (top/bridge/fcc/hcp), the metal coordination on which CO molecules bind, also have considerable effects on the binding energy. The change of CO binding energy due to the underlying metal can be attributed to both ensemble effect or ligand effect [3]. However, it is hard to de-convolute the adsorption energy into these two contributions rigorously due to the complex morphology change induced by PdAu segregation. Instead, we took a local approximation that takes into account the change in CO binding energies due to different local environment. We found that the metal atoms that influence binding energy dominantly are those that either are directly bonded to CO molecule (black circles in Figure 1), or their nearest neighbors (grey circles in Figure 1). The different arrangements of metal atoms beyond that range, as well as metal atoms in the sub-layer, lead to small fluctuations of binding energies of related sites, usually less than 0.1eV. These fluctuations are neglected in the MC simulations. Table I enumerates the CO adsorption energy on PdAu(111) surface as a function of binding sites and local metal coordination. Within the RPBE functional, the most stable binding site for CO is a three-fold site involving three Pd atoms. The energy difference between fcc and hcp is less than 0.05 eV and we consider them to be isoenergetic. For top and bridge adsorption configurations, changing the bonding metal from Pd to Au leads to a reduction of adsorption energy by more than 1 eV. Neighboring metals also tend to influence the binding energies on the order of 0.4 eV. There is a systematic trend that as the number of neighboring Au atoms increase, there is a corresponding reduction in binding energy.

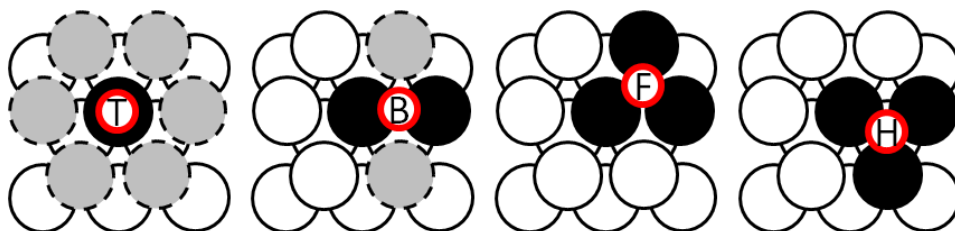


Figure 1. Red circles with labels indicate four types of CO adsorption sites : top(T), bridge(B), fcc(F) and hcp(H) on a PdAu(111) surface. Black circles represent the metal atoms involved in the adsorption site while grey circles represent neighboring metal atoms that influence the binding energy at the corresponding site. Circles indicate either Pd or Au atoms.

Table I. Calculated CO adsorption energies as a function of directly bonded metal atoms and neighboring metal atoms

Adsorption Geometry	Adsorption Site	Neighboring Metal Atoms	Binding Energy (eV)
top	Pd	6 Pd	1.35
	Pd	5 Pd, 1 Au	1.23
	Pd	4 Pd, 2 Au	1.20

	Pd	3 Pd, 3 Au	1.15
	Pd	2 Pd, 4 Au	1.12
	Pd	1 Pd, 5 Au	1.01
	Pd	6 Au	0.97
	Au	6 Pd	0.20
	Au	5 Pd, 1 Au	0.18
	Au	4 Pd, 2 Au	0.15
	Au	3 Pd, 3 Au	0.12
	Au	2 Pd, 4 Au	0.10
	Au	1 Pd, 5 Au	0.05
	Au	6 Au	0.00
bridge	Pd-Pd	2 Pd	1.63
	Pd-Pd	1 Pd, 1Au	1.52
	Pd-Pd	2 Au	1.47
	Pd-Au	2 Pd	1.05
	Pd-Au	1 Pd, 1Au	0.97
	Pd-Au	2 Au	0.80
	Au-Au	2 Pd	0.29
	Au-Au	1 Pd, 1Au	0.15
	Au-Au	2 Au	0.07
fcc/hcp	Pd-Pd-Pd	/	1.78
	Pd-Pd-Au	/	1.35
	Pd-Au-Au	/	0.73
	Au-Au-Au	/	0.10

It has been confirmed experimentally that average CO binding energy on transition metal surfaces decrease with increasing coverage, due to both through space repulsion and substrate mediated metal sharing effect [12]. Previous theoretical calculations indicate that CO molecules sitting on neighboring sites of platinum surface experiences roughly a repulsion of 0.3 eV [13]. We used the same parameters in Ref [13] to model CO lateral interactions in this study and found that the same CO repulsion functional produces reasonable agreement with DFT data.

Monte-Carlo Simulation of PdAu with CO Coverage

Figure 2 shows the ground states of PdAu alloy with different amount of CO coverage as determined by the MC and verified by DFT simulations. Due to the repulsion between CO molecules, adsorbates tend to form a relatively uniform distribution. The surface is Au rich under zero coverage because Au has lower surface energy and tends to segregate to surface. With CO coverage up to 0.5 ML, successive CO adsorption leads to Pd segregation to the surface. All CO molecules occupy a three-fold site with three Pd coordination, which are the most stable binding site. This is because the energy gained by switching CO adsorption from Au to Pd site is large enough to overcome the surface energy difference between Au and Pd. The total energies of the system as a function of CO coverage are plotted in Figure 3 (a). The red and blue curves indicate the contribution from CO adsorption and metal segregation, respectively. Since the surface energy of Au

is smaller than Pd, with every successively adsorbed CO and more Pd pulled to the surface, there is a corresponding increase in the energy of the metal substrate. A fit to the total binding energy curve yields an estimated energy gain for bringing out one Pd atom to the surface under this coverage range of around 1.0 eV. This indicates that adsorbate-induced segregation is strong in PdAu alloy. For CO coverage between 0.5 ML and 0.75 ML, the CO repulsion becomes more pronounced due to a more crowded surface. The thermodynamic driving force to bring out Pd atom reduces from 1.0 eV to 0.3 eV. It can be seen that thermodynamically, maximum CO coverage of PdAu can achieve 0.75 ML, where the surface layer is already a Pd monolayer. However, due to the significantly reduced driving force for Pd segregation under high CO coverage and the barrier for metal diffusion in the substrate, there might be kinetic barriers to achieving the 0.75 ML CO coverage. Our simulation also indicates the saturation coverage of CO cannot reach full monolayer. Beyond 0.75 ML, CO lateral repulsion makes additional CO adsorption no longer energetically favorable and turns the total energy trend around. Figure 3 (b) shows the concentration of surface Pd and sub-surface Pd versus adsorbed CO molecules. It can be noted that there is a compensation effect between surface concentration and sub-surface concentration, so that the Pd concentration in the first two layers roughly stays constant up to CO coverage of 0.5 ML. Beyond 0.5 ML, the concentration of sub-surface Pd atom reaches a constant of 0.25 ML and the surface segregation of Pd atoms comes from deeper layer in the slab. These calculations identify the correlation between the CO coverage and the morphology of the metal which is otherwise hard to determine experimentally.

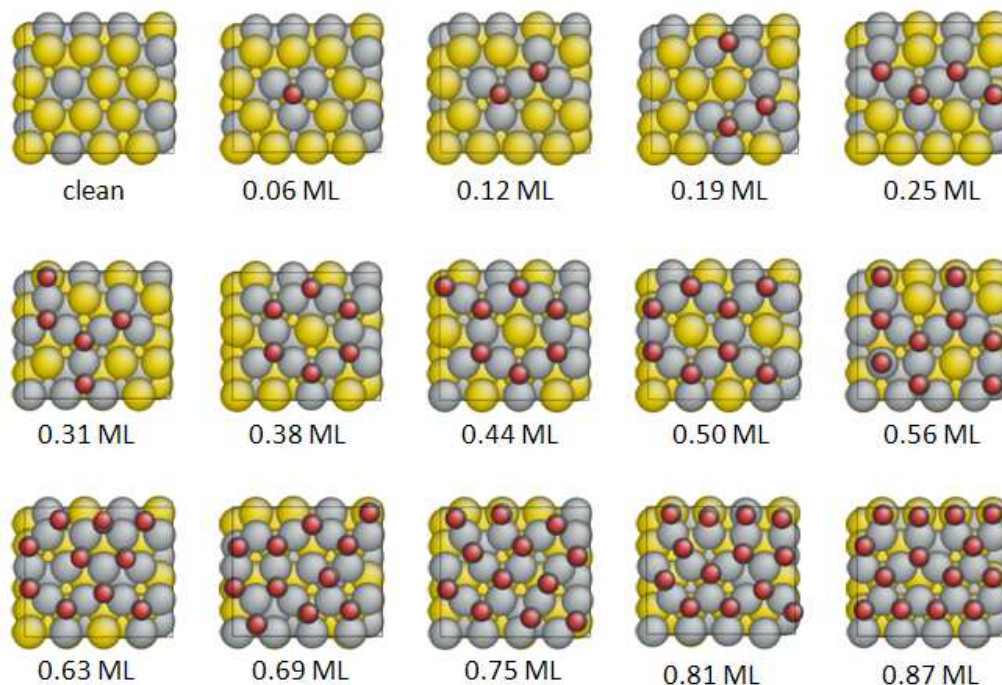


Figure 2. (a) Ground states of PdAu alloy with different amount of CO coverage obtained from MC simulations. Yellow atoms represent Au, light grey represent Pd atoms, dark grey represent carbon atoms and red represent oxygen atoms.

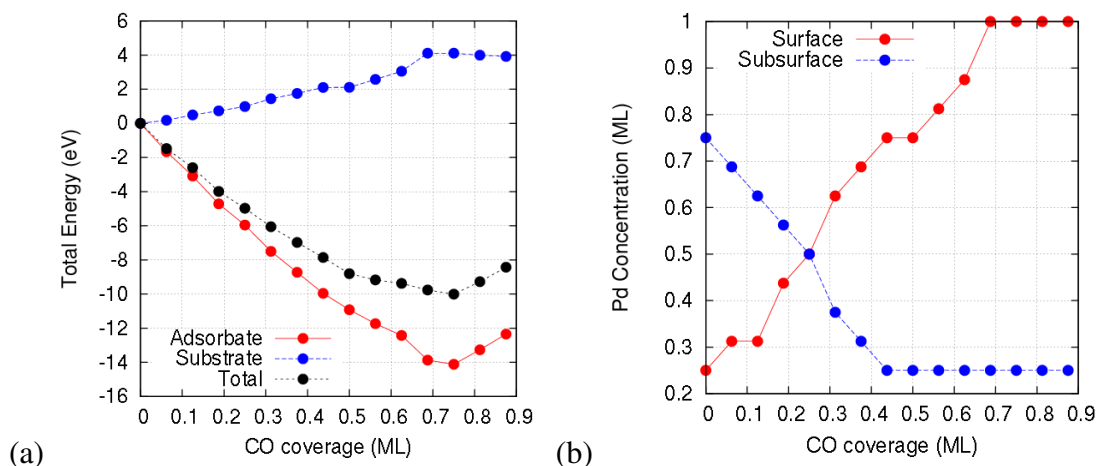


Figure 3. (a) Total system energy and the corresponding substrate and adsorbate energy as a function of CO coverage. (b) Surface and sub-surface Pd concentration as a function of CO coverage.

CONCLUSIONS

The segregation behavior of PdAu bimetallic alloy under different CO coverage conditions is studied by DFT calculations and Monte-Carlo simulations. It is shown that PdAu alloy transitions from Au-rich surface to Pd-rich surface with increasing CO coverage. The maximum CO coverage is 0.75 ML and the corresponding surface is a Pd monolayer. Our simulation also reveals a quantitative relationship between the CO coverage and the concentration of Pd atoms in the surface and sub-surface layer.

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