Elucidating and Predicting the Chemisorption Properties on Catalytic Alloy Surfaces. Applications to PdAu Alloys

Craig Plaisance[1] and Matthew Neurock[1]*
[1]*University of Virginia, Charlottesville, VA 22903*
*mn4n@virginia.edu

Introduction

It is well-established that alloying can lead to significant improvements in the activity as well as the selectivity for various catalytic systems than either metal alone [1]. Alloys of palladium and gold, for example, are known to be active and selective catalysts for a number of reactions including vinyl acetate synthesis as well as alkene and alkyne hydrogenation. The effects of alloying can systematically be broken down into ensemble, ligand, and lattice effects. Ensemble effects describe interactions between an adsorbate and metal atoms of the ensemble that it is directly bound to – as the composition of the ensemble changes, so does the binding energy. Ligand effects describe the influence of metal atoms neighboring the adsorption site and are weaker than ensemble effects. Lattice effects describe the change in binding energies due to strain induced by the expansion or contraction of the underlying lattice as its composition changes. Although much work, both experimental [2] and computational [3], has been performed relating to alloy surfaces, there is still a lack of understanding of the atomic-level fundamentals of how specific alloy surfaces and ensembles interact with specific adsorbates.

Methods

We have used density functional theory (DFT) calculations carried out using the Vienna ab-initio Simulation Package [4] to follow the changes in binding for simple adsorbates containing hydrogen, carbon, nitrogen, and oxygen for changes in the Pd/Au alloy compositions and configurations. The adsorbates include C, CH, CH_2, CH_3, CH_3C, CH_3CH, CH_3CH_2, CN, CO, H, N, NH, NH_2, NO, O, and OH which demonstrate different characteristic modes and sites for adsorption. The atop, bridge, fcc-hollow, and hcp-hollow adsorption sites were considered for all of the adsorbates considered. Ensemble and ligand effects were studied by replacing one or more Pd atoms in the top two layers of the slab with Au. Calculations were first carried out on a periodic four layer slab with the metal atoms frozen to their positions in the optimized Pd(111) slab and the adsorbates allowed to fully relax. A second set of calculations was then carried out where the top two layers of the slab also allowed to relax. This was done to deconvolute the electronic alloy effects from the geometric alloy effects.

Results and Discussion

Ensemble effects were found to be the largest of the three alloy effects, with the binding energy becoming weaker by 0.25 – 1.40 eV for each Au atom incorporated into the ensemble. The magnitude of the ensemble effect was found to be greater for binding sites with higher coordination numbers and decreases as substituents are added to the adatom of the adsorbate. Surface ligand effects were significantly weaker, with the binding energy weakening by less than 0.28 eV for each Au atom substituted into the surface layer. Subsurface ligand effects were weaker still, with the binding energy weakening by less than 0.09 eV for each Au atom substituted into the subsurface layer.

It was found that the ensemble and ligand effects for systems containing more than one Au atom are very well approximated by a pair-wise model. The model takes the form

$$E = E_{Pd} + \sum_{i}^{Au} \Delta E_i^{Ens} + \sum_{i} \sum_{j}^{Au} \Delta E_{i,j}^{Lig}$$

The first sum is over all Au atoms in the ensemble (those metal atoms that are directly bound to the adsorbate) and accounts for the ensemble effects. In the second sum, the index *i* runs over all metal atoms in the ensemble and the index *j* runs over all Au ligands that are nearest neighbors of atom *i* – this term accounts for the ligand effects. The maximum deviation of this model from DFT results was 0.04 eV.

When the surface was allowed to relax, the metal atoms of the ensemble relaxed outwards for bridge and three-fold sites with Au atoms moving more than Pd atoms. Additionally, Au atoms moved out of the surface by 0.06 – 0.07 A. Surface relaxation was found to decrease the magnitude of the ensemble effects. This occurred because Au atoms in the ensemble relaxed more than Pd atoms, leading to a higher relaxation energy for ensembles with more Au atoms. These results for the ensemble effects also fit the pair-wise model well.

The effects of surface relaxation on ligand effects was complicated and did not display any obvious trends. These results did not fit the pair-wise model as well as the frozen-surface calculations, especially for the subsurface ligand effects. When replacing the entire subsurface layer with Au, the binding energies became weaker by up to 0.36 eV. However, when replacing only on subsurface atom with Au, the binding energies did not show a clear trend of becoming weaker or stronger. This may occur because the surface layer buckles upwards when an Au atom is placed below it - this buckling causes a local expansion of the surface layer, resulting in a strengthening of binding energy which cancels out the weakening of the binding energy due to electronic ligand effects.

Significance

A quantitative understanding of how the composition and the specific atomic configuration of specific surface alloys and ensembles influence chemisorption properties and reactivity will provide important insights as to how alloys influence catalysis and how they may be designed to enhance catalytic performance. This study provides fundamental understanding to these effects and suggests an accurate coarse-grained chemical model that can be employed in ab initio based kinetic Monte Carlo simulations of catalytic performance.

References

1. R.A. van Santen, M. Neurock, "Molecular Heterogeneous Catalysis", Wiley, Weinheim (2006).
2. M. Chen, D. Kumar, C.-W. Yi, D.W. Goodman, *Science* 310 291 (2005).
3. V. Pallassana, M. Neurock, *J. Catal.* 191 301 (2000).
4. G. Kresse, *Phys. Rev. B* 54 11169 (1996).