

ELUCIDATING CATALYTIC REACTION PATHS ON ALLOY SURFACES

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Summary

Density functional theory was used to study the effects of Pd/Au surface alloy composition on the reaction energies and activation barriers for a range of different hydrocarbon conversions. The direct effects of active site composition on adsorption and reaction energies and transition state energies were examined as well as indirect effects resulting from the modification of lateral adsorbate interactions by alloy induced changes in surface coverage. The direct effects are separated into contributions from the adsorption ensemble, the ligands of the adsorption ensemble, and the modification of the lattice constant by bulk composition. A model based on pair-wise interactions is proposed to parameterize these effects.

Keywords

Computational Catalysis

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 The composition of the surface affects both reaction energies and activation barriers by altering the way species bind to the surface. The effects of alloying on binding energies 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. In addition to direct effects on reaction and activation energies, the composition of the surface can indirectly affect these by modifying the coverage of other adsorbates on the surface, leading to changes in adsorbate-adsorbate interactions. For example, it is believed that addition of Au to a Pd catalyst for the synthesis of vinyl acetate monomer enhances the activity by reducing the surface coverage to allow ethylene to adsorb and react.² Although much work, both experimental³ and computational,⁴ 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 and transition states and how this modifies lateral interactions between adsorbates.

This work examines the effect of composition of a Pd/Au alloy surface on the binding energies of adsorbates and transition states, decomposing them into contributions

from the ensemble, the ligands, and the underlying lattice. Lateral interactions between adsorbates are also examined for different surface configurations. Simple adsorbates composed of carbon, nitrogen, oxygen, and hydrogen were studied which demonstrate different characteristic modes and sites for adsorption. Reactions relevant to the synthesis of vinyl acetate monomer were examined. A pair-wise model is proposed to parameterize these alloy effects and a framework is developed to determine reaction rates from the energies of different surface configurations.

Methodology

The Vienna ab-Initio Simulation Package⁵ was used to calculate the energies of adsorbates and transition states on the metal surfaces. The computational details are given in reference⁶. The nudged elastic band method⁷ was used to find a rough estimate of the minimum energy pathway and estimate the structure of the transition state which was further refined using the dimer method.⁸

Results and Discussion

The effect of ensemble composition was studied on the binding energies of adsorbates bound to atop, bridge, and fcc/hcp three-fold sites by sequentially substituting Au atoms for Pd atoms in the ensemble. The 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 for an atom in the adsorption ensemble correlated with the strength of the bond between the adsorbate and that atom. The more

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bonds an adsorbate atom formed with the surface, the weaker each individual bond became and the ensemble effect became weaker. Adsorbates with more substituents formed weaker bonds to the surface and were also more weakly affected by ensemble composition.

In most cases, substituting surface Pd atoms adjacent to the adsorption site with Au atoms resulted in a weakening of the binding energy of the adsorbate. These surface ligand effects were significantly weaker than the ensemble effects, with the binding energy weakening by less than 0.28 eV for each Au atom substituted into the surface layer. Replacing subsurface ligands with Au also led to a weakening of the binding energy, however, these 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.

These same observations hold for the effect of alloy composition on the binding energies of transition states to the surface. The active sites for reactions lack the symmetry of the simple adsorption sites, so a different value of the ensemble effect is associated with each non-equivalent surface atom in the ensemble. For each of these non-equivalent surface atoms, a type of scaling relationship can be determined between the change in reaction energy and the change in activation barrier. If the scaling constant is similar for all the metal atoms in the active site, then a Bronsted-Evans-Polanyi relationship will accurately relate the activation barrier to the reaction energy.

It was found that in the absence of surface relaxation, the ensemble and ligand effects for adsorbates and transition states 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. Adsorbate induced surface relaxation leads to more complicated nonlinear effects and is difficult to model with a simple expression.

The effect of alloy composition on surface coverage and lateral interactions was also studied. The method of ab-initio thermodynamics [ref] was used to determine the free energy of adsorbate configurations on surfaces with different Pd/Au compositions. The method was extended to also determine the free energy of configurations involving a transition state structure. The activation free energy barriers are used to calculate reaction rates, enabling the deterministic study of reaction kinetics on complex surfaces without resorting to a mean-field approximation.

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