

# FINAL TECHNICAL REPORT

**Project Title: First Principles Investigations for the Ensemble Effects of PdAu and PtAu Bimetallic Nanocatalysts**

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## RESEARCH OBJECTIVES

Heterogeneous nanocatalysts with particles a few nanometers in size hold great promise because of their large surface area ratios, the availability of enormous of active sites and enhanced resistance against poisoning. To rationally design and massively fabricate highly efficient yet low cost nanocatalysts, however, there are key fundamental challenges (1) how to control the shape, size, separation and surface morphology of nanostructures; (2) how to improve their thermal stability and durability; and (3) how to optimize the constituents and fabrication conditions for preeminent catalytic performance. Many synergistic studies indicate the usefulness of density functional calculations for understanding of catalytic properties of bimetallic surfaces for practical chemical reactions. The proper arrangement of active constituents is crucial towards attaining excellent selectivity and reactivity from bimetallic catalysts.

The main objective of our research is to establish fundamental concepts of nanoparticle formation and catalytic performance, which are useful for the improvement of experimental and industrial procedures. In the next phase, we focused on the chemical properties of FePd, PdAu and PtAu bimetallic surfaces and nanoclusters that have unprecedented features for catalysis applications. Along with experimental efforts of collaborators, we systematically calculated several model reactions and identified the key factors that govern reaction rates. In addition, our theoretical studies provided suggestions for the control of reaction dynamics at the atomic/electronic level.

## Project Results and Implications

Our results were summarized in 14 publications in international journals, as listed below. In addition, we presented these results in APS meetings, international conferences and other institutions.

### Formation of Pd second neighborhoods on PdAu surfaces and clusters

Although the presence of different ensembles can be inspected using the scanning tunneling microscope (STM), very few atomic resolution images have been reported. More often, the existence of different ensembles are probed with ethylene, CO and H, using various surface sensitive techniques such as infrared reflection absorption spectroscopy (IRAS) and temperature programmed desorption (TPD). It is known that Au tends to segregate toward bimetallic surfaces with transition metals even at moderate temperatures due to differences in their surface energies. However, the distribution morphology of PdAu surfaces appears to be rather complex. For example, contradicting results were reported for PdAu(111), including the ordered surface alloy phase, the Pd overlayer on Au(111), and random Pd-Au(111) alloy surfaces with varying Pd ensembles. From STM images and infrared data, Behm and coworkers concluded that the critical ensemble for CO adsorption on PdAu(111) is Pd monomer. This conclusion was supported by the extensive work of Goodman's group<sup>Error! Bookmark not defined.</sup>; they found only one feature at 2087 cm<sup>-1</sup> in the IRAS for CO/PdAu(111) when the sample is annealed up to 800 K.

To attain a clear understanding of ensemble formation on the PdAu(111) and PdAu(001) surfaces, we performed systematic density functional calculations. The thermal stability of different Pd configurations on the surface is characterized by the formation energy as

$$\Delta E_{Pd} = -[E_{PdAu} - E_{Au-slab} + N_{Pd}(E_{Au-bulk} - E_{Pd-atom})]/N_{Pd} \quad (1)$$

Here,  $E_{PdAu}$ ,  $E_{Au-surf}$ ,  $E_{Au-bulk}$  and  $E_{Pd-atom}$  represent the total energies of the PdAu surface, clean Au slab, bulk gold (per atom), and isolated Pd atom, respectively.  $N_{Pd}$  is the number of surface Pd atoms in the unit cell. As seen in Fig. 1 for a few selected surface ensembles on PdAu(111), our results explained the absence of nearest Pd neighborhoods since they produce lower formation energies. The Pd-Au bond is found to be slightly ionic, and is stronger than Au-Au and even Pd-Pd bonds. As a consequence, Pd atoms tend to take positions where the number of Pd-Au bonds maximizes. Although the disturbance of Pd substituent is effectively screened by the Au lattice, not much beyond its first neighborhoods in plots of charge density and density of states, the formation of second neighbor Pd ensembles is slightly preferential compare to isolated Pd monomers.

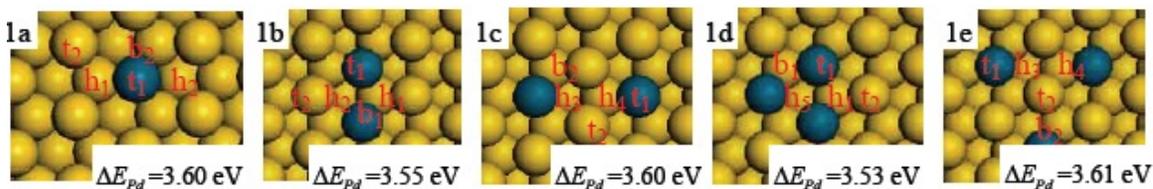


FIG. 1: The calculated formation energies of selected ensembles of Pd dopants (in blue or dark) in the surface layer of PdAu(111).

It is interesting to note that the potential energy surface of CO adsorption on the Pd second neighborhoods shows steep wells above Pd. Quantitatively, the CO adsorption energy is 1.1-1.3 eV on the Pd sites whereas it rapidly reduces to 0.3 eV on the adjacent Au sites from the density functional calculations for CO<sub>ad</sub>/PdAu(111). Therefore, surface Pd atoms serve as strong attractive centers for foreign adsorbates. The calculated CO stretch frequencies on ensemble 1a, 1c and 1e are very close, 2043-2056 cm<sup>-1</sup>, as compared to experimental value, 2087 cm<sup>-1</sup> (the deviation of 40 cm<sup>-1</sup> is caused by deficiency of DFT). Evidently, it is difficult to distinguish these three ensembles through TPS and IRAS with CO<sub>ad</sub> since it only interacts with one Pd atom underneath in the vertical adsorption geometry.

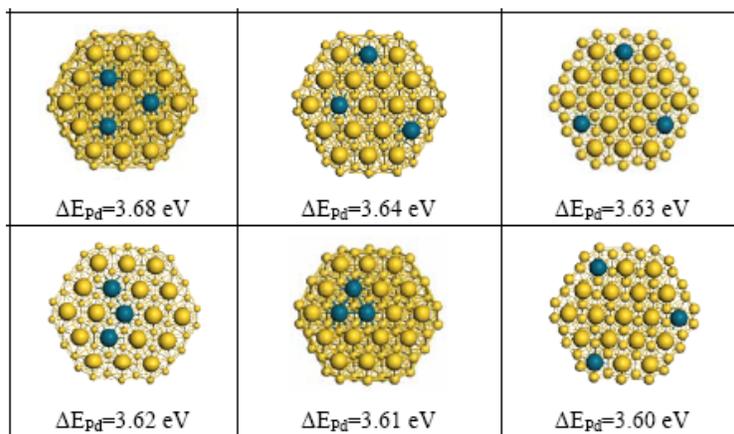


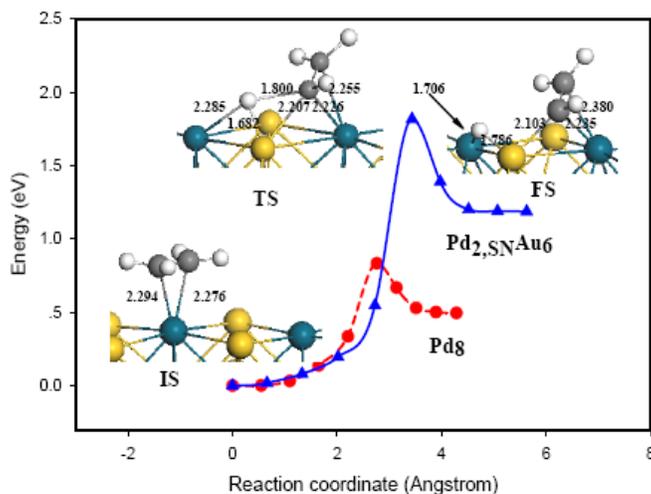
FIG. 2: The calculated formation energies of selected ensembles with three Pd dopants (in blue or dark) in the (111) facets of PdAu<sub>98</sub> cluster.

Furthermore, we have studied the distribution of Pd on the Au nanoclusters. Fig. 2 displays results of  $\Delta E_{Pd}$  for selected configurations with all atoms fully relaxed under the guidance of the calculated atomic forces. It appears that Pd atoms also prefer to form second neighborhoods at the centers of the Au(111) facets. Strikingly,  $\Delta E_{Pd}$  on the Au(001) facets (not shown here) are much smaller than those on the Au(111) facets, by as much as 0.08-0.13 eV per Pd atom. One may imagine that Pd atoms gather exclusively on the (111) facets of PdAu clusters under the thermal equilibrium whereas the (001) facets are left with pure Au. This is significant for catalysis since some reactions, e.g., VA synthesis, only occur on

the PdAu(001). To the same argument that Pd atoms prefer sites with more Au neighbors, they tend to avoid the edge and corner as found in our calculations. In different from PdAu surfaces, Au sites are also activated in PdAu nanoclusters due to the size reduction. For example, the CO adsorption energy enhances to 0.6-0.8 eV per CO molecule on Au and 1.5 eV on Pd of the PdAu<sub>98</sub> cluster.

What controls ethylene dehydrogenation on PdAu(001)?

Many chemical reactions involve the dehydrogenation of ethylene but the mechanism of this simple reaction is still elusive. Complete dehydrogenation of ethylene occurs easily on pure Pd surfaces, which results in the formations of Pd carbides on Pd surfaces or large Pd clusters. Although it was reported that the alloying of Au with Pd effectively prevents PdC<sub>x</sub> formation, it is unclear whether ethylene molecules partially decompose on PdAu. Clear understanding of ethylene dehydrogenation is essential to appreciating complex reactions such as VA synthesis. Through density functional calculations along with the Climbing Image Nudged Elastic Band (CI-NEB) approach, we addressed the consequence of lack of first Pd neighborhoods for the adsorption and dehydrogenation of ethylene on PdAu(001).



*Fig. 3. Reaction energy diagrams and atomic configurations for ethylene dehydrogenation on ensembles of Pd<sub>2,SN</sub> and Pd<sub>8</sub>. Some key bond lengths are given for initial state (IS), transition state (TS) and final state.*

As seen from Fig. 3, the activation energy for breaking the first C-H bond on a Pd second neighborhood (Pd<sub>2,SN</sub>) is extremely high, ~1.8 eV. In contrast, the corresponding energy barrier for this reaction on a Pd first neighborhood (Pd<sub>8</sub>) is only ~0.8 eV, even smaller than that on the clean Pd(001) surface, ~1.0 eV. The vinyl molecule and the eliminated H atom take the adjacent Pd-Pd or Pd-Au bridge sites in the transition and final states. Separate calculations indicated that the adsorption energies for hydrogen and vinyl on Pd-Pd bridge sites are, on

average, about 0.4 eV larger than those on Pd-Au bridge sites. The surge in activation energy on Pd<sub>2,SN</sub> stems primarily from an inability of this ensemble to provide sufficient attraction for vinyl and H in the transition state. Clearly, while ethylene can be dehydrogenated easily on Pd(001) and Pd first neighborhoods under the ambient condition, this reaction is likely prohibited on PdAu(001) where the Pd second neighborhoods are dominant. We also revealed a useful correlation among reaction energy, activation energy and adsorption energy.

#### *Origin of high activity and selectivity of PdAu(001) toward vinyl acetate synthesis*

The second neighbor ensembles on PdAu bimetallic surfaces may trap several reactants in a small region, necessary for imminent chemical reactions. Depending on whether ethylene dehydrogenates before or after its combination with acetate, two possible reaction pathways were proposed for VA synthesis: (i) ethylene is first dehydrogenated to vinyl species, which then couples with a coadsorbed acetate species; and (ii) ethylene inserts directly with acetate nucleophile to form an ethyl acetate-like intermediate which undergoes a  $\beta$ -H elimination afterwards. One of the most important consequences of the inactivity of PdAu(001) towards ethylene dehydrogenation is that one needs only focus on the second pathway for studies of VA reaction. The challenge is to determine why Pd second neighborhoods are more effective in catalyzing this reaction than Pd first neighborhoods, e.g., a Pd monolayer.

Our density functional calculations revealed that the activation energy for the formation of ethyl acetate-like intermediate on a Pd second neighbor pair is only 1.17 eV, as shown in Fig. 4. This modest barrier indicates that two Pd atoms in the Pd<sub>2,SN</sub> ensemble are already highly robust to facilitate the combination of ethylene and acetate nucleophile. This is in good agreement with experimental findings of Goodman et al. By contrast, the energy barrier for this reaction on Pd<sub>ML</sub>/Au(001) is 1.30 eV. This indicates that large Pd ensembles such as a Pd monolayer are unfavorable for VA production, because they bind to reactants “too” strongly. The adsorption energy of ethylene on Pd<sub>ML</sub>/Au(001) is 1.01 eV, even slightly larger than that on the clean Pd(001) surface, 0.94 eV. This overbidding makes reactants more difficult to adjust their orientations and positions for the subsequent reactions. Furthermore, VA molecules may easily take off from Pd<sub>2,SN</sub> with a small adsorption energy, 0.52 eV. In contrast, the adsorption energy of VA on Pd<sub>ML</sub>/Au(001) is 0.98 eV, which is expected to somewhat slow down the production of VA.

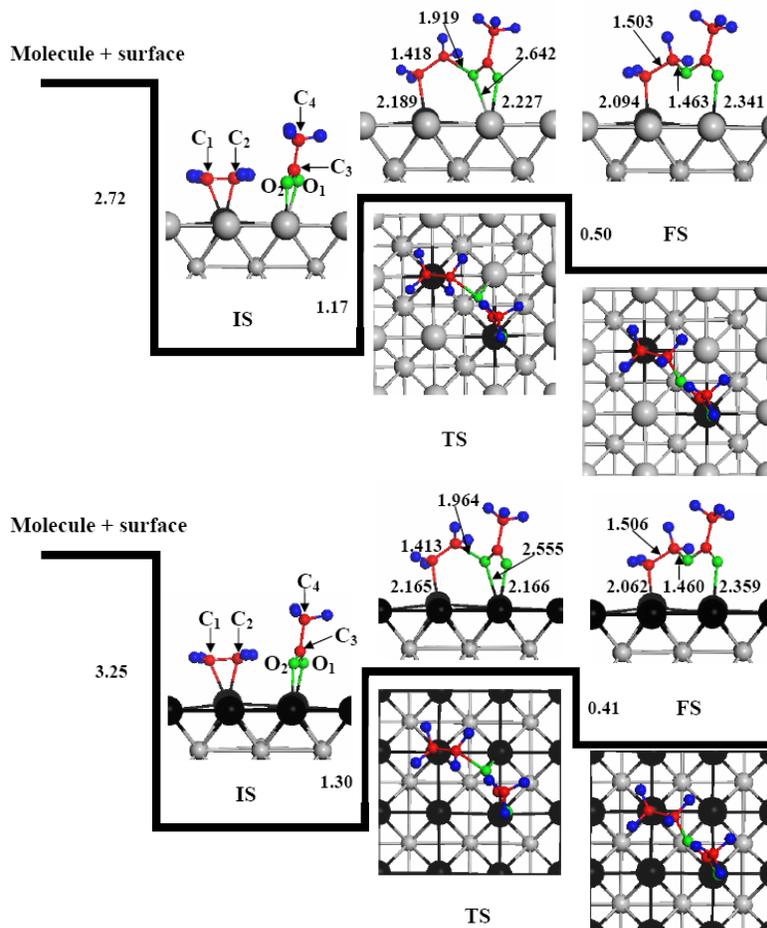


FIG. 4: Energies (in eV) and geometries of initial, transition, and final states for the coupling between ethylene and acetate on  $Pd_{2,SN}$  ensemble and Pd monolayer on the Au(001) surface. The key bond lengths (in Å) are inserted in positions nearby.

#### Decomposition of methanol on the PtAu(111) bimetallic surface

Direct methanol fuel cells (DMFC's) are ideal power sources for small devices such as cellular phones and laptops since they have low operating temperature, 50°C-120°C, and no requirement for a fuel reformer. The oxidation of methanol to hydrogen ions and carbon dioxide on anodes requires highly efficient catalysts. One important consideration for the design of new catalyst is how to rapidly reduce the  $CO_{ad}$  population, the product of methanol dehydrogenation, so as to maintain the activity of the reaction cycle. To this end, bimetallic catalysts may outperform the traditional Pt anode catalysts since their physical properties can be tuned using many parameters such as surface morphology, composition ratio and particle size.

We investigated two pathways for methanol dehydrogenation reactions on the PtAu(111) bimetallic surface. For the first pathways,  $CH_3OH \rightarrow CH_3O \rightarrow CH_2O$

→  $CHO \rightarrow CO$ , the activation energies for different reaction steps are 0.98 eV, 0.28 eV, 0.53 eV and 0.63 eV, respectively. These values are much larger than the corresponding energies on the clean Pt(111) surface are 0.81 eV, 0.25 eV, < 0.10 eV, and 0.23 eV. The major difference between Pt and PtAu catalysts is the existence of a sizable energy barrier for the decomposition of  $CH_2O$  on PtAu(111), 0.53 eV. This may bestow enough opportunity for direct oxidation of formaldehyde on PtAu(111) so as to avoid CO production. It is clear that the most difficult step is breaking the OH bond of methanol on both Pt(111) and PtAu(111). The imminent C-H scission from methoxy is very easy, with the activation energy as small as 0.28 eV. As a result, the reverse reaction  $CH_3O + H \rightarrow CH_3OH$  is unlikely to occur despite the fact that the energy barrier for this process is shallow, 0.22 eV.

For the second reaction path, the activation energies for reaction steps,  $CH_3OH \rightarrow CH_2OH \rightarrow CHOH \rightarrow COH \rightarrow CO$ , are 0.81 eV, 0.66 eV, 0.91 eV and 0.81 eV, respectively. The cleavage of H from CHOH appears to be the most difficult step. Although the activation energies for the rate limiting steps in the two paths are close, we would expect that the first reaction path prevails since it has only one major reaction barrier whereas the second path has three major barriers to overcome.

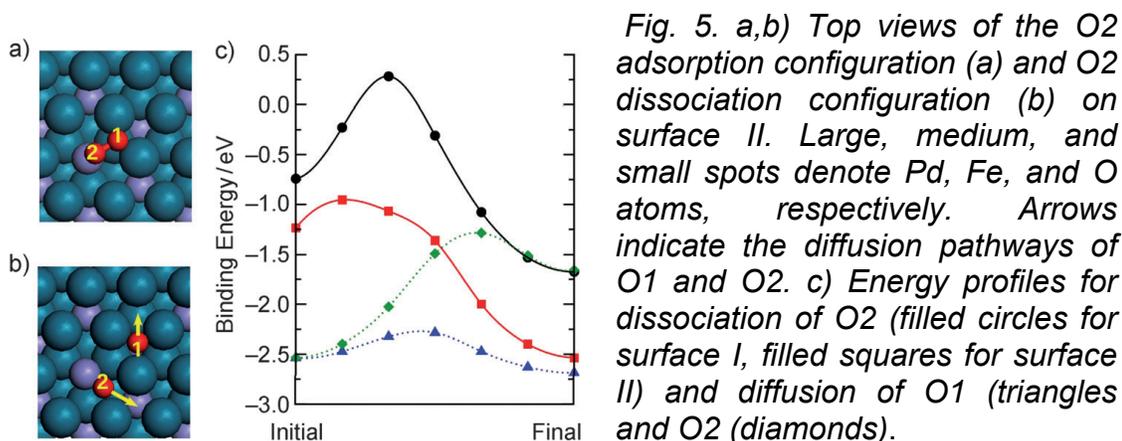
We also investigated  $CH_2OH$  dehydrogenation to  $CH_2O$ . The activation energy for this reaction is 0.96 eV, much higher than that for  $CH_2OH \rightarrow CHOH$ , 0.66 eV. Moreover, the reaction  $CH_2OH \rightarrow CH_2O$  is endothermic with a reaction energy of 0.38 eV. Therefore, it is unlikely that the two reaction paths will combine in the middle of the process.

### Catalytic performance of $Pd_3Fe(111)$ for oxygen reduction reaction

Observation and understanding of unusual surface structures of  $Pd_3Fe(111)$  are important for the exploitation of Pd-based alloys and efficient catalysts. Because of the small amount of Fe and large amount of Pd on the  $Pd_3Fe(111)$  surface, it is possible that a synergistic effect exists to take advantage of the capability of Fe sites for strong oxygen adsorption and dissociation and the capability of the Pd layer for fast removal of oxygen species by protonation. A strong correlation was found between the electrocatalytic activity with the surface Fe concentration, with the highest performance at approximately 10% Fe.

Development of improved cathode catalysts would be aided by a fundamental understanding of the ORR mechanism. The ORR systems are complex and ultimately require considering fully the effects of water, solvent ions, changing electrical potentials, and a detailed description of the composition and structure of all the chemical phases present at the electrode surface. As the first step, we performed DFT calculations to explore  $O_2$  adsorption and reaction on the flat  $Pd_3Fe(111)$  surfaces, with a complete Pd surface layer (no surface Fe, denoted as  $S_I$ ) or with 6.25% of surface Fe (denoted as  $S_{II}$ ). Our calculations (Figure 5)

show that after O<sub>2</sub> dissociation at the Fe site, one O atom can diffuse easily across areas with pure Pd (represented by the diffusion of O1) with a small energy barrier of 0.25 eV. In contrast, the barrier for the second O atom to diffuse away from the Fe atom (represented by the diffusion of O2) is as high as 1.25 eV. This high barrier may result in irreversible adsorption of an oxygen atom to the Fe site, causing site-blocking of further reactions. Intriguingly, this pre-adsorbed O atom does not hinder further O<sub>2</sub> dissociation at the corresponding Fe site at all, and the energy barrier for O-O bond breaking around the O-Fe site is 0.40 eV. Furthermore, the follow-up O diffusion out of the surface Fe region is significantly promoted, with the energy barrier decreasing from 1.25 to 0.75 eV. Therefore, partial covering of O atoms near surface Fe not only preserves high activity of O<sub>2</sub> dissociation but also enhances the O atom diffusion near surface Fe. This feature could balance the O<sub>2</sub> dissociation and O diffusion, so that the ORR process continues dynamically at a high rate.



*Fig. 5. a,b) Top views of the O<sub>2</sub> adsorption configuration (a) and O<sub>2</sub> dissociation configuration (b) on surface II. Large, medium, and small spots denote Pd, Fe, and O atoms, respectively. Arrows indicate the diffusion pathways of O1 and O2. c) Energy profiles for dissociation of O<sub>2</sub> (filled circles for surface I, filled squares for surface II) and diffusion of O1 (triangles and O2 (diamonds)).*

## Summary

As described through several examples above, we have performed high quality theoretical studies for the catalytic properties of various bimetallic surfaces and nanosystems. Many synergistic studies indicate the usefulness of density functional calculations for the understanding of catalytic properties of bimetallic surfaces. In general, catalytic reactivity of bimetallic surfaces depends on the ligand effects due to charge transfer, orbital hybridization and lattice strain. Extensive experimental and theoretical studies have established correlations among the adsorption energies of simple molecules, core level shift and the position of the d-band center with respect to the Fermi level of bimetallic surfaces. On the other hand, our studies stressed the importance of the geometric (or ensemble) effects related to particular arrangements of active constituents. The extraordinarily high reactivity and selectivity of the PdAu(001) bimetallic catalyst towards vinyl acetate synthesis, for instance, mainly stems from the presence of second neighbor Pd pairs on Au(001).

Unique changes in the electronic and chemical properties in nanostructure materials offer enormous opportunities for innovative heterogeneous catalysts with excellent performance. Microscopic understanding and control of their key features, essential for the long-sought goal of high activities with the utmost selectivity, are still major scientific challenges. To this end, DFT calculations and MD simulations for growth and chemical properties of innovative nanocatalysts will provide imperative information. Studies of bimetallic catalysts are cutting-edge and the present proposal is timely to provide theoretical guidance. Most model reactions are related to hydrogen production fuel cell technology, solar energy harvesting, and pollution reduction, major missions of DOE. Further studies along this direction are necessary to understand the synergy between “ligand” and “geometry” effects in bimetallic catalysts at the microscopic scale.

## Publications

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### **Education and training**

The project has provided partial or full support for:

Postdoc: Juexian Cao, now Professor in Xiangtan University, China

Postdoc: Dingwang Yuan, now Professor in Hunan University, China

Student: Aniketa Shinde, now in U West Virginia