

## Correlating Electronic and Chemical Properties of Monolayer

### Bimetallic Surfaces

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#### Introduction

It is well known that bimetallic surfaces often show novel properties that are not present on either of the parent metal surfaces. The modification effect is especially important at the admetal coverages in the submonolayer and monolayer regime. However, it is difficult to know *a priori* how the electronic and chemical properties of a particular bimetallic surface will be modified relative to the parent metals. There are at least two critical factors that contribute to the modification of the electronic and chemical properties of a metal in a bimetallic surface. First, the formation of the hetero-atom bonds changes the electronic environment of the metal surface, giving rise to modifications of its electronic structures. Second, the geometry of the bimetallic structure, such as the average metal-metal bond length, is typically different from that of the parent metals, resulting in strain effects that are known to modify the electronic structure of the metal through changes in orbital overlap.

In the past few years our research group has performed systematic experimental and Density Functional Theory (DFT) modeling of a wide range of bimetallic systems, including both single crystal surfaces and supported catalysts [1-7]. We have provided conclusive evidence that, depending on experimental conditions, the admetal can occupy the host surfaces in at least two configurations, on the surface to produce a surface monolayer, and in the subsurface between the first and second layer. DFT modeling results clearly indicate that the surface d-band center is significantly different for the two types of surface alloys. In addition, both DFT modeling and experimental results reveal a general correlation between the position of the surface d-band center and the adsorption energy for a wide range of atomic and molecular adsorbates.

#### Results and Discussion

In the current presentation we will use several probe reactions to demonstrate the unique chemical and catalytic properties of bimetallic systems. We will use the hydrogenation of alkenes, which is a reaction that requires relatively weak bonding of atomic hydrogen and alkenes, to demonstrate the utilization of bimetallic surfaces to enhance the hydrogenation *activity*; we will also use the selective hydrogenation of the C=O bond in unsaturated aldehydes to illustrate the possibility of controlling the *selectivity* with bimetallic surfaces. Next, we will present results for controlling the activity and selectivity of bimetallic surfaces for the reforming of oxygenates (alcohols and glycols), which is a reaction that requires relatively strong bonding of both hydrogen and oxygenates. Finally, we will present thermodynamic stability and kinetic

measurements regarding the *stability* of bimetallic surfaces in the presence of oxygen and hydrogen.

#### Significance

Overall, these results demonstrate the possibility of selecting catalytic materials with desirable *activity, selectivity and stability* based on the center of d-band of bimetallic surfaces, making it possible to predict bimetallic formations/structures with desirable chemical properties.

#### References

- [1] Hwu et al. *J. Am. Chem. Soc.* 124 (2002) 702
- [2] Kitchin et al. *Phys. Rev. Lett.* 93 (2004) 156801
- [3] Kitchin et al. *J. Chem. Phys.* 120 (2004) 10240
- [4] Khan et al. *Catal. Lett.* 105 (2005) 233
- [5] Skoplyak et al. *J. Phys. Chem. B* 110 (2006) 1686
- [6] Menning et al. *J. Phys. Chem. B* 110 (2006) 15471
- [7] Huang et al. *J. Catal.* 246 (2007) 40