

**Title:** Computational Chemistry-based identification of Ultra-Low Temperature Water-Gas-Shift Catalysts

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**Objectives:**

The primary route to hydrogen production from fossil fuels involves the water-gas shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ), and an improvement of the efficiency of WGS catalysts could therefore imply a significant leap forward towards the realization of hydrogen economy. *The primary objective of this project is the identification of thermodynamically stable, bimetallic, Near Surface Alloy (NSA)-based WGS-catalysts that provide high activity and poison-resistance, and allow low temperature of operation.*

**Accomplishments to date:**

Calculations completed in the earlier stages of this project had succeeded in evaluating the Binding Energies (BE's) of WGS relevant intermediates (e.g.: CO, O and OH) on a set of 17 catalytically relevant Transition Metal (TM) surfaces. A large number of bimetallic alloys can be synthesized from this set of 17 TMs and hence we employed several "screening" criteria to identify promising bimetallic NSAs deserving further study. Our primary criterion was the thermodynamic stability of these NSAs, both *in vacuo* and also in the presence of the stronger-binding-adsorbates to be expected in significant coverages under typical reaction conditions for WGS. A total of 40 NSAs were found to survive the strict criteria of being stable under the influence of all three species CO, O and OH. DFT calculations using the first-principles code DACAPO were performed for the adsorption of CO, O and OH on the most-stable, close-packed facets of these NSA-catalysts. The resultant BE-database was utilized for guiding the targeted discovery of novel high-activity WGS catalysts.

Previous theoretical calculations for WGS had identified  $\text{H}_2\text{O}$  activation (more specifically the step  $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ ) as a Rate Determining Step (RDS) on a variety of TMs. In our quest to identify catalysts that would allow facile water activation we evaluated the minimum energy pathway (MEP) and hence the activation energy for this step on a set of pure metals (Cu, Ag, Au, Pt and Ir) and promising NSA catalysts: this included the Pt-exposing overlayers Pt\*/Pd, Pt\*/Au, Pt\*/Ir and Pt\*/Ru, Pt\*/Rh and also the sub-surface alloys Cu/Pt and Cu/Pd. Sulfur poisoning is a potential concern for WGS catalyst and hence the S-resistance of these catalysts was also studied: several NSAs were found that bind S weaker than Cu, the current WGS catalyst, yet provide facile  $\text{H}_2\text{O}$  activation.

Specifically, the Cu/Pt catalyst was identified as the most promising improved WGS catalyst to be identified during this project. Cu/Pt shows an enhancement of Cu concentration in the first sub-surface of the Pt host and this system has been shown to be thermodynamically stable in CO-rich environments and hence CO-induced reconstruction and segregation is not expected in this catalyst. Further, this NSA is able to dissociate water relatively easily but binds the products of H<sub>2</sub>O dissociation (OH + H) weaker than Cu. The formate intermediate (HCOO) is known to be rather stable on conventional Cu-based WGS catalysts and high coverages of this species can poison the catalyst surface and impair catalyst activity. CO is another potential poison for WGS catalysts. The Cu/Pt NSA that we identified binds formate weaker than Cu and CO weaker than Pt thereby making it less prone to site-blocking and poisoning by these species. Sulfur adsorption calculations indicate this catalyst possesses resistance to S-poisoning comparable to that of conventional Cu. Our assertions of the superior nature of the Cu/Pt catalyst were experimentally verified by collaborators using a variety of techniques including XPS, TPD and STM.

### **Future work:**

The funding for the current project was completely used up by October 2007 and hence further calculations could not be pursued. Analogous to the Cu/Pt system (that was studied in detail during this project) several other NSA-based bimetallic catalysts have been identified as potentially promising WGS catalysts. Provided funding becomes available, detailed kinetic calculations for the elementary steps of WGS (with an emphasis on H<sub>2</sub>O activation) on such a set of promising NSAs is warranted with the objective of expanding our set of thermodynamically-stable, high activity, poison-resistant WGS catalysts.

### **List of Published Journal Articles:**

1. “A Cu/Pt Near-Surface Alloy for improved water-gas shift catalysis”, Knudsen, J.; Nilekar, A. U.; Vang, R. T.; Schnadt, J.; Kunkes, E. L.; Dumesic, J. A.; Mavrikakis, M.; Besenbacher, F. *J. Am. Chem. Soc.* **2007**, *129*, 6485.

### **Awards/Distinctions for the PI:**

1. **Samuel C. Johnson Distinguished Fellowship.**
2. Editorial Board of *Surface Science*
3. Editorial Board of *Annual Review of Chemical & Biological Engineering*
4. **Visiting Professor**, Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark (Fall 2006).
5. Featured in NERSC News (March 2007):  
[http://www.nersc.gov/news/nerscnews/NERSCNews\\_2007\\_03.pdf](http://www.nersc.gov/news/nerscnews/NERSCNews_2007_03.pdf)
6. Member of the **Advising Board** for the Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, Lyngby, Denmark (1/07- ).

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