

# Monday Afternoon, November 13, 2006

## Surface Science

### Room 2002 - Session SS1-MoA

#### Catalysis for the Hydrogen Economy

Moderator: G. Fisher, Delphi Research Labs

2:00pm **SS1-MoA1 Catalytic Hydrogen Production**, *J.K. Norskov*, Technical University of Denmark, Denmark; *J. Greeley*, Technical University of Denmark

INVITED

The possibility of using molecular hydrogen as a fuel focuses attention on the way it is produced. Methods include catalytic conversion of hydrocarbons and electrochemical or photochemical water splitting. Certain enzymes, hydrogenases and nitrogenases, catalyze hydrogen evolution. Attempts at using density functional theory calculations to understand both the inorganic and biological catalysts will be described. It will also be shown how the insight may be used to identify new catalysts in this area.

2:40pm **SS1-MoA3 Hydrogen Production from Ethanol Over Bimetallic Catalysts**, *P.Y. Sheng, A. Yee, W. Chiu, H. Idriss*, University of Auckland, New Zealand

Hydrogen is one of the most plausible alternative energy sources that can be widely used in the near future if sustainable ways of generating it are found. This work focuses on the reactions of ethanol, as an example of a bio-fuel, on the surfaces of platinum, palladium and rhodium supported on ceria (of size 10 to 20 nm). The bimetallic compounds: Pt-Rh, Rh-Pd, and Pt-Pd were also investigated. The addition of any of the above metals to CeO@sub2@ was found to suppress the oxidation of ethanol to acetates at room temperature, as there are fewer surface oxygen atoms available to oxidize the ethanol (the remaining oxygen atoms did not produce efficient oxidation). Ethanol dehydrogenation to acetaldehyde was facilitated by the presence of Pt or Pd; at higher temperatures the acetaldehyde condensed to other organic compounds, such as crotonaldehyde. By contrast, in the presence of Rh only traces of acetaldehyde or other organic compounds were seen on the surface, and detectable amounts of CO were found upon ethanol adsorption at room temperature. This indicates the powerful nature of Rh in breaking the carbon-carbon bond in ethanol. The effects of prior reduction were also investigated and clear differences were seen: for example, a shift in reaction selectivity is observed for the bimetallic Rh-containing catalysts. Methane was the dominant hydrocarbon on the reduced catalysts while acetaldehyde was the main product for the non-reduced ones. Hydrogen formation was monitored during steady state ethanol oxidation and Pt-Rh and Rh-Au were found to be the most active catalysts.

3:00pm **SS1-MoA4 Design and Stability of Surface Alloys used for Catalytic Conversion of Fossil Fuel to Hydrogen**, *J. Knudsen<sup>1</sup>, R.T. Vang*, University of Aarhus, Denmark; *J. Schnadt*, University of Aarhus, Denmark, Sweden; *E.K. Vestergaard, T.M. Pedersen, B. Hammer, T. An, I. Stensgaard, E. Laegsgaard*, University of Aarhus, Denmark; *A.U. Nilekar, M. Mavrikakis*, University of Wisconsin-Madison; *F. Besenbacher*, University of Aarhus, Denmark

Clean, cheap and efficient production of high-purity hydrogen is an essential prerequisite for the emerging hydrogen economy. The vast majority of the present hydrogen production comes from catalytic conversion of fossil fuel, which relies heavily on the steam reforming (SR) reaction and the Water-Gas-Shift (WGS) reaction. Supported Ni particles are commercially used as catalysts for the SR reaction, whereas supported Cu particles are currently used for the low-temperature WGS reaction. In this study vacuum deposition of Cu onto Pt(111) at 800 K is used to synthesize stable near-surface alloys (NSA) of Cu/Pt(111). A combination of scanning tunneling microscopy (STM), Core-level photoemission (XPS), Thermal desorption spectroscopy (TDS) and Density functional theory (DFT) is used to characterize the NSAs, and it is found that Cu atoms are stabilized sub-surface, leaving a surface layer free of Cu atoms. Very interestingly, we find that the WGS activity of our new NSA is superior to that of Cu(111), and it is, therefore, very likely that real Cu/Pt near-surface particles could be used as new and improved catalysts for the WGS reaction. Finally, fast high-pressure STM experiments in a high CO pressure are used to examine the stability of this new Cu/Pt(111) near-surface alloy for the WGS reaction, and a previously found Au/Ni(111) surface alloy, which can be used for the SR reaction. From these experiments we

conclude that the Cu/Pt(111) NSA remains stable in high pressure of CO in contrast to the Au/Ni(111) surface alloy, which is found to phase separate into small Au clusters on a Ni(111) substrate due to formation of Ni-carbonyls, which remove Ni from the surface.

3:20pm **SS1-MoA5 Thermodynamic Investigations into the Redox Properties of Mixed-Oxide Catalysts Relevant to Hydrogen Production**, *R.J. Gorte*, University of Pennsylvania

INVITED

Many of the reactions for hydrocarbon reforming, including steam reforming and water-gas shift, can be thought of as redox reactions. It is therefore not surprising that catalytic activities can be enhanced significantly by including a redox catalyst, such as ceria. In most cases, the redox catalysts are in the form of a mixed oxide, such as ceria-zirconia, and the thermodynamic properties for oxidation and reduction of these mixed oxides are usually not known. In this talk, I will discuss our investigations into the redox properties of selected materials, including solid solutions of ceria and zirconia. Reduction isotherms were determined over a temperature range using TPR methods and Coulomb Titration. For ceria-zirconia, the thermodynamic properties were found to be a strong function of composition but were independent of sample surface area and calcination temperature, so long as the oxide structure was maintained. While the enthalpy of reduction for ceria-zirconia solutions is less than that of pure ceria, at least some of the interesting properties of this material are associated with entropy effects.

4:20pm **SS1-MoA8 Electrode Catalysts of Polymer Electrolyte Fuel Cell using Carbon Nanotube**, *J. Nakamura, E. Yoo, T. Watanabe*, University of Tsukuba, Japan

The high-priced and limited Pt constitutes a high barrier to commercialization of fuel cells. Pt is essential for the electrode catalyst of polymer electrolyte fuel cells (PEFCs). Reduction in Pt usage is one of the key requirements for the commercialization of fuel cells for use in everyday life, because of its high price and limited availability, and the difficulty of finding suitable substitutes. We have reported that use of carbon nanotube (CNT) as an electrode material results in high performance with low loading of Pt. That is, the electric power of 12 wt% Pt/CNT was found to be higher than that of 29wt% Pt/carbon black. This is due to efficient formation of triple phase boundary (electrode/electrolyte/gas). Recently, we observed that Ru/Pt/CNT shows higher tolerance for CO poisoning compared to Ru/Pt/carbon black. This suggests that the interface between carbon and alloy catalysts is very different so that the Ru-Pt alloy phase is modified in terms of catalytic nature. The shape of metal catalyst particles is elongated on CNT surfaces, while catalysts on carbon black or defected carbon surfaces is spherical. This is the consequence of the difference in the state of the interface. In general, the electric double layer is formed at the interface between metallic surfaces, where electrons flow from materials with low work function to those with high work function. The electric double layer causes attractive interaction at the interface. The observed support effect of CNT is ascribed to the strong interaction between flat graphene sheet and Pt-Ru alloy particles, leading to the modification of catalytic nature. In this presentation, we report and discuss the effect of carbon surface below metal catalysts upon the performance of electrode catalysts by showing the results of CNT supported electrode catalysts and model system of metal catalysts/HOPG (Highly oriented pyrolytic graphite).

4:40pm **SS1-MoA9 Effect of Hydrogen on the Stability of Ti on an Al Surface\***, *R. Bastasz*, Sandia National Laboratories; *W.P. Ellis*, Los Alamos National Laboratory; *R. Stumpf, J.A. Whaley*, Sandia National Laboratories

The thermal stability of Ti atoms evaporated onto an Al(100) surface was studied using the surface-sensitive technique of ion scattering spectroscopy (ISS). Measurements were made in vacuum and in the presence of an atomic deuterium beam directed at the sample. When heated in vacuum, Ti begins to disappear from the surface at substrate temperatures below 100°C and is completely absent at temperatures above 250°C. When a similar measurement is made while the sample is being exposed to a flux of deuterium atoms, the Ti persists on the surface to noticeably higher temperatures. Diffusion coefficients for Ti into Al were obtained from ISS data in both cases at selected substrate temperatures in the range 50-150°C. The activation energy for diffusion of Ti from the Al(100) surface appeared to be altered in the presence of D. The experimental results are interpreted using density functional theory, which indicates that H-Ti interactions stabilize surface Ti. @FootnoteText@ \*This work was supported by the US Dept. of Energy under contract DE-AC04-94AL85000.

<sup>1</sup> Morton S. Traum Award Finalist

## Author Index

**Bold page numbers indicate presenter**

— A —

An, T.: SS1-MoA4, **1**

— B —

Bastasz, R.: SS1-MoA9, **1**

Besenbacher, F.: SS1-MoA4, **1**

— C —

Chiu, W.: SS1-MoA3, **1**

— E —

Ellis, W.P.: SS1-MoA9, **1**

— G —

Gorte, R.J.: SS1-MoA5, **1**

Greeley, J.: SS1-MoA1, **1**

— H —

Hammer, B.: SS1-MoA4, **1**

— I —

Idriss, H.: SS1-MoA3, **1**

— K —

Knudsen, J.: SS1-MoA4, **1**

— L —

Laegsgaard, E.: SS1-MoA4, **1**

— M —

Mavrikakis, M.: SS1-MoA4, **1**

— N —

Nakamura, J.: SS1-MoA8, **1**

Nilekar, A.U.: SS1-MoA4, **1**

Norskov, J.K.: SS1-MoA1, **1**

— P —

Pedersen, T.M.: SS1-MoA4, **1**

— S —

Schnadt, J.: SS1-MoA4, **1**

Sheng, P.Y.: SS1-MoA3, **1**

Stensgaard, I.: SS1-MoA4, **1**

Stumpf, R.: SS1-MoA9, **1**

— V —

Vang, R.T.: SS1-MoA4, **1**

Vestergaard, E.K.: SS1-MoA4, **1**

— W —

Watanabe, T.: SS1-MoA8, **1**

Whaley, J.A.: SS1-MoA9, **1**

— Y —

Yee, A.: SS1-MoA3, **1**

Yoo, E.: SS1-MoA8, **1**