

# Tuesday Afternoon, November 10, 2009

## Surface Science

Room: N - Session SS3-TuA

### Catalysis: Mechanisms & Morphology

Moderator: B.R. Cuenya, University of Central Florida

2:00pm **SS3-TuA1 High Catalytic Activity of CeO<sub>x</sub>/Au(111) and Au/CeO<sub>x</sub>/TiO<sub>2</sub>(110): Special Properties of CeO<sub>x</sub> Nanoparticles**, *J.A. Rodriguez, J.B. Park, J. Graciani*, Brookhaven National Laboratory, *J. Evans*, Universidad Central de Venezuela, *D.J. Stacchiola, S.J. Ma, P.J. Liu*, Brookhaven National Laboratory, *J. Fdez-Sanz*, Universidad de Sevilla, Spain, *J. Hrbek*, Brookhaven National Laboratory **INVITED**

This talk will focus on a series of studies investigating the catalytic activity of CeO<sub>x</sub>/Au(111) and Au/CeO<sub>x</sub>/TiO<sub>2</sub>(110) for the water-gas shift (WGS, CO + H<sub>2</sub>O → H<sub>2</sub> + CO<sub>2</sub>) reaction and CO oxidation. Au(111) is inactive for the WGS. The deposition of ceria nanoparticles on Au(111) produces a highly active WGS catalysts. An even better catalysts is produced after depositing Au and CeO<sub>x</sub> nanoparticles on TiO<sub>2</sub>(110). The titania substrate imposes non-typical coordination modes on the ceria nanoparticles. In the CeO<sub>x</sub>/TiO<sub>2</sub>(110) systems, the Ce cations adopt an structural geometry and an oxidation state (+3) which are quite different from those seen in bulk ceria or for ceria nanoparticles deposited on metal substrates. The increase in the stability of the Ce<sup>3+</sup> oxidation state leads to an enhancement in the chemical and catalytic activity of the ceria nanoparticles. The co-deposition of ceria and gold nanoparticles on a TiO<sub>2</sub>(110) substrate generates catalysts with an extremely high activity for the production of hydrogen through the WGS or for the oxidation of carbon monoxide. The exploration of mixed-metal oxides at the nanometer level may open new avenues for optimizing catalysts through stabilization of unconventional surface structures with special chemical activity.

2:40pm **SS3-TuA3 Kinetics and Elementary Steps of the Reverse Water-Gas Shift Reaction over Pt Catalysts**, *L.G. Cameron, C.T. Campbell*, University of Washington, *L. Grabow, M. Mavrikakis*, University of Wisconsin

The kinetics of the reverse water gas shift (RWGS) reaction (CO<sub>2</sub> + H<sub>2</sub> → CO + H<sub>2</sub>O) have been measured over clean and annealed Pt powder at a variety of conditions, and the surface coverage of adsorbed intermediates was verified by transient techniques. Under conditions where the surface coverage is very low and the reaction is occurring on essentially adsorbate-free Pt, the RWGS rate is 1000-fold faster than the rate of dissociative CO<sub>2</sub> adsorption (CO<sub>2</sub> → CO + O<sub>ad</sub>), estimated from measurements of the reverse rate and equilibrium constant for this elementary step. This proves that the dominant mechanism for the RWGS reaction is not via dissociative CO<sub>2</sub> adsorption. The energetics estimated from DFT calculations of potential alternate pathways on Pt(111) suggests that CO<sub>2</sub> is instead activated by reaction with H<sub>ad</sub> to make a COOH<sub>ad</sub> intermediate, which dissociates to make CO<sub>ad</sub> and OH<sub>ad</sub>. A microkinetic model based on these DFT energetics reproduces well the measured absolute rate per Pt atom, its activation energy, and its dependences on CO<sub>2</sub> and H<sub>2</sub> partial pressures. This offers strong support for this alternate “carboxylate” pathway as dominating the mechanism. Estimates of the degrees of rate control of this reaction’s elementary steps and intermediates will also be discussed.

Work supported by DOE-OBES Chemical Sciences Division.

3:00pm **SS3-TuA4 A DFT Study of Methanol Synthesis by CO<sub>2</sub> Hydrogenation on Cu Nanoparticles and Surfaces**, *Y. Yang*, SUNY at Stony Brook, *P.J. Liu, M. White*, Brookhaven National Laboratory

The synthesis of methanol from CO<sub>2</sub> and H<sub>2</sub> (CO<sub>2</sub>+3H<sub>2</sub>→CH<sub>3</sub>OH+H<sub>2</sub>O) has attracted considerable attention. It is not only environmentally important due to its application in the conversion of greenhouse gas, CO<sub>2</sub>, it is also of great industrial significance because the product, methanol, can serve as a raw material for the synthesis of other organic compounds, besides being used as a liquid fuel. Commercially, the reaction is performed on a catalyst containing Cu, ZnO and Al<sub>2</sub>O<sub>3</sub> at a high temperature (220-240°C) and high pressure (50-100 bar). There is a need to understand the reaction mechanism in order to develop more active and selective catalysts even though the mechanism is still controversial. In this study, density functional theory (DFT) was employed to elucidate the reaction mechanism on the Cu(111) surface and the promotion effect of nano-size Cu compared to bulk Cu.

Cu<sub>29</sub> nanoparticles, exposing a combination of (100) and (111) faces in a pyramidal structure, is the model we used to study the reaction pathways on the Cu nanoparticles. For comparison, the reaction mechanism on the Cu(111) surface is also studied. It was found out that on both systems, the reaction undergoes via formate (HCOO) and dioxomethylene (H<sub>2</sub>COO).

The reaction rate is controlled by hydrogenation of HCOO and H<sub>2</sub>COO. In accordance with experimental findings, our results show that the Cu<sub>29</sub> nanoparticles display a superior activity over Cu(111). The better behavior of Cu<sub>29</sub> is associated with the low-coordinated Cu sites, which provide a reasonably strong binding to the intermediates.

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4:00pm **SS3-TuA7 Electronic Structure Effect in Modified Reactivity of Pt/Cu(111)**, *T. Anniyev, S. Kaya, H. Ogasawara*, Stanford Synchrotron Radiation Lightsource, *S. Koh, P. Strasser*, University of Houston, *M. Toney, A. Nilsson*, Stanford Synchrotron Radiation Lightsource

A key role in the activity of transition metal catalysts is the degree of interaction of metal d-bands with the adsorbed atoms/molecules [1]. It has been suggested that d-band center is a single effective measure of this interaction [2]. In this work we demonstrate how strain induced electronic structure changes can be used to tune the catalytic activity of the Oxygen Reduction Reaction (ORR). The limiting factor in the performance of the Pt-based PEM fuel cells is the low rate of the ORR taking place at the cathode. It has recently been shown that electrochemically leached PtCu catalysts, which have strained Pt rich shell due to dissolution of Cu, exhibit uniquely high reactivity for this reaction [3]. Using a surface science approach we have investigated the electronic structure effect in the enhanced ORR activity using Pt monolayers epitaxially grown on Cu(111) as a model system. We show that compressive strain and host substrate-induced changes in the Pt d-band center are responsible for the changes in chemisorption strength of adsorbed oxygen. Electronic nature of chemisorbed oxygen atoms on strained Pt monolayers has been investigated by probing oxygen projected density of states below and above the Fermi level using X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS), respectively. Combined oxygen K-edge XAS and XES results of oxygen on strained Pt monolayers show lowering of the adsorbate projected density of states and a complete filling up of antibonding states above Fermi level indicative of weakened metal-oxygen bond relative to that of oxygen on Pt(111). The weakening of the metal-oxygen bond is correlated with the broadening and lowering of the Pt d-band probed by valence band X-ray photoemission spectroscopy (XPS). The observed results are explained in terms of the d-band model.

#### References

- [1] B. Hammer and J. K. Norskov, Theoretical surface science and catalysis—calculations and concepts, *Adv. Catal.* 45, 71 (2000).
- [2] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (John Wiley & Sons, New York, 1994).
- [3] S. Koh and P. Strasser, Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface de-alloying, *J. Am. Chem. Soc.*, 129 (42), 12624-12625 (2007).

4:20pm **SS3-TuA8 In Situ Study of Heterogeneous Catalysis on Oxide Support: CO Oxidation on Au/TiO<sub>2</sub> Catalysts**, *S. Porsgaard*, Lawrence Berkeley National Lab and University of Aarhus, Denmark, *P. Jiang, F. Borondics, M. Köber*, Lawrence Berkeley National Lab, *S. Wendt*, University of Aarhus, Denmark, *H. Bluhm*, Lawrence Berkeley National Lab, *F. Besenbacher*, University of Aarhus, Denmark, *M. Salmeron*, Lawrence Berkeley National Lab

It has been known for more than a decade that the system of gold nanoparticles on a TiO<sub>2</sub> support (Au/TiO<sub>2</sub>) is an active catalyst for a variety of reactions even below room temperature.[1] However, there is still little agreement on several important questions such as the role of the substrate, the charge state of gold, and the role of oxygen vacancies, even for the simplest reaction of CO oxidation.

In this study we focus on the questions related to the electronic band structure of the substrate. We chose a model system of evaporated Au nanoparticles on a rutile TiO<sub>2</sub>(110) single crystal substrate. The morphology of the evaporated Au nanoparticles were studied by STM, and it turned out to be strongly dependent on the pre-treatment of the TiO<sub>2</sub> surface.[2]

For traditional surface science, the pressure gap between the studies in ultra high vacuum (UHV) and the industrial relevant reaction conditions is an important challenge. To overcome this problem, we have used in situ X-ray Photoelectron Spectroscopy (in situ XPS)[3] to study the evolution of the adsorbed chemical species and the electronic band structure of the rutile TiO<sub>2</sub>(110) during the individual steps in the reaction under pressures up to 1 Torr.

However, XPS on semiconductor substrates is challenging especially in the presence of gases. We have designed novel samples and test experiments to overcome these drawbacks. These results show that most in situ

experiments on semiconductor substrates require extraordinary precautions. Now, we are able to avoid the newly discovered pitfalls, and we are able to present decisive results on the previously debated problems, e.g. the ongoing discussion about the charge state of gold and the role of oxygen vacancies.

[1] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, J.M. Genet, and B. Delmon, "Low-Temperature Oxidation of CO over Gold Supported on TiO<sub>2</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub>," *Journal of Catalysis*, vol. 144, Nov. 1993, pp. 175-192.

[2] D. Matthey, J. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Laegsgaard, B. Hammer, and F. Besenbacher, "Enhanced bonding of gold nanoparticles on oxidized TiO<sub>2</sub>(110)," *SCIENCE*, vol. 315, Mar. 2007, pp. 1692-1696.

[3] D. Ogletree, H. Bluhm, G. Lebedev, C. Fadley, Z. Hussain, and M. Salmeron, "A differentially pumped electrostatic lens system for photoemission studies in the millibar range," *REVIEW OF SCIENTIFIC INSTRUMENTS*, vol. 73, Nov. 2002, pp. 3872-3877.

4:40pm **SS3-TuA9 Search for Chemicurrent during CO Oxidation on Pt/GaN and Pt/TiO<sub>2</sub> Nanodiodes**, *J.R. Creighton, E.J. Heller, K.H.A Bogart, M.E. Coltrin, E.N. Coker, K.C. Cross*, Sandia National Laboratories  
In 2005, Gabor Somorjai's group demonstrated the capture of chemical energy liberated during carbon monoxide oxidation on Pt and Pd surfaces by using a structure they described as a "catalytic nanodiode" [1-2]. This device is a Schottky diode where the metal contact is made of an ultrathin (~5 nm) catalytic metal, deposited on a wide bandgap semiconductor such as GaN or TiO<sub>2</sub>. During the exothermic oxidation of CO, some fraction of the chemical energy may be dissipated by creation of hot electrons in the catalytic metal, and some of these electrons are potentially collected on the semiconductor side of the Schottky barrier. In principle, this "chemicurrent" formed by hot electron generation, transport, and collection represents the conversion of chemical energy directly into electrical energy. For some conditions using a Pt/TiO<sub>2</sub> nanodiode, a remarkable conversion efficiency of 3 electrons per 4 CO<sub>2</sub> produced was measured [1]. We have fabricated several versions of catalytic nanodiodes using GaN and TiO<sub>2</sub> films deposited and characterized in-house. During CO oxidation on Pt/GaN and Pt/TiO<sub>2</sub> nanodiodes we also detect a current that is unambiguously a result of the chemical reaction. We measure current densities up to 100 nA/mm<sup>2</sup> and reaction conversion efficiencies in the range of 10<sup>-5</sup>-10<sup>-3</sup> electrons per CO<sub>2</sub>, which are quantitatively similar to reports in more recent publications [3-4]. However, the behavior of this chemical signal as a function of diode impedance indicates that it is derived from a **voltage source**, and not from a current source. In fact, the chemical signal is primarily, if not entirely, due to the thermoelectric voltage generated and/or modified by the exothermicity of the reaction. We have yet to find any conclusive evidence supporting true "chemicurrent" formation during CO oxidation on Pt/GaN or Pt/TiO<sub>2</sub> nanodiodes.

References:

- [1] Z.J. Xiao and G.A. Somorjai, *J. Phys. Chem. B* 109 (2005) 22530.  
[2] J. Xiaozhong, A. Zuppero, J.M. Gidwani, and G.A. Somorjai, *J. Amer. Chem. Soc.* 127 (2005) 5792.  
[3] J.Y. Park, J. R. Renzas, B.B. Hsu, and G.A. Somorjai, *J. Phys. Chem. C*, 111 (2007) 15331  
[4] J.Y. Park, J. R. Renzas, A.M. Contreras, and G.A. Somorjai, *Topics in Catalysis*, 46 (2007) 217

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5:00pm **SS3-TuA10 MORTON S. TRAUM AWARD FINALIST: Morphology and Chemical Reactivity of Bi-Metallic Au-Pd Clusters**, *E. Gross\*, M. Asscher*, The Hebrew University of Jerusalem, Israel

Bi-metallic clusters have unique catalytic properties, since one metal can modify the electronic and thus the catalytic properties of the other metal. Here we describe a unique preparation method of bimetallic Pd-Au nano-clusters. The growth mode is based on initial evaporation of metal atoms on top of amorphous solid water adsorbed on SiO<sub>2</sub>/Si(100) substrate at 100K under ultra high vacuum (UHV) conditions. The ice buffer layer separates the small metallic seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth of nano-clusters in a Buffer Layer Assisted Growth (BLAG) mechanism.

Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) measurements revealed that by modifying the clusters preparation procedure either segregated or alloyed Pd-Au clusters

can be formed. The composition of the different clusters was also verified by optical surface plasmon resonance (SPR) absorption measurements.

Temperature Programmed Reaction (TPR) measurements have shown that adsorption of acetylene on top of Pd-Au alloy clusters has led to efficient conversion to ethylene. Benzene was also formed at an order of magnitude smaller rate. Pd-Au alloy clusters have demonstrated significantly higher reactivity than the monometallic clusters. Increasing the surface defects density by Ar<sup>+</sup> ion sputtering enhanced the thermal stability and sintering resistance properties of the Pd-Au clusters.

5:20pm **SS3-TuA11 Reactivity of NO<sub>2</sub> with BaO Nanoclusters Grown on YSZ(111) and CeO<sub>2</sub>(111)/YSZ(111) Probed by *in situ* High-Resolution XPS**, *Z.Q. Yu*, Nanjing Normal University, China, *P. Nachimuthu*, Pacific Northwest National Laboratory, *M. Nandasiri, S.V.N.T. Kuchibhatla*, Pacific Northwest National Laboratory, *Y.J. Kim*, Hanbat National University, Korea, *M.H. Engelhard, V. Shutthanandan, W. Jiang, J. Szanyi, S. Thevuthasan*, Pacific Northwest National Laboratory  
Catalysts for NO<sub>x</sub> storage and reduction (NSR) are being developed to reduce the NO<sub>x</sub> emission from gasoline based internal combustion engines. BaO is considered to be potential NSR catalysts because of its strong interaction and an effective trapping of NO<sub>2</sub>. BaO is more reactive when BaO is present as non-stoichiometric BaO clusters rather than bulk BaO. In order to understand the reactivity, BaO was grown on YSZ(111) and CeO<sub>2</sub>(111)/YSZ(111) substrates by molecular beam epitaxy. *In-situ* reflection high-energy electron diffraction, *ex-situ* x-ray diffraction, atomic force microscopy and x-ray photoelectron spectroscopy have confirmed that the BaO grows as nanoclusters on YSZ(111). During and following the growth under UHV conditions, BaO remains in single phase. The reaction of NO<sub>2</sub> with the BaO nanoclusters in different sizes on YSZ(111) and CeO<sub>2</sub>(111)/YSZ(111) substrates was investigated using *in situ* high-resolution x-ray photoelectron spectroscopy (XPS). The adsorption of NO<sub>2</sub> on the BaO nanoclusters at room temperature and the formation of Ba(NO<sub>3</sub>)<sub>2</sub> species at room temperature and above were probed. In addition the *in situ* XPS data collected from the BaO nanoclusters prior to and following the reaction with NO<sub>2</sub> were utilized to understand the morphology of BaO nanoclusters and the formation of Ba(NO<sub>3</sub>)<sub>2</sub> species using Quasestougaard V5.1 software. These results are compared with the reported data from NO<sub>2</sub> reaction with BaO film deposited onto an Al<sub>2</sub>O<sub>3</sub>/NiAl(110) substrate.

\* Morton S. Traum Award Finalist

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Anniyev, T.: SS3-TuA7, **1**  
Asscher, M.: SS3-TuA10, **2**

## — B —

Besenbacher, F.: SS3-TuA8, **1**  
Bluhm, H.: SS3-TuA8, **1**  
Bogart, K.H.A.: SS3-TuA9, **2**  
Borondics, F.: SS3-TuA8, **1**

## — C —

Cameron, L.G.: SS3-TuA3, **1**  
Campbell, C.T.: SS3-TuA3, **1**  
Coker, E.N.: SS3-TuA9, **2**  
Coltrin, M.E.: SS3-TuA9, **2**  
Creighton, J.R.: SS3-TuA9, **2**  
Cross, K.C.: SS3-TuA9, **2**

## — E —

Engelhard, M.H.: SS3-TuA11, **2**  
Evans, J.: SS3-TuA1, **1**

## — F —

Fdez-Sanz, J.: SS3-TuA1, **1**

## — G —

Grabow, L.: SS3-TuA3, **1**  
Graciani, J.: SS3-TuA1, **1**

Gross, E.: SS3-TuA10, **2**

## — H —

Heller, E.J.: SS3-TuA9, **2**  
Hrbek, J.: SS3-TuA1, **1**

## — J —

Jiang, P.: SS3-TuA8, **1**  
Jiang, W.: SS3-TuA11, **2**

## — K —

Kaya, S.: SS3-TuA7, **1**  
Kim, Y.J.: SS3-TuA11, **2**  
Köber, M.: SS3-TuA8, **1**  
Koh, S.: SS3-TuA7, **1**  
Kuchibhatla, S.V.N.T.: SS3-TuA11, **2**

## — L —

Liu, P.J.: SS3-TuA1, **1**; SS3-TuA4, **1**

## — M —

Ma, S.J.: SS3-TuA1, **1**  
Mavrikakis, M.: SS3-TuA3, **1**

## — N —

Nachimuthu, P.: SS3-TuA11, **2**  
Nandasiri, M.: SS3-TuA11, **2**  
Nilsson, A.: SS3-TuA7, **1**

## — O —

Ogasawara, H.: SS3-TuA7, **1**

## — P —

Park, J.B.: SS3-TuA1, **1**  
Porsgaard, S.: SS3-TuA8, **1**

## — R —

Rodriguez, J.A.: SS3-TuA1, **1**

## — S —

Salmeron, M.: SS3-TuA8, **1**  
Shutthanandan, V.: SS3-TuA11, **2**  
Stacchiola, D.J.: SS3-TuA1, **1**  
Strasser, P.: SS3-TuA7, **1**  
Szanyi, J.: SS3-TuA11, **2**

## — T —

Thevuthasan, S.: SS3-TuA11, **2**  
Toney, M.: SS3-TuA7, **1**

## — W —

Wendt, S.: SS3-TuA8, **1**  
White, M.: SS3-TuA4, **1**

## — Y —

Yang, Y.: SS3-TuA4, **1**  
Yu, Z.Q.: SS3-TuA11, **2**