

Wednesday Morning, November 12, 2014

Nanometer-scale Science and Technology

Room: 304 - Session NS-WeM

Nanoscale Catalysis and Surface Chemistry

Moderator: Jeremy Robinson, Naval Research Laboratory

8:00am NS-WeM1 **Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenations**, Charles Sykes, Tufts University
INVITED

Hydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies. Typical heterogeneous catalysts often involve noble metals and alloys based on platinum, palladium, rhodium and ruthenium. While these metals are active at modest temperature and pressure, they are not always completely selective and are expensive. We have demonstrated that single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultrasensitive catalyst. We used high resolution imaging to characterize the active sites and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of molecular hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultrasensitive catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the unique synergy of the system.

8:40am NS-WeM3 **In Situ FTIR Spectroscopic Observation of the Formation of Gold Ketenylidene during Carboxylic Acid Oxidation on a Au/TiO₂ Nanoparticle Catalyst**, Monica McEntee, W. Tang, M. Neurock, J.T. Yates, Jr., University of Virginia

Gold nanometer diameter particles supported on reducible oxide supports exhibit catalytic activity at temperatures as low as 90 K.[1] Numerous studies[2-4] have theorized that the catalytic activity occurs at the metal-support interfacial sites. In 2011, Green *et al.*[5] discovered, using infrared (IR) spectroscopy, a dual catalytic site for molecular oxygen adsorption and subsequent activation with one O atom bonded to the Au and the other O bonded to the Ti⁴⁺ site of the TiO₂ support. Here I show, using IR spectroscopy and density functional theory (DFT), the oxidation of three carboxylic acids (acetic, propionic and butyric acid) on a Au/TiO₂ catalyst with ~3 nm diameter Au nanoparticles producing gold ketenylidene, Au₂C=C=O, species. The initial step in all three acid oxidation processes is the dissociation of O₂ at the Au-Ti⁴⁺ dual site to form reactive O adatoms at the interface. Next, in sequential steps, α -CH and β -CH bonds specifically next to the COO group in each acid are oxidatively dehydrogenated to produce unsaturated, C=C, species. C-C and C-O bond scission occur next yielding adsorbed ketenylidene, Au₂C=C=O, an exotic species formed just before full oxidation. Control oxidation experiments on the TiO₂ support alone produce no Au₂C=C=O species verifying the reaction occurs at the Au/TiO₂ interface. Also, isotopically-labelled O₂ and acid experiments confirm the Au₂C=C=O is composed of specifically α -C and β -C atoms and O atoms from the acid.

References

1. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0 °C. *Chem. Lett.* **1987**, 405-408.
2. Rodriguez, J.; Ma, S.; Liu, P.; Hrbek, J.; Evans, J.; Perez, M. Activity of CeO_x and TiO_x nanoparticles grown on Au (111) in the water-gas shift reaction. *Science* **2007**, *318*, 1757-1760.
3. Molina, L.; Rasmussen, M.; Hammer, B. Adsorption of O₂ and oxidation of CO at Au nanoparticles supported by TiO₂(110). *J. Chem. Phys.* **2004**, *120*, 7673.
4. Camellone, M. F.; Zhao, J.; Jin, L.; Wang, Y.; Muhler, M.; Marx, D. Molecular Understanding of Reactivity and Selectivity for Methanol Oxidation at the Au/TiO₂ Interface. *Angew. Chem., Int. Ed.* **2013**, *52*, 5780 – 5784.
5. Green, I. X.; Tang, W.; Neurock, M.; Yates Jr., J. T. Spectroscopic observation of dual catalytic sites during oxidation of CO on a Au/TiO₂ catalyst. *Science* **2011**, *333*, 736-739.

9:00am NS-WeM4 **Fabrication and Photocatalytic Activity of Metal-loaded TiO₂ Nanometer Scale Particles**, Paolo Reyes, Y. Liu, J.C. Hemminger, University of California Irvine

We will describe methods to generate TiO₂ nanoparticles supported on HOPG substrates. We then utilize photoelectrochemical deposition to

selectively decorate the TiO₂ particles with metal nanoparticles. These samples are easily amenable to characterization with SEM and TEM imaging as well as electron spectroscopy surface analysis methods. The introduction of noble metals adsorbed on TiO₂ substrates can affect the intrinsic catalytic properties of the metal oxide, however previous research has been focused on single species of adsorbed noble metals (e.g. Pt, Au, Co, etc.) and the result impact on the photocatalytic activity. Typical effects from noble metals include lowering the band-gap requirement of TiO₂ (3.2 eV) in order for electron excitation from the valence band to the conduction band to occur. Our current research focuses on the fabrication and study of two or more noble metal nanoparticle species loaded onto TiO₂ particle arrays and to observe the impact on the catalytic activity, chemistry, electromagnetic field enhancements. The presence of two or more noble metal species may affect the catalytic properties of TiO₂ in interesting ways, such as Au nanoparticles allowing visible light to be absorbed, and Pt particles allowing more efficient photo-chemistry in degrading pollutants. In this work, we photodeposit Pt and Au particles onto TiO₂ particles situated on highly oriented pyrolytic graphite (HOPG). Au and Pt particles are found to be on average 4.7 nm in diameter. Preliminary experiments on bi-metallic loaded particles have been conducted in order to study photocatalytic properties via pollutant degradation rate. Methylene Blue (MB), a common organic dye, is used to observe photocatalytic activity of these particles through UV-induced photo-degradation. Bare TiO₂ particles are known to be photoactive, however the introduction of noble metal species show an increase of MB degradation over time. We are currently observing MB degradation rates with dual-loaded TiO₂ nanoparticles. Previous work in our group has proven that polarized Raman spectroscopy performed on Ag nanoparticle arrays yields a significant increase in signal

1. Wei Luo, W. Van der Veer, P. Chu, D. L. Mills, R. M. Penner, and J.C. Hemminger, *Journal Of Physical Chemistry C*, 2008. : p. 11609-11613.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant number: DE-FG02-96ER45576

9:20am NS-WeM5 **Size-dependent Trends in CO and O₂ Adsorption on Pd Nanoparticle Catalysts**, Hemma Mistry, L.K. Ono, University of Central Florida, B. Roldan Cuenya, Ruhr-University Bochum, Germany

Due to the striking dependence of many catalytic reactions on particle size and shape, a thorough understanding of structure-dependent reactivity trends in the interaction of adsorbates with model nanoparticles (NPs) is key to designing highly active and selective catalysts. Palladium NPs are highly active for important reactions such as CO oxidation and methane combustion. However, conflicting reports exist in the literature on the change in CO and O₂ adsorption strength on Pd NPs of different size. In this study, temperature programmed desorption (TPD) was used to investigate the binding strength of O and CO on Pd NPs supported on SiO₂/Si(111). A range of clusters with Pd deposition thicknesses between 1.5 and 15 Å were investigated and compared to Pd(111). Our results indicate that both O and CO binding strength increase dramatically with decreasing particle size, and the presence of distinct binding sites on the smaller NPs was revealed by CO TPD.

9:40am NS-WeM6 **Mixed Structures of CO and H on Ru(0001) as Precursor States for Fischer-Tropsch Synthesis**, Barbara Lechner, X. Feng, S. Carenco, Lawrence Berkeley National Laboratory, P.J. Feibelman, Sandia National Laboratories, M.B. Salmeron, Lawrence Berkeley National Laboratory

The Fischer-Tropsch reaction is of great importance in the industrial synthesis of hydrocarbon fuels and as such has motivated a large number of studies on the microscopic processes underlying the reaction. However, while the adsorption and interaction of the two reactants, carbon monoxide and hydrogen, on model catalyst surfaces has been investigated in detail for decades, several fundamental questions still remain, in particular that of the nature of the precursor species [1]. In addition, CO and H have been shown to segregate into different domains on single crystal surfaces [2-4], raising the question whether the reaction only takes place at the interface of these domains.

Here we investigate the co-adsorption of CO and H on Ru(0001) using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and density functional theory calculations with the goal of a more detailed understanding of the forces driving the formation of the precursor state in the Fischer-Tropsch reaction. CO and H co-adsorbed at 77 K show a largely unordered structure in STM, while subsequent annealing to 150-300 K results in dense CO islands compressed and separated by H atom regions that decrease in size with increasing annealing temperature. Unexpectedly, further annealing to 300-350 K gives rise to a mixed phase of CO and H in a 1:1 ratio. XPS measurements confirm a change in bonding geometry upon

annealing. We believe that studying the transition from a segregated to a mixed phase is an important step toward tracing the microscopic reaction pathway.

[1] R. A. van Santen, A. J. Markvoort, I. A. W. Filot, M. M. Ghouri, E. J. M. Hensen, *Phys.Chem. Chem. Phys.* 15, 17038 (2013).

[2] D. E. Peebles, J. A. Schreifels, J. M. White, *Surf. Sci.* 116, 117 (1982).

[3] B. Riedmuller, D. C. Papageorgopoulos, B. Berenbak, R. A. van Santen, A. W. Kleyn, *Surf. Sci.* 515, 323 (2002).

[4] I. M. Ciobica, A. W. Kleyn, R. A. van Santen, *J. Phys. Chem. B* 107, 164 (2003).

11:00am **NS-WeM10 *In Situ* Investigation of Oxidation State and Reactivity of a Cu Model Catalyst by Simultaneous Mass Spectrometry and Indirect Nanoplasmonic Sensing**, *Hans Fredriksson, H.J.W. Niemantsverdriet*, Eindhoven University of Technology, Netherlands

The activity of a catalyst depend on a wide range of factors such as elemental composition, particle dispersion and the oxidation state of the active material. All of these properties can change during operation, reversibly or irreversibly, thereby severely influencing the catalysts performance. It is therefore of great importance to learn how the fundamental properties of a catalyst change during use and to correlate these changes with changes in activity and selectivity. This requires simultaneous, in-situ measurements of both fundamental catalyst properties and activity, a far from trivial task. Here we present a novel quartz-tube micro flow-reactor in which optical spectroscopy and mass spectroscopy can be performed simultaneously. The optical setup is based on indirect nanoplasmonic sensing, which utilizes the localized surface plasmon resonances of Au-discs embedded in Si₃N₄ to detect subtle changes in the oxidation state of a material. We investigate CO-oxidation on a model catalyst consisting of Cu nanoparticles formed by thin film evaporation and subsequent annealing. From these measurements we demonstrate the correlation between oxidation state of the Cu-catalyst and onset temperature for CO₂ formation in gas mixtures with various CO/O₂ ratios. The changes in oxidation state were then confirmed by XPS.

11:20am **NS-WeM11 Controlling Surface Reactivities of TiO₂ (110) by Nanoscale Strain Field**, *Zhisheng Li, D.V. Potapenko, R.M. Osgood*, Columbia University

Strain is found to be an ubiquitous quantity in nanostructured surfaces and on supported catalysts. Therefore, understanding the influence of strain on surface properties is crucial for rational design of catalytic materials. The study of the interaction of nanoscale strain and adsorbate reactivity presents two experimental challenges, generating an intense strain field and differentiating strain effects from effects induced by change in other surface properties. In this work, we generate a patterned, nanoscale strain field on TiO₂ (110) surface by low energy bombardment of single crystal TiO₂ samples with argon ions at 1000°C. The interstitial argon diffuses so as to self-assemble into highly pressurized argon clusters and distort the surrounding lattice a few nanometers below the surface. As a result, the top surface layers of the crystal have a convex morphology while retaining their unstressed surface structures, thus introducing nanometer-size surface protrusions. The strain level obtained on the protrusions can be as large as ~4%. The locally varying strain field across the protrusion is ideal for strain effects study. By combining scanning tunneling spectroscopy (STM) imaging and continuum model, we show that the adsorption energy of hydrogen binding to surface bridge-bonded oxygen (BBO) is significantly altered by local lattice strain. In particular, strain causes, oxygen vacancies (BBOv) to be absent from the strained area. Our results thus provide direct evidence of the influence of strain on atomic-scale surface properties and thus help guide future research in catalysis materials design

11:40am **NS-WeM12 NSTD Recognition Award Lecture: Probing Local Optoelectronic Properties of Porphyrin-Gold Molecular Interfaces with STM/STS**, *X. Chen, E.H. Morales, T.-H. Park*, University of Pennsylvania, *M.J. Therien*, Duke University, *Dawn Bonnell**, University of Pennsylvania

INVITED

Porphyrin molecules are a group of organic compounds that exist extensively in natural biological systems, and they manifest rich electronic and photonic properties, raising the possibility of optoelectronic device applications. In this research thiolated Zinc-porphyrin oligomer molecules were linked to Au(111) surface in a vertical device configuration, embedded within an alkanethiol self-assembled monolayer. Spectroscopic measurements were done to determine the electronic orbital structures of different Zinc-porphyrin oligomer single molecules via scanning tunneling microscope. With lasers of different wavelength coupled to the tunneling

junction, both ground state and excited state electronic orbital structures of Zinc-porphyrin single molecule were measured.

Authors Index

Bold page numbers indicate the presenter

— B —

Bonnell, D.A.: NS-WeM12, **2**

— C —

Carenco, S.: NS-WeM6, **1**

Chen, X.: NS-WeM12, **2**

— F —

Feibelman, P.J.: NS-WeM6, **1**

Feng, X.: NS-WeM6, **1**

Fredriksson, H.: NS-WeM10, **2**

— H —

Hemminger, J.C.: NS-WeM4, **1**

— L —

Lechner, B.A.J.: NS-WeM6, **1**

Li, Z.: NS-WeM11, **2**

Liu, Y.: NS-WeM4, **1**

— M —

McEntee, M.: NS-WeM3, **1**

Mistry, H.: NS-WeM5, **1**

Morales, E.H.: NS-WeM12, **2**

— N —

Neurock, M.: NS-WeM3, **1**

Niemantsverdriet, H.J.W.: NS-WeM10, **2**

— O —

Ono, L.K.: NS-WeM5, **1**

Osgood, R.M.: NS-WeM11, **2**

— P —

Park, T.-H.: NS-WeM12, **2**

Potapenko, D.V.: NS-WeM11, **2**

— R —

Reyes, P.: NS-WeM4, **1**

Roldan Cuenya, B.: NS-WeM5, **1**

— S —

Salmeron, M.B.: NS-WeM6, **1**

Sykes, E.C.H.: NS-WeM1, **1**

— T —

Tang, W.: NS-WeM3, **1**

Therien, M.J.: NS-WeM12, **2**

— Y —

Yates, Jr., J.T.: NS-WeM3, **1**