

Tuesday Afternoon, November 1, 2011

Surface Science Division
Room: 109 - Session SS-TuA

Supported by DOE contract No. DE-FG02-93ER14331

Catalysis on Metals and Alloys

Moderator: G. Fisher, University of Michigan

2:00pm **SS-TuA1 La_{1-x}Ce_xMnO₃ Perovskites: Structural Features and Performance for Preferential CO Oxidation Reaction**, *S.S. Maluf*, Federal University of Sao Carlos, Brazil, *B.E. Hayden*, University of Southampton, UK, *C.R.M. Afonso*, Federal University of Sao Carlos, Brazil, *E.M. Assaf*, University of Sao Paulo, Brazil, *P.A.P. Nascente*, Federal University of Sao Carlos, Brazil

The perovskite structure is characterized by a large capacity to stabilize unusual valence states of different metal ions and can also accommodate variable amounts of different lattice defects. Several lanthanum transition metal based perovskites, represented as La_{1-x}A_xMO₃, have been known as very good oxidation catalysts in a variety of reactions. Particularly, LaMnO₃ perovskites have shown to be the most active. The catalytic activity of these compositions in different reactions can be further enhanced by the substitution of lanthanum by cerium. The catalysts were prepared by co-precipitation method, from aqueous solutions of La, Mn, and Ce nitrates with Na₂CO₃/NaOH solution (pH 10). The prepared samples were La_{1-x}Ce_xMnO₃ (x = 0, 0.05, and 0.10) and were characterized by EDS-SEM, surface area-BET method, X-ray diffraction (XRD), and temperature programmed reduction (TPR). The catalytic activity was tested over the temperature range of 130–230°C in a fixed-bed tubular glass micro-reactor, with 200mg of catalyst. The reaction products were analyzed in-line by gas chromatography. The amounts of the constituent metals obtained by EDS were in agreement with expected values; the presence of cerium did not change the surface area of the samples (26–27m² g⁻¹). The X-ray diffraction lines corresponded to cubic LaMnO₃ structure; the replacement of La did not change the diffractograms. Peaks of cerium oxide were not observed, suggesting the incorporation of Ce ions into the LaMnO₃ lattice. The sample with the highest content of cerium presented an increase on thermal stabilization of Mn³⁺ ions, and Mn⁴⁺ species were reduced to lower temperatures. The SEM results indicated that the presence of cerium decreased slightly the grain size (from 56 to 43 nm) and the range of distribution sizes is homogeneous and the most grains are spherical. All samples presented the same catalytic behavior, starting their activities at 130°C, and their activities increased with the temperature. At 150°C, the sample with 5% of Ce presented a slight advantage compared to other samples, and this was more significant at 230°C, indicating that the promoter effect of cerium can be observed for higher reaction temperatures. The results suggested that the replacement of La by Ce caused an increase of cationic/anionic vacancies and also in the Mn⁴⁺/Mn³⁺ ratio change, and consequently the catalytic behavior for CO oxidation changed, facilitating the CO adsorption.

Acknowledgements

The authors thank FAPESP for financial assistance, Ilika Technologies and University of Southampton for the XRD analyses.

2:20pm **SS-TuA2 Faceted Metal Surfaces: Surface Chemistry and Growth of Metallic Nanoclusters**, *W. Chen, Q. Shen, R.A. Bartynski*, Rutgers University

In this work, surface faceting is used to prepare a nanoscale model catalyst for surface reactions and a nanoscale template for growth of metallic nanoclusters. Faceting occurs when an initially planar surface converts to a “hill and valley” structure exposing new crystal faces of nanometer scale dimensions. Nanoscale three-sided pyramids exposing (311), (31-1) and (110) faces with tunable facet sizes are formed on an initially planar Ir(210) surface upon annealing in O₂ and a clean faceted Ir(210) surface can routinely be prepared in situ by heating in H₂. Surface reaction of NO+CO has been carried out on clean planar Ir(210) and clean faceted Ir(210) with varying facet size (5–14nm). Both planar and faceted Ir(210) favor reduction of NO by CO with high selectivity to N₂, which is accompanied by simultaneous oxidation of CO. The reaction is not only structure sensitive on faceted Ir(210) versus planar Ir(210) but also exhibits size effects on faceted Ir(210) for average facet size ranging from 5nm to 14nm without change in facet structure. Strong interaction between NO and CO at high NO exposure and IML CO pre-coverage results in “explosive” evolution of N₂ and CO₂ on planar Ir(210). Annealing Ru(11-20) in NO₂ leads to formation of ridge-like faceted surface exposing (10-11), (10-1-1), (01-11) and (01-1-1) faces. Faceted O/Ru(11-20) facilitates growth of nanoscale metallic clusters at room temperature which preferentially nucleate within valleys of the faceted surface.

2:40pm **SS-TuA3 Modeling the Complexities of Heterogeneous Catalysts**, *D.W. Goodman, Matt Lundwall*, Texas A & M University
INVITED

In the past several decades, surface science methodologies have contributed significantly to our understanding of reaction mechanisms of heterogeneous catalysts. From fundamental studies on metal single crystals to investigations of metal oxide supported metal clusters, the relative complexities of metal catalyst systems have continued to evolve in complexity and likeness to industrial catalysts. Studies on metal single crystals have aided researchers in understanding the effect of surface structure on catalyst reactivity and selectivity for a number of important reactions. More recently model systems consisting of metal clusters deposited on planar oxide surfaces under ultra high vacuum conditions have facilitated the study of metal particle size and support effects. These model systems are useful for carrying out kinetic investigations, yet are amenable to surface spectroscopic techniques, thus enabling investigations under realistic pressures and at working temperatures. This talk will present selected investigations of catalytic reactions on single crystal and model supported catalysts with emphasis on recent work addressing the nature of the active site in structure sensitive reactions.

4:00pm **SS-TuA7 Nanocatalysis: New Developments in Catalytic Performance of Size- and Shape-Controlled Metal Nanoparticles**, *B. Roldán Cuenya*, University of Central Florida

Tailoring the chemical reactivity of nanomaterials at the atomic level is one of the most important challenges in catalysis research. In order to achieve this elusive goal, fundamental understanding of the geometric and electronic structure of these complex systems at the atomic level must be obtained. To study these effects, homogeneous size- and shape-selected Pt nanoparticles (NPs) were synthesized by means of diblock copolymer encapsulation.

The influence of the nanoparticle *shape* on the reactivity of Pt nanocatalysts supported on nanocrystalline γ -Al₂O₃ will be described. Nanoparticles with similar size distributions (~0.8–1 nm) but with different shapes were found to display distinct reactivities for the oxidation of 2-propanol. A correlation between the number of undercoordinated atoms at the nanoparticle surface and the onset temperature for 2-propanol oxidation was observed, demonstrating that catalytic properties can be controlled through shape-selective synthesis. Furthermore, the complex interaction between catalysts and reactants was investigated under *operando* conditions via X-ray absorption fine-structure spectroscopy. Platinum oxides were found to be the active species for the partial oxidation of 2-propanol (<140°C), while the complete oxidation (>140°C) was catalyzed by oxygen-covered metallic Pt NPs. Our findings highlight the decisive role of the nanoparticle structure and chemical state in oxidation catalytic reactions.

4:20pm **SS-TuA8 Oxidative-Coupling Reactions via Nucleophilic Attack on Gold Surface**, *B. Xu**, *C.M. Friend, R.J. Madix*, Harvard University

Metallic gold owes its centuries-old mystique and intrinsic value to its chemical inertness toward bulk compound formation. In the past decade, however, it has been discovered that the surface of gold is far from inert, and that gold can catalyze important chemical transformations – particularly with the assistance of molecular oxygen or other oxidizing agents. These processes are of particular significance because they may occur at remarkably low temperatures and pressures, suggesting the possibility of energy efficient and environmentally benign reaction conditions using metallic gold catalysts. Recently, there has been a focus on selective oxidation of alcohols to aldehydes, oxidative self-coupling of alcohols to form esters and, most recently, acylation via amine-formaldehyde coupling. Our work under ultra-high vacuum (UHV) condition on the well defined model system of Au(111) surface has unequivocally proved that surface adsorbed atomic oxygen is critical in facilitating a range of nucleophilic coupling-reactions among alcohols, aldehydes and amines. A general reaction mechanism for this class of coupling-reactions is established: surface alkoxy or amide is formed via the deprotonation of the corresponding alcohol or amine by surface atomic oxygen, which can subsequently nucleophilically attack the aldehydes (formed in situ from alkoxy or introduced directly) and produce the corresponding ester or amide. The product distribution of our low-pressure experiments match remarkably well with gas phase reactions carried out in the ambient

* Morton S. Traum Award Finalist

condition as well as liquid phase reactions, proves the generality of the mechanism.

4:40pm **SS-TuA9 Understanding the Enhanced Activity for Methanol Reaction on Titania-supported Au Clusters**, *D.A. Chen, S.A. Tenney, B.A. Cagg, M.S. Levine*, University of South Carolina, *S. Hong, T.S. Rahman*, University of Central Florida

The growth and chemical activity of Au clusters deposited on rutile TiO₂(110) were studied by scanning tunneling microscopy, temperature programmed desorption and density functional theory calculations. Methanol reaction on 0.25 ML Au clusters produces formaldehyde as the major product at 535 K with methanol desorption observed at the same temperature; water and hydrogen evolution are detected below room temperature, as well as methyl radical evolution at 575 K. On the titania surface itself, methanol reaction also produces methyl radical around 600 K. Formaldehyde production reaches its maximum value between 0.25 and 2 ML but decreases dramatically as the coverage is increased to 5 ML. This behavior suggests that formaldehyde is produced at the Au-titania interface since formaldehyde production does not occur at pure Au sites. STM experiments confirm that the 0.25 ML Au coverage has the greatest number of Au-titania interfacial sites at the perimeter of the clusters. For higher coverages of 2 and 5 ML, cluster coalescence diminishes the number of Au-titania sites, and this is consistent with the decreased formaldehyde yield at higher Au coverages. When the titania surface is reoxidized with ¹⁸O₂ prior to Au deposition and exposure to methanol, lattice oxygen is incorporated into the water that is evolved at low temperature. We propose that the role of the titania support is to facilitate the formation of the reactive methoxy intermediate via abstraction of the hydroxyl hydrogen in methanol by lattice oxygen. Density function theory calculations also indicate that methoxy is the intermediate formed at the Au-titania interface after O-H bond scission is induced by lattice oxygen.

5:00pm **SS-TuA10 Oxygen Chemisorption, Formation, and Thermal Stability of Pt Oxides on Pt Nanoparticles Supported on SiO₂/Si(001): Size-Effects**, *L.K. Ono, J.R. Croy, H. Heinrich, B. Roldan Cuenya*, University of Central Florida

The changes induced in the structure and chemical state of size-selected Pt nanoparticles (NPs) supported on ultrathin SiO₂ films upon exposure to oxygen have been investigated by atomic force microscopy, transmission electron microscopy, in situ X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD). For low atomic oxygen dosings, chemisorbed oxygen species were detected on all samples. Exposure to higher atomic oxygen coverages at room temperature lead to the formation and stabilization of PtO_x species (PtO₂ and PtO). On all samples, a two-step thermal decomposition process was observed: PtO₂ → PtO → Pt. For NPs in the 2-6 nm range, the NP size was found to affect the strength of the O-binding. Contrary to the case of Pt(111), where no oxides were detected above 700 K, 10-20% PtO was detected on the NP samples via XPS at the same temperature, suggesting the presence of strongly bonded oxygen species. In addition, for identical atomic oxygen dosings, decreasing the NP size was found to favor their ability to form oxides. Interestingly, regardless of whether the desorption of chemisorbed oxygen species or that of oxygen in PtO_x species was considered, our TPD data revealed higher O₂ desorption temperatures for the Pt NPs as compared to the Pt(111) surface. Furthermore, a clear size-dependent trend was observed, with an increase in the strength of the oxygen bonding with decreasing NP size.

5:20pm **SS-TuA11 Alloy Surface Reactivity on Cu_xAu_yPd_{1-x-y} Composition Spread Alloy Films**, *A.J. Gellman, J.B. Miller, P. Kondratyuk, D. Priyadarshini*, Carnegie Mellon University, *B.D. Morreale*, National Energy Technology Laboratory

The key features of Cu-Au-Pd alloys relevant to their application as hydrogen purification membranes are the ability to dissociatively adsorb H₂ and the ability to transport H atoms through their bulk. We have developed tools for the preparation of Cu_xAu_yPd_{1-x-y} composition spread alloy films (CSAFs) as libraries for high throughput study of their catalytic surface properties. These ternary Cu_xAu_yPd_{1-x-y} CSAFs expose a broad and continuous distribution of compositions for spatially resolved analysis of their properties. Electron backscatter diffraction has been used to verify the structure of the films across their composition spread and to demonstrate that they have the atomic structure expected on the basis of their phase diagram. LIES has been used to study surface segregation as a continuous function of composition, (x,y), demonstrating that segregation is preferred in the order Au>Cu>Pd at the clean alloy surfaces. A multichannel microreactor array has been used to spatially resolve the surface activity for H₂ dissociation by measuring the kinetics of H₂-D₂ exchange as a function of alloy composition. This reveals that while both Cu and Au poison surface activity, Cu is more effective than Au at suppressing H-D exchange activity. This work demonstrates the potential value of CSAFs as platforms for study

of alloy surface chemistry and for comprehensive study of their properties across composition space.

5:40pm **SS-TuA12 Pd Ensemble Effects on Enhancing Low Temperature CO Oxidation and Tolerance on AuPd Alloys: A First Principles Study**, *H.C. Ham, J.A. Stephens, G.S. Hwang*, University of Texas at Austin

In the oxidation reaction of fuels such as CO-contained hydrogen, methanol and formic acid at the low temperature region (300 ~ 400K) at the anode side of polymer electrolyte membrane fuel cell, the precious catalysts such as Pd and Pt have suffered the gradual loss in the catalytic activity due to the blocking of active sites (Pd/Pt) by CO molecules (the so-called CO poisoning effect). To handle this issue, alloying precious catalysts by other transition metals has been suggested as one of solutions since the synergetic alloying effects such as the creation of unique mixed-metal surface sites [ensemble effect] and electronic structure change by metal-metal interactions [ligand effect] can provide an avenue for preventing CO poisoning and enhancing CO oxidation at the low temperature.

In this talk, we will present our recent first-principles results on the role of Pd ensembles on the AuPd alloy in enhancing CO oxidation and tolerance at the low temperature. Using spin-polarized DFT-GGA calculations, for the first time, we elucidate that the reactivity toward CO+O₂ oxidation at the low temperature on various CO-precovered Pd ensembles (such as monomer, dimer, trimers and tetramers) is a strong function of surface Pd arrangements on the AuPd surface. In particular, the small-sized ensembles like dimer or compact trimer are responsible for enhancing the low temperature CO+O₂ oxidation by the increased availability of free Pd sites and facile O₂ activation on CO-precovered Pd ensembles. We will also show the importance of the interplay of ensemble and ligand effects in reducing the CO poisoning of the catalysts through the comparison study on the energetics, charge transfer, geometric and electronic structures of CO between Pd and Pt ensembles. Finally, we will present geometric parameter effects (such as strain and facet) on the CO tolerance of Pd ensembles, which can provide the proper criteria for designing the nano-sized Au-based bimetallic catalysts.

This study hints on how the surface arrangements of atoms and the influence of ensembles on the reaction kinetics and energetics can offer insight to properly tailor CO-tolerant Au-based bimetallic catalysts for fuel cell applications.

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