

# Monday Afternoon, November 10, 2014

## Surface Science

Room: 309 - Session SS+EN-MoA

## Metals, Alloys and Oxides: Structure, Reactivity & Catalysis

Moderator: Jason Weaver, University of Florida

2:00pm **SS+EN-MoA1 High Throughput Discovery and Optimisation of Metal Alloy Electrocatalysts**, *Brian Hayden*, University of Southampton **INVITED**

High-throughput synthesis and screening methodologies provide a powerful tool for the optimisation of alloy electrocatalysts. Libraries of thin film metal alloys have been synthesised using MBE sources to produce compositional gradient thin films in masked fields on micro-fabricated electrochemical screening chips. Examples will be given of ternary metal alloy catalysts designed as alternatives to platinum for the oxygen reduction reaction at the cathode in PEM Fuel Cells. The combination of ab-initio theory and high throughput synthesis and electrocatalyst screening is also shown to provide a powerful combination in the search for alternative catalysts to platinum for hydrogen oxidation at the anode. The approach has also been extended to the development of PdCu and PdSn alloys for the electro-reduction of nitrate, alloys which exhibit strong compositional dependencies which can be related to the redox behaviour of the surfaces. A full structural characterisation allows a direct comparison of catalytic activity to not only composition but also to the structure and phase of the alloy. In addition to measuring the total activity of the electrocatalysts, a secondary screen has been developed adapting the Differential Electrochemical Mass Spectroscopy (DEMS) method to assess the specificity of the reaction to produce the desired gas phase product.

2:40pm **SS+EN-MoA3 Methanol Oxidation on Pt-Re Surfaces: Ambient Pressure XPS and Reactor Studies**, *A.S. Duke, R.P. Galhenage, K. Xie*, University of South Carolina, *S.A. Tenney, P. Sutter*, Brookhaven National Laboratory, *Donna Chen*, University of South Carolina

Methanol oxidation has been investigated on Pt-Re bimetallic surfaces in order to understand how the addition of Re promotes activity on Pt in alcohol reforming and other oxidation reactions. Pt-Re alloy surfaces were prepared by depositing Re on Pt(111) or polycrystalline Pt foils and annealing to 1000 K. Scanning tunneling microscopy studies demonstrate that the deposited Re islands diffuse into the Pt(111) surface upon annealing, and low energy ion scattering studies indicate that the top monolayer consists mainly of Pt. XPS investigations were carried out at the X1A1 beamline at the National Synchrotron Light Source under methanol oxidation conditions of 200 mtorr  $O_2$ /100 mtorr methanol between 300 and 550 K, and gaseous products were monitored using a mass spectrometer. Methanol oxidation was studied on clean Pt(111), the Pt-Re alloy and Re films grown on Pt before and after surface oxidation at 450 K. The main products on all surfaces were  $CO_2$  and  $H_2O$  with formaldehyde, CO and  $H_2$  as minor products. On the unoxidized surfaces, the selectivity toward  $H_2$  and CO production increased above 500 K. Deposition of atomic carbon during reaction was suppressed on the Pt-Re alloy surfaces as compared to pure Pt, and the oxidized Pt-Re alloy was found to reach maximum activity at the lowest temperatures. The Re films were unstable under methanol oxidation conditions at temperatures above 450 K due to the sublimation of Re oxides, but the Re in the Pt-Re alloy remained on the surface under the same conditions. Activity studies in a flow reactor coupled to the ultrahigh vacuum chamber showed that methanol oxidation activity increases with surface oxidation; unoxidized Pt and Pt-Re surfaces initially exhibit minimal activity until the surface becomes oxidized under reaction conditions.

3:00pm **SS+EN-MoA4 Ångstrom-resolved Real-Time Dissection of Electrochemically Active Noble-Metal Interfaces during Oxidation and Reduction**, *B.R. Shrestha, T. Baimpos, S. Raman, Markus Valtiner*, Max Planck Institut für Eisenforschung GmbH, Germany

Electrochemical metal-oxide|liquid interfaces are critically important for a variety of technological applications and materials for energy storage, harvesting and conversion. Yet, a real-time Ångstrom-resolved visualization of dynamic processes at electrified metal-oxide|liquid interfaces has not been feasible. Here we present a unique direct and real-time atomistic experimental view into dynamic processes at electrochemically active metal interfaces using white light interferometry in an electrochemical surface forces apparatus. This method allows to simultaneously decipher both sides of an electrochemical interface - the solution side and the metal side - in real-time under dynamically evolving reactive conditions, which are

typically found in technological systems *in operando*. Quantitative *in situ* analysis of the electrochemical oxidation and reduction of noble metal surfaces shows that the Å-thick oxide films formed on Au and Pt are reflecting high-*ik* materials, *i.e.* they are metallic or highly doped semiconductors, while Pd forms a transparent low-*ik* oxide during dynamic change of applied electrochemical potentials. In contrast, under potentiostatic growth conditions all electrochemically grown noble metal oxides are transparent, with thicknesses ranging from 2-10 Å. On the solution side the data simultaneously reveals hitherto unknown strong electrochemical depletion forces, which are due to a temporary charge imbalance in the electric double layer caused by the consumption or generation of charged species. The real time capability of our approach shows significant time lags between electron transfer, oxide reduction/oxidation and solution side equilibration during a progressing electrode process. Comparing the kinetics of solution side and metal side reactions provide detailed experimental evidence that noble metal oxide reduction initiates via hydrogen loading and subsequently proceeds via a dissolution/re-deposition mechanism. The presented approach may have important implications for designing emerging materials utilizing electrified interfaces such as fuel cells, batteries or super-capacitors.

3:40pm **SS+EN-MoA6 Catalytic Dehydration of 2-propanol on Size Selected  $(WO_3)_n$  and  $(MoO_3)_n$  Metal Oxide Clusters**, *Xin Tang*, Johns Hopkins University, *D. Bumüller, G. Gantefoer*, Universität Konstanz, Germany, *D.H. Fairbrother, K.H. Bowen*, Johns Hopkins University

Metal oxide nanoparticles and clusters are widely used as redox and acid/base catalysts in heterogeneous catalysis. The catalytic activity of the size selected metal oxide clusters  $(WO_3)_n$  and  $(MoO_3)_n$  ( $n = 1, 2, 3, 5, 30$ ) were studied as a function of their size. The 2-propanol dehydration reaction was conducted on both two cluster catalysts. Temperature programmed reaction (TPR) was utilized to characterize the catalytic activity of the deposited cluster catalysts. The cluster size, supporting substrates, and the chemical compositions of the clusters were found to play an important role in determining the catalytic activity of the metal oxide clusters. For tungsten oxide clusters on the annealed oxide films, the catalytic activity of the clusters was found to be linear correlated to the size of the cluster. In addition, lower catalytic activity was observed for  $(WO_3)_1$  monomer supported on the HOPG surface compared to the annealed oxide support. Meanwhile, molybdenum oxide clusters exhibited low catalytic activity toward 2-propanol dehydration reactions.

4:00pm **SS+EN-MoA7 Growth and Characterization of Ultrathin ZnO Layers on Au(111) – STM Study of Growth Mode and Adsorption of Water**, *Junseok Lee, X. Deng, D.C. Sorescu*, National Energy Technology Laboratory

Zinc oxide is an important material in the low-temperature synthesis of methanol. In this study, the growth mode of ZnO ultrathin films has been studied on the Au(111) surface using scanning tunneling microscopy (STM). The ultrathin ZnO layers have been found to grow by forming islands on Au(111). Different growth conditions during reactive deposition resulted in ZnO islands whose thickness ranging from one to four layers. The STM results and the density functional theory (DFT) calculation have been used to model the observed phenomena. STM results indicate that the brightness of the Moiré pattern of the ZnO layer on Au(111) surface is significantly modulated by the adsorption of water molecule at the positive tip bias. Various water adsorption sites have been identified in the STM results after annealing the sample to various temperatures that correspond to temperature programmed desorption (TPD) peaks. The DFT calculation results provide the most stable configurations of water molecules at each adsorption site.

4:20pm **SS+EN-MoA8 In Situ Imaging of the Dynamic Interaction of the Oxide with the Atomic Steps During the Oxide Growth on NiAl(100)**, *Hailang Qin*, SUNY Binghamton, *X. Chen*, Biola University, *P. Sutter*, Brookhaven National Laboratory, *G.W. Zhou*, SUNY Binghamton

Ultrathin oxide films on metal supports represent a unique combination of materials systems with potential applications ranging from heterogeneous catalysis to electronic devices. In particular, the oxidation of NiAl alloys has received extensive interest for its ability to form a well-ordered  $Al_2O_3$  film. Here we study the dynamic interaction of the atomic steps with the oxide stripes during their growth on single-crystal NiAl(100) at high temperature. With in-situ low-energy electron microscopy (LEEM) imaging and theoretical modeling, it is shown that the oxygen surface diffusion is the main mechanism controlling the oxide growth kinetics while the migration and shape evolution of the substrate steps follows the fluid-like Hele-Shaw flow governed by the attachment/detachment of Al atoms at step edges. When the oxide stripe encounters a series of step edges, the step edges are

“pushed” along with the oxide stripe growth and bent towards the growth direction of the stripe. However, the growing oxide stripes do not cross over the substrate steps; instead, they stay on the same terrace even after encountering a number of step edges. Such a process is reversible during the oxide decomposition. The scanning tunneling microscopy (STM) images of the oxide stripes and the atomic steps after the interaction further confirm that the oxide stripes stay on the same terrace after encountering multiple substrate steps, instead of crossing the step edges.

4:40pm **SS+EN-MoA9 Subsurface Oxygen on Ni(111) and Ag(111)**, *Daniel Killelea, J. Derouin, R. Farber*, Loyola University Chicago

Subsurface oxygen atoms are enigmatic sources of energetic reagents in the heterogeneously catalyzed partial oxidation of small hydrocarbons on metal surfaces. Subsurface oxygen atoms are absorbed in the seldedge of a metal, and may emerge to the surface at elevated temperatures to react with adsorbed molecules. Furthermore, when subsurface atoms emerge from beneath adsorbed molecules new reaction geometries are enabled that are otherwise inaccessible between reactants co-adsorbed to a surface. Although believed to be important reactive intermediaries, a systematic study of their fundamental chemistry has yet to be undertaken. To address this, we have selected two model systems for study; oxygen on Ni(111) and Ag(111). These are two systems that will provide basic details of subsurface absorption and reactivity, and further provide guidance for utilization of these species to selectively control chemistry. Subsurface atoms are key components of catalytic processes, but it remains unclear how they enhance reactions. The surface-subsurface dynamics will be elucidated using scanning tunneling microscopy (STM) to image the surfaces with and without subsurface O atoms. We will use the images to determine the presence of a bias for particular surfaces sites for the absorption / emergences processes and further study any structural or electronic effects of the subsurface O atoms on the host metal surface. To complement STM images, temperature programmed desorption and Auger electron spectroscopy will identify adsorbates and provide thermodynamic information. Our results will show mechanisms for subsurface migration and we will also probe the energetics of subsurface incorporation. Taken together, this new information seeks to narrow the gap our understanding between model and actual catalytic systems and enable chemists to accurately gauge the role of subsurface species in the transformation of plentiful feedstock into energy-rich chemicals over metal catalysts.

5:00pm **SS+EN-MoA10 Direct Imaging of the Amphoteric Nature of Rutile (110) Surfaces in Solution**, *Dapeng Jing, A. Song, M.A. Hines*, Cornell University

High-profile applications of nanocrystalline TiO<sub>2</sub>, such as next-generation solar cells and self-cleaning surfaces, have triggered extensive studies on the structure and chemical reactivity of rutile surfaces. But are UHV-prepared clean surfaces a good representation of technologically relevant surfaces? In this study, we show that a simple aqueous procedure produces near-ideal hydrocarbon-free rutile (110) surfaces characterized by well-defined terraces and nearly straight, single-layer-high steps without high-temperature annealing. The structure of rutile surfaces after water exposure is very different from that observed on UHV-prepared clean surfaces. In particular, the O vacancies that dominate the reactivity of surfaces in UHV are not present, as evidenced by both XPS spectra and STM images. This water-induced “healing” of O vacancies is consistent with chemical intuition. The step structures, too, are quite different. In addition, the amphoteric nature of the surface is directly observed in STM. Depending on the pH of the solution, a low density of protrusions decorate either the Ti rows or the bridging oxygen atoms, consistent with pH dependent protonation/deprotonation of the basic/acidic sites on the surface. No evidence of the corresponding counterions is observed.

5:20pm **SS+EN-MoA11 Water Splitting Kinetics at MgO(100) Terrace Sites**, *John Newberg*, University of Delaware

Understanding the surface chemistry of water with metal oxide interfaces has important implications in energy and environmental research. In order to understand surface kinetics and thermodynamics under environmental conditions, in situ molecular level studies are needed to assess adsorbate chemistry and coverage under conditions where adsorption and desorption occur concomitantly. In this talk we will outline a proposed precursor kinetic model to describe recently published ambient pressure XPS (APXPS) results for MgO(100) terrace hydroxylation observed under adsorption-desorption conditions. By combining APXPS with computational studies, mechanistic details for water dissociation on MgO(100) terrace sites are put forth.

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