Surface Science Division
Room A220-221 - Session SS+AS+HC+OX-WeA

Reactions at Alloy Surfaces and Single Atom Catalysis

Moderators: Erin Iski, University of Tulsa, Bruce E. Koel, Princeton University

2:20pm SS+AS+HC+OX-WeA1 Correlating Structure and Function for Nanoparticle Catalysts, *Graeme Henkelman,* University of Texas at Austin **INVITED**

Metal nanoparticles of only 100-200 atoms are synthesized using a dendrimer encapsulation technique to facilitate a direct comparison with density functional theory (DFT) calculations in terms of both structure and catalytic function. Structural characterization is done using electron microscopy, x-ray scattering, and electrochemical methods. Combining these tools with DFT calculations is found to improve the quality of the structural models. DFT is also successfully used to predict trends between structure and composition of the nanoparticles and their catalytic function for reactions including the reduction of oxygen and selective hydrogenation. This investigation demonstrates some remarkable properties of the nanoparticles, including facile structural rearrangements and nanoscale tuning parameters which can be used to optimize catalytic rates. In this presentation I will focus on a pair of random alloy bimetallic nanoparticles which have complete different trends in hydrogenation activity as a function of composition. Pd/Au is found to be tunable as a function of composition whereas Pt/Au is not. The reason behind these different behaviors will be discussed.

3:00pm SS+AS+HC+OX-WeA3 Surface Reactivity of PtAg and PdAg: From Single-Atom Alloys to Supported Nanoparticles, *Dipna Patel[1][2],* Tufts University*; C.R. O'Connor, R.J. Madix, C.M. Friend,* Harvard University*; E.C.H. Sykes,* Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt and Pd are catalytically active towards hydrogenation, they are often costly, and can suffer from poisoning by CO and coke. Previously, Ag based catalysts have been modified by alloying Pt or Pd for applications in highly selective heterogeneous catalysis. This has shown promise for catalyst design since Ag is cheaper and more resilient to poisoning. It is well known that ensemble size can dramatically change the catalytic pathway, however the atomic-scale structure of PtAg and PdAg alloys and their relation to catalytic activity is still unknown. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of Pt deposited on Ag(111) as a function of alloying temperature. At low temperatures, intermixing of PtAg is driven by a negative mixing enthalpy, resulting in different metastable states such as isolated Pt atoms in, and islands on, Ag terraces, as well as Pt rich brims located along Ag step edges. Increasing the alloying temperature results in an increased concentration of Pt atoms along Ag steps edges as well as direct exchange of Pt atoms into Ag terraces. At higher temperatures, there is sufficient thermal energy for Pt atoms to fully disperse in the Ag(111) surface layer as isolated atoms, forming single-atom alloys. STM characterization of the surface structure of PdAg alloys reveals the formation of large Pd islands on Ag(111). Using STM, we investigated H_2 activation on active Pd sites and spillover on to Ag(111). The characterization of PtAg and PdAg surface alloys enables us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and to inform catalyst design that optimizes catalytic selectivity.

3:20pm SS+AS+HC+OX-WeA4 Single-site Catalysts by Metal-ligand Complexation at Surfaces: From Model Systems in Vacuum to High-pressure Catalysis on Oxide Supports, *Steven L. Tait,* Indiana University

A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. Our group is working to apply principles of on-surface metal-organic redox assembly to develop a new approach to this problem. Metal-organic coordination networks at surfaces hold promise for selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. Studies of model systems in ultra-high vacuum allow for detailed characterization of the structure and chemistry of these systems. We tested chemical activity of vanadium single-site complexes that are stabilized by tetrazine-based ligands and found activity toward

dioxygen activation with a high degree of selectivity compared to vanadium nanoparticles. Reaction with O_2 causes an increase in V oxidation state from V^{II} to V^{IV}, resulting in a single strongly bonded V-oxo product and spillover of O to the Au surface [1]. The metal centers are stabilized in extended, ordered metal-organic complexes that self-assemble through an on-surface redox process on the Au(100) surface and are characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, and density functional theory. New results extend these chemical studies to more complex systems that include bimetallic sites and redox isomer systems [2-3], which will also be highlighted in this presentation.

We have also developed synthesis schemes to assemble quasi-square planar metal-organic complexes on high surface area powdered oxides under ambient conditions through a modified wet-impregnation method. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and synchrotron-based X-ray absorption spectroscopy measurements of the coordination shell of the metal centers demonstrates single site formation rather than nanoparticle assembly [4-5]. These systems are shown to be active for the catalysis of hydrosilylation reactions at a level that is competitive with current homogeneous catalysts. They also show excellent activity for hydrogenation in flow reactor experiment.

1. Tempas, Morris, Wisman, *et al.*, *Chem. Sci.*, **9**, 1674-1685 (2018). DOI: 10.1039/C7SC04752E

2. Tempas, Skomski, Cook, *et al.*, *Chem. Eur. J.*, **24**, 15852–15858 (2018). DOI: 10.1002/chem.201802943

3. Morris, Huerfano, Wang, *et al.*, *Chem. Eur. J.*, **25**, 5565-5573 (2019). DOI: 10.1002/chem.201900002

4. Chen, Sterbinsky, and Tait, *J. Catal.*, **365**, 303-312 (2018). DOI: 10.1016/j.jcat.2018.07.004

5. Chen, Ali, Sterbinsky, *et al.*, *ChemCatChem*, *in press* (2019).DOI: 10.1002/cctc.201900530

4:20pm SS+AS+HC+OX-WeA7 Controlling the Local Coordination and Reactivity of Oxide-supported Atomically Dispersed Pt-group Species, *Phillip Christopher,* University of California at Santa Barbara **INVITED**

The synthesis of oxide supported Pt-group catalysts typically produces metal particles with dimensions of a few nanometers. Recent work has shown that Pt-group species can co-exist as nanoparticles and single atoms, and that careful synthetic approaches can produce exclusively single atoms. Interest in the reactivity of supported isolated Pt-group metal atoms stems from the maximized metal utilization efficiency, unique reactivity or selectivity, connection to organometallic catalysis, and the potential for making well-defined active sites. It has proven challenging to characterize the intrinsic catalytic activity of these dispersed active sites on oxide supports at a level that relates local electronic and geometric structure to function. The difficulty arises from their atomic dispersion, heterogeneity in the local coordination of active sites on most catalysts (i.e. isolated species sit at different sites on the support), dynamic changes in local coordination under reactive environments, and often the low loading of metal that is required to achieve site isolation.

In this talk I will describe a synthetic approach to produce isolated Pt-group atoms that exhibit uniformity in their bonding environment on an oxide support and show how a combination of microscopy, spectroscopy and theory can be used to describe the local coordination of these species. Then I will describe two different approaches to control the local environment of Pt-group atoms: (1) through varied pre-treatment that tunes the local coordination and oxidation state of the single atom, and (2) through the site selective deposition of single atoms near well-defined acid sites on oxide supports. Detailed characterization by a combination of spectroscopy and microscopy is used to develop structure-function relationships for these well-defined single atom active sites in the context of CO oxidation, methanol carbonylation and ethylene hydroformylation. This work highlights the ability to tune the local environment of single Pt-group atom active sites on oxide supports in analogous ways to the engineering of organometallic catalysts.

5:00pm SS+AS+HC+OX-WeA9 Coordination Defines Reactivity of a Model Single-atom Catalyst: Ir$_1$/Fe$_3$O$_4$(001), *Zdenek Jakub[3], J. Hulva, M. Meier, U. Diebold, G.S. Parkinson,* TU Wien, Austria

The development of single-atom catalysts (SACs) was originally motivated by saving of the precious metal, but an equally intriguing characteristic of

the ideal SAC is potentially high selectivity due to the high number of identical active sites. The coordination of the active metal center is known to play a crucial role in homogeneous catalysis, and in this talk, I will demonstrate that similar effects can be observed on a model single atom catalyst: $Ir_1/Fe_3O_4(001)$. Using scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), temperature programmed desorption (TPD), x-ray photoemission spectroscopy (XPS) and DFT calculations, I will show that the coordination of single Ir_1 adatoms can vary depending on preparation, and that the local environment has dramatic consequences for the ability of the catalyst to adsorb CO. As deposited at room temperature, Ir atoms take 2-fold coordination to the surface oxygen atoms. Upon annealing, they incorporate into the first surface layer (5-fold coordinated Ir_1), and then into the first subsurface layer (6-fold coordinated Ir_1). The 2-fold adatoms can form both monocarbonyls and dicarbonyls, but the 5-fold Ir only binds a single CO. The structures are understood by analogy to square planar Ir(I) and octahedral Ir(III) complexes, respectively. The 6-fold Ir is coodinatively saturated, and thus deactivated for CO adsorption. These results show that control of the local coordination environment is critical to design so-called single-atom catalysts, and that incorporation into the support can be as critical a deactivation mechanism as thermal sintering.

5:20pm SS+AS+HC+OX-WeA10 Capturing the Early Stages of Oxidation on Low-Index Ni and Ni-Cr Surfaces, *William H. Blades, P. Reinke,* University of Virginia

The early stages of oxidation and corrosion of alloys control the structure and development of the oxide layer and therefore decisively influence its protective function. To this end, we have studied thenanoscale evolution of surface oxides prior to the formation of a complete layer. The oxidation of Ni(100), Ni(111), and Ni-Cr(100), Ni-Cr(111) surfaces was captured by sequential oxidization and measured with scanning tunneling microscopy/spectroscopy (STM/STS). The early-stage oxidation, and the influence of alloy composition and crystallographic orientation on surface reactivity, was studied by comparing pure Ni(100/111) and Ni-Cr(100/111) surfaces. Alloy thin films (8-18 wt.% Cr) were prepared on MgO(100/111) and exposed to oxygen up to 400 L at 773 K. Under these conditions, oxide nucleation is predicated by the development of oxygen adlayers on both the pure Ni(100/111) surfaces. The formation of a c(2x2)-O chemisorbed phase on the Ni(100) surface causes the step edges to facet into {100} segments, kinetically limiting NiO growth. However, no such faceting is observed on the Ni(111) surface and the nucleation and growth of NiO begins after only 300 L of O_2. Our experiments demonstrate that the addition of small amounts of Cr completely change the oxidation pathways. On the Ni-Cr(100) surface, the nucleation and growth of NiO initiates along the step edges, forming low-angle NiO wedges with a NiO-Ni(7x8) superstructure. Terrace oxide growth commences with the nucleation of small oxide particles, driven by the presence of Cr, which grow into large oxide nodules after further oxidation. NiO growth extends into the terraces and takes a NiO-Ni(6x7) cube-on-cube interfacial relationship. Several novel surface reconstructions are observed and are tentatively attributed to Cr(100)-O reconstructions, suggesting surface segregation and phase separation of BCC Cr. Similarly, nano-sized oxide particles nucleate on the Ni-Cr(111) terrace and step edges, while single atomic NiO rows extend across the surface. Oxide nodules, similar to those found on the Ni-Cr(100) surface are observed and grow laterally along the terraces. Each of these aforementioned surface oxides present unique electronic signatures, and STS maps are used to quantify the spatial variations in their density of states and band gaps. The electronic heterogeneity of the surface underscores that the use a homogenous electric field to capture oxidation kinetics at the alloy-oxide interface should be revisited.

5:40pm SS+AS+HC+OX-WeA11 Evolution of Steady-state Material Properties during Catalysis: Oxidative Coupling of Methanol over Nanoporous $Ag_{0.03}Au_{0.97}$, *Matthijs van Spronsen,* Lawrence Berkeley National Laboratory*; B. Zugic,* Harvard University*; M.B. Salmeron,* Lawrence Berkeley National Laboratory*; C.M. Friend,* Harvard University

Activating pretreatments can be used to tune both surface composition and surface structure of bimetallic alloy catalysts. Careful selection of both gas mixtures and reaction temperatures can lead to surfaces that are able to achieve optimum selectivity and activity under steady-state reaction conditions. The activation-induced changes in material properties of a nanoporous (np) $Ag_{0.03}Au_{0.97}$ alloy and their subsequent evolution under steady-state conditions for CH_3OH oxidation are presented. Initial activation by oxidation in O_3 at 423 K leads to the formation of AgO and Au_2O_3 driving a strong Ag enrichment in the near-surface region, based on ambient-pressure X-ray photoelectron spectroscopy (AP XPS) and extended X-ray absorption fine structure (EXAFS) analysis. Exposing this oxidized np $Ag_{0.03}Au_{0.97}$ to the O_2/CH_3OH reaction mixture reduces both Ag and Au oxides and results in a surface alloy locally highly enriched in Ag. Both the oxides and the highly Ag enriched alloy unselectively oxidize methanol to CO_2. However, at the reaction temperature of 423 K, the Ag slowly realloys with Au. Although decreasing, the composition remains enriched in Ag in the top few nanometers under steady-state conditions. The Ag content in the surface is 29 at.% in steady state and the desired product, methyl formate, is selectively produced without significant deactivation. The activation and evolution of the active phase is not uniform: nanometer-scale patches of AgO, leading locally to Ag-rich alloys, were observed with environmental transmission electron microscopy (E TEM). These local Ag-rich AgAu alloy regions are critical for initiation of the catalytic cycle through O_2 dissociation. Calculations based on density-functional theory (DFT) indicate that the O on the surface assist in stabilizing the Ag. Moreover, an essential factor for retaining this local enrichment in Ag is the modest reaction temperature of 423 K. At higher temperatures, bulk diffusion induces sintering and redistribution of the Ag, leading to a loss of activity. These findings demonstrate that material properties determining catalytic activity are *dynamic* and that metastable (kinetically trapped) forms of the material may be responsible for catalysis. Hence, catalytic activity and selectivity depend on the pretreatment, reaction temperature and gas composition. These observations provide guiding principles concerning the activation of heterogeneous catalysts for selective oxidation.

6:00pm SS+AS+HC+OX-WeA12 Reduction and Oxidation of Transition Metal Oxides: From Tailoring the Surface and Interface Properties to the New Crystalline Phases Formation, *Dominik Wrana,* Jagiellonian University, Poland*; C. Rodenbücher,* Forschungszentrum Jülich GmbH, Germany*; K. Cieślik, B.R. Jany,* Jagiellonian University, Poland*; K. Szot,* Forschungszentrum Jülich GmbH, Germany*; F. Krok,* Jagiellonian University, Poland

In the recent years transition metal oxides have attracted tremendous interest, mostly due to the manifold real applications, ranging from (photo)catalysis, through memristive and neuromorphic device development, to energy storage and production. A specific quality which makes them so versatile is the ease by which their electronic and structural properties can be controlled by changing a cation's reduction state.

In this presentation we will present an overview of the impact that thermal reduction and oxidation have on the surface properties, which enable a precise control over the valence state of prototypical binary and ternary oxide representatives: TiO_2 and $SrTiO_3$. We will focus on the preparation methods under regular UHV conditions and upon additionally reduced oxygen partial pressure.

Reduction of both crystals results in the formation of oxygen vacancies and therefore d-electrons, which leads to changes in the work function and a corresponding rise in electrical conductivity, which could be tuned over many orders of magnitude [1]. A newly developed SPM-based technique, combining LC-AFM and KPFM, allows both measurements to probe the same area of the reduced $TiO_2(110)$ surface [2], helping understanding of the nanoscale resistive switching . Besides the change in electrical properties, the surface structure evolves towards nonstoichiometric reconstructions [1], due to the increased oxygen deficiency. Surprisingly, not only is oxygen flow possible during UHV annealing of the oxide crystal, but also incongruent cation sublimation can be triggered, as demonstrated for the perovskite oxides like $SrTiO_3$ [3]. Extremely low oxygen partial pressure (ELOP), achieved by the use of an oxygen-getter, initiates $SrTiO_3$ crystal decomposition and the formation of stable monocrystalline cubic TiO nanowires with a c(4x4) reconstructed surface [4]. Such bottom-up growth of conductive TiO nanostructures could be an alternative to other costly methods, resulting in the creation of the $TiO/SrTiO_3$ interface, with a sharp transition between Ti^{2+} and Ti^{4+} states, proven by atomically-resolved electron microscopy. This oxide heterostructure provides an interesting metal/insulator junction with a 0.6 eV work function difference [5], opening many new possibilities for (photo)catalysis and aiding in the search for exotic interface states.

[1] Wrana, D. et al. (2018) *Applied Surface Science*, *432*, 46-52.

[2] Rodenbücher, C. et al. (2018) *APL Materials*, *6*(6), 066105.

[3] Rodenbücher, C. et al. (2017) *physica status solidi (RRL)–Rapid Research Letters*, *11*(9), 1700222.

[4] Wrana, D. et al. (2019) *Nanoscale*, *11*(1), 89-97.

[5] Wrana, D. et al. (2019) Beilstein Arch., 201912.

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