Wednesday Afternoon, November 1, 2017

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 24 - Session HC+SA+SS-WeA

Bridging Gaps in Heterogeneously-Catalyzed Reactions
Moderator: Yu Lei, University of Alabama in Huntsville

2:20pm HC+SA+SS-WeA-1 Oxygen Reduction Reaction Activity for Pt/Co/Pt(111) and Pt/Co-N/Pt(111) Model Catalyst Surfaces Fabricated by Arc-plasma Depositions, *S Kaneko, R Myochi, S Takahashi, N Todoroki, Toshimasa Wadayama,* Graduate School of Environmental Studies, Tohoku University, Japan*; T Tanabe,* Graduate School of Engineering, Tohoku University, Japan

Comprehensive understanding of oxygen reduction reaction (ORR) activity enhancement mechanisms for Pt-based alloy (Pt-M) catalysts is a key for developing highly-efficient, low-Pt-loading cathode catalysts for polymer electrolyte fuel cell. To clarify the effects of the alloy surface structures (e.g., Pt shell atomic arrangements, Pt/M ratio etc.,) on activity and durability, a number of studies have been performed. We have, thus, investigated ORR properties for the well-defined Pt-based bimetallic single crystal surface alloys prepared by vacuum depositions of metals on single crystal substrates in ultra-high vacuum (UHV) [1]. In this study, ORR activities are investigated for Pt/Co and Pt/Co-N model catalysts prepared on Pt(111) substrate by alternative arc-plasma depositions (APDs) of Pt and Co (Co-N).

The UHV-APD-EC apparatus is described elsewhere [2]. Pt and Co (Co-N) layers were alternately deposited onto a clean Pt(111) substrate by the APDs at 573K in UHV. As for the preparations of Co-N layers, Co was deposited by APD under 0.1 Pa of N_2. Total thickness of the Pt/Co(Co-N) and thickness of the topmost-surface Pt and bottom Co layers are fixed to be 6 nm, 1.6nm, and 0.4nm, respectively; the $Pt_{1.6nm}/Co_{0.4nm}/Pt_{3.6nm}/Co_{0.4nm}/Pt(111)$ (denoted as U_Co_4A), U_Co_8A, U_Co_16A, and U_Co_32A samples are prepared. Structural analysis is performed by in-plane XRD, cross-sectional TEM. Then, the Pt/Co/Pt(111) and Pt/Co-N/Pt(111) samples were transferred to an N_2-purged glove box without air exposure. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted in N_2-purged and O_2-saturated 0.1M $HClO_4$ in the glove-box. To discuss EC stability, square-wave potential cycling between 0.6(3s) ~ 1.0(3s) V vs. RHE was applied.

ORR properties (initial activity & durability) of the samples closely correlate with the Co (Co-N) thickness underlying the topmost Pt layer. For example, the activity enhancement factor for the U_Co_16A is highest (13-fold vs. Pt(111)) for the Pt/Co/Pt(111). ORR activity enhancement well corresponds to in-plane lattice distance estimated by the XRD. The results suggest that the ORR enhancements are determined by compressive surface strains that work on the topmost Pt(111) layers induced by underlying Co (Co-N) layers.

We wish to acknowledge the NEDO and JSPS.

[1] T.Wadayama et al., Electrochem.Commun. **12**, 1112 (2010). N.Todoroki et al., PCCP, **15**, 17771 (2013). M.Asano et al., ACS catal. **6**, 5285 (2016).

[2] S. Takahashi et al., PCCP, **17**, 18638 (2015). S. Takahashi et al., ACS Omega **1**, 1247 (2016).

2:40pm HC+SA+SS-WeA-2 The Mechanism of Oxygen Induced p(2×3) Reconstruction on Mo(112), *Teng Ma,* Shenyang Agricultural University, PR China

Oxygen induced reconstruction and oxidation of Mo(112) surface has shown various surface structures in model catalysis and surface studies. Because of its complexity, the p(2 × 3) reconstruction has been modeled as several patterns and its formation mechnism was not well clarified. In this report, a critical precursor of forming p(2 ×3) reconstruction has been observed by using STM, XPS and HREELS methods. For the Mo(112) surface exposed to $5.0×10^{-8}$ mbar O_2, the formation of the p(2×3) reconstruction is a process of two consecutive steps, during which the clean metallic surface experience the initial oxidation to form dispersed oxide particles at nanoscale, and then reduction and structural rearrangement of molybdenum oxides to the ordered nanostructures. The features of surface structures are also temperature dependent, a mixture of dispersed nanoparticles of molybdenum oxide and one-dimensional nanostructures occurs after O_2 dose at 605 K, while two-dimensional nanostructures or the p(2×3) reconstruction occurs until above 710 K. Our results would give a good explanation about some hurdled questions about the appearance of

LEED streaky points and antidomain dislocations in the STM images of the p(2× 3) reconstruction.

3:00pm HC+SA+SS-WeA-3 Gas-Liquid Scattering Studies of Atmospheric Reactions at the Surfaces of Sea-Spray Mimics, *M Shaloski, J Gord,* University of Wisconsin - Madison*; S Staudt,* University of Wisconsin-Madison*; S Quinn, T Bertram,* University of Wisconsin - Madison*; Gilbert Nathanson,* University of Wisconsin-Madison **INVITED**

Heterogeneous reactions between atmospheric gases and sea-spray aerosols are fascinating examples of complex interfacial processes involving water, ions, and surface-active molecules. These reactions are also important because of the controlling role they play in regulating pollution and greenhouse gases in the troposphere. Of particular interest is the atmospheric molecule N_2O_5, created indirectly by fossil fuel burning. During the day, N_2O_5 is photolyzed to NO_2 and NO_3, ultimately producing O_3 and then OH· radicals that destroy CH_4. During the night, N_2O_5 can be removed by dissolving into sea-spray aerosols near coastal regions. This dissolution is followed by rapid hydrolysis to HNO_3 or reaction with Cl^- to produce $ClNO_2$, a gas that potentially supplies reactive Cl atoms and returns half of the NO_2 to the atmosphere. The fate of N_2O_5 upon collision with an aerosol droplet is enormously difficult to predict because the droplets are chemically diverse and often possess an outer layer of lipid-like organic molecules. Such surface-active species can inhibit or even enhance uptake and reactivity by orders of magnitude.

We have implemented gas–liquid scattering experiments to investigate the dynamics of these interfacial N_2O_5 reactions. By directing a well-defined beam of N_2O_5 at a stream of salty water emerging from a liquid microjet in vacuum, we can track the uptake and reactivity of N_2O_5 with seawater and sea-spray mimics. We have also used similar experiments involving liquid glycerol to explore the ability of cationic and zwitterionic surfactants to increase ion concentrations of Br^- or Cl^- at the surface and to stabilize reaction intermediates created by N_2O_5. These studies provide insight into interfacial ionization and bimolecular reactions at the surfaces of complex liquids found in the atmosphere.

4:20pm HC+SA+SS-WeA-7 In-situ Investigation of Methane Activation on MO_x/CeO_2 (111) Surfaces {M=Co, Ni and Cu} using Ambient-Pressure XPS, *J Rodriguez, Zongyuan Liu,* Brookhaven National Laboratory

Natural gas has transformed the energy landscape of this nation and has fast become a cheap and abundant fuel stock. Methane is the primary component of natural gas but is difficult to convert it to upgraded fuels or chemicals due to the strong C-H bond in methane (104 kcal/mol). This challenge constitutes one of the most difficult problems in heterogeneous catalysis. We have discovered a catalyst with small Ni nanoparticles supported on ceria that has shown promising activity for both methane activation and dry reforming of methane. Then we expanded the study to other transition metals (Co and Cu) supported on ceria in order to rationalize the structure-reactivity relationships for methane activation. Due to the chemically inert nature of methane, the experiment needs to be conducted at elevated pressure via the utilization of Ambient Pressure of XPS. Nanoparticles or clusters of Co and Cu were deposited onto the well-defined CeO_2(111) surface. Strong metal-oxide interactions were found upon annealing the deposited surfaces to 700 K, leading to the generation of MO_x. In-situ AP-XPS showed that the CoO_x/CeO_2(111) interacted strongly with 50 mTorr of methane, resulting in the formation of Co/CeO_x(111), while no obvious changes were observed on the CuO_x/CeO_2(111) surface (figure 1). By comparing it with the NiO_x/CeO_2(111) surface, it can be found that the methane activation on these MO_x/CeO_2 (111) surfaces follow the order: Co > Ni > Cu. The methane dry reforming activity was also investigated on the CoO_x/CeO_2(111) surface by sequentially adding another 50 mTorr of CO_2 into the system. The slight reoxidation of the ceria surface indicates the participation of CO_2 in the catalytic cycle by the following steps: $CH_4(g) \rightarrow CH_{4-x}(a) + H(a)$ with x=1-4; $CO_2(g) \rightarrow CO(a) + O(a)$; $C(a) + O(a) \rightarrow CO(g)$; $H(a) + H(a) \rightarrow H_2(g)$.

4:40pm HC+SA+SS-WeA-8 Ambient Pressure XPS Study of Catalytic Conversion of Carbon Dioxide by CuO_x Nanoparticles Photodeposited on TiO_2 Nanoparticles, *Djawhar Ferrah, R Galhenage, J Bruce, A Babore, J Hemminger,* University California, Irvine

The chemical conversion of carbon dioxide to useful products has attracted great interest both from a scientific and industrial perspective. It is widely known that Cu is active for the catalytic hydrogenation of CO_2. However, the detailed structure and oxidation state of the active site is not well understood. Recently, Cu nanostructures were reported to be a promising catalyst for hydrogenation of CO_2. The main challenge in the development of Cu based transition - metal nanoparticles is thereby bring selectivity and

efficiency to heterogeneous catalysis. Due to the wide range of accessible oxidation states (Cu^0, Cu^I, Cu^{II}, and Cu^{III}), CuO_x-nanoparticules can promote and undergo a variety of reactions which enable reactivity via both one- and two-electron pathways. The size and shape of the particles can play an important role in reactant adsorption and activation at defects and dangling bonds.

In this study, we investigated the reaction mechanisms in carbon dioxide conversion with CuO_x nanoparticles synthesized through the photodeposition process on TiO_2 nanoparticles supported on HOPG. We utilize ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to monitor the surface chemistry during in-situ catalytic reaction of CO_2 and H_2 (H_2O) on the surface under ambient pressure conditions. To track the structural and morphological evolution of catalytic nanoparticles, SEM and TEM investigation will be reported.

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, as follows: The specific development of CuOx nanoparticles on TiO2 nanoparticles was supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993; The ambient pressure XPS experiments were carried out at the CSX2 end station at NSLS-II. RG is supported by funding from the Provost Office of the University of California, Irvine.

5:00pm **HC+SA+SS-WeA-9 Atomic-Scale Characterization of Pt/Ag Surface Alloys**, *Dipna Patel, E Sykes,* Tufts University

Catalytic hydrogenation reactions are important in many industrial applications. While Pt is catalytically active towards hydrogenation, it is very costly, can suffer from poisoning by CO, and coke. On the other hand, bulk Ag is catalytically inert towards hydrogenation reactions, but cheaper than Pt and more resilient to poisoning. Previously, Ag based catalysts have been modified for applications in highly selective heterogeneous catalysis. By analogy to our single-atom alloy approach in other systems such as Pt/Cu and Pd/Cu, alloying Pt into Ag has the potential to greatly enhance catalytic selectivity while reducing the cost of precious metal required to catalyze industrially relevant reactions and reduce poisoning. The atomic-scale surface structure of dilute Pt-Ag alloys has not been reported to date. Using scanning tunneling microscopy (STM) and STM-based spectroscopies, we characterized the surface structure and local geometry of low coverage Pt deposited on Ag(111) as a function of temperature. At low temperatures, intermixing of Pt-Ag 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. This characterization of Pt-Ag surface alloys will enable us to correlate reaction activity and selectivity to the atomic-scale structure of the alloy and potentially tune catalytic selectivity and resilience to poisoning via both ligand and ensemble effects.

5:20pm **HC+SA+SS-WeA-10 Structural Consequences of High Oxygen Coverages on Rh(111)**, *Rachael Farber[1,2], M Turano, D Killelea,* Loyola University Chicago

Partial oxidations of small molecules over metal surfaces are central to many heterogeneously catalyzed reactions. However, the identity of the actual surface species that promote or hinder these reactions has remained elusive for a variety of reasons. Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, they are now believed to be effective promoters of selective catalysis.

We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Our approach is to first elucidate the uptake of oxygen on Rh(111) and the surface structures formed for a range of oxygen coverages and then characterize them with a variety of techniques under ultra-high vacuum conditions. Exposure to O_2 yields coverages up to 0.5 monolayers (ML), and higher coverages, well in excess of 1 ML, were achieved by dosing with gas-phase atomic oxygen (AO). The surface oxygen coverage was determined with Auger electron spectroscopy (AES), the total oxygen abundance with temperature programmed desorption (TPD), and the surface structures with low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

Careful control of the exposure parameters allowed for the selective growth of the RhO_2 surface oxide, surface adsorbed oxygen, and subsurface oxygen. The combination of AES, TPD, LEED, and STM revealed that despite total oxygen coverages in excess of 3 ML, the surface oxygen coverage was less than 1 ML and the thermodynamically favored surface phase was the (2x1)-O adlayer corresponding to a surface oxygen coverage of 0.5 ML. The RhO_2 surface oxide was observed to form during extended oxygen exposures, but the (2x1) adlayer persisted. Our findings highlight the complexity of the surface chemistry of oxygen on transition metals and reveal the consequences of incorporating oxygen into the near-surface region of the solid. Furthermore, formation of the surface oxide was shown to rely not only on the presence of defects, but also on high concentrations of oxygen absorbed below the surface of the metal.

5:40pm **HC+SA+SS-WeA-11 Reactivity and Electronic Properties of Supported Metal Oxide and Sulfide Clusters**, *Michael White,* Brookhaven National Laboratory; *X Meng, K Goodman,* Stonybrook University; *P Liu,* Brookhaven National Laboratory **INVITED**

Small clusters exhibit electronic and chemical properties that can differ significantly from that of the bulk and offer a unique opportunity for preparing novel catalysts whose reactivity can be modified at the atomic level. Here, we use mass-selected cluster deposition to prepare model "inverse" catalysts comprised of small metal oxide (M_xO_y: M = Ti, Nb, Mo, Ce, W) and sulfide (M_xS_y: M = Mo, W) clusters deposited on Cu, Cu_2O/Cu and Au surfaces for studies the water-gas-shift reaction (WGSR) and for CO/CO_2 activation. A key advantage of cluster deposition is that it allows control over cluster stoichiometry which provides a means of introducing oxygen/sulfur "vacancies" and varying the average cation oxidation state. Recent work has focused on the correlation of electron transfer at the cluster-support interface and activity for water dissociation, the latter being a key step in the WGSR mechanism. Electron transfer is probed by XPS core level spectra and 2PPE photoemission measurements of coverage-dependent work function shifts to extract surface dipoles. All the oxide clusters on Cu(111) exhibit negative surface dipoles, indicative of Cu to cluster charge transfer, with smaller dipoles for sub-stoichiometric and reducible oxides (Ti, Nb). Temperature programmed reaction (TPR) experiments show that the Ti_xO_y and Nb_xO_y clusters promote water dissociation on Cu(111), with the 'reduced' Ti_xO_y clusters being more active, while both stoichiometric and reduced Nb_xO_y clusters are active. Overall, these results suggest that local cation coordination is most important for determining water activity. Recent ambient pressure XPS ($CO+H_2O$, 100's mTorr) measurements at NSLS-II show that small Ti_nO_{2n} (n = 3, 4, 5) clusters on Cu(111) are active for the WGSR reaction through the observation of reaction-induced O-vacancy formation (Ti^{3+} 2p) and the appearance of formate intermediates (C 1s) at room temperature. Results will also be presented on investigations of CO_2 activation on alkali modified surfaces of Mo_6S_8 clusters on Au(111), which had been previously predicted to be active for CO_2 hydrogenation to methanol. Combined TPR and XPS measurements show that co-deposition of K-atoms and Mo_6S_8 clusters strongly enhances CO_2 adsorption above room temperature, whereas the CO_2 is only weakly bound on the bare clusters. The results will be compared with DFT calculations of the possible CO_2 binding sites for the K-cluster-Au interfaces.

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