## Surface Science
## Room Hall D - Session SS-TuP
## Surface Science Poster Session

**SS-TuP1 Adsorption and Decomposition Properties of Dimethyl Trisulfide Over Au(111)***, **Isao Nakamura**,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; M. Tokunaga,* Kyushu University, Japan*; T. Fujitani,* National Institute of Advanced Industrial Science and Technology (AIST), Japan

It is known that dimethyl trisulfide (DMTS) is mainly responsible for an off-flavor that develops during the storage of Japanese sake. Recently, we found that the supported gold catalysts are effective for the adsorption and removal of DMTS. In this study, in order to clarify the reaction properties of DMTS over gold, we investigated the adsorption and decomposition of DMTS using the Au(111) single-crystal surface.

First, we examined the influence of the exposure temperature on the adsorption properties of DMTS. X-ray photoelectron spectroscopy (XPS) results indicated that DMTS is dissociatively adsorbed as $CH_3S$ and $CH_3SS$ species at 100–300 K. Furthermore, both the dissociative adsorption rate and the saturation coverage were the same regardless of the exposure temperature.

In contrast, the thermal decomposition properties of $CH_3S$ and $CH_3SS$ strongly depended on their formation temperatures. On the Au(111) surface formed at 100 K, the $CH_3S$ was shown to be associatively desorbed as dimethyl disulfide (DMDS), and the production of ethane and atomic sulfur by the cleavage of C–S bond in $CH_3SS$ were confirmed from temperature-programmed desorption and XPS measurements. Thus, $CH_3S$ and $CH_3SS$ reacted individually. On the other hand, the reaction of $CH_3S$ with $CH_3SS$ to produce DMDS and atomic sulfur was also confirmed for the surface at 150 K. At 200 K or 300 K, only the reaction of $CH_3S$ with $CH_3SS$ was observed. We consider that the difference in the decomposition reaction is due to that the adsorption structure of $CH_3S$ and $CH_3SS$ species on Au(111) changes by their formation temperatures. That is, the $CH_3S$ and $CH_3SS$ species are present in separate islands each other at 100 K, whereas the adsorption structure of $CH_3S$ and $CH_3SS$ becomes random with rising their formation temperatures.

**SS-TuP2 Spectroscopically Monitoring the Surface and Crystallinity of Titania Nanopowders Treated with Hydrogen Peroxide: an Endeavor in Simplifying the Atomic Picture of Complex Substrates***, **Maria Kipreos**, M. Foster,* University of Massachusetts, Boston

Metal oxide substrates are often riddled with defect sites, imperfections in metal-oxide atomic arrangements. One such defect is an oxygen vacancy at the surface. Commonly, the substrate is exposed to $O_2$ to reestablish the proper metal-oxygen coordination. Much like $O_2$, hydrogen peroxide may be used to oxidize the surface of metal oxide nanopowders, such as titania ($TiO_2$), as well as drive off impurities remaining and or derived from the synthesis of these materials, to establish a more pristine surface. Various commercially available nanosized rutile and anatase structured titania nanopowders are treated with hydrogen peroxide and any changes in crystallinity are monitored using a confocal Raman microscope as well as powder X-ray Diffraction. In situ DRIFTS coupled with a high temperature reaction chamber is used to assess any changes in the substrate upon treatment, including evolving water and hydroxyl features on the surface and the disappearance of impurities, both as the pretreatment conditions change and as a function of substrate temperature.

**SS-TuP3 Efficacy of $Ar^+$ CIRD Removal of Adsorbed O from Rh(111)***, **Marie Turano**, R.G. Farber, D.R. Killelea,* Loyola University Chicago

Subsurface oxygen ($O_{sub}$) on Rh(111) is formed via gas-phase deposition of atomic oxygen (AO). Total O coverages of over 3 ML equivalence are possible, and results in an oxygen saturated surface and $O_{sub}$. In order to study the geometric and electronic effects of $O_{sub}$ on a surface alone requires a technique to remove the adsorbed oxygen ($O_{ad}$) while retaining $O_{sub}$ and minimizing damage to the metal surface. Here, we present results from our development of collision-induced recombinative desorption (CIRD) of $O_{ad}$ from Rh(111) using $Ar^+$ ions from a commercial sputter gun. We show that with proper selection of the $Ar^+$ energy and electronic bias of the metal surface, $O_{ad}$ can be removed leaving behind a cleared Rh(111) surface still charged with $O_{sub}$. We characterized the surface with a combination of structural probes (LEED, STM) and temperature programmed desorption to quantify total oxygen and Auger electron spectroscopy for the surface coverage.

**SS-TuP4 Adsorption and Oxidation of n–Butane on the Stoichiometric $RuO_2$(110) Surface***, **Tao Li**, R. Rai, Z. Liang,* University of Florida, Gainesville*; M. Kim, A. Asthagiri,* Ohio State University*; J.F. Weaver,* University of Florida, Gainesville

The surface chemistry of late transition-metal (TM) oxides has drawn significant attention due to the observation and prediction of facile C-H bond cleavage of molecularly adsorbed n-alkanes at low temperatures. Previous studies have shown that PdO(101) readily promotes the dissociation of alkanes by a mechanism in which adsorbed σ-complexes serve as precursors to initial C-H bond cleavage. Density functional theory (DFT) calculations further predict that the formation and facile C-H bond activation of alkane σ-complexes should also occur on $RuO_2$ and $IrO_2$ surfaces, suggesting that the σ-complex mechanism is a common pathway for alkane activation on late TM oxides.

In this study, we investigated the adsorption and oxidation of n-butane on the stoichiometric $RuO_2$(110) surface using temperature-programmed reaction spectroscopy (TPRS) and DFT calculations. At low coverage, molecularly adsorbed n-butane achieves a binding energy of ~100 kJ/mol on $RuO_2$(110), consistent with a strongly bound σ-complex that forms through dative bonding interactions between the n-butane molecule and coordinatively unsaturated (cus) Ru atoms. We find that a fraction of the n-butane reacts with the $RuO_2$ surface during TPRS to produce CO, $CO_2$, and $H_2O$ that desorb above ~400 K and present evidence that adsorbed σ-complexes serve as precursors to the initial C−H bond cleavage and ultimately the oxidation of n-butane on $RuO_2$(110). From measurements of the product yields as a function of surface temperature we estimate that the initial reaction probability of n-butane on $RuO_2$(110) decreases from 9% to ~4% with increasing surface temperature from 280 to 300 K and show that this temperature dependence is accurately described by a precursor-mediated mechanism. From kinetic analysis of the data we estimate a negative, apparent activation energy of −35.1 kJ/mol for n-butane dissociation on $RuO_2$(110) and an apparent reaction prefactor of $6 \times 10^{-8}$. The low value of the apparent reaction prefactor suggests that motions of the adsorbed n-butane precursor are highly restricted on the $RuO_2$(110) surface. DFT calculations confirm that n-butane forms strongly bound σ-complexes on $RuO_2$(110) and predict that C−H bond cleavage is strongly favored energetically. The n-butane binding energies and energy barrier for C−H bond cleavage predicted by DFT agree quantitatively with our experimental estimates. Our results support the idea that the σ-complex mechanism is a common pathway for alkane activation on late TM oxide surfaces that expose pairs of cus metal and oxygen atoms.

**SS-TuP5 Step-type Dependence of Water Desorption from Single-Crystalline Ag Surfaces***, **Sabine Auras**,* Leiden University, Netherlands*; J. Janlamool,* Chulalongkorn University, Bangkok

Many heterogeneously catalyzed reactions have been shown to be strongly structure dependent.[1] Catalytically active materials can feature a wide spectrum of defect densities on the same sample and may include various step types.[2] Thus, curved crystals with continuously changing average step densities provide a good alternative to flat single crystals for the investigation of surface structure dependencies.[3] In this study we use two curved Ag single crystals to exemplify the strength of this approach to studying structure dependencies. The crystals have two different apex orientations. One Ag crystal with a [111] apex contains two different step sites on either side of the center, generally referred to as the (100) and (111) or A and B step types. The step density gradually increases until at the edges of the crystal we reach 5-atom wide (111) terraces. The crystal with the [100] apex has only one step type, that resembles the B step type from the first crystal, but has adjacent (100) terraces. We study the surface structure of the clean crystals with LEED and STM and show that the surface behaves as may be expected with single-atom high steps.

Subsequently, water adsorption to the steps and their effect on the water-metal interface are investigated using spatially resolved Temperature Programmed Desorption. As Ag binds water only weakly, effects resulting from the available steps are expected to be rather small . We show how the different step types affect the desorption of water and how it would be nearly impossible to measure the effects using multiple flat Ag samples.

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2. Walter, A.L.; Schiller, F.; Corso, M., et al. X-ray photoemission analysis of clean and carbon monoxide-chemisorbed platinum(111) stepped surfaces using a curved crystal. *Nat. Commun.* **2015***, 6*, 8903.

3. (a) Besocke, K.; Krahl-Urban, B; Wagner, H. Dipole moments associated with edge atoms; A comparative study on stepped Pt, Au and W surfaces, *Surf. Sci.***1977**, *68*, 39–46.

(b) Hopster, H.; Ibach, H.; Comsa, G. Catalytic oxidation of carbon monoxide on stepped platinum(111) surfaces, *J. Catal.***1977**, *46*, 37–48.

(c) Pluis, B.; van der Gon, A.W.D.; Frenken, J.W.M.; van der Veen, J.F. Crystal-Face Dependence of Surface Melting, *Phys. Rev. Lett.***1987**, *59*, 2678–2681.

**SS-TuP6 Topographical Changes of Liquid-Metal Alloys as a Function of Temperature***, **Nelson Bello,*** University of Massachusetts, Boston*; I. Tevis,* SAFI-Tech*; M. Thuo,* Iowa State University*; M. Foster,* University of Massachusetts, Boston

Gallium-indium metal alloys are remarkable materials that, at the eutectic composition, are liquid at room temperature and form a very thin (0.7 nm) passivating oxide film on the surface. This makes them valuable in the field of molecular electronics as soft conformal electrical contacts and as, potentially, self-repairing wires. For this project, EGaIn is put through a fluidic shearing process that produces 3-layered core-shell nano/micro-spherical particles composed of a chemisorbed organic outer layer on an oxide film around the liquid metal core that prevents their coalescence. We used Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) to monitor topographical changes in these particles as a function of temperature. The liquid metal has a different rate of expansion from the oxide shell, and AFM coupled with SEM are especially well-suited to monitor these changes both as a function of the rate of change of the temperature and the thickness of the oxide film. The nature of the external coating can also be tuned through exposure of the particles to strong oxidants or shearing the metal in the presence of different surfactants. The effect of the different film coatings and the expansion of the particles upon application of heat will be discussed.

**SS-TuP7 Interaction of Ethylene with Partially Chlorinated $RuO_2$(110) Surfaces***, **Zhu Liang**, T. Li, R. Rai, J.F. Weaver,* University of Florida

Partial replacement of surface oxygen atoms with chlorine atoms may provide a means for modifying the activity and selectivity of oxide surfaces toward hydrocarbon oxidation. In this study, we investigated the adsorption and oxidation of ethylene on partially chlorinated $RuO_2$(110) surfaces using temperature programed reaction spectroscopy (TPRS) and X-ray photoelectron spectroscopy (XPS). Chlorination of the $RuO_2$(110) surface occurs when exposing the stoichiometric surface to gaseous HCl at 700 K, where the bridging oxygen atoms are selectively replaced by chlorine atoms. The degree of chlorination is controlled by the amount of HCl gas introduced, and characterized by XPS. Compared with stoichiometric $RuO_2$(110), we find that bridging Cl atoms weaken the binding and suppress the oxidation of ethylene, without shifting the selectivity toward partially oxidized products. We also find that on-top oxygen atoms significantly enhance the activity of both s-$RuO_2$(110) and chlorinated $RuO_2$(110) surfaces toward the complete oxidation of ethylene. The enhanced reactivity arises from an increase in the ethylene coverage achieved on the O-rich surfaces as well as more facile C–H bond cleavage of ethylene via H-transfer to on-top vs. bridging oxygen atoms. Our results provide evidence that ethylene molecules achieve high coverages on the O-rich surfaces by preferentially binding to stranded Ru sites located between on-top oxygen atoms, and that such configurations are responsible for the high activity of the O-rich $RuO_2$ and $RuO_xCl_y$ surfaces. These findings demonstrate that the relative reactivity of on-top vs. bridging oxygen atoms plays a decisive role in determining the chemical activity of partially-chlorinated $RuO_2$ surfaces, and that high reactivity can be achieved on O-rich $RuO_xCl_y$ surfaces.

**SS-TuP8 Supramolecular Assemblies of Halogenated Molecules on the Si(111) $\sqrt{3}\times\sqrt{3}$-Ag and Cu(100) Surfaces***, **Renjie Liu,*** Lakehead University, Canada*; C. Fu, A.G. Moiseev, D.F. Perepichka,* McGill University, Canada*; M.C. Gallagher,* Lakehead University, Canada

The surface-confined assembly of two-dimensional (2-d) covalent organic frameworks (COF) has gained much attention [1]. One approach to COF formation is the adsorption of halogenated aromatic precursors onto a noble metal surfaces, followed by dehalogenation of the precursors, and subsequent covalent coupling. We have studied the adsorption of a halogenated organic molecule, 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (TIPT), on both the Cu(100) and Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag surfaces by scanning tunneling microscopy (STM). Recently, we found that the Si $\sqrt{3}$–Ag surface can provides an inert, high-mobility template for the adsorption of halogenated organic molecules [2].

STM images reveal that TIPT monomers are quite mobile on the Cu(100) surface at room temperature. At low coverage, molecules readily migrate and accumulate at step edges. We observe very few supramolecular features at the surface, and these structures often decompose after repeated STM scanning. In contrast to the as deposited samples, after annealing to 420°K more robust open pore structures are observed. The structure and size of these molecular frameworks are consistent with covalent linking. We have also studied TIPT adsorption on the $\sqrt{3}$-Ag surface. The structure of these films as a function of coverage and annealing temperature will be discussed.

1. D.F.Perepichka, and F. Rosei, *Science* **323**, 216–217 (2009).

2. R. Liu et al., *Surf. Sci.* **647**, 51–54 (2016).

**SS-TuP9 Synthesis and Reduction of Graphene Oxide***, **Heike Geisler**, J.M. Bachor, N.A. LaScala,* SUNY College at Oneonta

Graphite oxide was successfully synthesized from graphite powder using the modified Hummers method*. The graphite oxide was then exfoliated to yield graphene oxide which was subsequently reduced to give reduced graphene oxide. This employed two different chemical reduction methods, and one effective combination of the two. The two methods being a weaker sodium borohydride/calcium chloride catalyst and a hydrogenation through hydrogen produced from the reaction of hydrochloric acid and aluminum. This can be seen through the removal of various functional groups from our graphene oxide sample after each reduction method, as shown in FTIR spectra of each sample. While the reduction methods employed did remove a number of oxygenated functional groups on the graphene oxide sheet, we still observe the presence of hydroxyl and some carboxylic acids that persist through. We also notice the appearance of a well-defined peak at ~1600 cm$^{-1}$ representing the conjugated system in the combined reduction method.

** W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339*

**SS-TuP10 Nanomechanical Properties of Eutectic Gallium-Indium Particles by Atomic Force Microscopy***, **Syeda Akhter,*** University of Massachusetts, Boston*; I. Tevis,* SAFI-Tech*; M. Thuo,* Iowa State University*; M. Foster,* University of Massachusetts, Boston

Eutectic Gallium-Indium (EGaIn) alloy is a liquid metal at room temperature that, under air, forms a passivating native thin (~0.7 nm) oxide layer. This oxide layer plays an important role in the overall mechanical properties of the alloy. The metallic and physical properties of EGaIn make it effective at conducting, and dissipating, heat away from temperature sensitive components. Being a deformable liquid metal, EGaIn is consistently electrically conductive even when a supporting polymeric channel is excessively stretched. EGaIn particles, with a liquid core and a thin oxide shell, are created with diameters that range from 6.4 nm to >10 µm using fluidic shearing. The mechanical properties, such as the flexibility of the oxide shell, especially on nano- and micro-particles, are unknown. Atomic Force Microscopy, however, is a versatile instrument for imaging surface topography as well as for characterizing material properties, such as elasticity and film thickness at the micro- and nanoscale via force-distance curves (F-D curves). F-D curves are the result of interactions, upon contact, between an AFM tip and the surface of the sample due to the elastic force of the cantilever and values can be measured with resolutions up to pico-Newtons. This poster describes our studies on mechanical properties of EGaIn thin film and particles of various sizes via AFM F-D curves.

**SS-TuP11 Reactivity of $CO_2$ at Single-site Vanadium in Metal-Organic Coordination Networks at Surfaces***, C. Tempas, B. Cook,* Indiana University*; **David Wisman,*** Indiana University; NAVSEA Crane*; T. Morris, A. Polezhaev, D. Skomski, K. Smith, K. Caulton, S.L. Tait,* Indiana University

Driven by growing concern of the effect of greenhouse gases on the environment, $CO_2$ chemistry has become an increasingly active area of research. The interaction of $CO_2$ with metal-organic complexes offers opportunities for $CO_2$ recycling, but those chemistries have not been developed in surface catalysts, which could offer much higher efficiency. We have developed a prototypical metal-organic network that shows chemical activity toward $CO_2$ by co-depositing bis-pyridinyltetrazine (DPTZ) and metallic vanadium on a Au(100) surface. These organize at room temperature into highly-ordered one-dimensional metal-organic chains. We characterized the assembly by high-resolution scanning tunneling microscopy. The chains align in specific orientations relative to the underlying gold surface due to their interaction with the gold. The assembly occurs by a redox-active self-assembly process, in which the vanadium oxidizes to the +2 state and there is corresponding reduction of the ligand, as observed by X-ray photoelectron spectroscopy. Exposure to $CO_2$ gas leads to a shift in the vanadium oxidation state to +4; the shift is gradual with increasing $CO_2$ exposure. The 1D chains generally remain intact during the $CO_2$ exposure, but become somewhat less ordered with increasing exposure time. Following gas exposure, the surface was annealed at various temperatures. At annealing temperatures of 250 °C and greater we observe desorption of the ligand and the shift of vanadium back to the +2 state, indicating a residual vanadium-oxo species on the surface. Developing single-site metal center surfaces systems with chemical activity toward $CO_2$ may lead to the development of new methods for $CO_2$ capture and recycling, as well as providing more general insight into the development of next-generation catalysts.

**SS-TuP12 $CO_2$ Optical Phonons for Constraining Mixing in Interstellar Ices***,* ***Ilsa Cooke****,* University of Virginia*; K.I. Öberg,* Harvard University

$CO_2$ is an important ice species in interstellar environments, often the second most abundant ice after $H_2O$. Astronomical infrared spectra of interstellar objects have revealed abundant $CO_2$ in a variety of protostellar environments as well as in cold dark clouds. The $CO_2$ $v_2$ band has been used as a tracer of thermal processing due to its dependence on the ice temperature and local environment; however, there are still uncertainties involved in fitting the laboratory $v_2$ band to astronomical spectra. We report laboratory spectra of the $CO_2$ longitudinal optical (LO) phonon mode for a series of $CO_2$ ices at low temperature and for ice mixtures with polar ($H_2O$) and non-polar (CO, $O_2$) components. We show that the LO phonon mode is particularly sensitive to the mixing ratio of various ice components of astronomical interest. These spectra may be useful in constraining the bulk environment of $CO_2$ in astronomical ices as well as for tracing ice mixing in laboratory experiments.

**SS-TuP17 Probe the Degradation Mechanism of Hybrid Perovskite by *In Situ* DRIFTs***, Q. Peng, X. Yu,* ***Amanda Volk****,* University of Alabama

Methylammonium Lead Iodide Perovskite ($MAPbI_3$) is a promising photoelectronic material for photovoltaics and LEDs. However, the stability of $MAPbI_3$ under the external application environments is a big concern. The underlying mechanism of decomposition of $MAPbI_3$ is not well understood yet. In this poster, we will use *in-situ* Diffuse reflectance infrared fourier transform spectroscopy for the first time to understand the surface reaction mechanism in the decomposition of $MAPbI_3$ in various related applications environments. With the unique setup and high-surface-area configuration, our results showed that the degradation rate is strongly affected by the temperature and chemical composition of the application environments. The degradation mechanism of $MAPbI_3$ changes with the application environments. Our results provide a fresh view of the degradation pathways of $MAPbI_3$ and will help optimize the synthesis of $MAPbI_3$ and provide potential solutions for stabilizing $MAPbI_3$.

**SS-TuP19 Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption at Surface versus Subsurface***,* ***Sara Isbill****, S. Roy,* University of Tennessee, Knoxville

While transition metals are commonly used to catalyze the oxidation of small organic compounds, the mechanisms of these reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions by silver surfaces, several aspects of the catalysis, particularly the different ways in which oxygen interacts with the silver surface have yet to be elucidated. This understanding is critical to determine the catalytically active oxygen-silver species that interacts with the reactants. It is also important to know how these active species change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage, such that the conditions can be tuned to design the most effective catalysts. In the present study, density functional theory (DFT) was used to probe atomic-oxygen adsorption at the surface and subsurface of Ag(111) and Ag(110) surfaces. The main goal was to investigate the competition between surface and subsurface oxygen at different oxygen coverages, and study their participation in oxidation catalysis by silver surfaces. On the Ag(111) surface, it was found that adsorption energies for all surface and subsurface sites decreased with coverage; however, surface adsorption was compromised much more than subsurface adsorption. This difference causes a flip in preference from surface adsorption at low coverages to subsurface adsorption at high coverages. Calculated potential energy curves of oxygen moving from surface to subsurface on Ag(111) and Ag(110) show a complex interplay between adsorption energies and energy barriers that is sensitive to monolayer coverage. Results provide valuable insight into the competition between surface adsorption and subsurface adsorption of oxygen on the silver surface, the role of subsurface oxygen in catalysis by the silver surface, and the importance of charge transfer in the adsorption and dynamics of oxygen on the silver surface.

**SS-TuP20 Isotope Fractionation Effect in Secondary Ions Mass Spectroscopy Analysis for Boron Quantification***,* ***Yibin Zhang****,* GLOBALFOUNDRIES U.S. Inc.

Secondary Ion Mass spectroscopy (SIMS) analysis is heavily used in semiconductor, lighting/LED, solar/PV industries for routine manufacturing and research/development due to its versatility, fast turnaround time and excellent accuracy/precision. There are some factors that affect the accuracy of SIMS quantification. Fractionation is one of them. It is very important for isotope abundance measurement and for applying RSFs from one isotope to another. If fractionation is ignored during SIMS quantification by applying RSFs from one isotope to another, over 10% error could be introduced. Boron is a useful dopant for such semiconductors as silicon, germanium, and silicon carbide. Having one fewer valence electron than the host atom, it donates a hole resulting in p-type conductivity. Then to accurately monitor Boron concentration in semiconductor manufacturing process is very important. In this study, the Boron isotope fractionation was investigated on Cameca IMS WF, Cameca 7f, Quad SIMS. A methodology to quantify Boron was demonstrated by applying RSF from $^{10}B$ implanted standard to unknown sample by monitoring $^{11}B$.

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