Surface Science
Room 104E - Session SS+AS+HC-MoM

Mechanistic Insights on Surface Reactions in Catalysis and at Novel Interfaces

Moderator: Bruce D. Kay, Pacific Northwest National Laboratory

8:20am **SS+AS+HC-MoM1 Study of Metal-Organic Complexation at Metal and Metal Oxide Surfaces by HREELS*, Miao Wang*,** *C. Williams, S.L. Tait,* Indiana University

The ordering of organic molecules at surfaces and the formation of ordered metal nanostructures at surfaces have been extensively studied for the advancement of organic photovoltaics, nanoscale molecular electronics, and catalysts. There are many chemical systems that benefit from the combination of organic ligands with single-site metal centers to design and tune specific chemistries, but metal-organic complexation at surfaces has not yet been significantly studied. Molecular ligands on a surface with specific binding pockets can bind metal centers to achieve uniform oxidation states, as has been shown in prior studies by our group and by other groups. The goal of these studies is to improve selectivity in heterogeneous catalysts and to develop other novel surface chemistries. With that end in mind, we present new experiments with metal-organic coordination on oxide support surfaces. Most of the metal-organic surfaces studies have been done on metal surfaces to facilitate surface analysis. We have studied the redox assembly of 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) and Pt on oxide surfaces, including rutile $TiO_2(110)$ using High Resolution Electron Energy Loss Spectroscopy (HREELS), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). HREELS characterizes vibrational modes, which can provide key information about adsorbate interactions and metal-organic interactions at surfaces. DPTZ and Pt were sublimated onto the surface from a Knudsen-type evaporator. Submonolayer DPTZ vibrational modes were observed on Ag(111) (C-H bending modes at 400 cm^{-1}, 618 cm^{-1} and 772 cm^{-1}; ring deformation modes at 966 cm^{-1}, 1145 cm^{-1} and 1354 cm^{-1}) and on $TiO_2(110)$ (a ring deformation mode at 1580 cm^{-1} and a C-H stretching mode at 3060 cm^{-1}). To see the vibrational modes of adsorbates on TiO_2, a Fourier deconvolution technique was applied to remove multiple excitations of surface phonon. Annealing DPTZ on Ag(111) at 170 °C caused significant changes to the HREEL spectra (C-H bending modes at 400 cm^{-1} and 740 cm^{-1}, ring deformation modes at 1100 cm^{-1}, 1445 cm^{-1}, 1574 cm^{-1}, a C-H stretching mode at 3080 cm^{-1}), but no observable changes were seen for DPTZ on $TiO_2(110)$ until the sample was annealed at 290 °C. Adding equimolar Pt onto submonolayer DPTZ on Ag(111) caused similar vibrational changes to be observed, but at a lower temperature of 140 °C. HREELS studies of the Pt-DPTZ complex on $TiO_2(110)$, Au(100), and other surfaces are ongoing. By studying the redox assembly of metal-organic complexes on these surfaces, strategies can be developed to customize and tune the reactivity of novel surface catalysts.

8:40am **SS+AS+HC-MoM2 Studies of Single-site Catalysts on Powdered Oxide Support through Redox Assembly*, Linxiao Chen*,** *J.P. McCann, S.L. Tait,* Indiana University

High levels of reaction selectivity for selective alkane functionalization are generally difficult to achieve with metal nanoparticle heterogeneous catalysts, due to the variety of metal biding sites available. Motivated by the desire towards the development of uniform single-site metal centers at surfaces, our group has been working on the redox assembly of metal-organic systems at surfaces. On a single crystal gold surface, electrons are transferred from platinum to the ligand 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ). Utilizing this unique redox chemistry, long-range ordered 1D chains with an alternating metal-ligand structure were assembled at deposition of DPTZ with pre-adsorbed metallic platinum. All platinum sites are oxidized into Pt(II), and stabilized in the binding pocket between two DPTZ with identical chemical environment. Here, aiming at practical applications in catalysis, a novel solution-phase synthetic strategy was developed based on wet impregnation approach, in attempt to reproduce the similar metal-ligand structure on high-surface-area powdered oxide catalyst supports. X-ray photoelectron spectroscopy verified that the redox chemistry is applicable to real supports, and is crucial in the successful deposition of DPTZ despite a weak ligand-support interaction. The surface structure is further elucidated by X-ray diffraction and surface titration. It was concluded that the mobility of the metal and ligand on a rough support surface, and the existence of residual Cl from Pt precursors represent major challenges. This metal-ligand structure can be manipulated by tuning strength of interaction between the supports, metal and ligand. Initial catalytic tests with the methane oxidation reaction exhibited C-H activation ability and selectivity similar to traditional highly-dispersed Pt catalysts. We have compared these catalysts and explored the limitations of single-site metal-organic complexes at oxide supports. Though being significantly stabilized by the favored coordination geometry and the redox chemistry, the thermal stability of the metal-ligand structure needs to be further enhanced.

9:00am **SS+AS+HC-MoM3 Controlled Reactions of Coordination Complexes on Oxide Surfaces*, Susannah Scott,*** University of California at Santa Barbara **INVITED**

The reactions of coordination complexes with functional groups on oxide surfaces (acidic and basic hydroxyl groups, Lewis acidic cations and Lewis basic oxide anions) can lead to anchored metal complexes with a high degree of uniformity when conducted under carefully controlled conditions (low-to-moderate temperatures, absence of moisture and/or O_2). Detailed characterization of these sites using spectroscopic methods, elemental analysis and reactivity studies leads to information about their structure and insight into the underlying structure of the oxide surface. Experiments with gold and silver complexes such as $Me_2Au(acac)$ and Ag(acac) reveal that interactions with surface hydroxyls involving strong H-bonding to ligand donor atoms are primarily responsible for their dispersion as isolated metal sites. By modulating the hydroxyl density via thermal pretreatment, it is possible to control not only the surface density of metal atoms, but also their subsequent mobility. In the case of nucleation and subsequent autocatalytic growth of metal nanoparticles, it is possible to exert control over particle size via the initial metal complex-oxide surface interaction.

9:40am **SS+AS+HC-MoM5 Adsorption and Activation of CO_2 on Cu(997) at Low Temperature*, Jun Yoshinobu,*** The University of Tokyo, Japan

Adsorption and activation of carbon dioxide on Cu(997) were investigated by infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). CO_2 molecules are *physisorbed* on Cu(997) at temperatures below 70 K. However, the vibrational spectra of adsorbed CO_2 depend significantly on the substrate temperature; IR spectra of CO_2 vibrational modes at 70 K show asymmetric Fano line shapes. On the other hand, at 85 K, the dissociation of CO_2 into CO was observed on Cu(997) by IRAS and XPS, but not on Cu(111). In addition, the reaction of CO_2 on Cu(997) surface at 340 K under CO_2 gas pressure of 0.8 mbar was investigated by ambient pressure XPS. A main reaction product on the surface was identified as carbonate (CO_3), based on estimation of the composition ratio of oxygen to carbon. CO_3 was produced on the surface through the reaction of CO_2 with atomic oxygen formed from CO_2 dissociation.

10:00am **SS+AS+HC-MoM6 D_2O Interaction with Planar ZnO(0001) Bilayer Supported on Au(111): Structures, Energetics and Influence of Hydroxyls*, Xingyi Deng,*** *D.C. Sorescu, J. Lee,* National Energy Technology Laboratory

Ultrathin oxides with single or few atomic layers are considered new types of due to the emergence of film-specific structures with properties distinct from their bulk counterparts. ZnO(0001) bilayer grown on Au(111) adopts a planar, graphite-like structure via an intralayer relaxation from the bulk wurtzite structure. In this work, we investigate the interaction between D_2O and the planar ZnO(0001) bilayer grown on Au(111) with temperature programed desorption (TPD), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. D_2O molecules adsorbed on this planar surface form two ordered overlayers, a (3 × 3) and a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$, not seen before on any of the bulk ZnO single crystal surfaces. The apparent activation energies of desorption (E_d) estimated from TPD peaks agree well with the adsorption energy values calculated from DFT. The DFT calculations also reveal that both overlayers are mediated by extensive hydrogen bonding among the molecules but with different packing densities. The hydroxyl groups, accumulating very slowly on the ZnO(0001) bilayer surface under the standard ultrahigh vacuum (UHV) environment, strongly suppress the formation of the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ overlayer but have less impact on the (3 × 3) overlayer. We suggest that the difference in packing densities of the overlayers leads to these findings such that only the (3 × 3) overlayer with a more open structure can accommodate small amounts of the adsorbed hydroxyls.

10:40am **SS+AS+HC-MoM8 Nanoscale Silicon as a Catalyst for Graphene Growth: Mechanistic Insight from In-Situ Raman Spectroscopy**, ***Keith Share**, R.E. Carter,* Vanderbilt University*; P. Nikolaev, D. Hooper,* Air Force Research Laboratory*; L. Oakes, A.P. Cohn,* Vanderbilt University*; R. Rao,* Air Force Research Laboratory*; A.A. Puretzky,* Oak Ridge National Lab*; D.B. Geohegan, B. Maruyama,* Air Force Research Laboratory*; C.L. Pint,* Vanderbilt University

Nanoscale carbons are typically synthesized by thermal decomposition of a hydrocarbon at the surface of a metal catalyst. Whereas the use of silicon as an alternative to metal catalyst could unlock new techniques to seamlessly couple carbon nanostructures and semiconductor materials, stable carbide formation in bulk silicon prevents the precipitation and growth of graphitic structures. Here, we provide evidence supported by comprehensive *in-situ* Raman experiments that indicates nanoscale grains of silicon in porous silicon (PSi) scaffolds act as catalysts for hydrocarbon decomposition and growth of few-layered graphene at temperatures as low as 700 K. Self-limiting growth kinetics of graphene with activation energies measured between 0.32 – 0.37 eV elucidates the formation of highly reactive surface-bound Si radicals that aid in the decomposition of hydrocarbons. Nucleation and growth of graphitic layers on PSi exhibits striking similarity to catalytic growth on nickel surfaces, involving temperature dependent surface and subsurface diffusion of carbon. This work elucidates how the nanoscale properties of silicon can be exploited to yield catalytic properties distinguished from bulk silicon, opening an important avenue to engineer catalytic interfaces combining the two most technologically-important materials for modern applications – silicon and nanoscale carbons.

11:00am **SS+AS+HC-MoM9 Functionalization of Graphene on Ru(0001) with Atomic Oxygen**, ***Zbynek Novotny**,* Pacific Northwest National Laboratory*; F.P. Netzer,* Karl-Franzens University, Austria*; Z. Dohnálek,* Pacific Northwest National Laboratory

Well-defined, monodispersed catalysts supported on oxidized carbon nanotubes are a promising class of new materials for heterogeneous catalysis. While such systems exhibit lower complexity compared to traditional catalysts, many questions, such as the reproducible preparation of carbon nanotubes and the range of functionalities used for anchoring of the clusters, make determination of their oxidation state and structure difficult. An analogous model system, graphene, can be prepared and studied under UHV conditions with great control. We employ scanning tunneling microscopy (STM) to study chemical functionalization of supported graphene on Ru(0001) with atomic oxygen. On Ru(0001) graphene forms a defect-free moiré structure with a periodicity of 3 nm, offering variety of distinct, regularly-spaced adsorption sites. Three different regions can be distinguished in STM images: bright regions (C atop of Ru) with the largest distance to the underlying Ru metal, dark hcp regions where graphene is closest to the metal, and medium-bright fcc regions where graphene is slightly further away compared to the hcp regions. Interestingly, for temperatures above 114 K, atomic oxygen (AO) is preferentially observed within the medium-bright fcc regions but in a minority of cases also in the hcp regions. The onset of AO mobility is observed at 400 K, where AO is occasionally moving inside the fcc region, or away from the less-stable hcp region towards the bordering fcc region. At higher temperatures (450-500 K), a dramatic increase in AO diffusion is observed allowing for AO transport between neighboring fcc regions through the hcp region. Upon encounter, the AO groups form stable immobile dimers and large clusters. The high-resolution time-lapsed data is used to assign the AO adsorption configuration to the on-top bonded enolate groups rather than the expected bridge-bonded epoxys. Our ongoing effort focuses on quantifying the enolate diffusion barrier and understanding their interactions with adsorbates such as H_2O, CO, and CO_2. The high thermal stability of enolate groups, and their large periodic separation (~3 nm) makes functionalized graphene/Ru(0001) an ideal model system for model studies of monodispersed catalysts.

11:20am **SS+AS+HC-MoM10 Interaction of BaO with H_2O, CO_2 and NO_2 Studied with APXPS and NEXAFS**, ***Osman Karslioglu**, I. Zegkinoglou, L. Trotochaud, H. Bluhm,* Lawrence Berkeley National Laboratory

Barium is a constituent of several technologically important materials such as NO_x storage and reduction (NSR) catalysts in automobiles, getters for UHV applications, perovskite catalysts for electrochemical reactions and high-temperature superconductors. Interaction of barium compounds with simple molecules such as H_2O, CO_2 and NO_2 is thus of practical importance. We studied the interaction of in-situ prepared BaO with H_2O, CO_2 and NO_2 as a function of temperature and pressure using ambient pressure X-ray photoelectron spectroscopy (APXPS) and near-edge X-ray absorption fine structure (NEXAFS). Using in-situ preparation proved essential for preparing clean BaO, as the compound is extremely reactive even with minute amounts of H_2O and CO_2. We report the first experimental O K-edge X-ray absorption spectrum of clean BaO, for which the published spectra in the literature are more consistent with $BaCO_3$.

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