

Tuesday Afternoon, October 29, 2013

Surface Science

Room: 201 A - Session SS-TuA

Metals and Alloys: Structure, Reactivity & Catalysis

Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS-TuA1 A Density Functional Theory Study of Stability and Reactivity of H-C=O and C-OH Surface Reaction Intermediates on Pt(111) and Effects of Water on the Intermediates**, *L. Arnadottir*, Oregon State University

Two forms of the reaction intermediate with H:C:O stoichiometry were studied on Pt(111) using density functional theory. Three cases were studied: the intermediate on a clean surface, the intermediate and one water molecule on the surface and the intermediate with a water bilayer. Both the H-C=O (formyl) and C-OH configurations were found to be stable on clean Pt(111) and when coadsorbed with a single water molecule. On the clean surface interconversion between the two forms goes through stable a CO_{ads} and H_{ads} intermediates so although both HCO and COH are stable on the clean surface they will not interconvert without coadsorbed water. In the presence of coadsorbed water molecule the activation barrier for the interconversion from HCO to COH was found to be much lower or 0.62 eV. The HCO configuration is stable in the presence of a water bilayer with slight preference for bridge over atop adsorption site. The COH configuration is unstable under the water bilayer and dissociates into CO_{ads} and H that structurally diffuses into the water bilayer. That suggest that, in the presence of water, the HCO form will be the only stable form of the reaction intermediate of H:C:O stoichiometry. Various reactions paths for both of the reaction intermediates with OH and H₂O eventually leading to CO or CO₂ formation are also investigated.

2:40pm **SS-TuA3 Energetics of Elementary Reaction Steps of Importance in Clean Fuels Production and Utilization on Pt(111) by Microcalorimetry**, *C.T. Campbell*, University of Washington **INVITED**

Until recently, the heats of formation of some of the simplest adsorbed molecular fragments such as -CH, -CH₂, -CH₃, -OH, -OCH₃, -OOCH and -C(CH₃)₃ were not known on any metal surface. However, these simple adsorbates are ubiquitous catalytic reaction intermediates involved in many industrially important reactions that are catalyzed by platinum-group metals, including water-gas shift, steam reforming of hydrocarbons and oxygenates, combustion and selective oxidation reactions of all sorts, methanation and Fischer-Tropsch, methanol synthesis and decomposition, several fuel cell reactions and photocatalytic water splitting. Here we summarize the first measurements of the heats of formation of these adsorbed intermediates on Pt(111) using single crystal adsorption calorimetry. We also use these heats of formation to predict reaction energies for important elementary steps in catalysis on Pt, which give insights into catalytic reaction pathways. The results will also be compared to Density Functional Theory (DFT) calculations, to assess which DFT methods are most accurate. These experimental benchmark energies are aiding in the ongoing development of more accurate computational methods, like DFT with van der Waals corrections.

4:00pm **SS-TuA7 RAIRS Study on the Kinetics of NH Formation and Dissociation on Ru(0001)**, *I. Waluyo, Y. Ren, M. Trenary*, University of Illinois at Chicago

We used reflection absorption infrared spectroscopy (RAIRS) to experimentally study the kinetics of the NH formation and dissociation reactions on Ru(0001). These reactions are important in ammonia synthesis, for which ruthenium is one of the most effective catalysts. While theoretical values for the heats of adsorption of each species and the activation barriers for each step in the ammonia synthesis reaction have been extensively reported, there are few, if any, direct experimentally measured values for the activation barriers of the elementary steps in the reaction on Ru(0001). In our study, the evolution of the NH stretch peak at 3318 cm⁻¹ was monitored as a function of time during the course of the NH formation reaction between 320 and 370 K and NH dissociation between 370 and 400 K. An atomic N layer was prepared through the thermal decomposition of NH₃. During the NH formation reaction, the sample was continuously exposed to a constant background pressure of H₂ to compensate for the loss of surface H due to the associative desorption of H₂, which occurs in the same temperature range as NH formation. Both NH formation and dissociation were found to follow first-order kinetics, and the experimental rate constants show good agreement with the theoretical values. The experimentally determined activation energies of 69.6 and 104.9 kJ/mol for

NH formation and dissociation, respectively, are comparable to the theoretical values of 103.3 and 133.5 kJ/mol.

4:20pm **SS-TuA8 Calorimetric Measurement of Adsorption and Adhesion Energies of Cu on Pt(111)**, *S.L. Hemmingson, T.E. James, J.R.V. Sellers, C.T. Campbell*, University of Washington

Bimetallic catalysts are an important category of industrial catalysts that exhibit unique electronic and chemical properties from their parent metals. Pt-based bimetallic catalysts are the most commonly studied and well-characterized bimetallic systems, with many providing enhanced selectivity, activity, and stability for industrially significant reactions such as hydrogenation/dehydrogenation, CO oxidation, and the water-gas shift reaction. The modifications in the catalytic properties of Pt bimetallics are most significant when the admetal coverage is less than a single monolayer. Yet little is known about the strength of metal-metal bonds in some bimetallic catalysts because indirect energy measurement techniques such as temperature programmed desorption cannot be employed. This study employs a novel ultrahigh vacuum Single Crystal Adsorption Calorimeter (SCAC) to directly measure the adsorption energy of Cu overlayers on Pt(111) at 300 K. A pulsed and collimated Cu atomic beam is generated using an electron beam-heated source and deposited onto a Pt(111) single crystal surface. The measured heats of adsorption as a function of total Cu coverage were interpreted with respect to the known layer-by-layer growth mechanism of Cu overlayers on Pt(111). Two distinct Cu coverage regimes of heat of adsorption have been observed. From 0 to just above one monolayer (ML), the heat decreases from 357.4 kJ/mol to 334.5 kJ/mol where Cu grows pseudomorphically on Pt(111). The high initial heat of adsorption indicates a strong Cu-Pt interaction for isolated Cu atoms which are stronger than the Cu-Cu metallic bond. As Cu coverage increases the heats decrease due to repulsive interactions between neighboring Cu atoms or lattice strain buildup. From 1.3 and 3 ML, where Cu grows layer-by-layer with the Cu(111) lattice spacing, the heats of adsorption increases slowly to the bulk heat of sublimation of Cu, 337.4 kJ/mol, due to lattice mismatch between the first Cu monolayer and the subsequent monolayers. By 3 ML no further lattice strain is felt by additional Cu. This represents the first ever direct measurements of late transition metal bimetallic adsorption energies.

4:40pm **SS-TuA9 History of Surface Science at AVS**, *R.M. Tromp*, IBM T.J. Watson Research Center **INVITED**

Surface science has a long and illustrious history. The development of surface science and of the AVS have often intersected, and even coincided. In this talk I hope to discuss some of these intersections and coincidences.

5:20pm **SS-TuA11 Growth and Activity of Pt-Based Bimetallic Clusters on Titania**, *D.A. Chen, R.P. Galhenage, H. Yan, K. Xie, A.S. Duke*, University of South Carolina

The nucleation, growth and surface composition of Pt-Co and Pt-Re bimetallic clusters on TiO₂(110) have been investigated as model systems for understanding how surface chemistry can be controlled by bimetallic composition and interactions between the clusters and the oxide support. Scanning tunneling microscopy studies demonstrate that bimetallic clusters can be formed from sequential deposition of the metals when the metal with the lower mobility on titania (Co or Re) is deposited first to serve as nucleation sites for Pt. For the Co-Pt clusters, the surface composition is slightly Pt-rich compared to the bulk, despite the lower surface free energy for Co compared to Pt. While Co-Pt clusters have similar surface compositions regardless of the order of deposition, the inter-diffusion of metals in Re-Pt clusters is inhibited when Pt is deposited on top of Re; for the reverse order of deposition, XPS data indicate that a Re-Pt alloy is formed. Temperature programmed desorption experiments with CO show that CO adsorbs at both Co and Pt sites on the bimetallic clusters. Methanol decomposition chemistry has also been studied as a function of changing bimetallic cluster composition. Methanol decomposition produces CO and hydrogen as the main products on both pure Pt and pure Co clusters. On the bimetallic Co-Pt clusters, the selectivity for methane production increases, and the desorption of H₂ at higher temperatures suggests that the intermediates have greater thermal stability.

5:40pm **SS-TuA12 An Atomic-Scale View of Carbon-Carbon Bond Formation on Cobalt Nanoparticles**, *E.A. Lewis, E.C.H. Sykes*, Tufts University

Fischer-Tropsch synthesis (FTS) has recently gained increased attention as it involves the formation of hydrocarbons (fuels) via the catalytic conversion of syngas (CO and H₂), which can be derived from renewable sources. FTS is often performed using cobalt-based catalysts, and although the exact mechanism of the reaction is not known, it has been shown that

the reactivity is affected by the adsorption state of reactants, as well as nanoparticle shape and size. Here we have used low-temperature scanning tunneling microscopy to study carbon-carbon bond formation during FTS. By using aryl-halides to form phenyl radicals on the cobalt surfaces, we can examine the preferred site for carbon-carbon bond formation. Initially at 5 K, the intact molecules form loosely-ordered arrays on the cobalt surfaces, but at 80 K, we find that phenyl radicals are stabilized in a series of highly ordered geometries on the cobalt terraces. Upon heating, a carbon-carbon bond is formed that results in surface-bound biphenyl. These results provide insight into the active site for carbon coupling during FTS, and we propose a mechanism that may explain the well-known phenomenon of surface roughening that occurs on cobalt surfaces under real FTS conditions.

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