

Surface Science

Room 203 - Session SS2-ThA

Gas-Surface Reaction Dynamics

Moderator: K.W. Kolasinski, University of Virginia

2:00pm **SS2-ThA1 Why is Formate Synthesis Insensitive to Copper Surface Structures?**, *J. Nakamura*, University of Tsukuba, Japan; *Y. Morikawa*, Osaka University, Japan; *G. Wang*, Nankai University, China

Unique structure sensitivity has been experimentally observed for the formate synthesis from CO@sub2@ and H@sub2@ (CO@sub2@ + 1/2 H@sub2@ ----> HCOOa) on copper surfaces and the reverse reaction of formate decomposition. That is, the reaction rate of formate synthesis and the activation energy are very similar among Cu(110), Cu(100), and Cu(111), meaning a structure insensitive reaction. On the other hand, the reverse reaction of formate decomposition on copper was a structure sensitive reaction with different activation energies. Also, an Eley-Rideal (E-R) type reaction mechanism has been suggested for the formate synthesis, in which CO@sub2@ molecule directly reacts with adsorbed hydrogen without passing through adsorption of CO@sub2@. Here, we report the results of ab initio density functional theory (DFT) calculation for the formate synthesis. The DFT-GGA calculation has reproduced adsorption energies and adsorption structure of bidentate formate experimentally measured on Cu(111), Cu(100), and Cu(110), which further reproduces the structure insensitive and structure sensitive features for formate synthesis and formate decomposition, respectively. The structure insensitivity is due to the presence of monodentate formate with similar adsorption energies on Cu(111), Cu(100), and Cu(110), giving a similar energetic pathway from CO@sub2,g@ + 1/2 H@sub2,g@ to monodentate formate. The structure sensitive feature for the decomposition of bidentate formate is due to a significant difference in the adsorption energy of bidentate formate depending on the Cu surface structure. The structure insensitivity is due to the E-R type reaction mechanism without passing through adsorption of CO@sub2@, which enables a similar reaction pathway with similar local structures as revealed in the snapshot for the structural change of intermediates.

2:20pm **SS2-ThA2 Experimental and Computational Probes of Transition States on Surfaces**, *A.J. Gellman*, *D.S. Sholl*, *P.P. Ye*, *X. Li*, Carnegie Mellon University

Transition states determine the rates of surface catalyzed reactions, however, direct characterization of surface transition states is challenging. Experimental measurements of substituent effects on reaction barriers have been combined with Density Functional Theory to probe the transition states to the @beta@-hydride elimination in ethoxy groups on Cu(111) and the hydrogenation of alkyl groups on Pt(111). Our results allow us to test the recently advanced proposition that surface reactions with reactant-like (product-like) transition states are relatively sensitive (insensitive) to the nature of the catalyst surface. The barrier to @beta@-hydride elimination in fluorine substituted ethoxy groups increases significantly as a result of fluorine substitution. This is ascribed to a transition state in which the @beta@-carbon atom is cationic with respect to the initial state ethoxy group. Comparison of the experimental values of @Delta@E@sub act@ and the predictions of DFT shows impressive agreement and verifies the predictions based on previous experimental measurements. Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups on the Pt(111) surface and the transition state to @beta@-hydride elimination in alkyl groups on the Pt(111) surface. Co-adsorption of hydrogen with alkyl groups and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The influence of the substituents on the activation barriers to hydrogenation has been correlated with the field and polarizability substituent constants of the alkyl groups in the form of a linear free energy relationship. This indicates that the @alpha@-carbon in the transition state is cationic with respect to the initial state alkyl group and that the reactant has greater charge density on the @alpha@-carbon than the transition state.

2:40pm **SS2-ThA3 Molecular Beam Studies of Rare Gas and HCl Collisions with Functionalized Self-Assembled Monolayers**, *B.S. Day*, *L.R. Fiegand*, *J.R. Morris*, Virginia Tech

INVITED

The research objectives of this work are aimed at elucidating the atomic-scale mechanisms of interfacial bonding, diffusion, and reactions that govern gas-surface interactions on organic surfaces. This challenge is

particularly formidable for functionalized organic surfaces where the complicated nature of the interface can result in a broad range of reaction pathways. The approach used in these studies for exploring gas-surface reaction mechanisms combines molecular beam scattering techniques with functionalized self-assembled monolayers. Together with surface analysis instrumentation, these techniques are designed to reveal insight into many aspects of the gas-surface interaction and help develop an atomic-level description of the transformation of reactants into products. This presentation will focus on recent investigations into the dynamics of rare gas and HCl collisions with self-assembled monolayers. Atomic beams of high-energy rare gases are employed to explore the initial gas-surface collision in the absence of reactivity. These studies reveal how the atomic-scale nature of organic surfaces determine the extent of interfacial energy transfer and the path to thermal accommodation. The atom scattering studies are used to help interpret the dynamics of reactive gas-surface collisions, such as HCl impinging on a hydroxylated surface. In this work, HCl is directed at OH-terminated self-assembled monolayers to learn about how gas-surface hydrogen-bonding forces influence the dynamics of the collision. Measurements of the HCl energy transfer, residence time, and proton exchange probability have provided new insight into the interactions of HCl with well-characterized hydroxylated surfaces.

3:20pm **SS2-ThA5 Gas-Surface Reaction Dynamics of NO on Iron Phthalocyanine Thin Films**, *S.R. Bishop*, *N.L. Tran*, *G.C. Poon*, *A.C. Kummel*, University of California, San Diego

Metallophthalocyanines (MPc) have been proposed for use in chemically sensitive field effect transistor (chem-FET) detectors for the measurement of ambient analytes such as NO@sub x@, NH@sub 3@, and O@sub 3@. However, the adsorption energies and mechanisms of the reaction between these gases and MPc thin films have not been studied. We have investigated the reaction dynamics between NO and monolayer Iron Phthalocyanine (FePc) grown on clean Au(111) surface. The sticking probabilities of 0.11 eV monoenergetic molecular beam of NO were measured on both clean Au(111) and ordered 6x6 monolayer-FePc deposited on clean Au(111) as a function of surface temperature. NO sticking on the Au(111) surface occurs through a precursor-mediated physisorption pathway. In comparison, NO sticking on the FePc film occurs via multiple pathways: direct chemisorption to the metal center and precursor-mediated physisorption. Although the metal center of the molecule accounts for only ~3% of the surface, the direct chemisorption pathway has a sticking probability of ~20%. This suggests that the NO molecules are steered to the reactive metal centers by other portions of the FePc molecule. By using a high translational energy molecular beam, the direct chemisorption pathway will be selectively probed.

3:40pm **SS2-ThA6 Extracting the Vibrational Ground State Reactivity of Methane on Ni(111) from Ensemble Averaged Experiments**, *D.R. Killelea*, *V. Campbell*, *A.L. Utz*, Tufts University

Beam-surface studies have uncovered key details of the dynamics of methane dissociation on transition metal surfaces. When the measured reactivity is averaged over the population distribution of vibrational states in the beam, the data may obscure the role of individual vibrational states in promoting reaction. Here, we measure the reactivity of CH@sub 4@ beams impinging on a Ni(111) surface. We vary the vibrational energy of the beams by changing the beam source temperature. We model the nozzle temperature effect for these data, and extrapolate to find the reactivity of CH@sub 4@ in its vibrational ground state (v=0). Our model predicts that at the low translational energies typical of thermal samples, vibrationally excited molecules account for the majority of observed reactivity.

4:00pm **SS2-ThA7 Variable (T@sub g@, T@sub s@) Measurements of Alkane Dissociative Sticking Coefficients**, *K.M. DeWitt*, *L. Valadez*, *K.W. Kolasinski*, *I. Harrison*, University of Virginia

A novel technique for measuring nonequilibrium dissociative sticking coefficients, S(T@sub g@, T@sub s@), with well-defined gas temperature, T@sub g@, and surface temperature, T@sub s@, is described, along with its application to activated dissociative chemisorption of CH@sub 4@ and C@sub 2@H@sub 6@ on Pt(111). Microcanonical unimolecular rate theory (MURT) is employed to analyze the sticking coefficients and to extract transition state characteristics. The MURT allows the S(T@sub g@, T@sub s@) sticking to be directly compared to other molecular beam and thermal equilibrium sticking measurements. Interestingly, measured S(T@sub g@ = 300 K, T@sub s@) for CH@sub 4@ on Pt(111) are several times larger than recent thermal equilibrium measurements, S(T@sub g@ = T@sub s@), on supported Pt nanocrystallite catalysts [J. M. Wei, E. Iglesia, J. Phys. Chem. B

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108, 4094 (2004)]. This is a surprising result that runs contrary to the popular notion that dissociative chemisorption should be enhanced at the coordinatively less saturated defect sites that should be more prevalent on the ~2 nm diameter Pt nanocatalysts than on a flat Pt(111) surface.

4:20pm SS2-ThA8 First Principles Resonance Energies and Widths of Ions near Surfaces: N-Body Dynamical Predictions of Charge-Transfer Probabilities for Scattered Ions, K. Niedfeldt, E.A. Carter, Princeton University; P. Nordlander, Rice University

By combining periodic density-functional theory calculations of adsorbate resonance widths and shifts with a many-body dynamical charge-transfer theory, we quantitatively assess charge-transfer rates for ions scattering off surfaces. This method goes beyond previous approaches, which have been limited to modeling metal surfaces with either jellium potentials or finite clusters. We consider Li⁺ scattering off Si(001), Mg(0001), Cu(001), and Al(001). When compared to experimental neutralization fractions for Li ion scattering off of Al(001), our method yields trends in neutralization as a function of scattering angle in better agreement than those derived from jellium models. Our results comparing Mg and Cu show that scattering off of Mg and Cu yield distinctly different charge-transfer probabilities. By contrast, jellium predicts identical scattering properties due to identical theoretical free-electron gas values. As expected, for Li ions scattering off Si(001), the Li 2s orbital interacts most strongly with the Si dimer dangling bonds. The charge-transfer rates for Li ions scattering off Si(001) exhibits extreme variations with lateral position, in contrast again to the jellium picture. Taken together, these results clearly indicate that more realistic ion-surface interaction models (such as provided here) are necessary to obtain even qualitatively correct trends in charge-transfer for many ion-surface interactions.

4:40pm SS2-ThA9 Formation of Multiply Charged Ions by Direct Recoil, X. Chen, Z. Srubek, J.A. Yarmoff, University of California, Riverside

Low energy ions that impact a solid surface can remove material by sputtering, which produces low kinetic energy particles through a collision cascade, or direct recoil (DR), which involves the emission of a relatively high-energy particle following a hard collision between the incident ion and a surface atom. An inner-shell promotion that places one of the atoms into an excited state is a possible consequence of the hard collision. In these experiments, we find a unique process in which the DR particle is emitted with two holes, i.e., as a doubly charged ion. Si²⁺ ions were incident on atomically clean Al(100). The absolute ionization probability of scattered Si and recoiled Al were measured with time-of-flight, while detailed spectra of the ion yield were collected with an electrostatic analyzer. All of the scattered Si was neutralized, as expected due to its large ionization potential. Spectra collected of the DR Al show, however, a combination of Al¹⁺, Al²⁺ and Al³⁺ ions. The multiply charged ions are attributed to a charge promotion of the Al 2p during the hard collision. The Al 2p level is promoted above the Fermi energy by interaction with the Si 2p level that lies just below, such that both electrons are transferred to the solid forming Al ions with two holes. Subsequently, some of the Al²⁺ may decay to Al³⁺ via autoionization, or pick up an electron to form Al¹⁺. This mechanism is verified by the observation of an energy threshold for the process, and by spectra of the electrons emitted as the excited states decay. This process of producing multiply charged DR ions is highly effective because of the small separation between the Al and Si 2p levels. Thus, it is expected that similar behavior would occur for other closely matched systems that will be investigated, such as P ions incident on solid Si.

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