Surface Science Division
Room 607 - Session SS2-WeA
Gas-Surface Dynamics

Moderator: B.D. Kay, Pacific Northwest National Laboratory

2:00pm **SS2-WeA1 Dissociative Sticking of Small Oxidant Molecules on a Simple Metal; NO, O@sub 2@, CO and N@sub 2@ on Al(111)**, *H. Ternow, **I. Zori@aa c@**, B. Kasemo,* Chalmers University of Technology, Sweden

Motivated by our combined interest in molecular dissociation mechanisms at surfaces and early stages of surface oxidation, we are studying the dissociative sticking of small oxidizing molecules on Al(111). Hydrogen dissociation on metal surfaces has been clarified in detail by a close interplay between state resolved molecular beam experiments and calculated dynamics of dissociation on multidimensional potential energy surfaces. In contrast, dissociation dynamics of O@sub 2@ on simple metal surfaces, e.g. Al(111) and Ag(110, is not well understood. Molecular beam experiments indicate in both cases activated dissociation, while the calculated PES-s so far do not show such features. We have in this work investigated dissociation of several small molecules on Al(111) surface to elucidate the nature of the activation barrier and to explore these molecules' properties as oxidants for oxide film formation. The observed dissociative sticking for the two isoelectronic molecules, CO and N@sub 2@, is consistent with the presence of a very high activation barrier. In contrast, dissociation of NO and O@sub 2@ shows a rather low apparent activation barrier. Vibrational excitation of the molecules enhances dissociation. In the case of NO dissociation an energy dependent N/O ratio on the metal surface is observed. These features are discussed referring to the known symmetry and spatial extention of the frontier orbitals on the two species. The alternative - or complementary - view of the dissociation event, based on a harpooning mechanism, is also discussed.

2:20pm **SS2-WeA2 Chemical Selectivity and Remote Dissociation-ICl/Al(111)**, ***K.A. Pettus**, A.C. Kummel,* University of California, San Diego

We have investigated the chemical selectivity of ICl adsorption onto Si(111)-7x7, a high work function surface, and Al(111), a low work function surface. ICl chemisorbs onto these surfaces by two mechanisms, abstractive chemisorption and dissociative chemisorption. Abstractive chemisorption, in which one halogen atom of ICl bonds to the surface while the other is ejected into the gas phase, is the dominant mechanism for both the ICl/Si(111)-7x7 and the ICl/Al(111) reactions. Multiphoton ionization (205 nm MPI) spectroscopy and time-of-flight (TOF) mass spectrometry were used to determine that the ratio of iodine-selective abstraction to chlorine-selective abstraction is at least 10:1 for both the ICl/ Si(111)-7x7 and ICl/Al(111) reactions. However, the dynamics leading to the chemical selectivity are quite distinct. For the ICl and Si(111)-7x7 reaction, a transition state is formed by the donation of electrons from ICl to an empty dangling bond on the Si(111)-7x7 surface. Since the highest molecular orbital (HOMO) of ICl consists of atomic iodine orbitals, the iodine atom is the more reactive atom and chemical selectivity occurs. The ICl/Al(111) reaction occurs by a very different mechanism, remote chemisorption. In this process, an electron is harpooned from the aluminum metal surface to the lowest unoccupied molecular orbital (LUMO) of ICl. The adsorption of the electron transforms ICl into an excited repulsive state of the negative ion, ICl-. The LUMO primarily consists of atomic iodine orbitals; therefore, iodine again is the more reactive atom and ICl/ Al(111) abstraction favors the adsorption of iodine.

3:00pm **SS2-WeA4 Quantum-State-resolved Studies of Elastic and Inelastic Scattering of H@sub 2@ from Cu and Pd**, ***G.O. Sitz**, E. Watts,* The University of Texas, Austin

The scattering of H2 from Cu and Pd surfaces was studied using molecular beam techniques and quantum state-specific detection methods. A comparison is made for an unreactive case, H2(v=0)/Cu, and two reactive cases, H2(v=1)/Cu and H2(v=0)/Pd. Rotational excitation was observed in the scattering of H2(v=0) from Pd(111) and Cu(110) and was found to depend on the surface temperature. This rotational excitation occurred even when there was insufficient translational energy to account for the gain in rotational energy, indicating that part of the excitation energy is transferred from the surface to the molecule. The effect of vibrational motion in the H2/Cu system was studied by preparing the incident molecules in the single rovibrational state (v=1, J=1). The absolute survival probability of this state was measured along with the probabilities for rotational excitation and vibrational relaxation. This information is used to estimate the probability of dissociation of the vibrationally excited state. These results are compared with recent quantum dynamical calculations for the scattering of this particular state.

3:20pm **SS2-WeA5 Atom Scattering From Atomic Surfactants**, ***G.M. Nathanson**, J.A. Morgan, W.R. Ronk, M. Manning,* University of Wisconsin, Madison **INVITED**

Scattering experiments show that the rate of energy transfer between atomic gases and atomic liquids can be controlled by altering only the composition of the outermost surface layer of atoms. In the case of the 0.2% bismuth/99.8% gallium liquid alloy, the surface composition can be varied from a nearly pure Bi monolayer at temperatures near 290 K to 80% surface Ga at 900 K. This Bi surface enrichment is due to the much lower surface tension of pure Bi than of pure Ga. We find that impinging argon and xenon atoms lose nearly the same amount of energy in collisions with pure liquid Bi as with the bismuth-covered Bi/Ga alloy created at low temperatures. With increasing temperature, the rate of collisional energy transfer increases nearly linearly toward the value for pure liquid Ga as the surface Bi atoms are replaced by Ga atoms. These results suggest that the Ga atoms underneath the surface Bi atoms do not play a direct role in controlling the exit energies of the inelastically scattered Ar or Xe atoms; the rate of approach to gas-liquid thermal equilibrium depends only on the composition of the outermost surface layer.

4:00pm **SS2-WeA7 Molecular Beam Studies of the Extrinsic Precursor State: Trapping of Alkanes on Alkane-Covered Pt(111)**, ***A.F. Carlsson**, R.J. Madix,* Stanford University

Adsorbed species can significantly affect probabilities of adsorption of incident molecules. The classic studies of CO adsorption on metals lead to the concept of the extrinsic precursor state, and the analysis of Kisliuk of this process is well known. However, there few systematic studies of the dynamics of this process and the way in which properties of the adsorbed state affect adsorption. Using a liquid helium cryostat to achieve surface temperatures upward from 25 K and molecular beam methods, we have studied the adsorption probabilities of methane and ethane on Pt(111) surfaces presaturated by the adsorption of another alkane from a low pressure ambient. Firstly, methane adsorbs on the clean surface with near-normal energy scaling. On all covered surfaces, except that saturated by ethane, methane traps with probabilities ranging from 0.8 to 0.9, dependent on incident angle and energy. Generally, the trapping probability depends weakly on incident angle and energy. The weak dependence on incident angle is attributed to surface corrugation produced by the adsorbed alkanes. In the case of methane trapping on an ethane-covered surface a threshold to adsorption is observed. Below 16 kJ/mol the trapping probability remains very small, but above this threshold the trapping probability increases to 0.9. This "activated" molecular adsorption is quite dramatic. Ethane, however, shows distinctly different effects. The differences are attributed to size effects, not binding energy differences. These and other observations will be discussed.

4:20pm **SS2-WeA8 Influence of Rotational Energy on Adsorption Probability for a Physisorbed System: C2H4 on Ag(001)**, ***M. Rocca**, Luca Vattuone, U. Valbusa,* University of Genova, INFM, CSFBT-CNR, Italy

We show that the population of the rotational degrees of freedom of gas molecules affects their adsorption probability also for a physisorbed state. The effect, expected to be very general, is demostrated for the case of ethylene interaction with Ag(001) where we observe that the physisorption probability is suppressed for molecules produced with a hot nozzle, characterized by a sustantially larger rotational quantum number. Chemisorption of ethylene is observed for nozzle temperatures above 870 K and occurs in two phases characterized by different vibrational electron energy loss spectra. The barrier to chemisorption is in the vibrational degree of freedom as can be inferred by comparing pure and seeded beam data. At still larger nozzle temperatures fragmentation of ethylene upon adsorption is observed.

4:40pm **SS2-WeA9 Vibrational-State-Selected Studies of Gas-Surface Dynamics**, ***A.L. Utz**, L.B.F. Juurlink, R.R. Smith, P.R. McCabe, C.L. DiCologero,* Tufts University

A recently developed experimental technique uses state-resolved infrared laser excitation to probe dissociative chemisorption dynamics with quantum state resolution. We combine a supersonic molecular beam source, infrared laser excitation of methane molecules in the beam, and UHV surface spectroscopies to quantify the reactivity of gas-phase reagents excited to single, selected vibrational states. This approach permits independent and precise control over the translational and vibrational energy content of gas-phase reactants, as well as the character of their vibrational motion. We report on our use of this approach to unravel the dissociative chemisorption dynamics of methane on Ni(100). We find that methane molecules excited to the v=1 level of the antisymmetric C-H stretching vibration, @nu@@sub 3@, are up to 1600 times more reactive than are molecules in the v=0 level. Over a translational energy range from 16 to 68 kJ/mol, the sticking probability for these molecules increases from 3x10@super -5@ to 2x10@super -2@, which indicates that the @nu@@sub 3@ state is only responsible in part for the reactivity of a thermal distribution of vibrational states. We will also compare the efficacy of @nu@@sub 3@ excitation with other coordinates for energy deposition in the methane/nickel system.

5:00pm **SS2-WeA10 Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions***, **T.K. Minton**, J. Zhang, D.J. Garton, J.W. Seale,* Montana State University

The interactions of energetic atoms with hydrocarbon surfaces are largely responsible for the degradation of polymeric materials in space and for the outcome of polymer etch processes. Molecular beam-surface scattering experiments show that non-equilibrium processes dominate both the initial and steady-state interactions when a hydrocarbon surface is bombarded with a beam containing fast oxygen atoms. Direct inelastic scattering is the most probable non-reactive interaction. The most likely initial interaction is gas-phase-like H-atom abstraction to form OH. Once formed, the OH may undergo further collisions and reactions with the surface, some of which produce H@sub 2@O. The initial reactive and non-reactive events may be described with a simple kinematic picture that allows us to determine the effective surface mass encountered by an incident O atom, as well as the fraction of the atom-surface collision energy (in the center-of-mass frame) that is converted into internal energy in the surface and in the recoiling gaseous species. During steady-state oxidation, CO and CO@sub 2@ are produced. Formation of these molecules is believed to account for the erosion, or mass loss, of a polymer under O-atom attack. The rate of CO and CO@sub 2@ production from the surface is significantly enhanced when high-energy (>9 eV) Ar atoms collide with a surface that is undergoing continuous oxidation. This observation suggests that collisional processes may be important in material etching.

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