Chapter 3. Chemical Reaction Dynamics at Surfaces

Academic and Research Staff

Professor Sylvia T. Ceyer, Dr. Yulin Li, Dr. David P. Pullman, Dr. Athanassios A. Tsekouras, Dr. Arthur L. Utz

Graduate Students

Sean P. Daley, David B. Gosalvez, Theodore R. Trautman, Julius J. Yang

Technical and Support Staff

Anne Stollerman

3.1 A New Mechanism for Dissociative Chemisorption on Si: Atom Abstraction

Sponsor

Joint Services Electronics Program
Contract DAAL03-92-C-0001

Project Staff

Professor Sylvia T. Ceyer, Dr. Yulin Li, Dr. David P. Pullman, Dr. Athanassios A. Tsekouras, David B. Gosalvez, Julius J. Yang

F_2 is known to adsorb on Si(100) at 300 K with close to unit probability in the zero coverage limit. We have shown that the adsorption mechanism involves both the common mechanism for dissociative adsorption, whereby both fluorine atoms of the molecule adsorb, and a new mechanism, fluorine atom abstraction. In the abstraction mechanism, the Si surface captures one of the fluorine atoms from the incident F_2 molecule, while the other F atom scatters back into the gas phase.

This observation was made in a UHV molecular beam surface scattering apparatus by monitoring the directly scattered F atom signal with a triply differentially pumped quadrupole mass spectrometer. The scattered F atom signal is readily distinguishable from the F^+ signal due to cracking of the unreacted F_2 in the electron bombardment ionizer by its time of flight spectrum. The directly scattered F atoms are significantly more energetic, indicating that some of the exothermicity of this reaction is channeled into translation.

We have also taken measurements of the abstraction mechanism as a function of the incident F_2 energy, incident angle, surface temperature, and fluorine coverage. In addition, we have shown that the Si dangling bonds are the sites for fluorine adsorption and are probably responsible for the abstraction mechanism. This was accomplished by directing a well-characterized, monoenergetic beam of He atoms at the surface covered with a monolayer of fluorine and monitoring the angular distribution of diffracted atoms. The results of He diffraction measurement show that the fluorine does not break the dimer bond characteristic of (2x1) reconstruction. While the binding of fluorine to the dangling bonds along with the maintenance of the surface Si dimer bond is not surprising, this study represents the experimental evidence for these adsorption sites.

The reaction of F_2 with Si(100) ceases after the dangling bonds are saturated at one monolayer of coverage. This lack of additional reactivity precludes build up of a sufficient layer of fluorine to produce the volatile etch product SiF_4 and therefore the use of F_2 as an etchant of Si. However, we have shown that if the kinetic energy of the incident F_2 molecule is increased above a threshold value of 4-5 kcal mol^{-1} (0.2 eV), the dissociation probability of F_2 with a fluorinated surface increases linearly with the normal component of the kinetic energy.

This additional reactivity at higher translational energies, which results in fluorine coverages greater than one monolayer, is the result of surmounting a barrier to dissociation on the fluorinated surface. Measurements of the He atom diffraction spectra as a function of the incident F_2 kinetic energy indicate that the barrier is associated with dissociative chemisorption on the second layer of Si atoms as well as on Si dimer atoms. These conclusions are based on the identical rate of linear decay for all diffraction features with increasing F_2 normal energy above the threshold. There is no preferential cleavage of the Si dimer atoms. These observations may represent the first experimental correlation of the barrier for dissociation with the sites for dissociation.

Publications

Ceyer, S.T., D.J. Gladstone, M. McGonigal, and M.T. Schulberg. "Molecular Beams: Probes of the Dynamics of Reactions on Surfaces." In *Physical Methods of Chemistry, Vol. IX A, Investigations of Surfaces and Interfaces.* 2nd ed. Eds. B.W. Rossiter and R.C. Baetzold. New York: Wiley, 1993. pp. 83-452.

Li, Y.L., D.P. Pullman, J.J. Yang, A.A. Tsekouras, D.B. Gosalvez, K.B. Laughlin, M.T. Schulberg, D.J. Gladstone, M. McGonigal, and S.T. Ceyer. "Observation of a New Mechanism for Dissociative Chemisorption: F Atom Abstraction on Si(100)." Submitted to *Phys. Rev. Lett.*

Li, Y.L., J.J. Yang, D.P. Pullman, and S.T. Ceyer. "Reaction Dynamics of F₂ on Si(100)." Paper presented at the Physical Electronics Conference, Irvine, California, June 20-25, 1992.

Pullman, D.P., Y.L. Li, J.J. Yang, and S.T. Ceyer. "Reaction Dynamics of F₂ on Si(100)." Paper presented at the American Chemical Society Meeting, Washington, DC, August 24-28, 1992.

Pullman, D.P., Y.L. Li, J.J. Yang, and S.T. Ceyer. "Reaction Dynamics of F₂ on Si(100)." Paper presented at the American Vacuum Society Meeting, Chicago, Illinois, November 9-13, 1992.

3.2 New Mechanisms for Surface Processes

Sponsor

Project Staff

Professor Sylvia T. Ceyer, Dr. Arthur L. Utz, Sean P. Daley, Theodore R. Trautman

We have recently shown that hydrogen can be embedded in the bulk of Ni by a new mechanism, collision induced absorption. A beam of monoenergetic Ar, Kr, or Xe atoms, produced by the supersonic expansion of the inert gas seeded in He, is directed at a monolayer of atomic hydrogen chemisorbed on Ni(111). We observed that impacts of the incident inert gas atoms induce absorption of chemisorbed hydrogen. The hydrogen absorbed is identified by appearance of a vibrational mode at 800 cm⁻¹ and appearance of a feature at 180-220 K in the thermal desorption spectrum. This is consistent with our previous study of atomic hydrogen absorption into this crystal.

We have extended this work to include a study of the dynamics of collision induced absorption. We probe these dynamics by measuring the cross section for absorption of chemisorbed H induced by the impact of Ar, Kr, or Xe atoms as a function of their incident energy and angle. The cross section is calculated from measurements of absorption rate in the limit of zero absorbance.

The absorption rate is measured in the following manner. An inert gas atom beam is directed at the crystal covered with a H monolayer. A partial pressure of 2×10^{-5} torr of H_2 is present in the chamber during exposure to the inert gas atom beam. The pressure of H_2 is necessary to replace the H lost from the surface as the result of absorption and a competing process, collision induced recombinative desorption. In addition, maintenance of a layer of surface H blocks the exchange between surface and bulk H that is observed to be also induced by collisions of the inert gas atoms. At the end of the exposure to the inert gas atom beam, the ambient H_2 is pumped away, and a thermal desorption measurement is carried out. The amount of H absorbed is determined by the integrated area of the low temperature feature. This measurement is made for Ar, Kr, and Xe atoms incident over a wide range of angles and total kinetic energies.

The collision induced absorption cross section is observed to depend linearly on the normal component of the kinetic energy of the incident Ar, Kr, and Xe atoms. Strict normal energy scaling of the cross section is observed, and the cross section for absorption induced by Xe is significantly larger than that for Kr or Ar. These two observations suggest that the cross section for collision induced absorption is directly proportional to the energy transfer to the Ni lattice:

$$\Sigma(E_i, \varphi_i, m) = A \; \Delta E(E_i, \varphi_i, m)$$

where ΔE is the energy transferred from the inert gas atom to the lattice, E_i is the incident energy, φ_i is the incident angle, m is the mass of the inert gas atom and A is a proportionality constant.

To test whether the absorption cross section does correlate with energy transfer to the lattice, the incident energy, incident angle, and mass dependence of the energy transferred from the inert gas atom to the Ni lattice is calculated and compared to that of the experimentally determined cross section. The energy transfer is calculated within a hard sphere-hard cube impulsive collision model which has been modified to include the multiple collisions that take

place when a heavier gas atom is incident on a lighter substrate atom. The mass of the Ni atom is taken as its atomic mass. Motion of the Ni atom is only allowed normal to the macroscopic plane of the surface, which is known to be an excellent approximation in an atom-surface collision. Once the Ni atom has suffered its first collision with the inert gas atom, it is assumed to recoil instantaneously back toward the incoming inert gas atom. However, the Ni atom recoils with only a fraction (0.8) of its momentum acquired by collision with the inert gas atom. The rest of the momentum is lost to the lattice and in this way energy is dissipated to the lattice in this calculation. A second collision of the recoiling Ni atom and the incoming inert gas atom occurs, and their new momenta are calculated. Again, the Ni atom is assumed to recoil instantaneously with a fraction (0.8) of its momentum after the second collision. A third collision may occur, depending on the mass of the incoming inert gas atom. The total energy transferred is calculated by summing the energy lost to the lattice by the recoiling Ni atom after each collision and the final energy of the Ni atom.

The energy transferred to the lattice by Xe, Kr, and Ar is plotted as a function of their normal energy on the same plot as the experimental cross sections. The energy transferred by Xe is scaled to the experimental cross section for Xe, allowing the proportionality factor A to be determined. The proportionality factor is then used to predict the cross sections for absorption by Ar and Kr based on the energy transferred to the lattice by Ar and Kr. The experimental dependence of the cross sections on the mass and normal energy agrees very well with that of the cross sections predicted on the basis of the amount of energy transferred to the lattice. The one adjustable parameter in this model, the fraction of momentum with which the Ni atom recoils away from the lattice, is set at 0.8, but this parameter gives good agreement with the data over a wide range of values between 0.1 to 0.95 for a Ni mass of 58.7. This excellent correlation between the cross section for collision induced absorption and the energy transferred to the Ni lattice suggest a surface deformation mechanism. The incident atom collides with the surface either directly on top of or close to the adsorbed H atom. The impact of the collision transfers energy to the surface which momentarily distorts it to open up channels or holes into which the hydrogen can readily diffuse and enter the bulk.

Publications

Maynard, K.J., A.D. Johnson, S.P. Daley, and S.T. Ceyer. "A New Mechanism for Absorption: Collision Induced Absorption." Faraday Discuss. Chem. Soc. 91: 437 (1991).

3.3 The Chemistry of Bulk Hydrogen

Sponsor

Project Staff

Professor Sylvia T. Ceyer, Dr. Arthur L. Utz, Sean P. Daley, Theodore R. Trautman

Using molecular beam techniques coupled with high resolution electron energy loss spectroscopy, we have recently demonstrated the synthesis and detection of hydrogen embedded in the bulk of Ni under low pressure, UHV conditions. These capabilities have enabled the chemistry of bulk hydrogen to be probed unambiguously for the first time. We have found that the bulk hydrogen atom has unique chemistry. In particular, we have shown that the species reactive with adsorbed CH_3 is not a surface bound H atom but a bulk H atom.

The experiment is performed as follows. Exposure of the Ni(111) crystal to atomic hydrogen not only results in hydrogen embedded within the Ni lattice but also in a monolayer of hydrogen adsorbed on the surface. The surface-bound hydrogen blocks sites necessary for the second reactant, adsorbed CH_3 that we synthesize by the dissociative chemisorption of CH_4. Therefore, the H adsorbed on the surface must be removed. The removal of the surface-bound H cannot be effected thermally because it is more stable than bulk H, recombining and desorbing between 340-390 K. Therefore, removal of the surface-bound H by the non-thermal process, collision induced recombinative desorption, is necessary. A 100 kcal/mol Xe atom beam is directed at the surface at a glancing angle. The impacts of the Xe atoms deform the surface and allow the hydrogen to recombine and desorb as H_2. In this manner, the surface is swept clean of hydrogen while the bulk hydrogen remains. The clean surface is then exposed to CH_4 incident at 17 kcal/mol. The CH_4 dissociatively adsorbs, producing adsorbed CH_3 and adsorbed hydrogen. With the reactants now synthesized, the surface temperature is ramped at 2K/s and the partial pressures of hydrogen and methane are measured. At exactly the same temperature at which hydrogen

desorbs from the bulk, 180 K, there is very intense desorption of CH_4. We have also carried out this reaction with a deuterium isotope embedded in the Ni lattice. In this case, the sole product observed is CH_3D. There is no formation of CH_4 or higher deuterated methanes. In the absence of bulk hydrogen, no CH_4 is observed to desorb.

Methane is formed solely by the reaction with bulk hydrogen. The surface bound hydrogen is unreactive with CH_3. The reaction likely proceeds by the direct recombination of a bulk H atom with CH_3 because the interstitial octahedral site in which the hydrogen atom is bound is directly beneath the threefold hollow site on which the CH_3 is bound. As the surface temperature is raised, the bulk hydrogen atom moves up toward the surface where it encounters the methyl radical. Because the hydrogen atom now has the correct orientation required by the transition state for sp^3 hybridization, it reacts with CH_3 and immediately desorbs as CH_4. The reaction of CH_3 with an adsorbed H atom probably does not occur because access of the H atom to the Ni_3-C bond is blocked. This result documents a new mechanism for a surface reaction—a reaction between an adsorbed and a bulk species—and it unambiguously demonstrates the importance of bulk hydrogen as a reactant in a heterogeneous catalytic reaction.

Publications

Johnson, A.D., S.P. Daley, A.L. Utz, and S.T. Ceyer. "The Chemistry of Bulk Hydrogen: Reaction of H Embedded in Ni with Adsorbed CH_3." Sci. 257: 223 (1992).