

4. Chemical Reaction Dynamics at Surfaces

Academic and Research Staff

Prof. S.T. Ceyer

Graduate Students

J.D. Beckerle, D. Gladstone, M.B. Lee, M. McGonigal, R.J. Simonson, S.L. Tang

Undergraduate Students

M. Hines

4.1 Dynamics of Activated Dissociative Adsorption

National Science Foundation (Grant DMR81-19292)

Sylvia T. Ceyer, John D. Beckerle, Melissa Hines, Myung B. Lee, Sau Lan Tang

Our efforts this year have centered around the construction, assembly and testing of the molecular beam-EELS apparatus which will enable us to study the dynamics of molecule-surface interactions. In particular, we are interested in understanding why dissociative chemisorption does not occur on transition metal surfaces where the adsorption is known to be exoergic. In many of these cases it is likely that dissociative adsorption is activated and thus, is not observed when the adsorption is attempted by allowing ambient molecules, whose energies are characterized by a 300 K Maxwell-Boltzmann distribution to impinge on the surface. The existence of a barrier along the lowest energy pathway is the condition for activated dissociative chemisorption. On many metal surfaces, however, dissociative adsorption is observed when the surface has been modified with low coordination number sites or promoter atoms. Whether these modifications lower the barrier for dissociative adsorption, increase the atom-surface binding energy or affect both quantities is unknown. In short, the features of the potential energy surfaces which are modified to promote dissociation are simply not known experimentally.

Because activation energy barriers are extrema on the potential surface they are experimentally accessible. It is proposed to verify the existence of and to measure the magnitude of these dominant features in an experimental arrangement in which a beam of molecules that are to be adsorbed on a surface and high resolution electron energy loss spectroscopy are coupled. With this arrangement, the effect of the energy of the incoming molecule on its probability of dissociatively chemisorbing can be determined. If there exists a barrier to dissociation, there will be a sharp onset in intensity of the dissociated species at some incident beam energy. This beam energy then constitutes the appearance threshold or magnitude of the energy barrier to dissociation. The orientation of the barrier relative to the surface can be determined by variation of the incident beam angle. The effect

of lateral interactions on the height of the barrier can be investigated by variation of the surface coverage.

Carbon monoxide dissociation on Ni(111) is the rate limiting step in the methanation reaction, $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$. This reaction occurs with measurable rates only at high surface temperatures (>500 K) and at high pressures (>1 atm). This observation suggests that CO dissociative adsorption is an activated process since the pressure must be high enough for the CO molecules to gain energy through multiple inelastic collisions with the hot surface prior to the collision which leads to dissociation. We have chosen to investigate this system on an apparatus which we have recently finished constructing. Preliminary results indicate that the dissociative adsorption of CO is indeed activated and that the barrier is at least 25 kcal. If we confirm this result, then the rate of the methanation reaction could be greatly increased by heating the reactants prior to their encounter with the nickel catalyst. We also have measured the decrease in the barrier height when a small quantity (<10% of a monolayer) of potassium is doped on the surface. It appears that this small amount of potassium decreases the barrier by two orders of magnitude. We are presently confirming these preliminary results.

4.2 Dynamics of Dissociative Adsorption

National Science Foundation (Grant CHE82-06422)

Research Corporation

Camille and Henry Dreyfus Foundation

Sylvia T. Ceyer, John D. Beckerle, Melissa Hines, Myung B. Lee, Sau Lan Tang

Investigations into the dynamics of the dissociative chemisorption process on transition metal surfaces are planned. The collision energy of the incident adsorbate is a convenient probe of the dominant features of the molecule-surface potential energy surface which governs the adsorption dynamics. High resolution electron energy loss spectroscopy and photon detection are sensitive detectors of the result of the dissociative adsorption event. The effect of translational energy and, where appropriate, internal energy on the extent of dissociative chemisorption will be studied for molecule-metal systems that are believed to dissociate via a precursor state, a direct, an activated and an electronic mechanism or are believed not to dissociate. The emphasis of these studies is on establishing a correlation between the nature of the potential energy surface for the molecule-surface interaction and the dynamics of dissociative adsorption.

4.3 Chemical Reaction Dynamics at Semiconductor Surfaces

Sylvia T. Ceyer, Marianne McGonigal, David Gladstone

An investigation into the reaction dynamics of atomic oxygen and atomic halogens with

semiconductor surfaces will be carried out with molecular beam-surface scattering techniques. These techniques enable the measurement of the mass distribution, the residence time distribution, the angular distribution, and the energy distribution of the product molecules. The goals of this research are to develop a kinetic model for the surface reaction, to determine the chemical identities of the reaction intermediates, to understand the mechanism of the desorption step and how it relates to the potential energy surface in the exit channel region and to investigate whether simple gas phase unimolecular decay theories may be applied to describe the angular and energy distributions of the desorbing molecule after chemical activation. The plans for this apparatus have been submitted to various machine shops.

4.4 Spectroscopic Studies of Small Molecule Adsorption on Rare Earth Single Crystal Metal and Metal Oxide Surfaces

Monsanto

Sylvia T. Ceyer, Robert J. Simonson

An investigation aimed at a spectroscopic study of the adsorption of small molecules on single crystal rare earth metal and metal oxide surfaces has begun. Such techniques as X-ray and ultraviolet photoelectron spectroscopy, Auger and high resolution electron energy loss spectroscopy, low energy electron diffraction and thermal desorption are being employed to determine the dissociative nature of the adsorption, the electronic structure and the binding site of the molecule, the kinetics of the desorption process and the binding energy of the molecule on the surface. These studies represent the first investigations into adsorption on single crystal rare earth metals even though these metals, their oxides and their intermetallics exhibit catalytic activity comparable to transition metal catalysts.

At the present time, we have temporarily side-tracked from these goals to investigate some interesting inner shell spectroscopy of the rare earths. We have observed and identified inner core to 4f transitions in an electron energy loss spectrum of a Gd single crystal. These resonances have been previously observed in X-ray absorption studies of polycrystalline rare earth metals. Since both these resonances and the Auger transitions can be observed in a single spectrum, we are attempting to identify the Auger transitions that can be attributed to direct recombination from the bound 4f excitations versus those that arise from continuum excitations.

Publications

- Ceyer, S.T., W. Guthrie, T.H. Lin, and G.A. Somorjai, "D₂O Product Angular and Translational Energy Distributions from the Oxidation of Deuterium on Pt(111)," *J. Chem. Phys.* **78**, 6982 (1983).
Ceyer, S.T. and J.T. Yates, *J. Elect. Chem.* **150**, 17 (1983).

