

## 4. Chemical Reaction Dynamics at Surfaces

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### 4.1 Bridge to Atop Site Exchange of CO Adsorbed on Ni(111)

*Center for Materials Science and Engineering*

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*Research Corporation*

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Our research group has shown that a rapid site conversion process occurs between CO adsorbed on the bridge and atop binding sites. Since equilibrium is established, measurements, by a surface vibrational spectroscopy (high resolution electron energy loss), of the relative populations of CO bound to the bridge and atop sites as a function of surface temperature yield the binding energy difference between these sites. The difference in the binding energies at different sites on a single crystal surface has been previously undetermined. The bridge site is found to be more stable by about 1 kcal/mole in the zero coverage limit. The binding energy decreases to about 0.4 kcal/mole as the coverage is increased to near saturation coverage. We have shown that this sensitivity to temperature and coverage is the origin of the conflicting conclusions in the literature regarding the CO binding sites on Ni(111).

### 4.2 Activated Dissociative Adsorption of CH<sub>4</sub> on Ni(111)

*Camille and Henry Dreyfus Foundation*

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*Synthetic Fuels Center of the Energy Laboratory at M.I.T.*

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We have shown that the dissociative adsorption of methane on a Ni(111) surface is translationally activated by approximately 17 kcal/mole. This was accomplished by monitoring the carbon Auger intensity as a function of the incident translational energy of the methane molecule. Supersonic molecular beam techniques are used to produce the CH<sub>4</sub> molecules with well-defined translational energies over a wide range. Below translational energies of 17 kcal/mole, CH<sub>4</sub> does not adsorb either dissociatively or molecularly on a Ni(111) surface at 300K. At 17 kcal/mole, dissociative adsorption is observed. The probability of dissociative adsorption rapidly increases as the translational energy is increased to 22 kcal/mole. Preliminary high resolution electron energy loss spectra of the resulting hydrocarbon layer indicate that a methyl radical and an adsorbed hydrogen atom are the products of the dissociative adsorption event. These measurements indicate that there is an ~17 kcal/mole barrier along the potential energy surface for the CH<sub>4</sub>/Ni interaction which rises above the zero of energy. The presence of this barrier likely necessitates the high pressure conditions required for realistic reaction rates in the steam reforming of methane over Ni catalysts. The significance of this work is that if the high pressure requirement can be bypassed by increasing the energy of the incident molecule, then high pressure industrially important reactions can be studied at low pressure, enabling well-developed surface science techniques to be applied directly to catalytic reactions important in the "real" world.

### **4.3 Chemical Reaction Dynamics on Semiconductor Surfaces**

*Sylvia T. Ceyer, David J. Gladstone, Marianne McGonigal, Michelle Schulberg*

The etching of semiconductor materials in halocarbon plasma environments is a complex chemical process. The purpose of the plasma is the production of radical species that are highly reactive with the semiconductor surface. Since many different species, including neutral dissociation products of the halocarbon to atomic halogens and halocarbon radicals and ions and fragment ions produced by electron bombardment, are produced in the plasma, the chemistry is difficult to probe in this environment. Our program is aimed at systematically probing with molecular beam reactive scattering techniques the role of the neutral radical species in the etching process.

In this experimental arrangement, a beam of reactant atoms is aimed at a semiconductor surface and the volatile product molecules are detected after desorption from the surface by a quadrupole mass spectrometer. Since the molecular beam allows the production of a single reactive neutral species, the chemistry of the reactive species can be studied in a controlled fashion. The product molecule is unperturbed by collisions before detection allowing the reaction probabilities and the nascent product distribution to be determined unambiguously. We are planning to determine the reaction probabilities of F, C1, O and H atoms, common neutral radical species present in plasma environments, with silicon and to determine the identities of their

reaction products and the dynamics of the chemical reaction.

The molecular beam surface scattering apparatus required for these experiments is complex and not available commercially. Therefore, our group has been designing, constructing and assembling the apparatus for the past three years. At this time, the apparatus is in the final stages of assembly. The three ton ultra-high vacuum main chamber has been pumped down. We are waiting for delivery of the detector chamber from a machine shop before experimentation can begin.

#### 4.4 Spectroscopic Studies of the Adsorption of $C_2H_4$ and $C_2H_2$ on Gd(0001)

*Center for Materials Science and Engineering*

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*Sylvia T. Ceyer, Robert J. Simonson, Jun Rong Wang*

We are studying the adsorption of  $C_2H_4$  and  $C_2H_2$  on Gd(0001) over a temperature range of 90–500 K. Ultraviolet photoemission spectroscopy suggests that both  $C_2H_2$  and  $C_2H_4$  form a hydrocarbon species with the C–C bond intact at temperatures below 200K. Above this temperature, adsorbed species dehydrogenate and a graphitic overlayer is formed. We will confirm the structure of the intermediate by a vibrational spectroscopy, high resolution electron energy loss spectroscopy.

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