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Molecular Beam and Surface Science Studies of Heterogeneous Reaction Kinetics
Including Combustion Dynamics

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Chicago, IL 60637 s-sibener@uchicago.edu**I. ABSTRACT**

This research program examined the heterogeneous reaction kinetics and reaction dynamics of surface chemical processes which are of direct relevance to efficient energy production, condensed phase reactions, and materials growth including nanoscience objectives. We have had several notable scientific and technical successes. Illustrative highlights include: (1) a thorough study of how one can efficiently produce synthesis gas (SynGas) at relatively low Rh(111) catalyst temperatures *via* the reaction $\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$. In these studies methane activation is accomplished utilizing high-kinetic energy reagents generated *via* supersonic molecular beams, (2) experiments which have incisively probed the partial oxidation chemistry of adsorbed 1- and 2- butene on Rh and ice, as well as partial oxidation of propene on Au; (3) investigation of structural changes which occur to the reconstructed $(23 \times \sqrt{3})$ -Au(111) surface upon exposure to atomic oxygen, (4) a combined experimental and theoretical examination of the fundamental atomic-level rules which govern defect minimization during the formation of self-organizing stepped nanostructures, (5) the use of these relatively defect-free nanotemplates for growing silicon nanowires having atomically-dimensioned widths, (6) a combined scanning probe and atomic beam scattering study of how the presence of self-assembling organic overlayers interact with metallic support substrates – this work has led to revision of the currently held view of how such adsorbates reconfigure surface structure at the atomic level, (7) an inelastic He atom scattering study in which we examined the effect of chain length on the low-energy vibrations of alkanethiol striped phase self-assembled monolayers on Au(111), yielding information on the forces that govern interfacial self-assembly, (8) a study of the vibrational properties of disordered films of SF_6 adsorbed on Au(111), and (9) a study of the activated chemistry and photochemistry of NO on NiO/Ni. Innovative STM and molecular beam instrumentation has been fabricated to enable this program.

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II. RELEVANCE TO THE DOE MISSION

This program was of direct relevance to the strategic DOE mission of developing enhanced processes for the efficient production of energy and reformed hydrocarbon feedstocks, with concomitant impact on the development of more environmentally sound processes than those that are in common use today. The proposed program generated fundamental new atomic-level knowledge of reaction mechanisms including microscopic rate constants by examining the underlying heterogeneous reaction dynamics which govern such processes. Directly associated with the above was a critical examination of new chemical processes of direct relevance to carbon management such as the one-step conversion of CH_4 to syngas. We envision the research that occurred under this program as being an "enabler" for related work in combustion research and carbon management, providing needed data -- not currently in hand -- on heterogeneous reaction mechanisms -- especially involving energetic reagents such as atomic oxygen.

In summary, the accomplishments described in this Final Technical Report have addressed several strategic areas of interest for DOE, namely heterogeneous catalysis, synthetic fuels, hydrogen production, carbon management, fundamental science for complex systems on the nanoscale including self-organization on mixed nano- and atomic-level length scales, and partial oxidation chemistry in condensed phase systems.

III. PERSONNEL: CURRENT AND PAST GROUP MEMBERS

Our research program has been quite successful in attracting and educating some of the best young scientific talent in the country, including undergraduates, graduate students, and postdoctoral fellows. We also wish to emphasize that we have been quite successful in attracting qualified women and minorities to our program.

Personnel Who Participated in this DOE Program:

(PD: Postdoctoral Fellow; GS: Graduate Student; UG: Undergraduate):

Steven J. Sibener, Carl William Eisendrath Professor and PI

Dr. Kevin Gibson (Research Scientist)

Dr. Ken Nicholson (PD)

Miriam Freedman (GS)

Miki Nakayama (GS)

Aaron Rosenbaum (GS, Ph.D., August 2005; Intel)

Irene Popova (PD, IBM Yorktown Heights/Fishkill)

Seth Darling (GS, Ph.D. August 2002; Glenn Seaborg Fellow at Argonne Natl. Laboratory)

Ben Zion (GS, Ph.D. December 2000; research staff at Penn State)

Tom Pearl (GS, Ph.D. August 2000; Asst. Prof. NC State)

Yi Wang (GS, MS degree)

Mark Viste (GS, Ph.D. June 1999; Medtronics)

Jennifer Gimmel (UG)

IV. SUMMARY OF ACCOMPLISHMENTS

1. Molecular Beam Studies of Enhanced Routes to SynGas Production Using Methane

Methane is an abundant natural resource for making larger hydrocarbons through the Fischer-Tropsch process. To do this, it is necessary to partially oxidize CH_4 to synthesis gas (hereafter syngas), CO and H_2 , ideally in a 1:2 ratio. One method for accomplishing this is the direct partial oxidation of methane, $\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$. We have explored, using our multiple-molecular beam reactive scattering techniques, detailed aspects of this reaction on $\text{Rh}(111)$. We find that this reaction initially proceeds with the activated direct dissociative chemisorption of methane followed by subsequent oxidative chemistry to yield $\text{CO} + 2\text{H}_2$ from the partial oxidation of CH_4 . Concurrent molecular beams of O_2 and CH_4 were used, with both beams having narrow kinetic energy distributions. The reaction is highly activated, with the fraction of CH_4 converted being strongly dependent on normal translational energy, approaching unity for energies greater than ~ 1.3 eV. No CO_2 was detected under the conditions used, a key observation for reaction efficiency and minimization of greenhouse gases.

Applied Reaction Dynamics: Efficient Single Collision Partial Oxidation of Methane to CO on $\text{Rh}(111)$, K.D. Gibson, M. Viste, and S. J. Sibener, *J. Chem. Phys.*, In Press (2006).

2. Reaction of Small Olefins with O(³P) Adsorbed on Rh, Ice, and Au

Using molecular beams, we have studied the reaction of O(³P) with 1- and 2-butene on the surface of Rh and ice, and propene on the surface of Au, in vacuum at cryogenic temperatures. For 1-butene, the products are 1,2-epoxybutane, butanal, and a trace of butanone. For the 2-butenes, the reaction products include cis- and trans-2,3 epoxybutane and butanone. The propene reaction yielded a mixture of propylene oxide, propanal, and acetone. These results, taken together, demonstrate that the surface serves as an efficient sink for the excess energy of these highly exoergic reactions, yielding the stabilized adduct products. These investigations have emphasized that significant differences occur in condensed phase reactions as compared to related gas phase oxidative reaction where fragmentation and rearrangement dominate due to the absence of other energy-dissipation channels. Our observations indicate that heterogeneous interfaces provide a mechanism for channeling away excess energy, therefore leading to adduct stabilization. These experiments will, ultimately, provide kinetic data that are needed for the accurate modeling and design of advanced combustion and catalytic reforming systems.

O(³P) Reactions with Small Alkenes Adsorbed on Rh, Au and Ice, K.D. Gibson and S. J. Sibener, *Surf. Sci.* 600, L76-79 (2006).

3. O-Atom Induced Reconstruction of the Au(111) Surface

Using He diffraction, we have investigated morphological changes of the reconstructed (23x√3)-Au(111) surface when small quantities of O atoms are adsorbed. The electronegative oxygen removes charge from the surface, which causes the surface to restructure and ultimately revert to the (111) structure. The extent of this deconstruction is dependent on the initial O coverage and the surface temperature. When the deconstruction is complete, the oxygen can be removed from the terraces by annealing, leaving the surface in the unreconstructed (111) structure. Ultimately, and at a much slower rate, the surface begins to reconstruct. These experiments are important as they demonstrate that catalytic interfaces cannot be viewed as static entities, but rather as having evolving structure upon the adsorption of strongly-interacting reactive gases. The manuscript has been completed except for a last low temperature STM image of O/Au, now in progress.

O-atom Induced Reconstruction of the Au(111) Surface, K. D. Gibson and S. J. Sibener, to be submitted.

4. Oxygen Induced Restructuring of Stepped Metals: Experiment and Monte Carlo Simulation of Nucleation-Controlled Step Doubling

In order to make effective use of the extreme density of nanoscale elements that form spontaneously in self-assembling architectures, one must address the associated issue of minimizing defect creation during the formation of such structures. In this project we have examined the competing roles that nucleation kinetics and two-dimensional growth processes play in nanostructure formation and defect minimization. We employed oxygen-induced step doubling of vicinal Ni(977) surfaces as our physical system, using elevated temperature scanning tunnelling microscopy and Monte Carlo simulations to extract the desired details of interface evolution. Two interesting topological defect features were observed on the surface after doubling reaches its asymptotic limit: (i) “frustrated ends,” which form when two counter-propagating step-doubling events that have a single step in common intersect, leaving a stable topological defect, and (ii) residual “isolated single steps,” which form when a single step is unable to partner with an adjacent step. Monte Carlo simulations were performed to better understand these results. These simulations indicate that control of the delicate and competing interplay of nucleation kinetics and two-dimensional growth kinetics is the key to the formation of more perfect interfaces. Such optimized interfaces can act as templates for guiding the hierarchical assembly of nanowires and other nanoscale molecular assemblies (see next section).

In Search of Nano-Perfection: Experiment and Monte Carlo Simulation of Nucleation-Controlled Step Doubling, Yi Wang, T. P. Pearl, S. B. Darling, J. L. Gimmell, and S. J. Sibener, *J. Applied Physics*, 91 (12): 10081-10087 (2002).

5. Reactive Deposition of Silicon Nanowires Templated on a Stepped Nickel Surface

We have employed STM to examine the initial stages of Si nanowire growth by reactive deposition of disilane (Si_2H_6) on Ni(977). At low dosing exposures, Si_2H_6 decomposes on the stepped surface and forms oriented nanoscale wires which decorate the substrate’s step edges. This method of gas-phase reactive deposition on a stepped surface, with the substrate acting as both catalyst and nano-template with easily tunable width (by varying the vicinal miscut angle) is a fruitful approach to creating massively-parallel nanoscale arrays of highly aligned structures.

Reactive Deposition of Silicon Nanowires Templated on a Stepped Nickel Surface, Yi Wang and S. J. Sibener, *J. Phys. Chem. B* 106, 12856-12859 (2002).

6. Coexistence of the $(23\times\sqrt{3})$ -Au(111) Reconstruction and a Striped Phase SAM

We have studied the effect of adsorption of a low-density alkanethiol monolayer on the state of the Au(111) reconstruction. It is commonly believed that the substrate deconstructs following formation of a thiolate self-assembled monolayer, but our results suggest this is not always the case. The diffraction from 1-decanethiol and 1-octanethiol striped phase monolayers is exploited to establish the surface nearest-neighbor spacing and to illustrate a unit cell corresponding to the long dimension of the $23\times\sqrt{3}$ reconstruction. Using our observed $0.198\text{ \AA}^{-1}$ peak spacing and the $11.5\times\sqrt{3}$ unit cell reported in the literature, we measure a substrate nearest-neighbor spacing of $2.76\text{ \AA}$ along the $[1\bar{1}0]$ direction, which represents the atomic spacing of the uniaxially-compressed, reconstructed gold surface. Moreover, 1/2-order peaks in the diffraction from decanethiol/Au(111) demonstrate a distinction between neighboring thiolate dimers. These peaks are not observed for octanethiol/Au(111). Therefore, the 1/2-order peaks are not an inherent characteristic of alkanethiol SAMs. The most likely explanation is a reconstructed substrate. Complementary STM data, **Figure 1**, indicate persistence of the reconstruction during growth of a decanethiol striped phase monolayer and no evidence for vacancy islands typically associated with deconstruction. Our model involving a still-reconstructed substrate is consistent with all available data, while alternative models fail to explain the results from our laboratory.

Coexistence of the $(23\times\sqrt{3})$ -Au(111) Reconstruction and a Striped Phase Self-assembled Monolayer, S.B. Darling, A.W. Rosenbaum, Yi Wang, and S.J. Sibener, *Langmuir* **18**, 7462-7468 (2002).

Figure 1. Left: Variable-Temp UHV-STM with exceptional stability at elevated temperatures suitable for examining a wide range of molecularly adsorbed and reacting systems. Right: image of 3L exposure of decanethiol adsorbed on reconstructed Au(111) which demonstrates the persistent reconstruction during adsorption of the low-density lying-down phase. Deconstruction occurs upon formation of the higher-density standing phase.

7. Surface Vibrations in Alkanethiol Self-Assembled Monolayers of Varying Chain Length

We have performed a series of single-phonon inelastic He atom scattering experiments, complemented by appropriate numerical simulations, in order to dissect the forces driving the self-assembly of alkanthiolate monolayers, including inter-chain and chain-substrate interactions which govern the self-assembly process. The striped phases of 1-decanethiol, 1-octanethiol, and 1-hexanethiol exhibit FT_z phonons at 8.0, 7.3, and 7.3 meV, respectively. Molecular dynamics simulations suggest that the frequencies of the low energy vibrations are relatively constant with respect to chain length, in agreement with experiment. We also suggest that the modestly increased energy of the C10 mode with respect to C8 and C6 comes from increased binding due to the commensurate structure that C10 has with respect to the Au(111) reconstruction. This work represents a step forward in understanding the forces that govern interfacial self-assembly.

Surface Vibrations in Alkanethiol SAMs of Varying Chain Length, A.W. Rosenbaum, M.A. Freedman, S.B. Darling, I. Popova, and S.J. Sibener, J. Chem. Phys. 120, 3880-3886 (2004).

8. Interfacial Dynamics of Disordered Mono and Bilayer Films of SF_6 Adsorbed on Au(111)

In this project we have examined the vibrational characteristics of mono- and bilayer films of SF_6 adsorbed on Au(111). We have done this to better understand the substrate-adsorbate and inter-adsorbate interactions of sulfur hexafluoride physisorbed on Au(111), and to examine the scaling properties of the operative interaction potentials which determine the condensed phase dynamics of this important molecular adsorption system. In particular, we have examined the low-energy single-phonon vibrations of disordered mono- and bilayers of sulfur hexafluoride physisorbed on Au(111) with inelastic helium atom scattering. At monolayer coverages, SF_6 exhibits a dispersionless Einstein mode at 3.6 ± 0.4 meV. We observed two distinct overtones of this vibration as both creation and annihilation events at 7.1 ± 0.7 meV and 10.9 ± 1.4 meV, respectively. The overtones are harmonic multiples of the fundamental Einstein oscillation. Bilayers of SF_6 exhibit a softer fundamental vibration with an excitation energy of 3.3 ± 0.3 meV. This softening, due to the weaker SF_6 binding, also results in reduced overtone energies of 6.6 ± 0.7 meV and 9.8 ± 0.6 meV. The disordered bilayer does not exhibit dispersion, indicating that the molecules are still behaving like Einstein oscillators and not beginning to act as bulk crystalline SF_6 . The results have improved our understanding of the adsorbate-substrate and

inter-adsorbate interactions which govern the properties of this model molecular physisorption system.

Vibrational Properties of Disordered Mono- and Bilayers of Physisorbed Sulfur Hexafluoride on Au(111), A. W. Rosenbaum, M. A. Freedman, and S. J. Sibener, *J. Phys. Chem. A* **110**, 5537-5541 (2006).

9. Activated Chemistry and Photochemistry of NO on NiO/Ni

These activities explored the mechanistic details of NO chemistry with NiO(111)/Ni(111). Intense and kinetic energy tunable molecular beams have led to the formation of unusual surface adsorbate structures exhibiting higher density (new bonding configurations); vibrational and photochemical studies have been performed on these new bonding arrangements. In particular, we have examined the adsorption behavior of NO on NiO(111) grown on Ni(111) at 110 K. High-resolution electron-energy-loss spectroscopy (HREELS) shows fundamental changes in the vibrational spectrum for the beam-dosed surface in comparison with the background dosed surface. Three vibrational peaks are observed after beam dosing, two of which are not observed after conventional background dosing. The peaks can be assigned to NO stretches for a previously observed NO state, a new NO bonding geometry and a new NO₂ surface species, previously unobserved under NO dosing. The difference is accounted for by increased NO uptake due both to kinetically activated adsorption and to increased exposure. UV photo-irradiation causes the emergence of a fourth vibrational peak. The emergence of this peak is explained by a mechanism of selective desorption of the original NO species and a reaccommodation of the beam-induced NO structure to a more relaxed state on the lower coverage surface. The measured desorption cross sections and wavelength dependence are in good agreement with previous studies indicating that desorption induced by electron transfer is the mechanism responsible for the observed behavior. These studies are improving our fundamental understanding of heterogeneous processes which are relevant to controlling NO_x in the environment.

Molecular Beam Induced Changes in Adsorption Behavior of NO on NiO(111)/Ni(111), B. D. Zion and S. J. Sibener, *J. Chem. Phys.*, submitted (2006); UV-Photodesorption of Novel, Molecular Beam-Induced NO Layers on NiO(111)/Ni(111), B. D. Zion and S. J. Sibener, to be submitted.

10. Instrumentation Development

During the past grant period we have completed the assembly of a new cryogenically cooled STM (LiqN₂ or LiqHe can be used). This facility is giving crucial support to our effort in interface reactivity. We have also recently completed a laser-ignition (7J CO₂ TEA laser) pulsed beam source for the production of O(³P) spanning the kinetic energies from sub-eV to multi-eV. This addition allows us to examine dynamical details of condensed phase oxidation reactions.

Variable-Temperature UHV-SPM Facility - Details: We have completed the construction of our new liquid-He cooled STM facility which can operate over the temperature range 20-1000K, giving us the ability to study the structure of complex molecular overlayers from their low-temperature adsorption states until desorption/decomposition occurs; **Figure 2**. It is built around a Besoke Beetle type design, with the actual STM coming from RHK Technologies. We have spent over a year refining the cooling system (in partnership with RHK) which now meets our expectations. The facility now consists of two chambers, one which holds the microscope, and one which is for materials preparation. A third chamber, for mounting a differentially-pumped molecular beam, is being designed at this time (some components have already been fabricated). We have successfully imaged standing up and lying-down SAMs, as well as the canonical Si(111)-(7x7) at near liquid-He temperatures. This new instrument joins our first UHV-STM, shown earlier in **Figure 1**, which is based on an Omicron micro design. This microscope offers excellent stability at elevated temperatures (the environment of the scan head and surface mount has been modified to be cylindrically symmetric, and is hence self-correcting for thermal drift).

Figure 2. Liquid-He Cooled Variable-Temp UHV-STM Facility (Left) with Close-up of STM

(Center). Right: First cryogenic STM image of Si(111)-(7x7) with the sample temperature held at 30 K. Tunnelling conditions: $I = 0.55\text{ nA}$, bias $V = +1.65\text{ V}$. Supersonic molecular beam dosing and surface analysis instrumentation not shown. The hemispherical analyzer (SPECS, Germany) along with related XPS and Auger instrumentation has now been installed and is fully operational.

IV. Publication Summary

In Search of Nano-Perfection: Experiment and Monte Carlo Simulation of Nucleation-Controlled Step Doubling, Yi Wang, T. P. Pearl, S. B. Darling, J. L. Gimmell, and S. J. Sibener, J. Applied Physics, 91 (12): 10081-10087 (2002).

Reactive Deposition of Silicon Nanowires Templated on a Stepped Nickel Surface, Yi Wang and S. J. Sibener, J. Phys. Chem. B 106, 12856-12859 (2002).

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