

Dear DOE- Please find below a final report for the grant DE-FG02-04ER15518, to the American Chemical Society, Geochemistry Division.

Sincerely-Jay Brandes, frn. Treasurer for the Geochemistry Division.

Symposium objectives:

This was a grant to support travel for scientists to present data and interact with others in their field. Specifically, speakers presented their data in a session entitled "*Interfacial Phenomena: Linking Atomistic and Macroscopic Properties: Theoretical and Experimental Studies of the Structure and Reactivity of Mineral Surfaces*". The session ran across three ½ day periods, March 30-31 2004. The session's organizers were David J. Wesolowski and Gordon E. Brown Jr. There were a total of 30 talks presented during the symposium.

The entire technical program, with abstracts, may be found at:  
<http://oasys2.confex.com/acs/227nm/techprogram/S13682.HTM>

Please find below a list of abstracts, participants and support values. Speakers are given in Bold. Only Speakers were supported.

Ander Nilsson **Structure and bonding of water on metal surfaces** \$800

**Anders Nilsson**, Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, M.S. 69, Menlo Park, CA 94025, Lars G.M. Pettersson, FYSIKUM, University of Stockholm, Stockholm, Sweden, and Hirohito Ogasawara, Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, M.S. 69, Menlo Park, CA 94025.

The current understanding of the first water layer on metal surfaces will be presented. The traditional buckled bilayer model for water adsorption on closed metal surfaces has been shown to be inconsistent with new experimental data for water on Pt(111) based on electron and x-spectroscopy studies coupled with density functional theory calculations. Instead it was found that the layer of water in contact with the metal is nearly flat where half of the molecules bind through the oxygen as usually assumed, but the other half bind through an unexpected attractive interaction with the hydrogen to the metal. New experimental evidence will be presented showing that water adsorbs in a non dissociated state on Ru(001) at monolayer coverage in disagreement with a recent theory study that proposed that water forms a half dissociated layer. Large differences in both reactivity and wetting behavior for different Cu surfaces will be discussed in terms of electronic structure of the substrate.

Vicki Grassian **Heterogeneous reactions of carbonate minerals with trace atmospheric gases** \$ 800

**Vicki H. Grassian**, Department of Chemistry, Department of Chemistry, University of Iowa, Iowa City, IA 52242  
Mineral dust aerosol makes up a large fraction of the tropospheric aerosol mass. This is significant because mineral dust aerosol can impact climate, biogeochemical cycles, human health and atmospheric chemistry. The focus of this talk is on the heterogeneous chemistry of carbonate containing mineral dust aerosol with several trace atmospheric gases including nitric acid, sulfur dioxide and acetic acid. These reactions are done under ambient conditions of temperature, pressure and relative humidity. Several experimental methods have been used to probe reactions at the calcite-air interface. These include transmission and ATR FT-IR spectroscopy, atomic force microscopy and scanning electron microscopy coupled with energy dispersive x-ray analysis. The results of our laboratory study can be used to explain data collected during two field campaigns (TRACE-P and ACE-Asia) that were conducted in spring '01. During these field campaigns, a large dust storm occurred and several reactions on mineral dust aerosol, in particular the carbonate component of the aerosol, were observed. Mechanisms of these reactions in the atmosphere can be deduced from the laboratory studies.

William Schneider **Cooperative interactions in chemisorption on oxides** \$800

**W. F. Schneider**, Physical and Environmental Sciences, Physical and Environmental Sciences, Ford Motor Company, 2101 Village Road, MD 3083/SRL, Dearborn, MI 48121-2053  
Adsorption on oxide surfaces is fundamental to many aspects of environmental chemistry and catalysis. Despite this importance, the chemical concepts underlying oxide adsorption are not as well developed as for metal surfaces. In our work, density functional theory methods are being used to elucidate the adsorption chemistry of species particularly relevant to atmospheric chemistry and environmental emissions control, including CO<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub>, on main group and transition metal oxides. We find that this chemistry can be understood in terms of a combination and acid/base and charge transfer interactions which, in some cases, can lead to dramatic "cooperative" enhancements in adsorption. These interactions depend sensitively on the electronic structure of the oxides and the properties of the adsorbates. In particular, differences in behavior among different oxides and different adsorbates can potentially be exploited in the design of more effective and selective emissions control materials.

Amy Anshultz **Size dependent reactivity of iron oxyhydroxide nanoparticles** \$800

**Amy J. Anschutz** and R. Lee Penn. Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455

Nanoparticle reactivity is critically important to the geochemical cycling of both natural and anthropogenic chemical species. Iron oxides and oxyhydroxides are common and important materials in the biogeochemical cycle of iron and other metals and molecular species at the Earth's surface. These materials commonly occur as nanoparticles in the 3-10 nm size range. Our work shows that the rate of redox using hydroquinone as the reducing agent and iron oxyhydroxide nanoparticles as reductant is strongly particle size and phase dependent. Redox reactions using ~3.5 nm 6-line ferrihydrite nanoparticles, ~9x70 nm needle-shaped goethite nanoparticles, and ~30x350 nm needle-shaped goethite particles show that the surface-area normalized rates of redox are fastest (by as much as 100x) in experiments using the 6-line ferrihydrite. Furthermore, the surface-area normalized rates of redox for the ~9x70 nm needle-shaped goethite nanoparticles is up to fourteen times faster than the rates for the ~30x350 nm needle-shaped goethite particles.

Steve Granick **Viscosity and hydrophobicity of interfacial water**

\$800

**Steve Granick**, Departments of Materials Science and Engineering, of Chemistry, and of Physics, Departments of Materials Science and Engineering, of Chemistry, and of Physics, University of Illinois, 104 S Goodwin, Urbana, IL 61801

Properties of water at interfaces are of widespread environmental, technological, and biological interest but the details are disputed. Using a surface forces apparatus, we have measured the frequency- and rate-dependent responses to impulses applied in the shear direction and also in the direction normal to this. From studies using an assortment of counterions (monovalent, divalent, trivalent), film thickness (from nanometers to micrometers), and wettability (from hydrophilic to controlled extents of hydrophobicity), a provocative picture emerges of a dynamical structure whose complex responses are qualitatively unlike those possessed by simpler Lennard-Jones fluids.

Keith Grubbins **Phase transitions and chemical reactions at the nano-scale:**

**Effects of confinement** \$ 800

Benoit Coasne<sup>1</sup>, **Keith E. Gubbins**<sup>1</sup>, Francisco Hung<sup>1</sup>, Erik Santiso<sup>1</sup>, and Malgorzata Sliwinska-Bartkowiak<sup>2</sup>. (1) Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695, (2) Institute of Physics, Adam Mickiewicz University, Poznan, 61-614, Poland

Nano-porous solids, such as activated carbons, silicas and the recently synthesized mesoporous solids, have important applications in separations, catalysis, as sensors and in the synthesis of nano-structured materials. The behavior of phases confined within such nano-scale cavities can be strikingly different from that of the bulk material, due to finite size and confinement effects. The influence of such confinement will be discussed for pores of simple geometry for phase transitions, with emphasis on freezing and melting, and for chemical reactions. Both experimental and molecular simulation results will be

presented, where available; the results show qualitative agreement. Finally, some recent attempts to develop more realistic molecular models of disordered nanoporous materials will be described, based on mimetic simulation and reconstruction techniques.

Andrew Madden    **Testing geochemical reactivity as a function of mineral size: Manganese oxidation promoted by hematite nanoparticles**    \$ 200

**Andrew S. Madden** and Michael F. Hochella Jr. Department of Geosciences, Virginia Tech, 4044 Derring Hall, Blacksburg, VA 24061

The rate of  $\text{Mn}^{2+}(\text{aq})$  oxidation on hematite surfaces in the presence of oxygenated water has been studied as a function of the hematite particle size, where the particles are in the nanometer size regime. Experimental results from this study suggest that the surface area normalized initial heterogeneous manganese oxidation rate is approximately one to one and a half orders of magnitude greater on hematite particles with average diameter and thickness of 7.3 nm and 1.5 nm than those with average dimensions of 37 nm by 8 nm. The acceleration of electron transfer rate for the reaction promoted by the smallest particles was rationalized in the framework of electron transfer theory, considering the effects of the changing surface geometric and electronic structure on the coupling between solid- $\text{Mn-O}_2$ , the reduction in reorganization energy for distorted octahedral Mn coordination environments, and the redox potential of the adsorbed Mn.

Participants in Bold were supported by the amounts listed above for travel to attend the Symposium.