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14. ABSTRACT Two related programs of experiments are described. Size-selected metal cluster ion deposition was used to prepare model catalysts, which were then studied by a variety of chemical and physical probes, in situ. Anomalous sintering of atoms on oxide surfaces was observed, and pre-formed clusters were found to be relatively stable with respect to heating and reactant exposure. Methods using ion beam scattering to probe both metal morphology, and adsorbate binding geometry were developed. The second thrust was using single-electron tunneling to try to image and probe the electronic structure of metal clusters on insulating supports. Significant new approaches to the methodology were developed, including dynamic tunneling force microscopy, which offers STM-spatial resolution and spectroscopy capabilities, but uses only a single electron that is tunneled rapidly back and forth between the sample and the microscope tip.					
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16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT none	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON Scott L. Anderson
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Objectives: The objectives were to study monopropellant decomposition chemistry on size-selected model catalysts, and to develop single-electron tunneling as a method to probe the geometric and electronic structure of clusters on insulating supports.

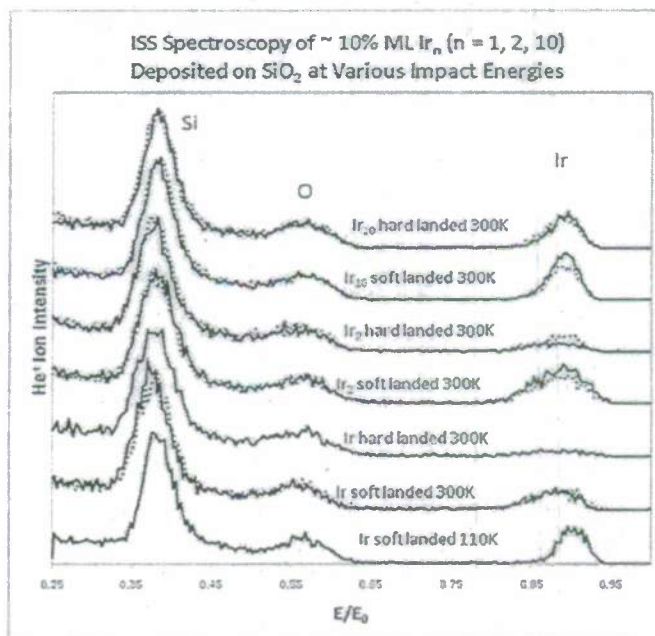
Status of effort: In the past year we have: 1. Completed study of Iridium cluster deposition on SiO_2 as a function of cluster size, impact energy, and substrate temperature. We examined implantation dynamics and effect of implantation on sintering during subsequent heating and exposure to hydrazine. 2. Developed the Dynamic Tunneling Force Microscopy/Spectroscopy method for looking small clusters on thick and relatively rough insulating substrates. We obtained preliminary images of Au, Pd, and Ir clusters on SiO_2 . 3. Studied oxidation of Pd clusters on a thin film alumina support as a function of cluster size and temperature, and subsequent activity for CO oxidation (work in progress).

Accomplishments/New Findings:

1. Cluster impact dynamics and chemistry.

SiO_2 surfaces were prepared with 0.1 ML of different size Ir_n ($n = 1, 2, 10$) deposited on 7 nm gate oxide on Si. This system was chosen partly because SiO_2 is the preferred substrate for the single electron tunneling work described below. The clusters deposit as neutral species in the zero oxidation state as shown by x-ray photoelectron spectroscopy. N_2H_4 was found to be reactive with defects in the SiO_2 , resulting in the formation Si-N functionality. N_2H_4 decomposition on the Ir could also be observed at higher Ir coverages. Ion scattering (ISS – see figure) was used to probe morphology.

At room temperature, iridium dimers and decamers soft landed on the surface were found to bind to the surface over Si sites in the form of flat two-dimensional islands, while atoms appeared to already possess enough surface mobility to agglomerate into large, three dimensional, clusters. If atoms are deposited at 110 K, they show much less diffusion, and appear to be mono-disperse. When heating the surfaces to 750 K, sintering to produce large, 3D clusters occurred in all cases. The presence of the reactive species, N_2H_4 , proved to be of little consequence with regard to agglomeration behavior at high temperature. To try to stabilize the clusters, surfaces were prepared with higher particle impact energies. At the higher collision energies, the particles partially or complete embed into the silica surface, but were observed to diffuse back to the surface and presumably agglomerate under the same heating conditions used in the case of the soft landed clusters. It appears that partially burying clusters in the substrate will not be sufficient to prevent sintering during the highly exothermic reaction conditions found

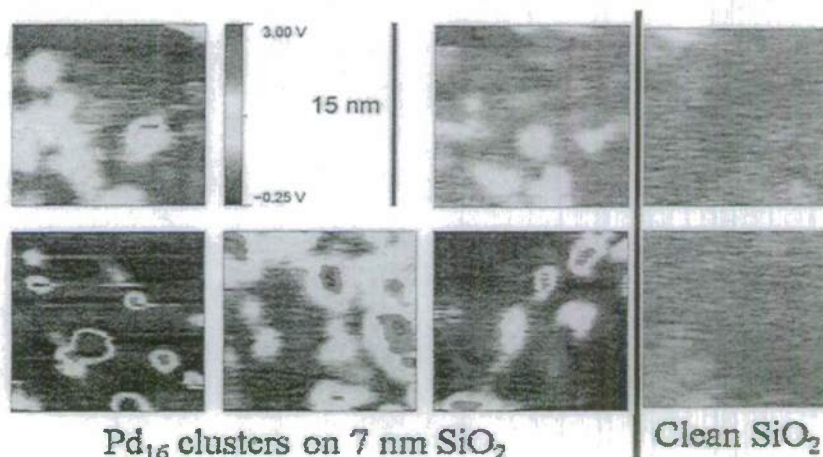


during hydrazine decomposition for the SiO_2 support. TPD was used to provide evidence of a surface-mediated adsorption mechanism for CO binding to the Ir sites during low temperature sample preparations, observed as a large attenuation of the Ir signal during ISS experiments.

2. Single electron tunneling imaging and spectroscopy.

We (the physics component of the project) had developed tools for single electron tunneling spectroscopy of states on insulator surfaces. The approach was based on using atomic force microscopy to locate features on the surface, and then force-detected single electron tunneling to probe energies at which transitions occurred. For the small metal clusters on thick oxide samples of interest for this project, it proved impossible to locate the small clusters (diameter ~ 1 nm) on the surface because thick oxide films typically have roughness comparable to the cluster diameter.

We, therefore, were forced to develop a new approach. We successfully demonstrated the "Dynamic Tunneling Force Microscopy" method for imaging. This technique basically uses force-detected tunneling of a single electron back and forth between the probe tip and the surface, under the influence of an AC bias, to generate an image of locations on the surface where states exist. Such states can include metal clusters. We have used the new method to image both defect states in the oxide surface, and samples with deposited clusters. On the later, we do see features that are not present on sample without deposited clusters, as shown in the figure. It is important to note that we do not completely understand the nature of the tunneling signal, and additional work will be necessary before we can confidently say that we have detected clusters.



3. Pd oxidation chemistry and catalytic combustion.

We have begun a set of experiments on oxidation of size-selected Pd clusters on alumina thin film supports. This work is relevant to AFOSR interest in catalytic combustion for hypersonic and other propulsion applications. So far the results are that oxidation of deposited $\text{Pd}_n/\text{alumina}$ is quite sensitive to cluster size, with clusters larger than Pd_5 oxidizing under O_2 exposure even at cryogenic temperatures, while smaller clusters appear inert under mild oxidizing conditions. We are presently examining oxidation of CO by the O_2 -exposed $\text{Pd}/\text{alumina}$ samples using a pulsed dosing technique. This reaction is moderately relevant for combustion catalysis, but the main motivation for starting with CO oxidation is that it has been extensively studied for a wide variety of real and model catalysts, as well as for Pd single crystal and bulk surfaces. It is, therefore, a good starting point in trying to probe the complex mechanism of catalyzed redox chemistry in $\text{Pd}_n/\text{alumina}$.

Personnel Supported:

Faculty:	Scott L. Anderson	(PI)
	Clayton C. Williams	(co-PI)
Students:	William E. Kaden	(chemistry graduate student)
	Jon Johnson	(physics graduate student)
	William Kunkel	(chemistry graduate student)

Publications:

Atomic scale imaging and spectroscopy of individual electron trap states by force-detected dynamic tunneling, J. Johnson and C.C. Williams, Nanotechnology (submitted)

Impact dynamics of Ir clusters on SiO₂ and effects on stability and reaction with hydrazine, William E. Kaden, William Kunkel, and Scott L. Anderson (in preparation).

Interactions/Transitions:

a. Conference presentation, seminars
(invited)

1. "Effects of particle size and particle-support interactions on the physical and chemical properties of metal/oxide model catalysts", Chemistry Colloquium, University of Chicago, Nov. 12, 2007
2. "Atomic Control of Catalysts", Chemistry Colloquium, Johns Hopkins University, March 25, 2008
3. "Nano Catalysis for Propulsion Applications", Air Force Laboratory Nano Review, Dayton, OH May 5, 2008.
4. "Nano Catalysis for Propulsion Applications", AFOSR Molecular Dynamics meeting, Tyson's Corner, VA, May 18-21, 2008
5. "Physical and Chemical Properties of Model Catalysts Prepared by Size-Selected Cluster Deposition", Int. Conf. on Clusters at Surfaces, Warnemuende, Germany, May 25-29, 2008

(contributed)

1. "Studies of Size Selected Metal Clusters on Surfaces of Interest", William Kaden, Tianpin Wu, Will Kunkel, Jon Paul Johnson, Clayton C. Williams & Scott L. Anderson, Nano Utah '07 (10/26/07), Salt Lake City, UT
2. "Studies of Size Selected Metal Cluster/Metal Oxide Model Catalysts", Bill Kaden, Will Kunkel, Tianpin Wu, Jon Paul Johnson, Clayton C. Williams, Scott L. Anderson, Grand Challenges of Electron Chemistry & Catalysis at Interfaces, (8/10/08 – 8/15/08) Santa Barbara, CA

b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. none

c. Transitions. none

New discoveries, inventions, or patent disclosures. none

Honors/Awards: Disting. Scholarly and Creative Research Award (U. of Utah) (2007)
Fellow of the American Physical Society (2005)