Ultra-High Resolution Electron Microscopy for Catalyst Characterization

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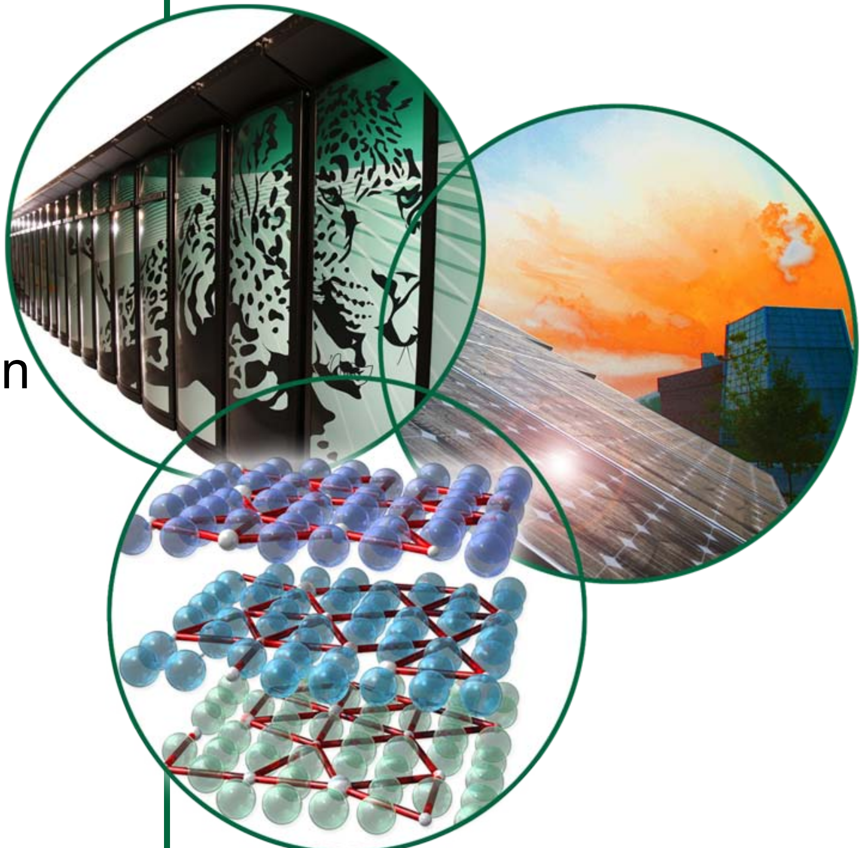

DOE 2010 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

June 9, 2010

Agreement PM029

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Timeline

- Project start date: 10/01/2004
- Project end date: 09/30/2012
- Percent complete: 75%

Barriers

- Development and optimization of catalyst-based aftertreatment systems are inhibited by the lack of understanding of catalyst fundamentals (*e.g., surface chemistry, deactivation mechanisms, particulate capture and oxidation)*
- Reducing or eliminating precious metal content
- Improving durability

Budget

- Total project funding
  - DOE share: $980,000
  - Contractor share: $105,000
- FY09 funding: $220,000
  FY10 funding: $168,000 (thru April 9, 2009)

Partners

- Eastman Chemicals, UOP, PNNL, UT-Austin, UT-San Antonio, UNewMexico, UMich, MIT, Protochips Co., UM-St. Louis, Ford Research Lab
- Proj. Lead: L. F. Allard

Project ID: PM029, Allard

Purpose of Work

- Advance frontiers of atomic and molecular characterizations of energy-related catalysts using world-class sub-Ångström imaging capability with EERE-funded aberration-corrected electron microscope, ultimately leading to a better understanding of factors influencing the behavior of catalytic species under use conditions, and thereby to better catalytic materials for exhaust after-treatment.

- Develop novel new capability for in-situ studies. Extend demonstrated unique capability for *in situ* heating to development of an environmental cell capability for gas reaction studies.

- Support catalyst characterization studies with many partners, including HTML User Program, ORNL VT projects, industry partners, university partners and national laboratory partners

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Barriers

- Catalytic process occur at the atomic level, with interactions between individual atoms, small clusters etc. We have a limited understanding of these processes. Sub-Ångström imaging in the electron microscope is the only way to obtain direct evidence of what is occurring.

- New capability for *in situ* reaction studies via novel environmental cell will depend on as-yet unproven technology being developed in collaboration with Protochips Co. Success with Protochips heaters offers much promise for similar success with reaction cell fabrication.

- The quality of imaging using the E-cell concept will depend on development of ultra-thin amorphous window material (~20nm thick or less) that will maintain their integrity inside the microscope, and will not significantly degrade the imaging process.

Approach

- Acquire and maintain the very best microscopy instrumentation for EERE catalyst/energy materials research. Example: ACEM.
- Develop and utilize the techniques necessary for advanced catalyst characterization. Example: *in situ* heating technology.
- Through professional contacts, information sources such as literature and meetings, communication with UT-B and DOE program managers, determine those research areas where the microscopy program can make significant and important contributions. Example: Support a variety of EERE programs.
- Use the above to set immediate and long-term microscopy program goals. Example: in-situ microscopy with environmental cell capability for reaction studies.
- Partner with industrial and university research teams when such partnerships will benefit both parties. Example: PNNL, UOP, UM-St. Louis, Eastman Chemicals, Ford Research
- Perform research, analyze data, and promulgate results to appropriate parties.

Performance measures and accomplishments

- Utilize atomic imaging capabilities of ACEM for catalyst studies at elevated temperatures (in-situ reactor)
- Utilize pseudo *ex situ* technique involving ACEM airlock reaction system for atmospheric pressure elevated temperature catalyst reaction studies
- Develop and implement environmental cell capability for in-situ gas reaction studies of catalytic materials
- Develop new double-tilt heating holder using Protochips Aduro™ heater chips, to allow precision orientation of catalyst supports during elevated temperature studies
- Design and implement new glove box with TV viewing capability to permit ACEM catalyst specimen loading and transfer under protective atmospheres
- Industrial and university partnerships formed
- Publications
- Invited presentations

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Collaborators in *in-situ* microscopy of catalytic materials

- Steven Bradley, UOP Co.
  Pt/Al-Si-Ti oxides, Pt-Sn bimetallics, correlate EM and EXAFS results
- Miguel Jose-Yacaman, UTexas-San Antonio
  Au-Pd nanoparticles, Pt/carbon, fundamental studies
- Abhaya Datye, Univ. of New Mexico
  Pt-Zn/alumina methanol reforming for hydrogen production
- Charles Peden, Ja-Hun Kwak, PNNL
  BaO/alumina, Pt/alumina, NOx traps
- David Nackashi, Protochips Co.
  WFO project: in-situ heater and environmental cell development
- Paulo Ferreira, UTexas-Austin
  Pt-Co/carbon fuel cell catalysts, new Li-ion battery materials
- Yang Shao-Horn, MIT
  Pt surface segregation in leached Pt-Co fuel cell catalysts
- Jimmy Liu, Univ. of Missouri-St. Louis
  Pd/ZnO, PtSn/C on-board methanol reforming, direct ethanol FC
- Yong Wang, Liang Zhang, PNNL
  Pt-Re bimetallics on multiwalled CNTs for aqueous phase reforming

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Our work also supports ORNL EERE programmatic research:

- Cummins catalyst characterization CRADA (Watkins)
  (zeolites, ammonia oxidation (new 2009))
- Catalysis by First Principles (Narula et al.)
  (Pt/alumina, CO and NO oxidation)
- HTML User Program projects (Lara-Curzio)
  (bimetallic catalysts for DEFCs, methanol reforming)

Other ORNL program collaborations:

- BES Nanocatalyst Characterization (Overbury)
  (Au/FeOx catalysts for H_2 purification and CO oxidation)

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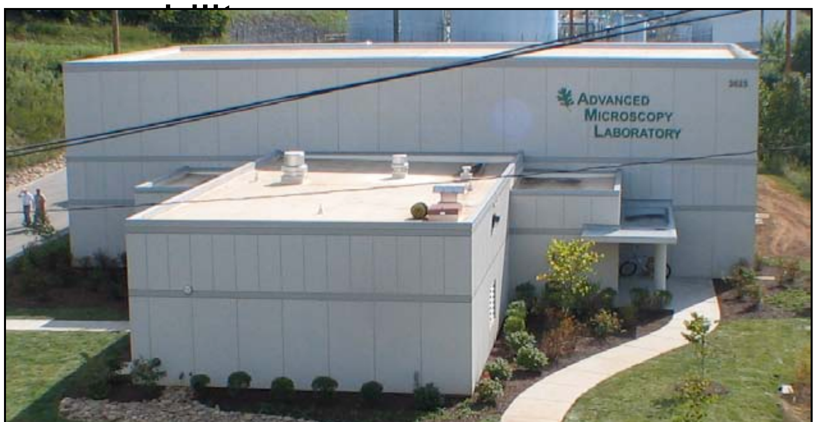
JEOL 2200FS-AC
Aberration-Corrected Electron Microscope

- Sub-Ångström resolution (0.7Å)
- Housed in Advanced Microscopy Laboratory
- Remotely operated (e.g. adjacent control room, London, Austin…)
- New thrust: in-situ studies with novel heating capabilities and developing “environmental cell”



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ORNL-Protochips Co. collaboration has resulted in significant advances in heater holder development

- We have designed and fabricated a new "double-tilt" holder for the ACEM which permits in situ heating and alignment of catalyst supports to perfect crystallographic orientations.

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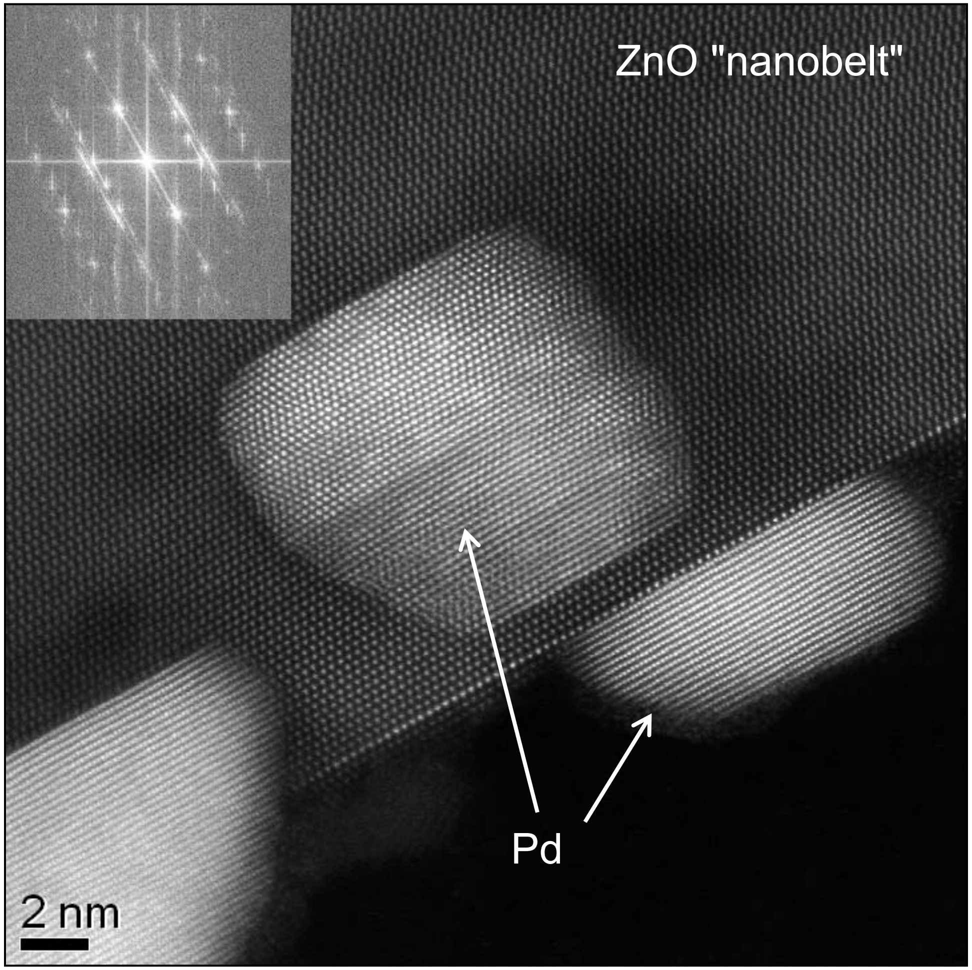
Double-tilt heater holder facilitates studies of catalysts having single-crystal supports, e.g. Pd on ZnO "nanobelts"



This example shows Pd nanoparticles formed by coalescence of fine Pd clusters during heating of ZnO nanobelt sample material to 500°C for 90min. Epitactical orientation relationships are analyzed with greater reliability with precision orientation of the support.

Progress in development of an environmental cell ("E-cell") capability

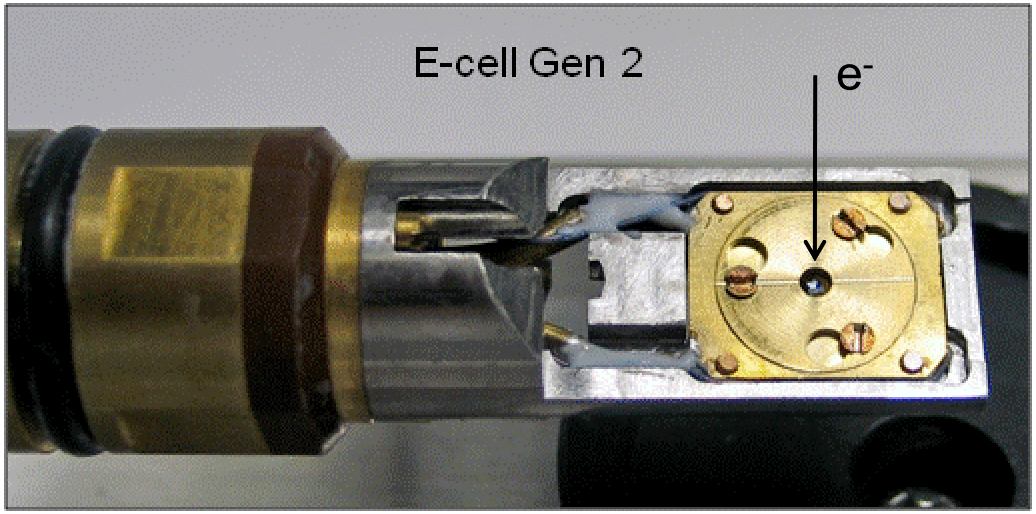
- The Aduro™ heater chip technology is amenable to use in a special holder designed to allow gases to be passed into a "Gen 2" cell composed of an amorphous SiN lower window, and an Aduro heater upper window on which catalyst material is deposited

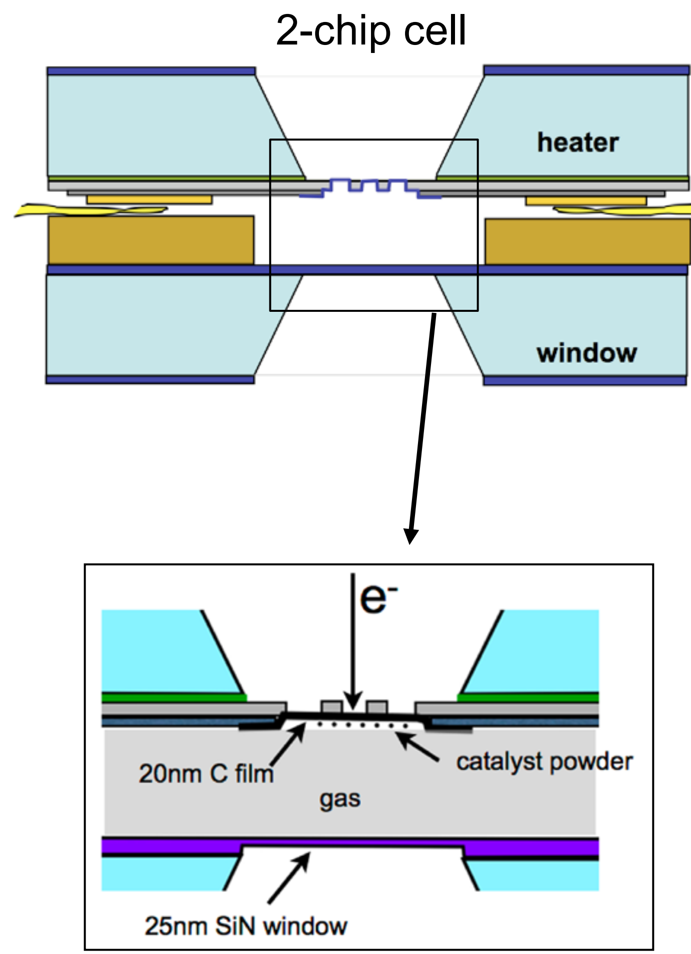
- The Aduro heater window has a thin carbon film supported over holes in the ceramic heater membrane; catalyst powder on the carbon is imaged in the ACEM

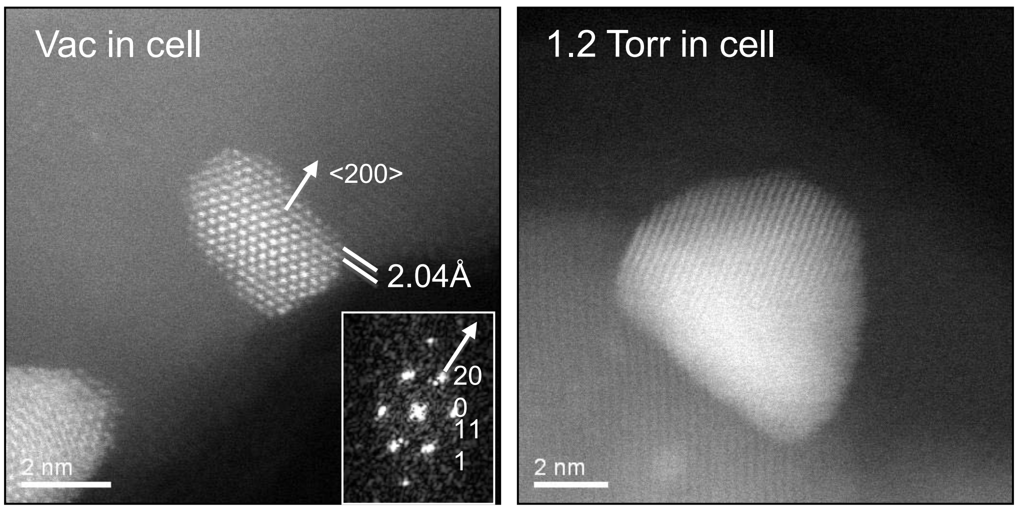
- With only 2 chips, the Gen 2 E-cell tip is 1.38mm thick, which allows unimpeded use in the ACEM.

- Tests of the E-cell show the ability to image at the atomic level, with significant gas pressure and at elevated temperatures (next slides)

E-cell development







a) Au nanoparticle in perfect <110> orientation; HA-ADF image at 500°C, with no gas in the E-cell; b) Similar HA-ADF image with 1.2Torr gas in E-cell, at 500°C.

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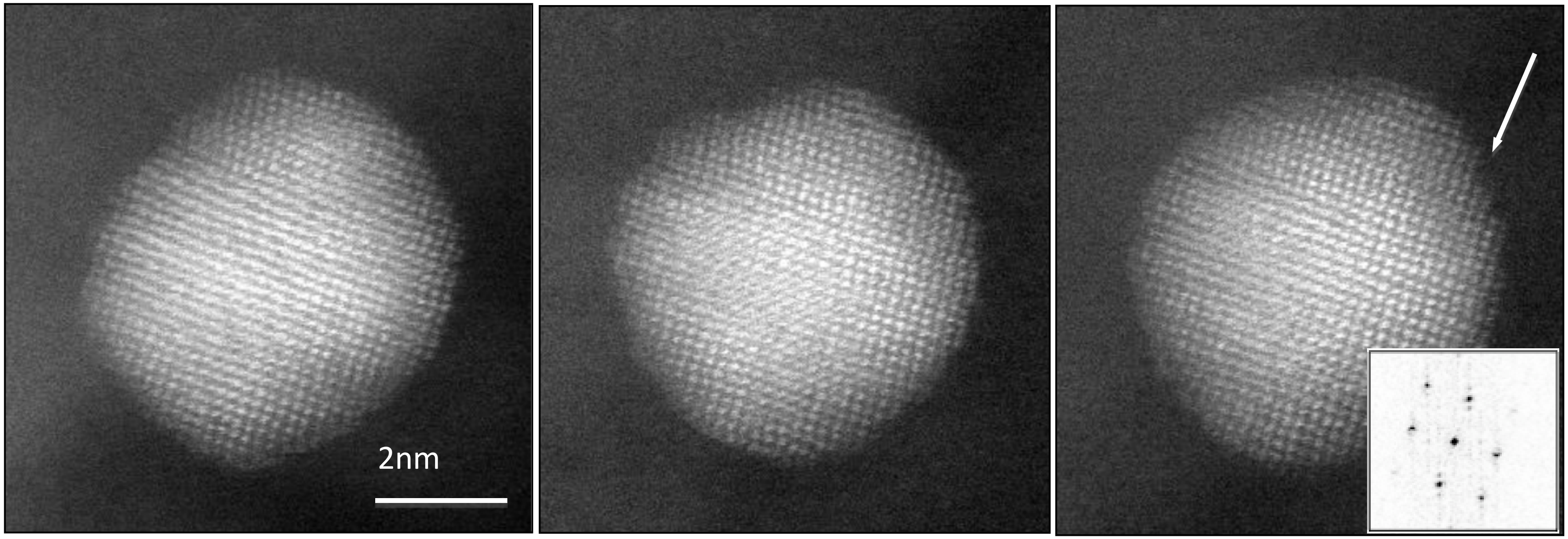
Atomic-resolution imaging at 2 Torr



Three frames from an image sequence ("movie") showing atomic resolution at 500°C with 2Torr reducing gas in E-cell. HA-ADF image of a gold nanoparticle in near-perfect <100> orientation. Arrow indicates presence of ledges with cube faces ({100} planes)

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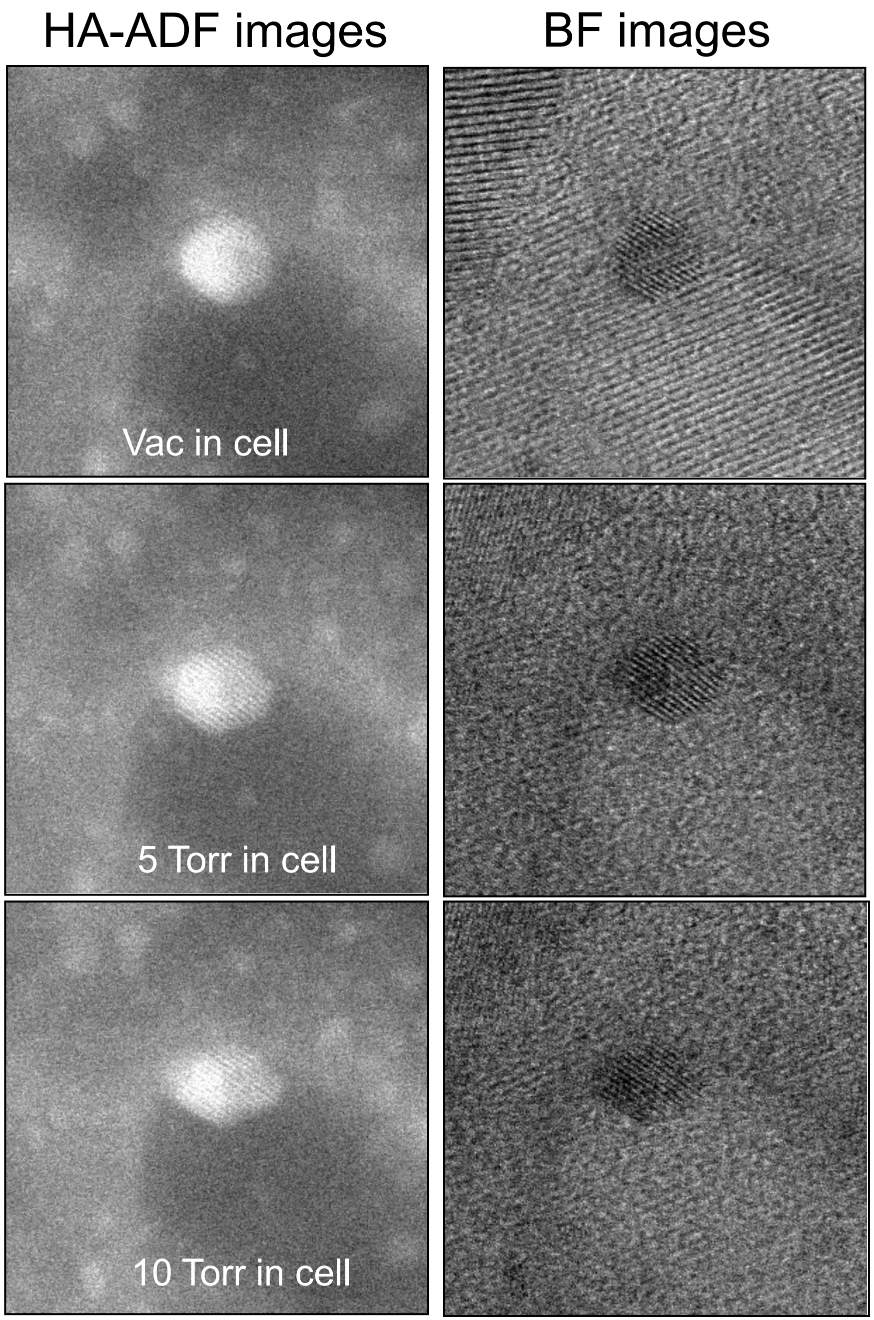

E-cell tests show ability to image crystal lattices with significant gas pressure in cell

Au nanoparticle internal to Fe_2O_3 support particle, imaged at 300°C in vac and in 4%H_2/Ar reducing gas

Lattice imaging at 10Torr pressure exceeds the capability of "environmental" TEMs

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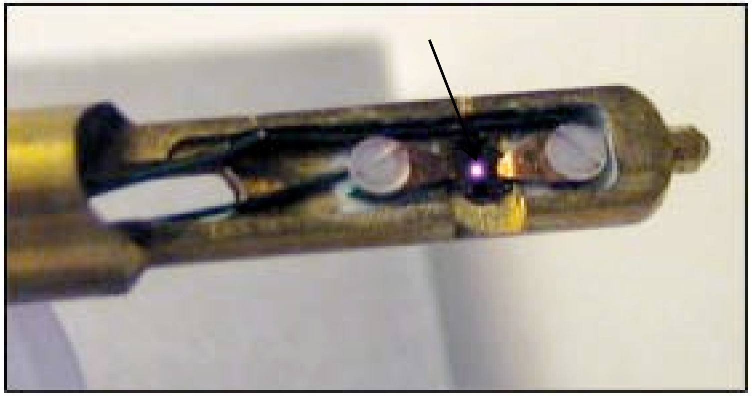
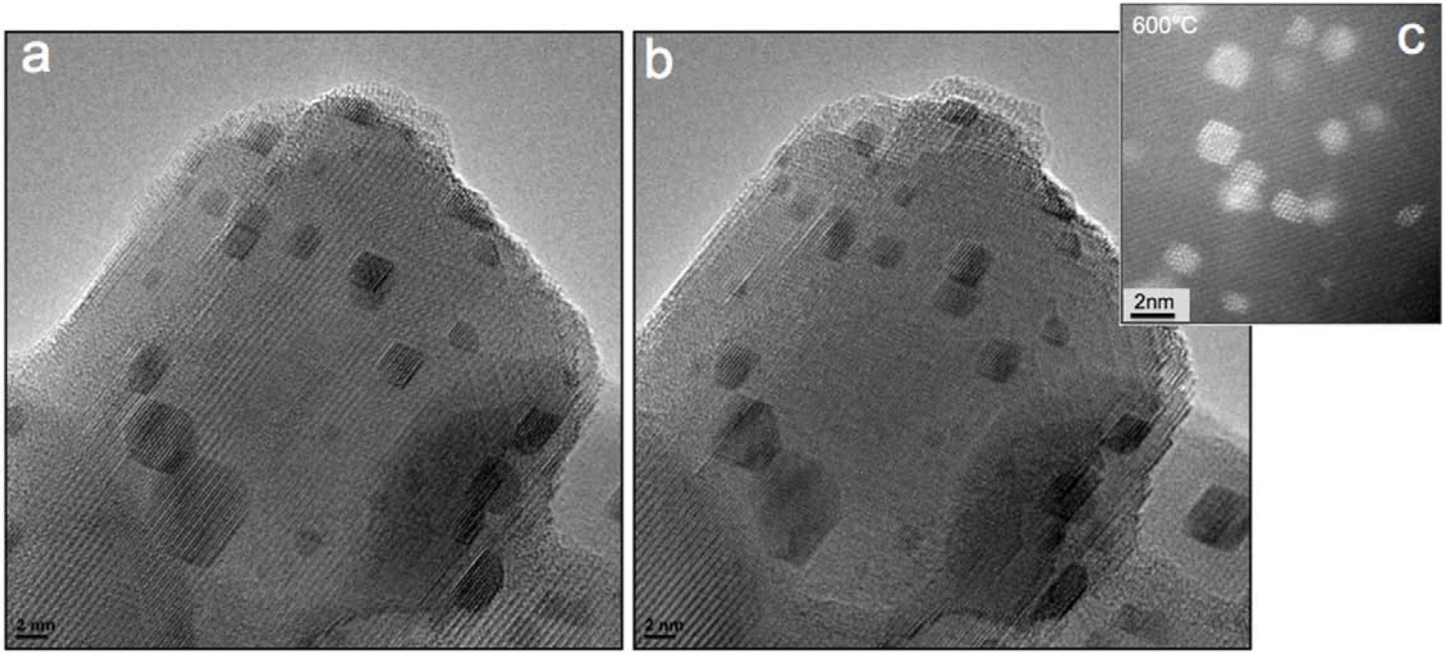
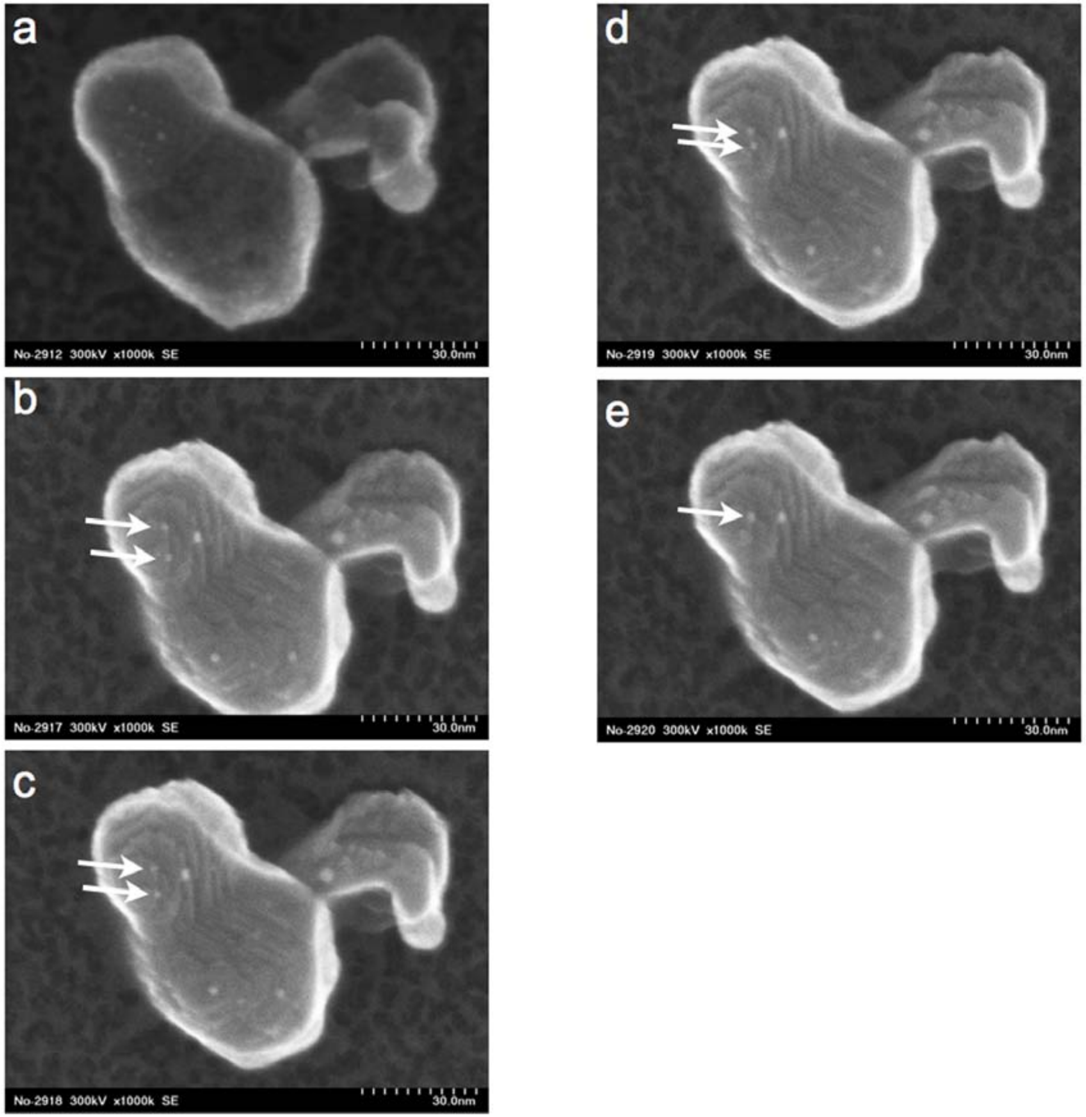
Hitachi HF-3300 TEM/STEM heater holder offers new capability for imaging catalysts at elevated temperatures.





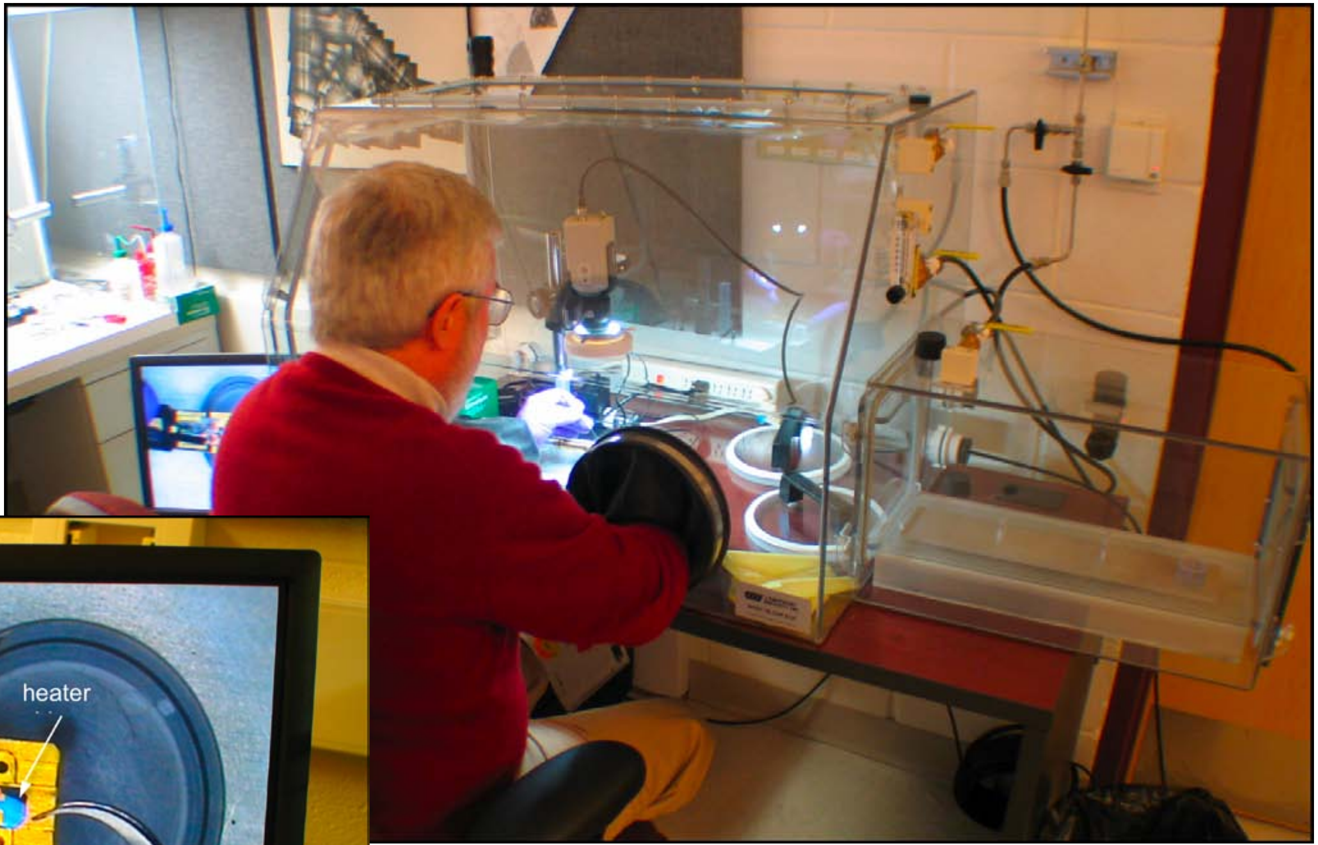
a,b) BF images recorded over time with Au/Fe_2O_3 catalyst at 600°C, showing 1-3nm Au particles, and some surface faceting of support. c) HA-ADF image of similar sample from ACEM, showing Au particles in bright contrast, but no evidence of faceting.

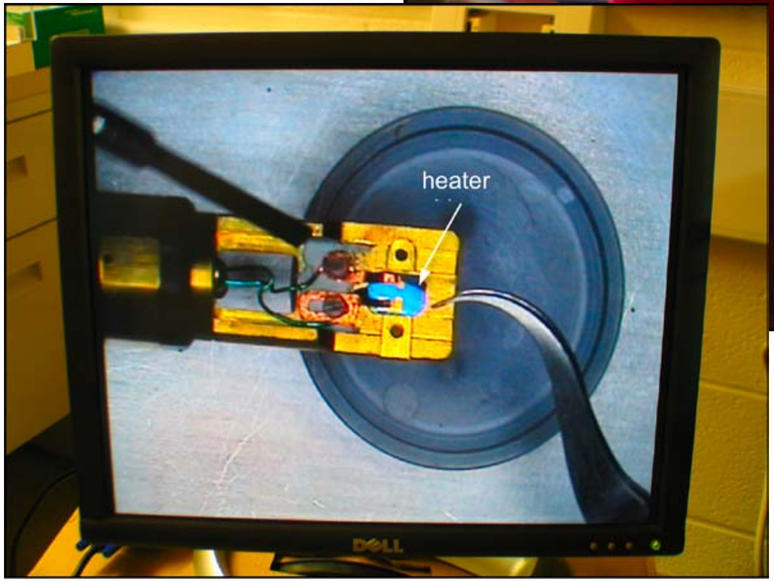
The high-resolution secondary electron imaging capability of the Hitachi give information on catalyst behavior not available with ACEM, or any other manufacturer's instrument presently in the field.



a) Au/FeOx catalyst particle imaged with secondary electrons in the Hitachi HF-3300 STEM/TEM. After heating at 600°C, a few Au nanoparticles in the 1nm range are seen, and little surface faceting. b-e) heating to 700°C causes surface facets to develop, and 1nm Au particles to move along ledges and coalesce, as arrowed.

ACEM sample loading glovebox capability has been implemented





Permits transfer of sensitive catalyst specimens to microscope under protective atmosphere

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Plans for FY2010-FY2011

- Continue work started FY 2009 in development of *in situ* gas reaction and double-tilt heating capabilities for catalyst reaction studies via aberration-corrected electron microscopy

  - leverage funding with Protochips Co.

- Utilize new in-situ capabilities for studies of the behavior of highly dispersed catalytic species on a variety of support materials, and nanoparticulates of controlled composition, to understand the changes in catalyst morphology as a function of treatment conditions, and ultimately the factors that control degradation of catalyst performance with use

  - Continue collaborations underway with top-line industry and university researchers

  - Initiate new work with industry collaborators (GM Research, Eastman Chemicals), leveraging funding via WFO projects

2009 Milestone review:

- Mar-09: Fabricate a glovebox facility with CCTV camera and airlock pass-thru to permit loading and transfer of air-sensitive catalysts to ACEM. (completed Sept-09)
- June-09: Test a new silicon drift x-ray detector system on consignment from Bruker Co. for use on the ACEM, to characterize catalyst compositions at elevated temperatures. (completed July-09, detector purchased Dec-09)
- Oct-09: Design and fabricate a prototype 'double-tilt' heating holder for the ACEM, required to permit accurate orientation of crystalline supports for more reliable characterizations. (completed Feb. 2010)
- Dec-09: Utilize our Protochips heater for the Hitachi TEM to conduct trial studies of bimetallic catalysts using EDS analysis and electron holography. (Heater holder tested in Hitachi TEM Sept-09, holography not complete)
- Mar-10: Develop protocols for most effective use of E-cell in imaging experiments to study gaseous reaction phenomena. (underway
- Sept-10: Submit for publication at least 6 articles in refereed journals on catalyst research activities.

Principal Technical Accomplishments-FY2009-10

- Prototype Gen 2 E-cell fabricated and tested showing remarkable imaging at high pressures and elevated temperatures.

- Prototype heater holder for Hitachi TEM designed, fabricated and tested successfully.
- Double-tilt heating holder designed, fabricated and tested successfully

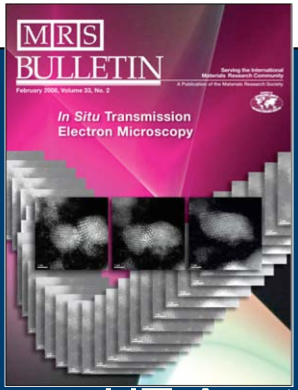
- New glovebox capability for specimen loading and transfer under protective atmospheres implemented

- Our work has resulted in numerous invited and contributed publications and presentations.

Summary: our work supports many entities…

PNNL

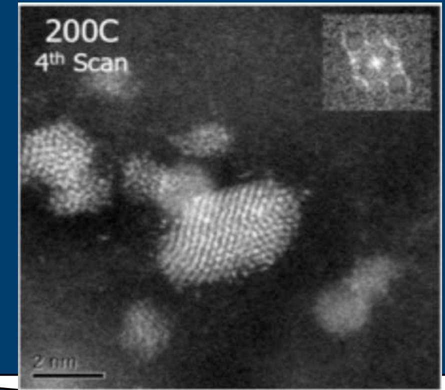
University…



UT-Austin,…

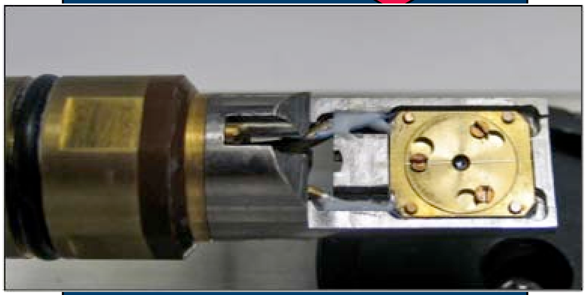
ACEM

Eastman Chemicals,…



Industry…

ORNL



Protochips

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