

Ultra-high Resolution Electron Microscopy for Catalyst Characterization

Dr. Lawrence F. Allard

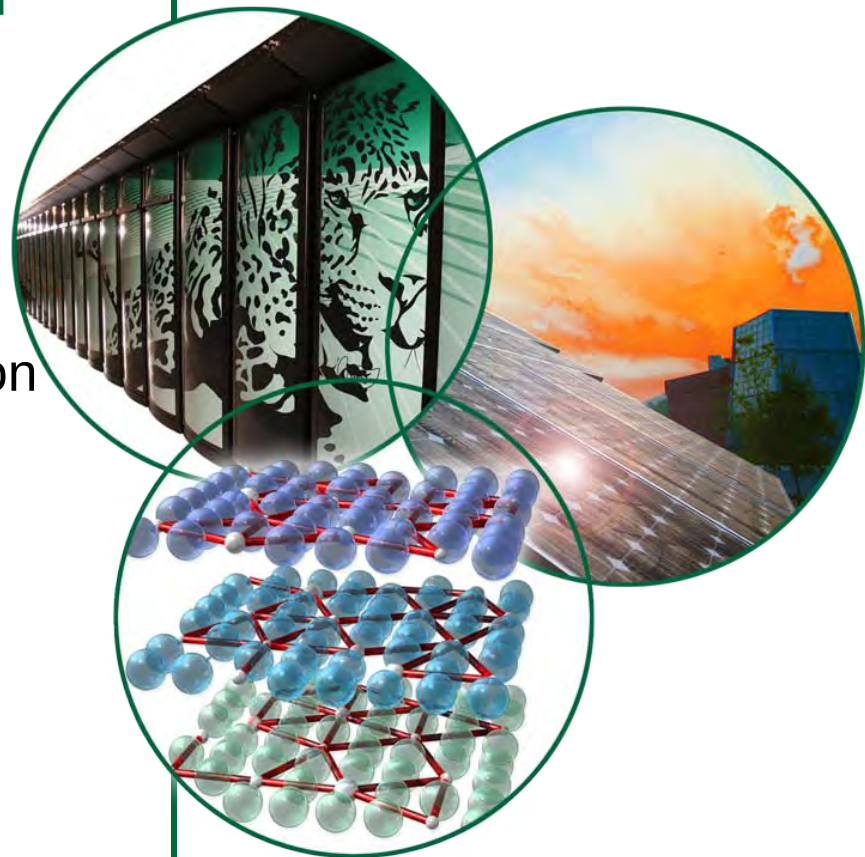
Materials Science & Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN

DOE 2010 Vehicle Technologies Annual
Merit Review and Peer Evaluation
Meeting

May 12, 2011

Project ID: PM029

This presentation does not contain any
proprietary, confidential, or otherwise
restricted information.



Agreement PM043



Timeline

- Project start date: 10/01/2007
- Project end date: 09/30/2012
- Percent complete: 80%

Budget

- Total project funding
 - \$1,176,000
 - (DOE: \$1,036,000,
 - Collaborators: \$140,000)
- FY10 funding: \$198,000
- FY11 funding: \$198,000

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

Partners

- Ford Research Lab, UMichigan, Eastman Chemicals, UOP, PNNL, UTexas-Austin, Purdue University, UNewMexico, MIT, Protochips Co., UM-St. Louis
- 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.

Project ID: PM029, Allard

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 utility of elevated temperature *in situ* experiments in reactive gas environments will depend on the robustness and integrity of the MEMS-based amorphous SiN window/heater devices we have developed. *In vacuo* failures that affect microscope operation cannot be tolerated.

Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

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 and gas-reaction 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, Univ. of Michigan, Purdue University.**
- Perform research, analyze data, and promulgate results to appropriate parties.

Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

Performance measures and accomplishments

- Develop Gen 3 environmental cell capability for *in situ* gas reaction studies of catalytic materials
- Utilize atomic imaging capabilities of ACEM for catalyst studies at elevated temperatures (*in situ* heating)
- Utilize pseudo *ex situ* technique involving ACEM airlock reaction system for atmospheric pressure elevated temperature catalyst reaction studies
- Modify and refine operation of new double-tilt heating holder that uses Protochips Aduro™ heater chips, and utilize holder to allow precision orientation of catalyst supports during elevated temperature studies
- Industrial and university partnerships formed
- Publications
- Invited presentations

Project ID: PM029, Allard

Collaborators in high-resolution and *in situ* microscopy of catalytic materials

- Steven Bradley, UOP Co.
Pt/Al-Si-Ti oxides, Pt-Sn bimetallics, fundamental studies of dynamics of cluster development
- Jimmy Liu, Univ. of Missouri-St. Louis
Pd/ZnO, Pt/FeO for CO oxidation; developments in single-atom catalysis
- Charles Peden, Ja-Hun Kwak, PNNL
Pt, Pt-BaO and VOx on alumina for NOx reduction
- David Nackashi, Protochips Co.
WFO project: *in situ* heater and environmental cell development
- Paulo Ferreira, UTexas-Austin
Studies of new Li-ion battery materials
- Yang Shao-Horn, MIT
Studies of interfacial structures in coated lithium transition-metal oxides
- Yong Wang, Liang Zhang, PNNL
Pt-Re bimetallics on multiwalled CNTs for aqueous-phase reforming
- Abhaya Datye, Univ. of New Mexico
Pt-Zn/alumina methanol reforming for hydrogen production
- Fabio Ribeiro, Purdue University
Elucidate active sites on catalysts based on Au and Pt nanoparticles

Project ID: PM029, Allard

Our work also supports ORNL EERE programmatic research in catalytic science:

- 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)
(Pt, Ba on alumina NOx traps, bimetallic catalysts for DEFCs, methanol reforming)

Other ORNL program collaborations:

- BES Nanocatalyst Characterization (Overbury)
(Au/FeOx catalysts for H₂ purification and CO oxidation, Cu-Au on alumina and silica catalysts for CO oxidation)

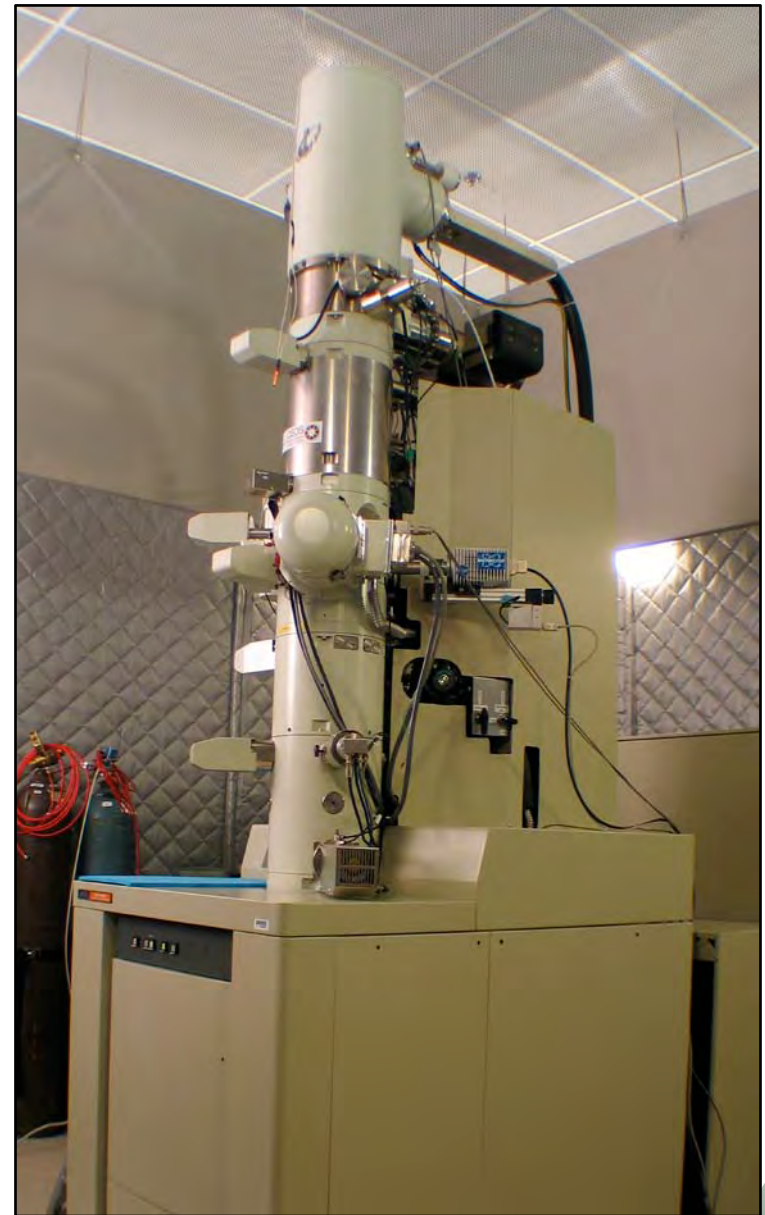
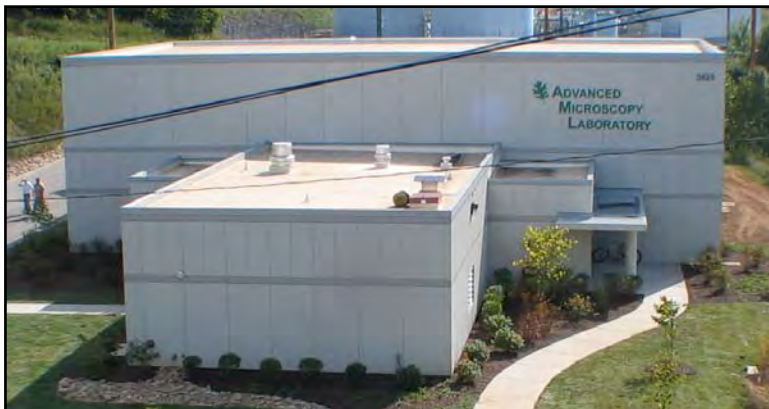
Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

JEOL 2200FS-AC

Aberration-Corrected Electron Microscope

- Sub-Ångström resolution (0.7Å)
- Housed in Advanced Microscopy Laboratory
- Advanced x-ray detector capability (first silicon-drift detector on an A-C microscope)
- New thrust: novel heating *in situ* studies with double-tilting and a new “environmental cell” capability



Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

Research Thrust Areas:

1. Develop "Gen 3" design of improved environmental cell (E-cell) for *in situ* gas reaction studies
2. Lead microscopy pursuit towards goal of "single-atom catalysis"
3. Couple high-resolution imaging with spectroscopy methods to elucidate locations of active sites on catalyst nanoparticles for reactions such as CO oxidation and the water-gas-shift reaction for hydrogen production
4. Pursue fundamental studies of cluster development kinetics and mechanisms via *in situ* heating
5. Investigate mechanisms of behavior of new experimental catalysts, such as "intelligent catalysts" based on perovskite structures for NO_x reduction reactions

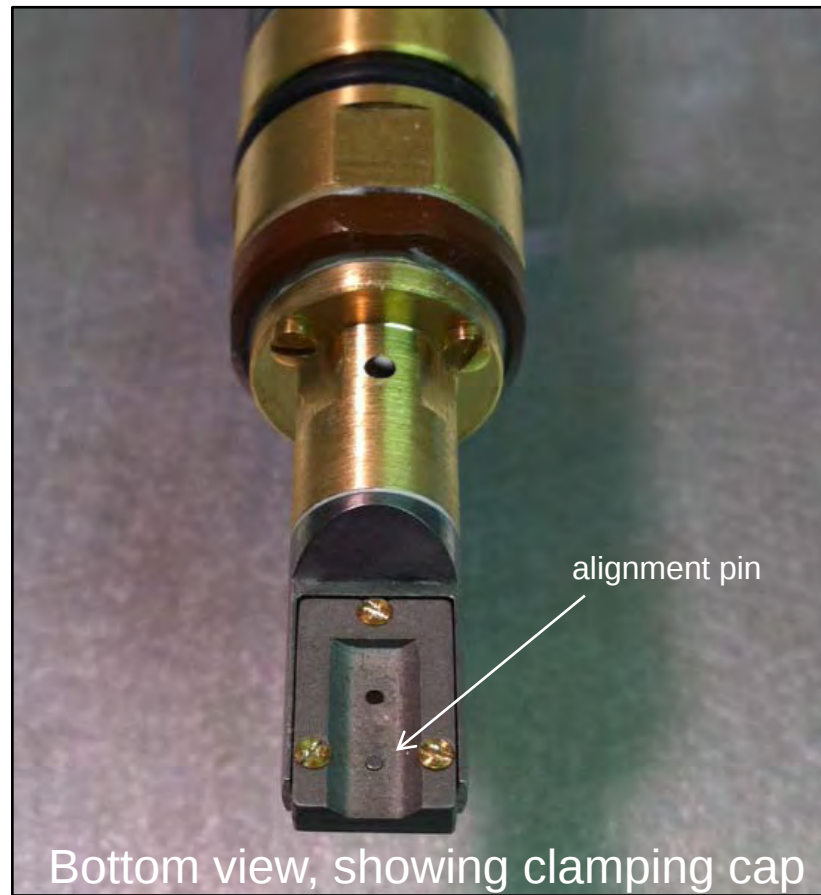
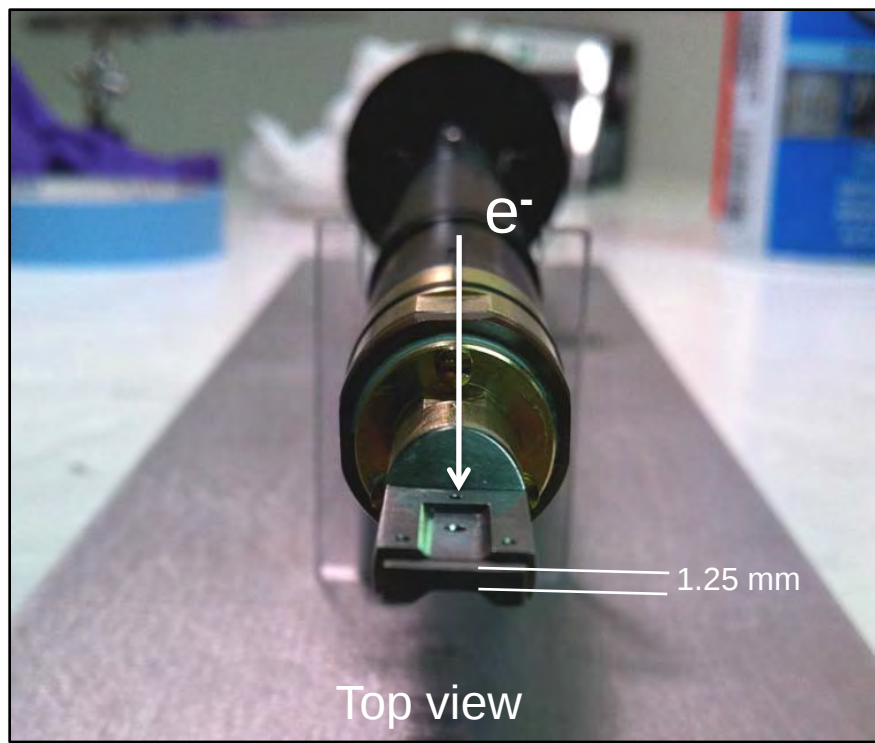
Some details from 1-3 are presented in the following slides...

1. Development of Gen 3 E-cell for *in situ* gas reaction studies

Some new Gen 3 E-cell design features:

- simplified mechanics of sample/heater chip/bottom window loading
 - better connection method from heater leads in specimen rod to electrode on heat chip
- total thickness reduced from 1.38mm to 1.25mm, allowing insertion of objective lens aperture if needed
- new design of gas delivery system for clean operation
- new design of "clamshell" cover for E-cell when inserted into ACEM
- improved heater chip design
 - microfabricate 30nm SiN continuous layer to seal heater and support catalyst material for microscopy
 - microfabricate "spacers" on heater chip to control volume of cell

Views of Gen 3 E-cell holder tip:

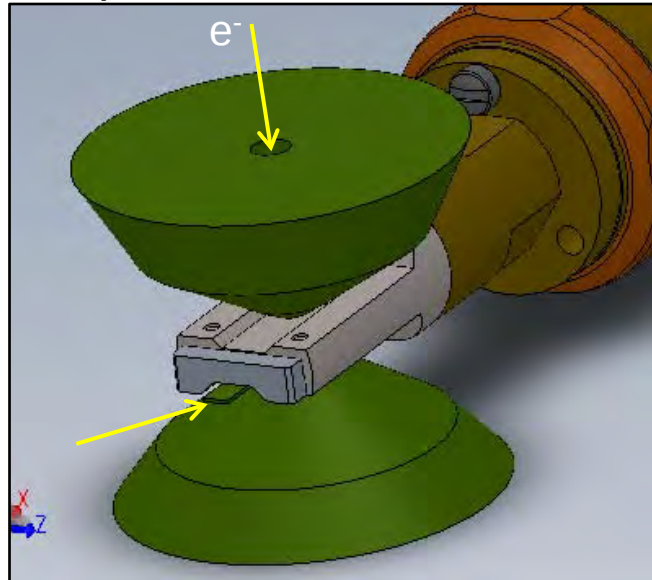


- Redesigned all titanium specimen tip
 - Total thickness of 1.25mm in pole piece area
 - Compatible with JEOL UHP pole-piece configuration (2mm gap), including in-lens aperture
 - Improved loading and unloading of bottom window and sample heater chip

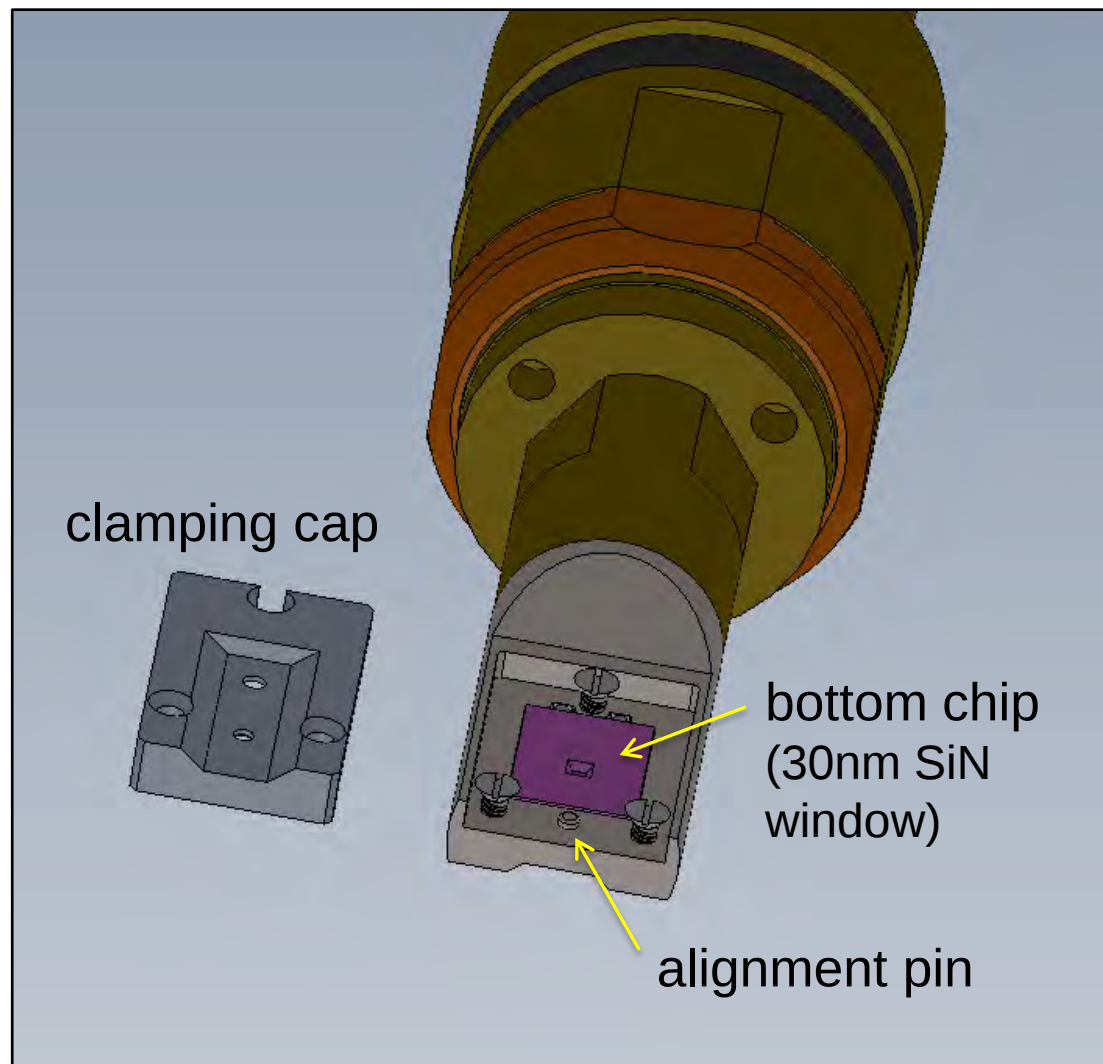
Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

Top view of holder



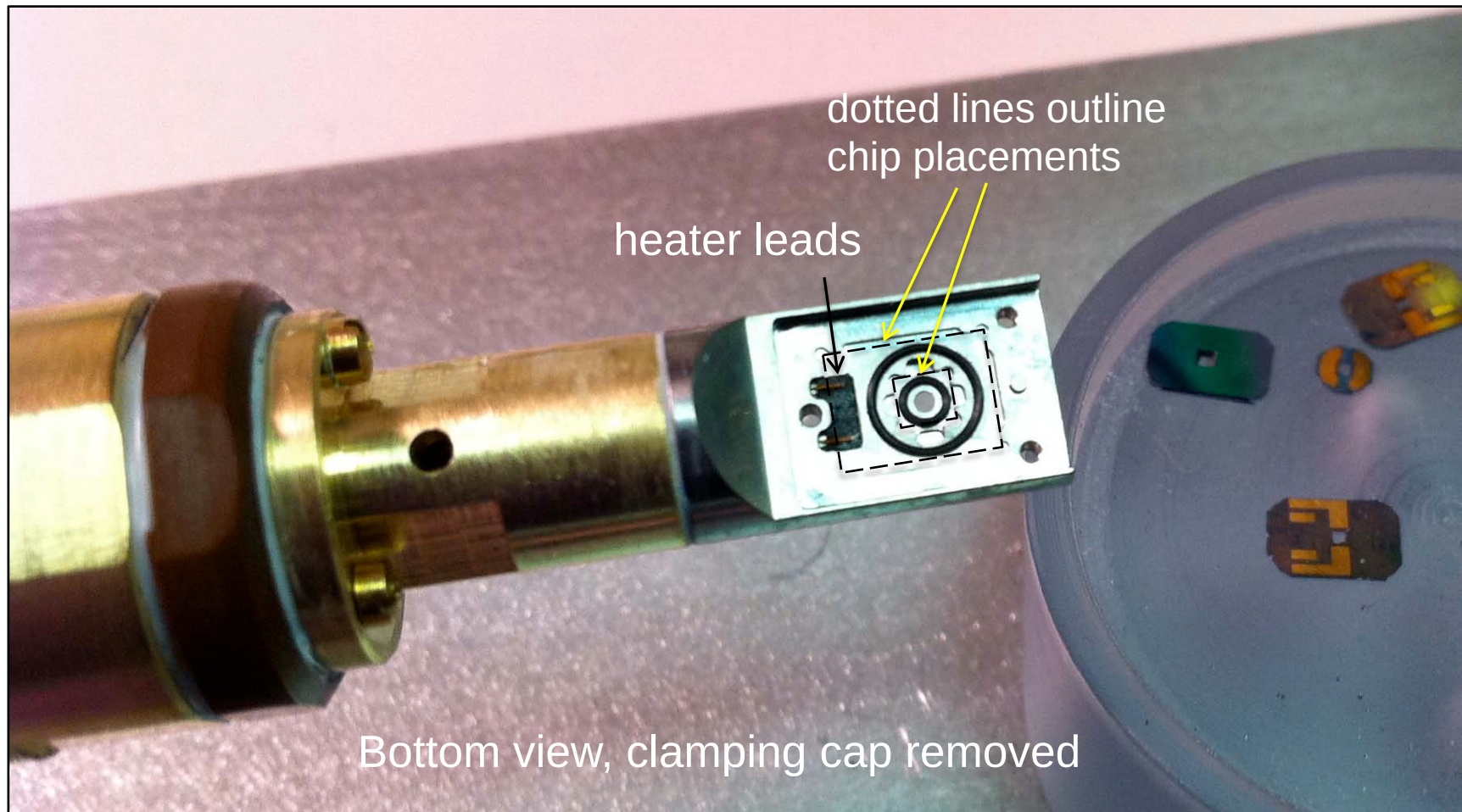
View of holder installed in microscope objective lens (represented by the green cones). Lower slot allows insertion of OL aperture (arrow).



CAD drawing showing bottom view of E-cell tip

Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting



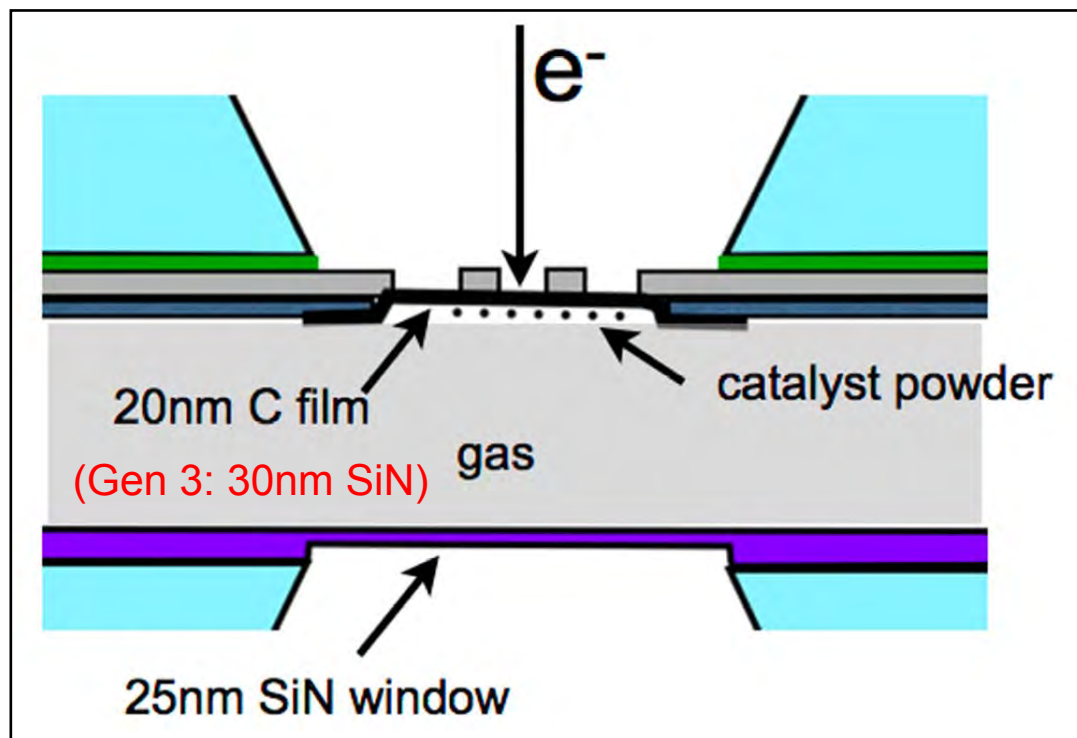
- New devices and pocket design (chips removed)
 - Two chip stack with 30nm SiN overlay (windows) for oxidation reactions
 - Self-aligned devices within the specimen tip pocket
 - Slightly reduced window area for strength to allow thinner SiN layer (e.g. 50nm→25nm)
 - No adhesives required for device mounting
 - "Spacers" microdeposited onto the heater chip accurately set volume of reaction zone

Project ID: PM029, Allard

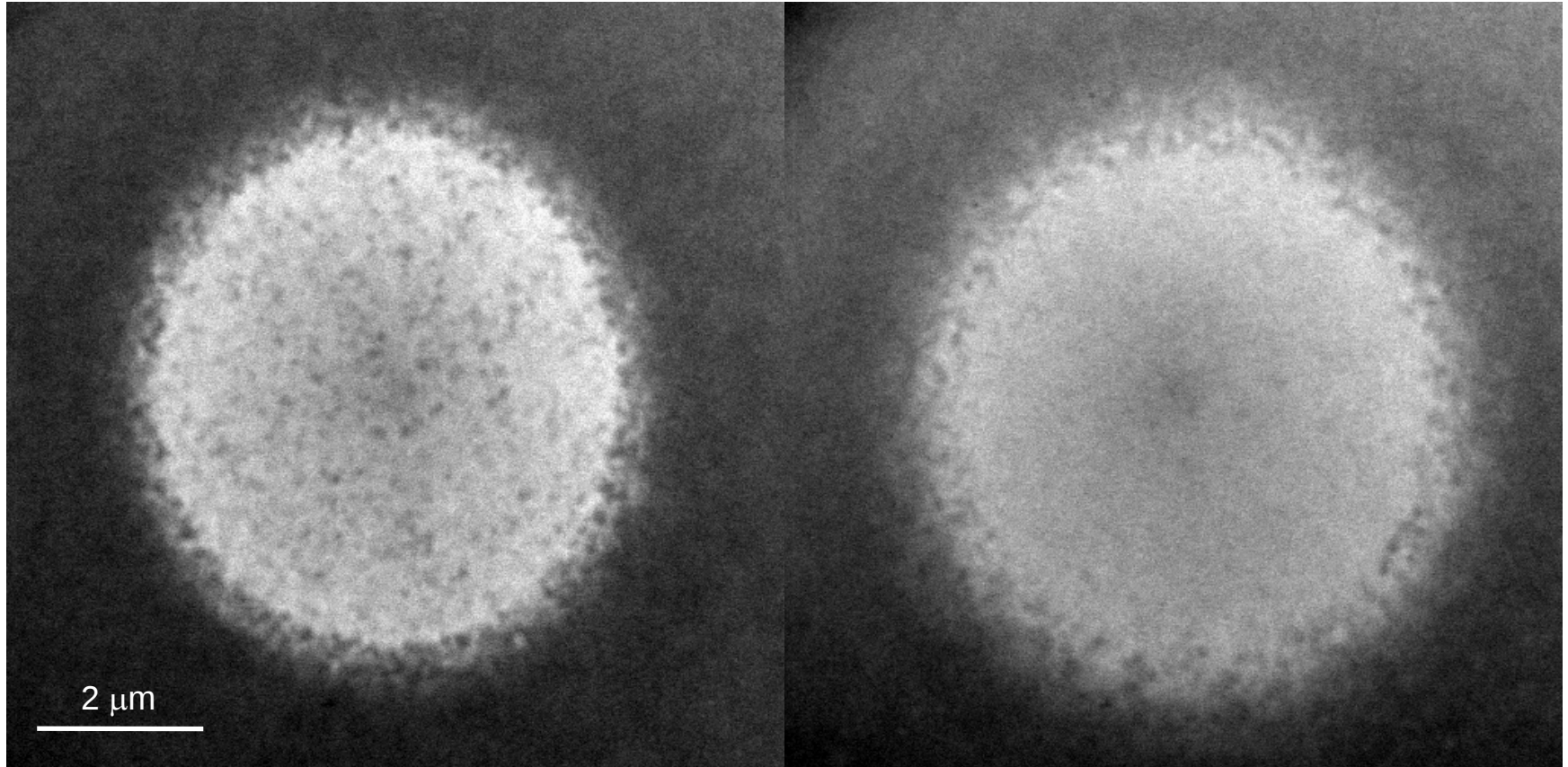
DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

Original gas cell geometry: continuous C film over holes in Aduro™ heater membrane, not amenable to oxidation experiments.

Gen 3 E-cell utilizes new Aduro chip design, with continuous amorphous **30nm SiN** film micro-fabricated over heater membrane.



Initial success in microfabrication of continuous SiN films on heater membranes

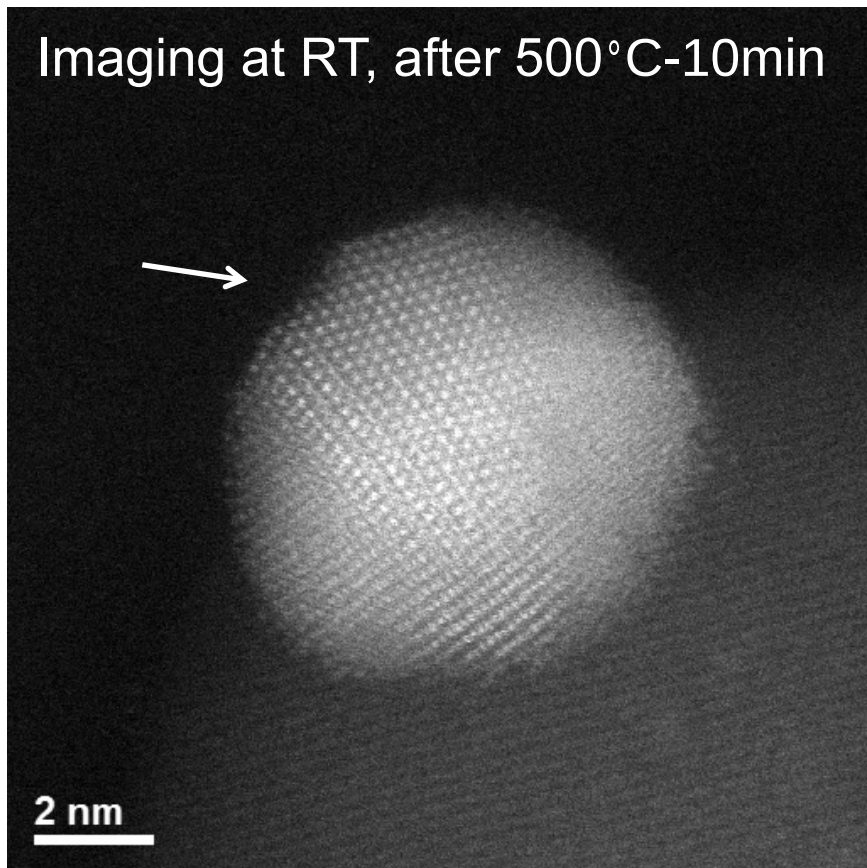


First SiN films were robust and continuous, but showed artifact structures (see next slide)

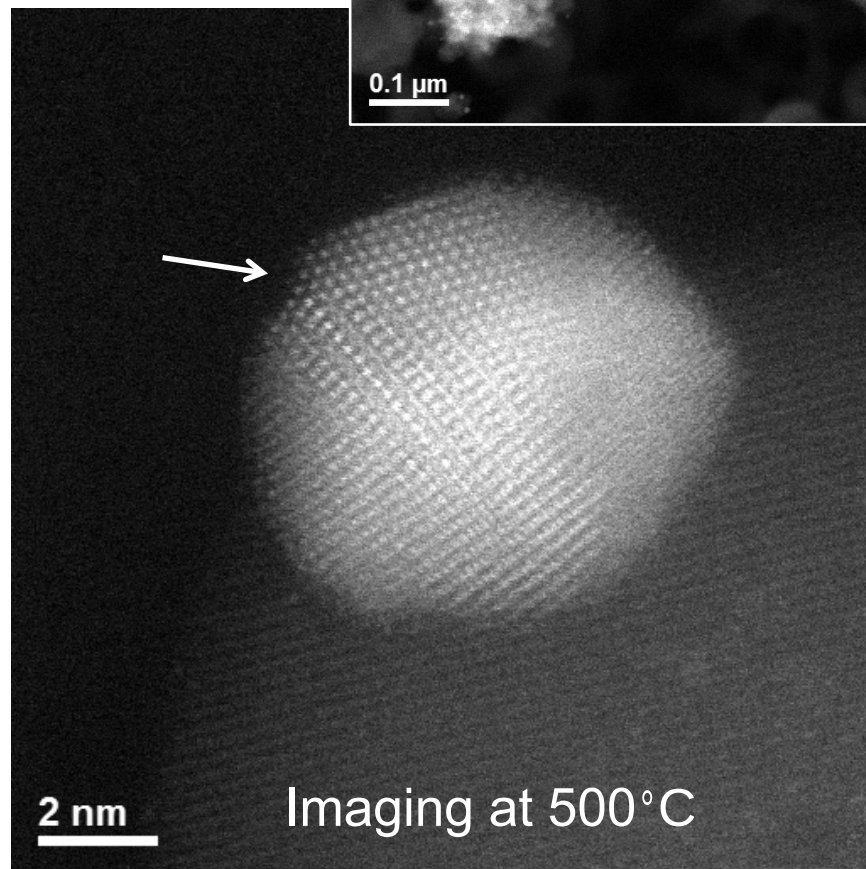
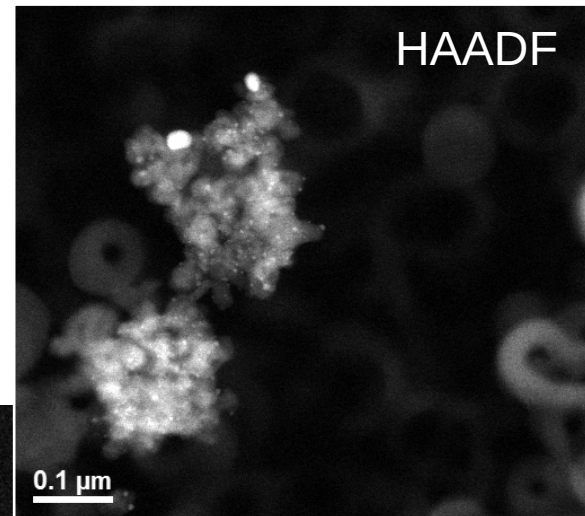
Recent advances in procedure have yielded much more uniform SiN films

Atomic imaging still possible thru ~25nm SiN film: Au on FeOx

Imaging at RT, after 500°C-10min

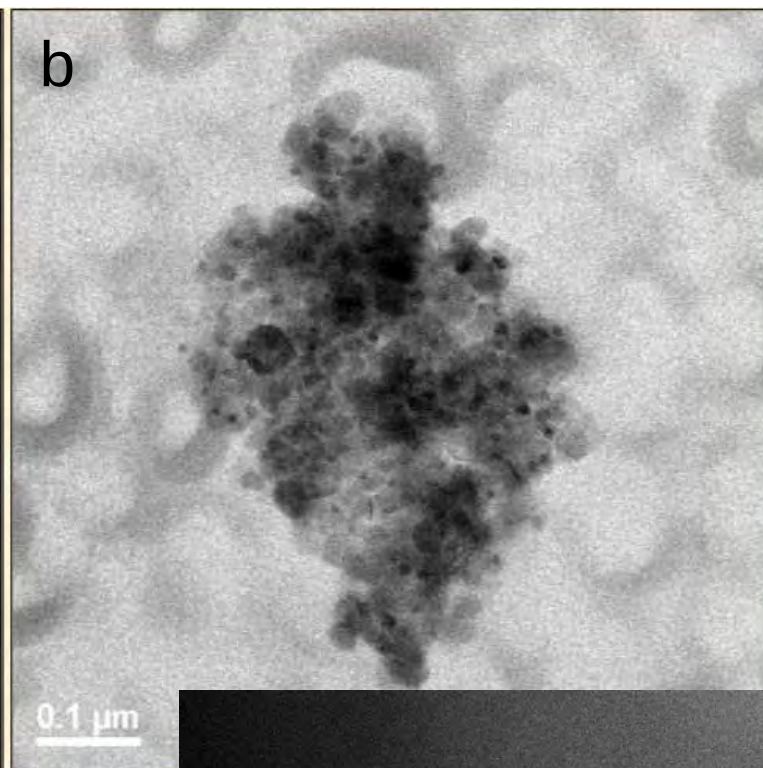
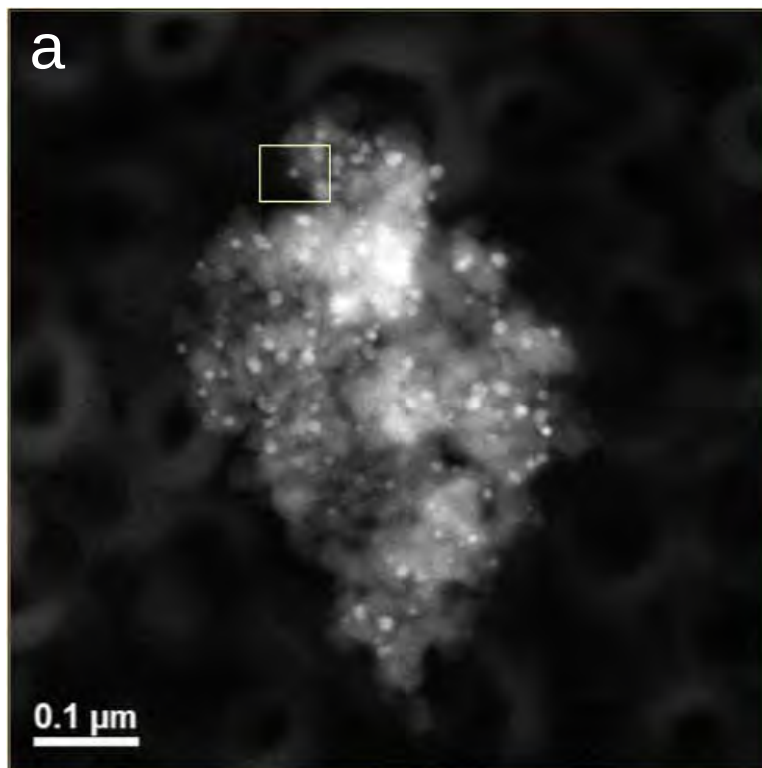


Note stability for atomic-level imaging maintained at elevated temperature (Au columns remained fully resolved). Some rearrangement of surface layer seen as arrowed.

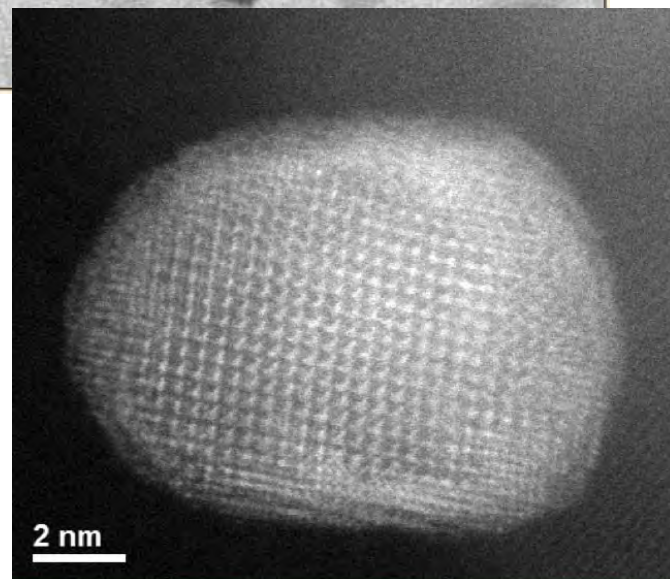


Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting



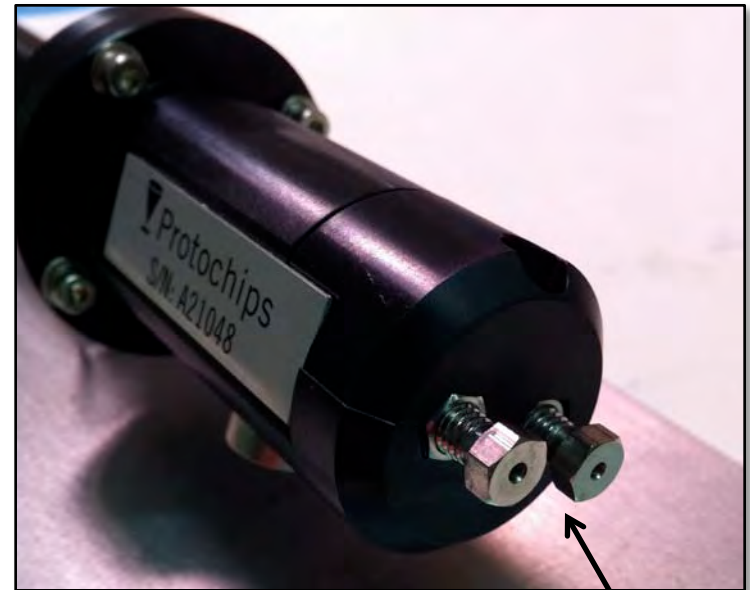
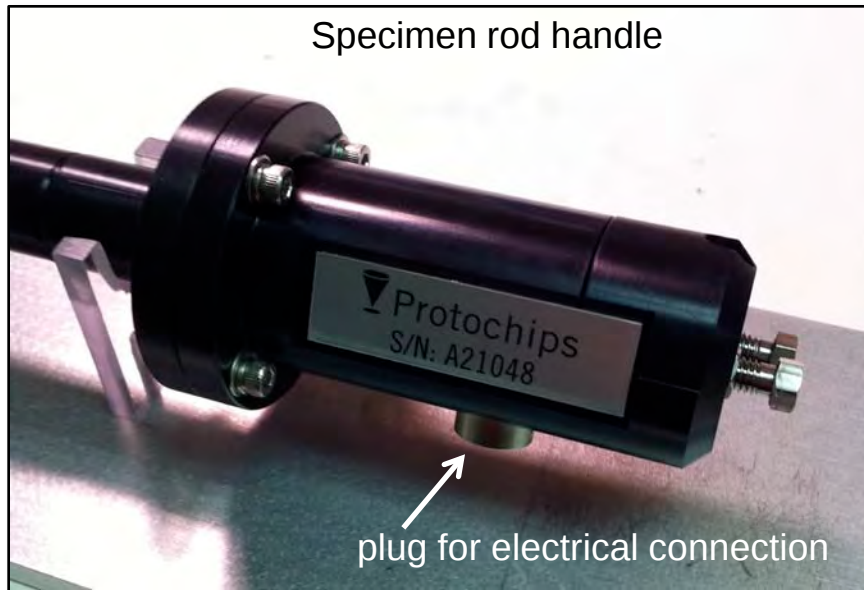
High-angle annular dark-field (a) and bright-field (b) images showing a CuAu/FeOx catalyst after heating in air for 10 min at 600°C; the SiN film was not visibly affected by this aggressive oxidation treatment. Inset box shows particle (R) with Cu oxide on surface.



Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

New holder replaces Cu/polymer tubing for gas deliver with stainless steel tubing and connectors, from gas manifold system through to the reactor zone



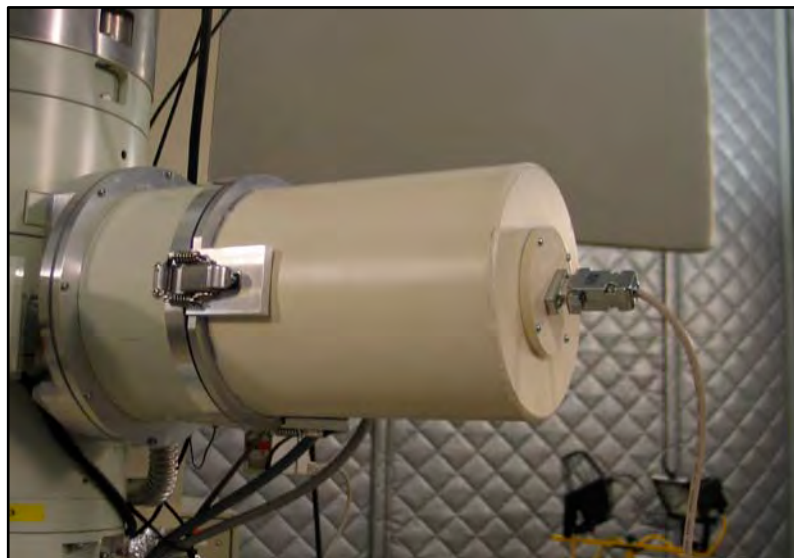
- Annealed stainless steel supply lines
 - Robust to greater variety of gases
 - Gas-tight fittings improved from polymer tubing compression fittings
 - Better control of contamination from polymer tubing
 - Capillary tubing for supply and return gas lines run the length of the holder
 - Fine stainless steel tubing connects from the holder to gas manifold

Project ID: PM029, Allard

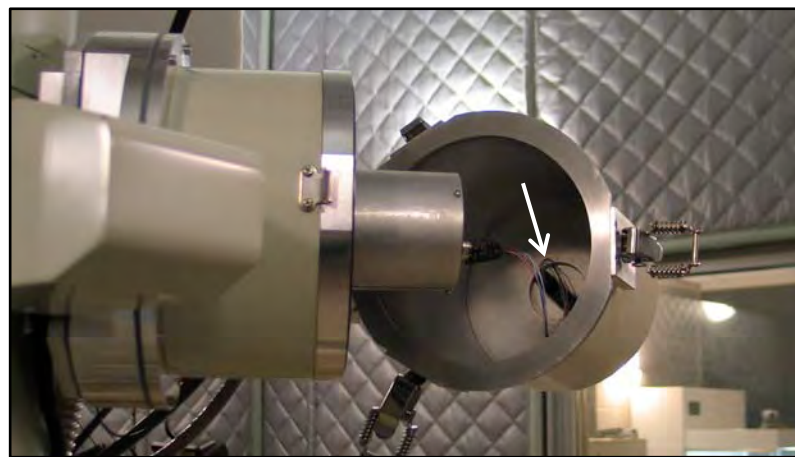
DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting



Original ACEM "clamshell" cover for specimen stage (seals holder against external disturbances such as pressure changes).



New clamshell, extended to permit internal connections for *in situ* holders. End flange is exchangeable depending on holder configuration.



Double-tilt heating holder with heater leads plugged into inside of new clamshell.

Summary of Gen 3 E-cell developments:

- New holder is thinner, allowing use of objective lens aperture
- Heater chip sample loading procedure much simplified
- New geometry of heater leads thru rod to cell is simpler and more robust
- Employing stainless steel gas lines and fittings thru entire system eliminates polymeric tubing that contributed to contamination problems
- Amorphous SiN coatings are deposited during microfabrication process; SiN shown to withstand aggressive oxidation treatments
- Full atomic resolution achievable thru SiN film
- "Spacers" microfabricated onto chips allow control of E-cell volume
- New "clamshell" cover for specimen stage airlock allows coupling of heater and E-cell holders while maintaining seal over specimen holder

2. The goal of "single-atom" catalysis:

- Typical catalysts have heavy metal species (e.g. Pt, Au, Pd, or bimetallics) dispersed as nanoparticles on supports such as oxides or carbon
- Catalytic reactions are adversely affected when nanoparticles grow, and reduce surface area, or number and location of active species
- An active catalyst with dispersed single atoms, if stable under reaction conditions, represents an ultimate catalyst (holy grail)
- Several collaborators are pursuing developments in understanding the potential for single-atom catalysis, or behavior of catalysts dispersed at the single-atom level
 - Prof. J. Liu, UM-St. Louis and colleagues at the Chinese Academy of Sciences (Pt on FeOx for CO oxidation, highlighted next)
 - Drs C. Narula and M. Moses-Debusk, ORNL (Pt/ θ -alumina)
 - Dr. S. Bradley, UOP Co. (Pt/alumina)

Single-atom catalysis: Remarkable performance of Pt₁/FeO_x for CO oxidation and preferential oxidation of CO in H₂

B. Qiao, A. Wang, X. Yang, **Lawrence F. Allard**, Z. Jiang, Y. Cui, **Jingyue (Jimmy) Liu**, J. Li and T. Zhang

(manuscript currently in review for publication by **Nature Chemistry**)

We report the first practical fabrication of a single-Pt-atom catalyst consisting of only isolated single atoms anchored onto iron oxide (FeO_x) nanocrystallites. This unprecedented single-Pt-atom catalyst exhibits very high activity and stability for both CO oxidation and preferential oxidation (PROX) of CO in H₂, attributed to the partially vacant 5d-orbitals of positively charged, high-valent Pt atoms.

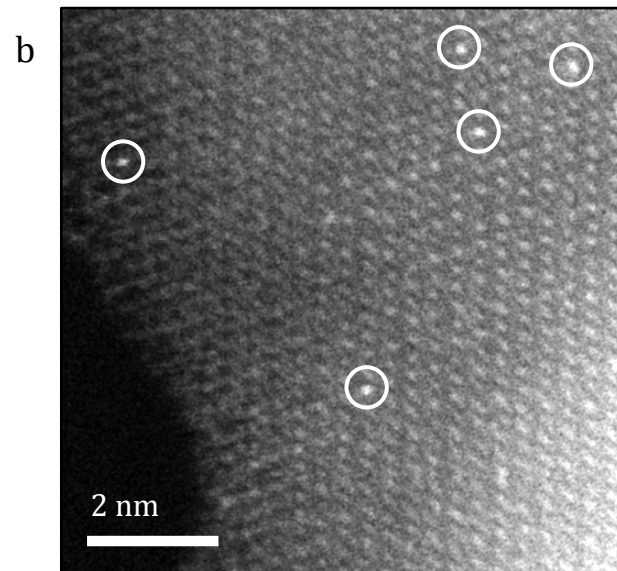
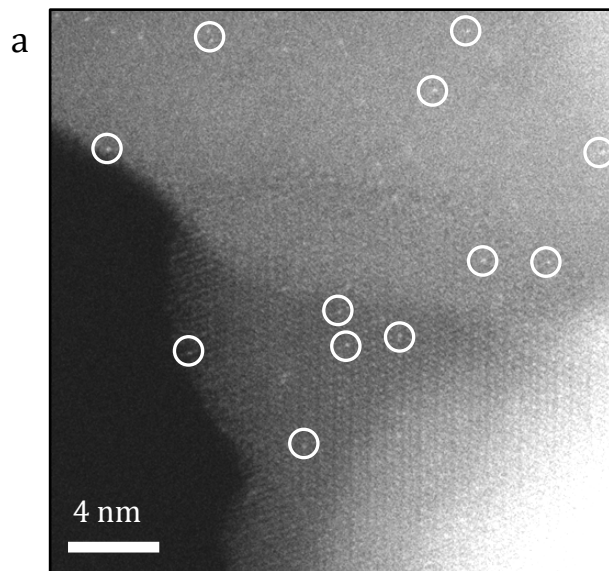
- Pt loading constrained to **0.17w%** (Sample A) vs **2.5w%** (Sample B) on high surface area FeO_x (290 m²/gm)
- Aberration-corrected STEM imaging on HTML's ACEM provided direct evidence that Sample A is composed of only isolated single Pt atoms, which are positively charged due to their strong interactions with the FeO_x support (evidence from several spectroscopic analysis techniques). These strong ionic and covalent interactions stabilize the single Pt atoms on the FeO_x support.
- All results suggested that the single Pt atoms embedded into the FeO_x surface have a high oxidation state due to coordination by the three surface O atoms, significantly different from the metallic Pt⁰ atoms in bulk Pt nanoparticles or clusters typical of most Pt-based catalytic materials.

Project ID: PM029, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

Sample A

a,b) Only single Pt atoms on surface of FeOx, in Fe positions on atomic columns



Sample B

c,d) a mixture of single atoms (white circles), the 2-d Pt "rafts" consisting of fewer than 10 Pt atoms (black circles), and the 3-d Pt clusters with sizes about 1 nm (white square) is clearly observed.

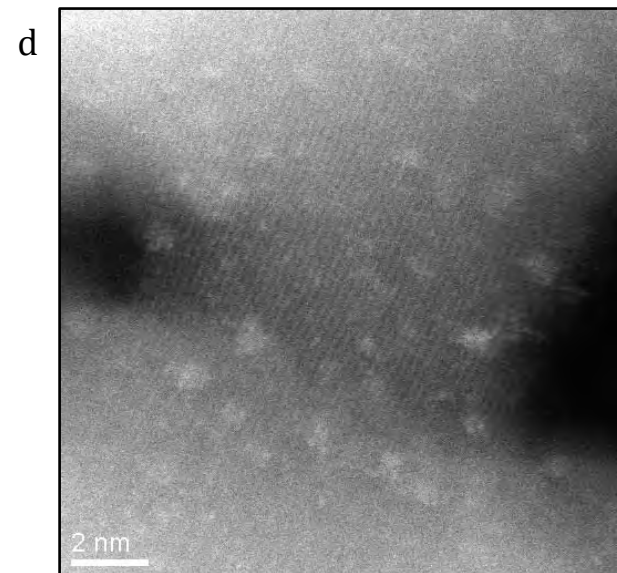
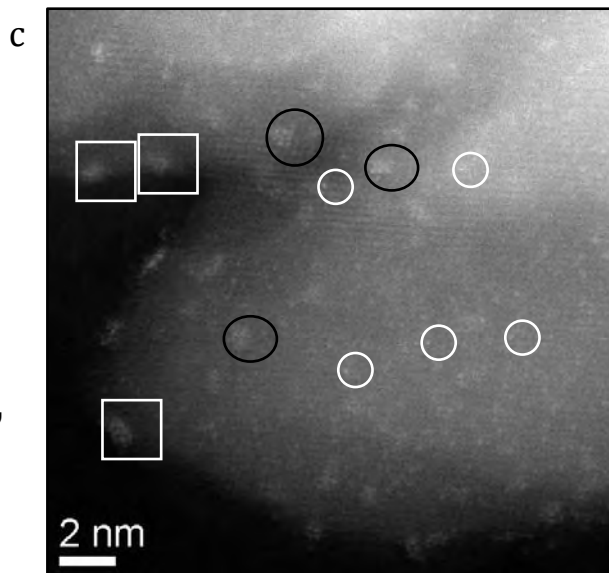


Table 1 Comparison of reaction rates and turnover frequencies (TOFs) of different samples

	Metal loadings (wt%)	Reaction type	Temperature (°C)	Specific rate×10 ² (mol _{CO} h ⁻¹ g _{metal} ⁻¹)	TOF×10 ² (s ⁻¹) ^b
Sample A	0.17	CO oxidation	27	43.5	13.6
Sample B	2.5	CO oxidation	27	17.7	8.01
Au/Fe ₂ O ₃ ^a	4.4	CO oxidation	27	21.7	4.76
Sample A	0.17	PROX	27	67.6	21.2
Sample B	2.5	PROX	27	20.3	9.15
Au/Fe ₂ O ₃ ^a	4.4	PROX	27	39.3	8.60
Sample A	0.17	PROX	80	99.2	31.1
Sample B	2.5	PROX	80	35.8	16.2
Au/Fe ₂ O ₃ ^a	4.4	PROX	80	80.3	17.6

Samples A and B tested against commercial Au/Fe₂O₃ catalyst used for CO oxidation and PROX reactions

Conclusions:

- We have synthesized and characterized a novel catalyst consisting of only single Pt atoms uniformly dispersed on high-surface-area FeO_x support.
- This catalyst shows extremely high activity for both CO oxidation and PROX reactions (used as test reactions).
- The chemical reactivity of our high-valent single Pt atoms is quite different from that of single Au atoms or cations on the same support.
- The more vacant d-orbitals of our single Pt atoms are responsible both for the strong binding and stabilization of single Pt atoms (due to the charge transfer from Pt atoms to the FeO_x surface), and for providing high-valent Pt atoms, which ultimately account for the excellent catalytic activity of the Pt_1/FeO_x catalyst.
- *The stabilization of single atoms on practical oxide supports via charge transfer is not limited to the Pt_1/FeO_x system, and can be further extended and made applicable to other precious metal systems.*
- **The discovery of this single-Pt-atom catalyst not only proves the concept of single-atom heterogeneous catalysis but also has a great potential to reduce the high cost of commercial noble metal catalysts in industry.**

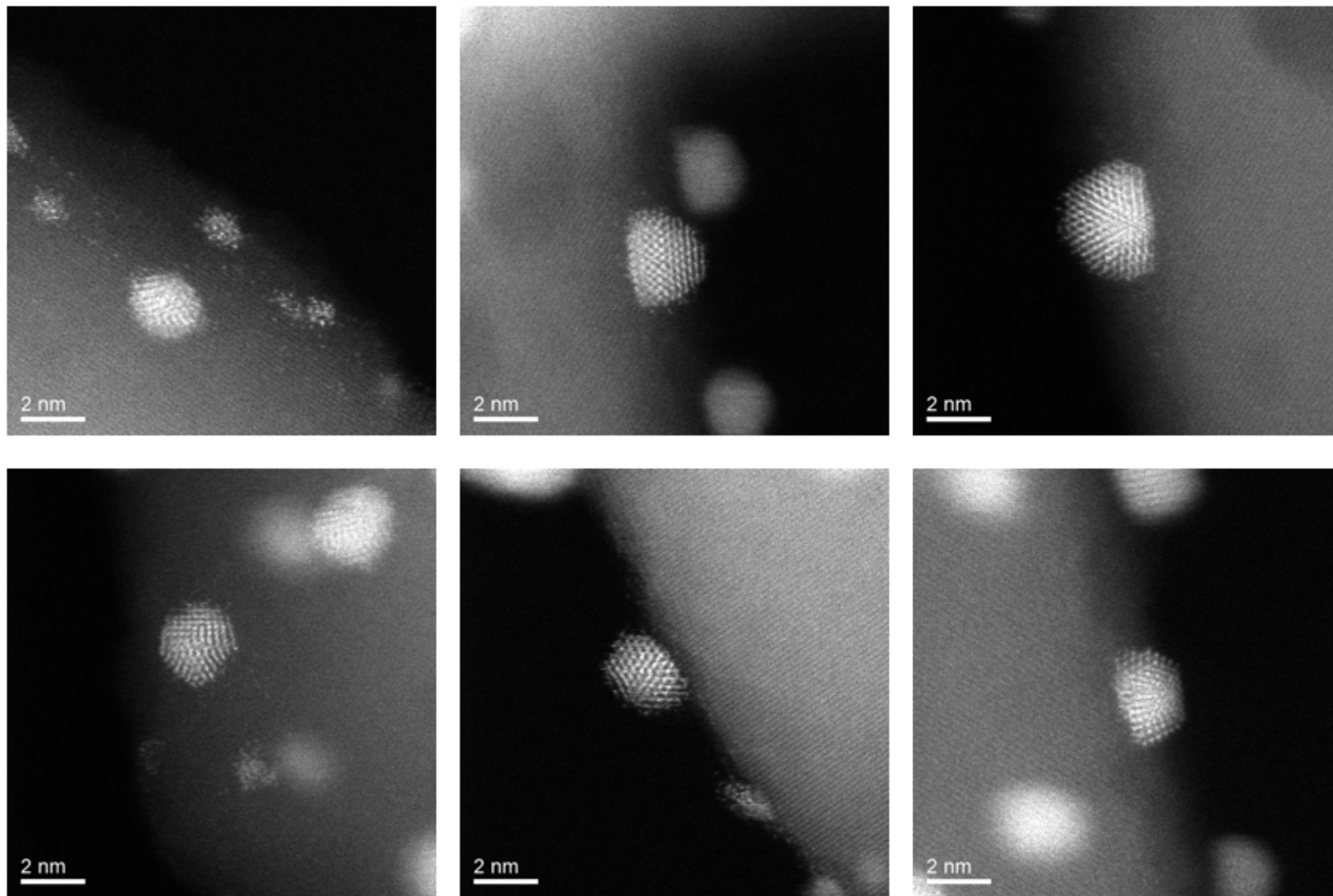
3. Determine locations of active sites on catalyst nanoparticles

Metallic Corner Atoms in Gold Clusters Supported on Rutile are the Dominant Active Site during Water-Gas Shift Catalysis

(work with Prof. F. Ribeiro and colleagues at Purdue University, published in J. American Chemical Society, 2010)

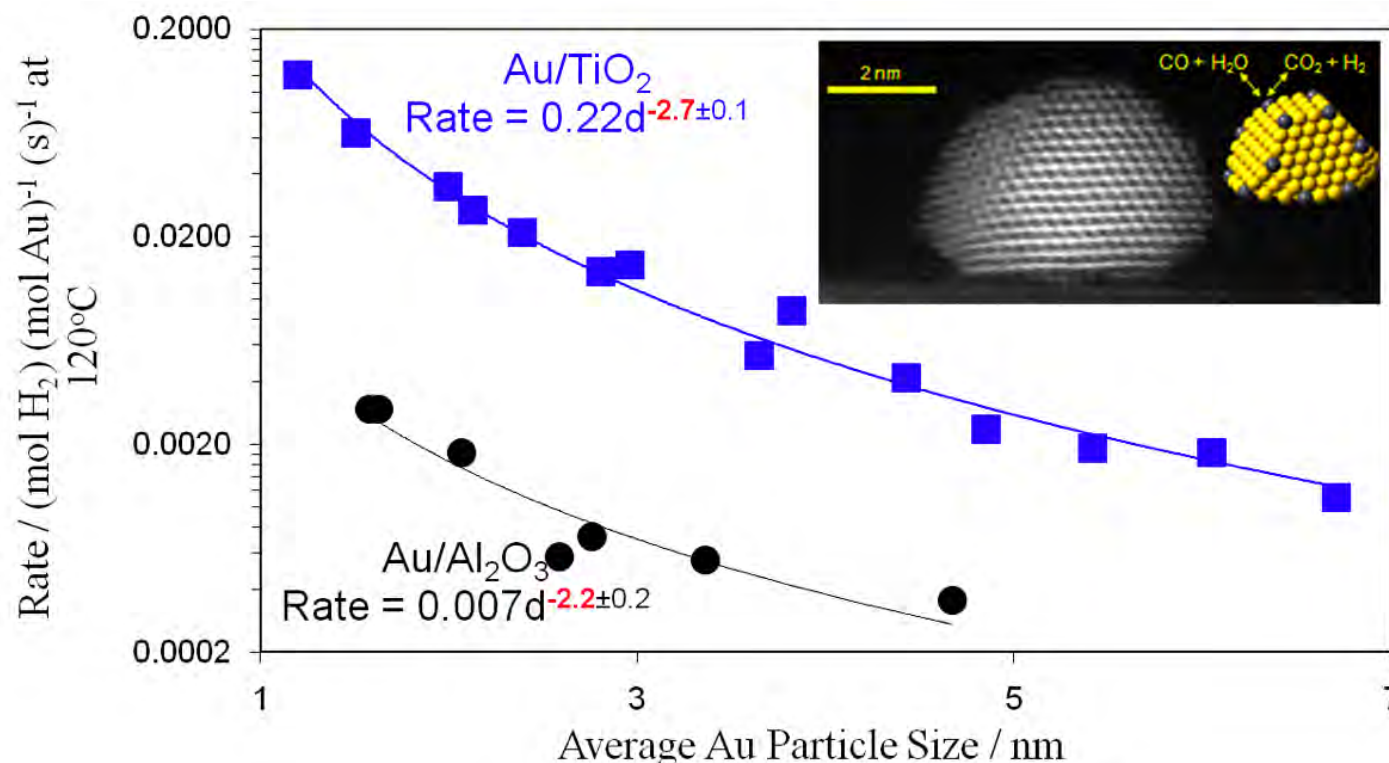
- Our high-resolution imaging is being used in conjunction with operando Fourier transform infrared (FTIR) and *in situ* diffuse reflectance infrared spectroscopy (DRIFTS) to elucidate the nature of the active sites for reactions over supported Au and Pt nanoparticles on alumina, titania and silica supports.
 - The inert nature of bulk gold as compared to gold nanoparticles makes gold catalysts ideal to study the origin of the activity of nanoparticles.
 - Lower-coordinated Au has been shown to exhibit higher reaction rates than bulk gold surfaces.
 - In literature concerning gold catalysis, perimeter sites, low-coordinated corner sites, cationic gold, and bilayers of gold have been proposed as the active species.
 - Our use of a model nonporous support enhances the ability to characterize the gold nanoparticles.
- Illustrated here is an example of the Au/titania and Au/alumina results

Project ID: PM043, Allard



Representative HAADF-STEM images of titania-supported Au particles. These images led to the determination of the model Au structure to correlate to spectroscopy results.

Project ID: PM043, Allard



The dependence of WGS rate per total mole of Au on model Al₂O₃ and TiO₂ as a function of average Au particle size.

A physical model of the gold clusters as truncated cubo-octahedra was used to determine the fraction of atoms in a gold cluster that have a specific number of gold neighbors. From the model, it is determined that these catalysts have more than one active site, the low-coordinated corner atoms and the perimeter Au atoms.

Project ID: PM043, Allard

Conclusions

- The dominant active site is shown to be the low coordinated corner Au atoms, which are ~7 and ~3 times more active than the perimeter Au atoms for Au/TiO₂ and Au/Al₂O₃ catalysts respectively.
- The conclusion that corner atoms are dominant sites implies that the rate on each cluster larger than approximately 1 nm in size is the same and that the total rate of a given sample is proportional only to the number of clusters, but not their size.
- The presence of the corner atoms with low Au-Au coordination is caused by the geometry of the nanoparticles.
- Thus, it is possible to explain the high rate per mole of Au of the nanoparticles without invoking explanations involving changes to the electronic nature of the nanoparticles with size.

Plans for FY2011-FY2012

- Test and evaluate Gen 3 environmental cell in both static gas and dynamic flow conditions
- Design, fabricate and test new manifold system to allow precise flow rate control through E-cell, and knowledge of the pressure during both static and flowing gas conditions (leverage funding with Protochips Co. WFO)
- 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

Project ID: PM043, Allard

2010 Milestone review:

- Mar-10: Develop protocols for most effective use of E-cell in imaging experiments to study gaseous reaction phenomena.
- Sept-10: Submit for publication at least 6 articles in refereed journals on catalyst research activities.

Project ID: PM043, Allard

DOE 2011 Vehicle Technologies Annual Merit
Review and Peer Evaluation Meeting

Principal Technical Accomplishments-FY2010-11

- Experience with Gen 2 E-cell operation leads to improved Gen 3 E-cell design and fabrication. Gen 3 design offers numerous operational improvements over Gen 2 design.
- Double-tilt heating holder utilized for in situ heating experiments that require precise alignments for reliable imaging.
- Use of in situ specimen holders in ACEM facilitated by implementation of newly fabricated specimen stage "clamshell" that permits electrical and gas connections to holders while maintaining seal over the holder.
- Incorporation of 30nm amorphous SiN films over heater membrane provides vacuum seal for E-cell while permitting atomic-level imaging and resistance to oxidizing environments.
- Our work has resulted in numerous invited and contributed publications and presentations.

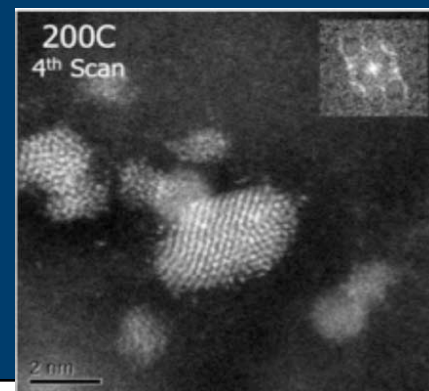
Project ID: PM043, Allard

Summary: our work supports many entities...

PNNL



Eastman Chemicals,...



Industry...

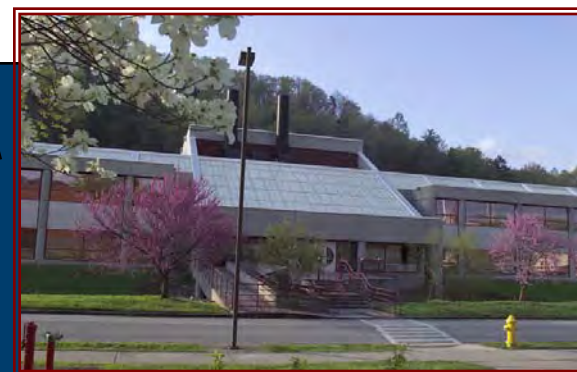
University...



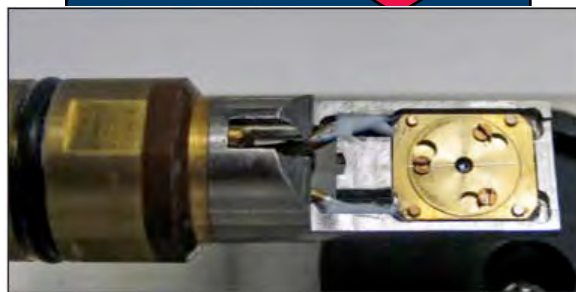
UT-Austin,...



ACEM



ORNL



Protochips

Project ID: PM043, Allard