Characterization of Catalyst Microstructures and Deactivation Mechanisms

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PM_9105

Characterization of Catalyst Microstructures and Deactivation Mechanisms

21CTP Technical Goal: Develop and demonstrate an emissions compliant engine system for Class 7-8 highway trucks that improves the engine system efficiency from ~42% today to 50% by 2010.

Project Objectives

Our goal is to utilize ultra-high resolution imaging and spectroscopy capabilities of the ORNL aberration-corrected electron microscope (ACEM) to characterize "real" and "model" diesel and automotive catalyst systems to better understand mechanisms controlling aging and poisoning behavior of exhaust emission reduction catalyst materials.

FY 2005 Focus

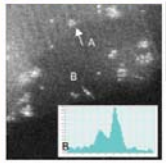
Study model metal cluster systems of known cluster size on oxide supports to develop capability to reliably characterize our experimental and real catalysts at sub-Ångstrom resolutions. Use ACEM to characterize series of real-world catalysts (supplied by Ford Research Lab) to determine aging behavior mechanisms.

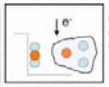
Planned Duration

October 2004 to September 2007

DOE Funding/Industry Cost Share

FY04: $200K; FY05: $190K





Cartoon showing arrangement of atoms in "dimer" B.

A: Tri-Re cluster seen in top view.
B: "Dimer" is actually a tri-Re cluster anchored to a ledge on the alumina, and imaged edge-on. Inset intensity profile confirms twice the intensity for lower "atom," indicating presence of 2 atoms.

ACEM annular dark-field image of tri-rhenium carbonyl clusters on γ-alumina support material.

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Accomplishments

- ORNL ACEM installed and demonstrated using model heavy metal cluster system to provide sub-Ångstrom imaging that allowed confirmation of presence of clusters containing 3 metal atoms in triangular configuration.
- Studies of real-world Lean NOx trap and diesel particulate NOx-reduction catalysts with ACEM confirmed atomic-level dispersions of Pt on baria-alumina-magnesia and ceria-zirconia components in washcoats, and allowed further characterization of these materials as a result of aging treatments.

Significant Future Milestones

Using ACEM imaging capabilities, unambiguously characterize for the first time the morphology of one or more nanometer or sub-nanometer metal particles in model catalyst system, and use the capability thus developed in the characterization of nano-dispersed catalyst particles in real automotive and diesel exhaust catalyst systems, to better understand aging mechanisms. (September, 2007)

Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
PM_9105	Materials Technology	HV Propulsion Materials	Applied Research	8-12-05

Objectives

- Our goal is to utilize ultra-high resolution imaging and spectroscopy capabilities of the ORNL aberration-corrected electron microscope (ACEM) to characterize “real” and “model” diesel and automotive catalyst systems, to better understand mechanisms controlling aging and poisoning behavior of exhaust emission reduction catalyst materials.
- The primary objectives of the proposed research are to continue to investigate the nature of the active sites of promising metal-oxide materials [e.g., Pt and Pd on ceria-zirconia materials for reactions in particulate traps to eliminate soot (with NTRC, in conjunction with the CLEERS program (Dr. Stewart Daw, et al.)] and “real” catalysts for NO_x trapping applications with Ford Research Laboratory (Drs. George Graham and John Hoard), to facilitate correlation of microstructure with performance.

Approach

- Study model metal cluster systems of known cluster size on oxide supports to develop capability to reliably characterize both experimental and real catalyst sample at sub-Ångström resolutions.
- Characterize series of real-world catalysts (supplied by Ford Research Lab) to determine aging behavior mechanisms. Utilize “spectrum imaging” capabilities to correlate x-ray maps with annular dark-field images, in order to determine relationship between heavy metal catalytic species and washcoat phases. Utilize ultra-high resolution imaging capabilities to determine atomic-level distributions of heavy metals on as-received samples.

Relevance to 21 CT Goals

- **Develop and demonstrate an emissions compliant engine system for class 7-8 highway trucks that improve the engine system efficiency from ~42% today to 50% by 2010**
- **Our work relates to the basic understanding of processes that affect the degradation of performance of exhaust aftertreatment materials such as Lean NOx Trap (LNT) catalysts and Diesel Particulate NOx Reduction catalysts. The performance of catalytic materials is largely dependent on events that occur at the atomic level in the catalyst, so an understanding of catalyst microstructures and changes that occur at the level of single atomic species and ultra-fine clusters is essential to development of new materials.**
- **Our ability to characterize a given model catalyst or "real" catalyst material from a supplier both before and after aging treatments in simulated exhaust conditions will be an essential component of the work to understand poisoning (e.g. by sulfur) and other degradation mechanism. Modern techniques of ultra-high resolution imaging and spectroscopic analysis at the sub-Ångström level, now available in our laboratory (and unique in EERE), gives us a strong potential to have an impact on catalyst system development in several arenas.**
- **Partners include Drs. Jim Parks and Stuart Daw of NTRC (CLEERS program research), with whom we are working to characterize supplier materials provided by Drs. John Hoard and George Graham of Ford Research Laboratory. Dr. Michael O'Keefe of Lawrence Berkeley National Laboratory is a long-time collaborator with whom we are developing the methodology for understanding imaging in the sub-Ångström range, in particular to develop the facility with which to accuarately characterize catalyst particle shapes in order to better understand catalytic mechanisms.**

Technical Accomplishments/ Progress/Results

- ORNL's EERE-funded ACEM installed and demonstrated using model heavy metal cluster system to provide sub-Ångstrom imaging that allowed confirmation of presence of clusters containing 3 metal atoms in triangular configuration.
- Studies of real-world Lean NOx trap and diesel particulate NOx-reduction catalysts with ACEM confirmed atomic-level dispersions of Pt on baria-alumina-magnesia and ceria-zirconia components in washcoats, and allowed further characterization of these materials as a result of aging treatments.
- Special holder for ACEM specimens designed and fabricated, to permit imaging the same catalyst areas before-after sequential reaction treatments.

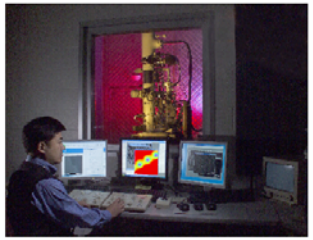
Accomplishments/Progress/ Results Slides

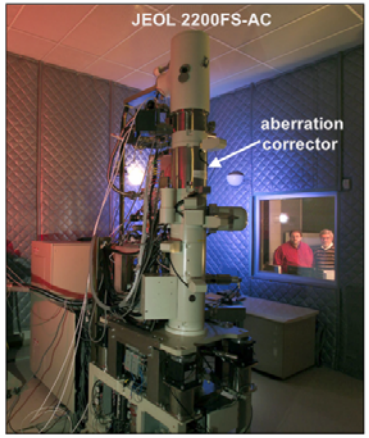
Some Background

- EERE provided $3M funding for the purchase of one of the first aberration-corrected combination scanning transmission and transmission electron microscopes in the nation (or world), called the “ACEM”.
- The JEOL 2200FS-AC equipped with a CEOS GmbH aberration corrector was delivered in 2004, and is nearing completion of installation and testing.
- General Plant Project (GPP, BES) funds were used to construct a special new laboratory, the Advanced Microscopy Laboratory, to provide the specialized environment for operation of the new microscope.
- The ACEM is being used in beginning studies of diesel and automotive catalysts in support of OFCVT NOx and particulate emission reduction program.

The ORNL Advanced Microscopy Lab (AML)…

…provides an ideal environment for sub-Ångstöm imaging





The HTML’s ACEM is operated remotely, from an adjacent control room

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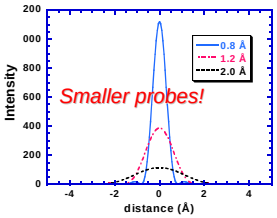
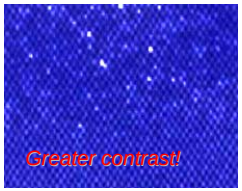
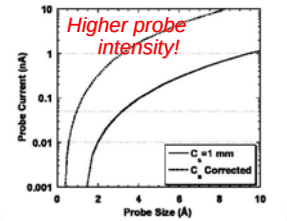
What does aberration correction of the STEM image buy us?

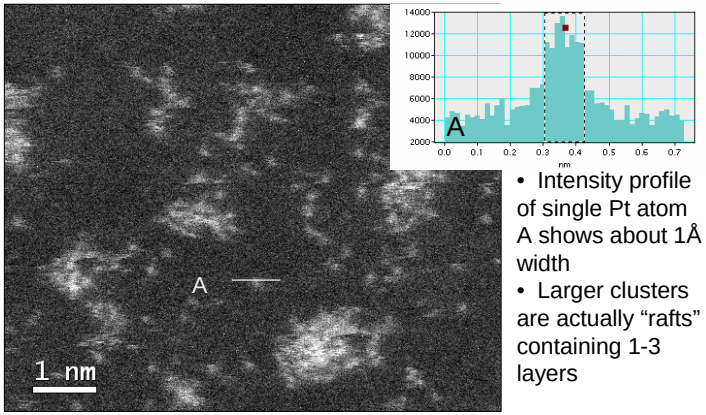




Sb atoms in Si



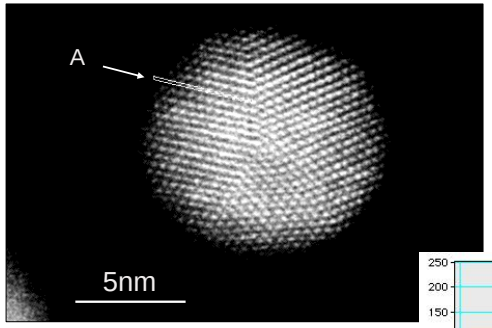
First demonstrated capability for EERE visualization of Pt atoms and clusters:



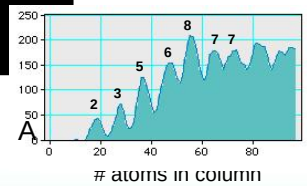
- Intensity profile of single Pt atom A shows about 1Å width
- Larger clusters are actually "rafts" containing 1-3 layers

HA-ADF STEM image of Pt on 11Å carbon film

Potential for 3-d shape analysis of catalyst nanoparticles using ACEM dark-field imaging techniques

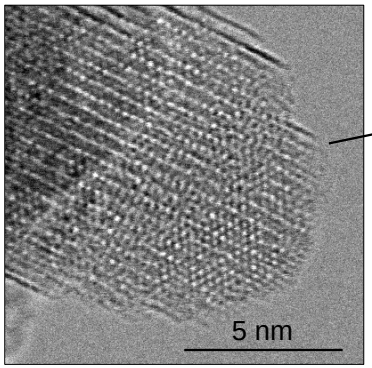


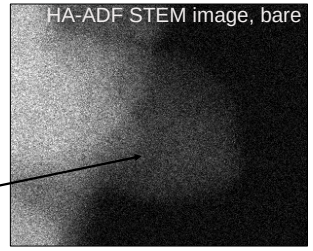
ORNL "ACEM" image of gold nanoparticle

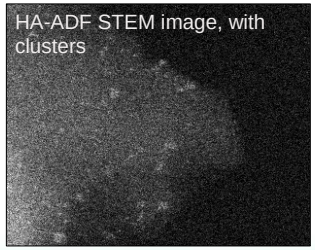


Analysis of STEM image of Au particle can provide information on particle shape. Carbon support film <u>does not</u> contribute to background in ADF image.

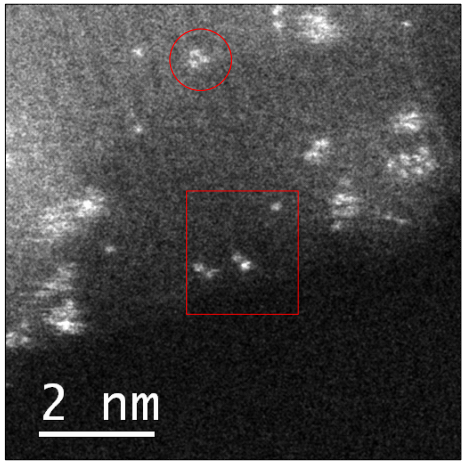
Tri-rhenium carbonyl clusters on γ-alumina



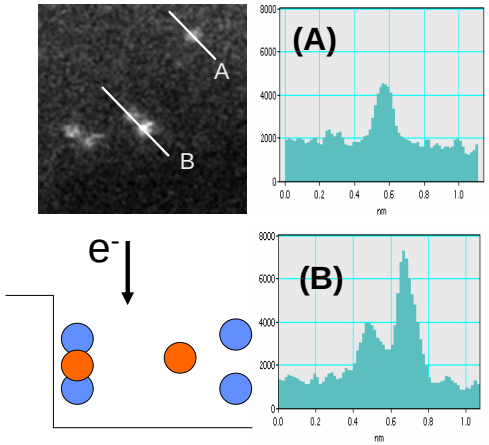




BF STEM image of <u>bare</u> alumina, shows high phase contrast



Isolated atoms and Re-3 clusters on alumina. See next slide for analysis of atoms in outlined square.



"Dimer" B is apparently a Re-3 cluster tethered to a ledge.

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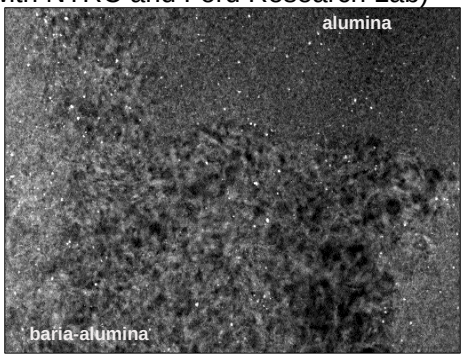
Example of characterization of “real” catalyst material:
Umicore LNT catalyst as-received and after “degreening”
(collaboration with NTRC and Ford Research Lab)

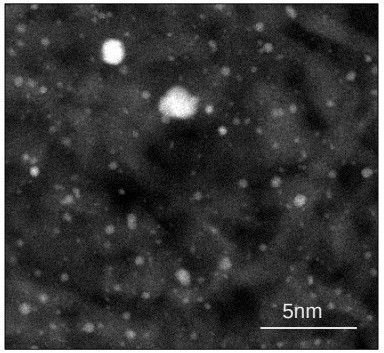
Umicore Co.
LNT catalyst
washcoat, as
received

HA-ADF image
from ACEM



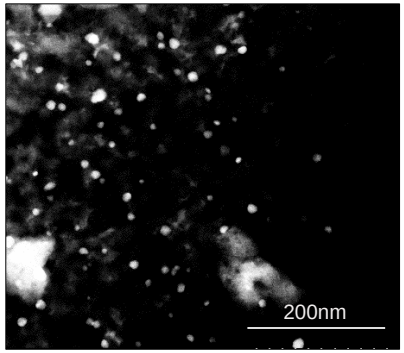
2nm Pt particles clearly seen in bright contrast, in alumina and baria-alumina phases

Umicore
LNT Fresh, alumina area



Note ultra-fine clusters are visible, down to near single atom level

Umicore
LNT “degreened”



Pt clusters grow to 5-20nm particles (note scale change)

Technology Transfer

- **Tech transfer activities**
  - –Presentation at CLEERS, DEER2005, Microscopy Society of America meetings
  - –Publications in refereed Journals
  - –Establishing collaboration with OEMs – e.g. Ford Research Lab
- **Collaborators**
  - – D. Blom (ORNL), C. Narula (ORNL): Experimental imaging and interpretation of results
  - – M. O'Keefe (LBNL): development of theory and methodology for ultra-high resolution imaging
  - – S. Daw (NTRC), J. Parks (NTRC), J. Hoard (FRL), G. Graham (FRL): Experiments on supplier materials
- **Consideration of manufacturing, materials, design, supply chain**
  - –Does not require changes in manufacturing, design, or supply chains
- **Timeframe for potential tech transfer**
  - –Ongoing

Future Work

- Using ACEM imaging capabilities, unambiguously characterize <u>for the first time</u> the 3-d morphology of one or more nanometer or sub-nanometer metal particles in a model catalyst system. (September 2006)
- Using unique ACEM energy-loss spectroscopy capabilities, develop and demonstrate the capability to determine chemical species and bonding characteristics of small metal clusters. (September 2006)
- Utilize specially constructed ACEM sample holder for studies of catalyst aging phenomena, by imaging the same areas before and after sequential aging treatments. (September 2006
- Use the capabilities thus developed in the characterization of nano-dispersed catalyst particles in real automotive and diesel exhaust catalyst systems (with FRL and NTRC collaborators), to better understand aging mechanisms. (September, 2007)

Publications, Presentations, Patents

- **L.F. Allard** and C.K. Narula, Electron Microscopy of LNT Materials: Microstructural Changes with Aging," Presentation at 2005 CLEERS Workshop, Dearborn, MI, May, 2005
- V. A. Bhirud, M. J. Moses, D. A. Blom, **L. F. Allard**, T. Aoki, S. Mishina, C. K. Narula, and B. C. Gates, "Alumina-supported Tri-rhenium Clusters Revealed by Aberration-corrected Electron Microscopy," *Microscopy and Microanalysis* (2005) (First Place Award winner in Physical Sciences competition)
- C.K. Narula. **L.F. Allard**, M.J.Moses, Y. Xu, W. Shelton, W.F. Schneider, G. Graham, and J. Hoard; "Lean NOx Traps - Microstructural Studies of Real World and Model Catalysts," DEER 2005, Palmer Hilton, Chicago, Aug. 21-25, (2005).
- M. A. O'Keefe, **L. F. Allard** and D. A. Blom, "HRTEM Imaging of Atoms at Sub-Ångström Resolution," *Journal of Electron Microscopy*, Special Issue in Memory of Prof. John M. Cowley, Aug. 25 (2005) p.1-12
- M. A. O'Keefe and **L. F. Allard**, "A Standard for Sub-Ångström Metrology of Resolution in Aberration-Corrected Electron Microscopes," *Microscopy and Microanalysis* **10** (2004) p.100
- **L. F. Allard**, D. A. Blom, M. A. O'Keefe et al., "First results from the Aberration-Corrected JEOL 2200FS-AC STEM/TEM." *Microscopy and Microanalysis* 10 (2004), p.110
- M. A. O'Keefe, **L. F. Allard** and D. A. blom, "Resolution Quality and Atom Positions in Sub-Ångström electron microscopy," *Microscopy and Microanalysis*, in press
- M.A. O'Keefe, E.C. Nelson and **L.F. Allard**, "Focal-Series Reconstruction of Nanoparticle Exit-Surface Electron Wave," *Microscopy and Microanalysis (*2003).