Project ID: LM031, Allard

Characterization of Catalysts for Aftertreatment and Biomass-derived Fuels:

Success Stories from the High Temperature Materials Laboratory (HTML) User Program

DOE 2010 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

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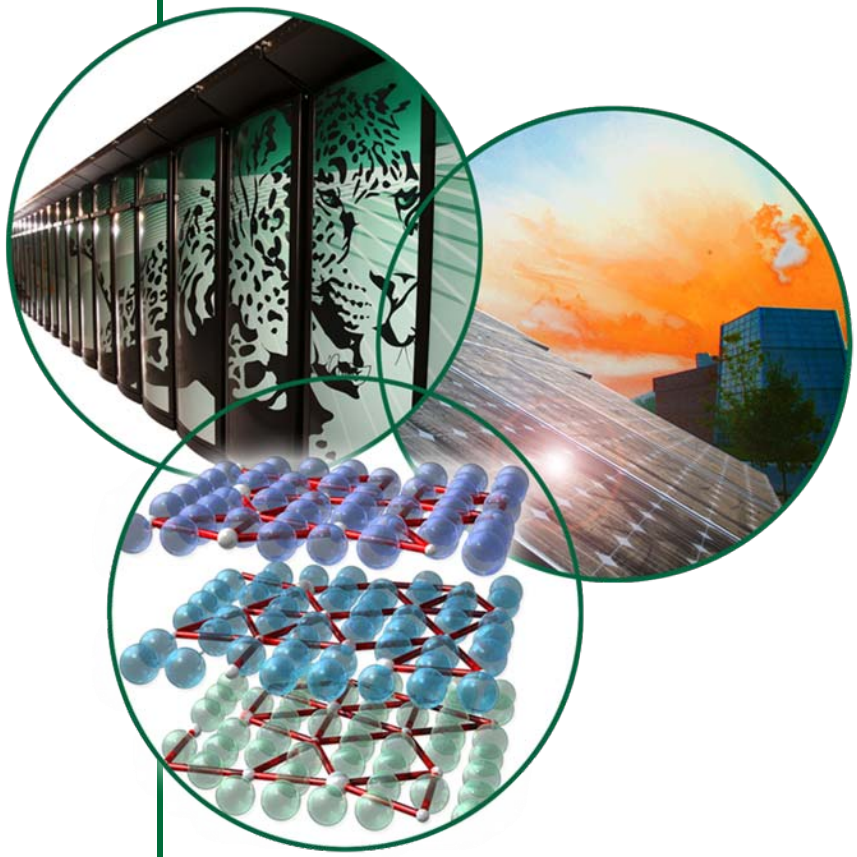

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The HTML User Program: Background

- The HTML is a National User Facility that supports the missions of DOE, EERE and the Vehicle Technologies Program in particular, by working with industry, universities, and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum. The HTML is organized into six user centers, which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization.
- Access to the HTML User Program is provided through the HTML User Program proposal process. Research proposals are reviewed by a committee and approved based on scientific merit, relevance of the proposed research to the mission of DOE's Vehicle Technologies Program, and feasibility. Projects have a well-defined scope, and research is completed within 24 months and normally involves one or more user visits to the HTML.
- Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, and users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature. A nonproprietary project is complete when the results are published in the open literature and/or presented at a professional conference. For proprietary research, the user owns the research data, and all costs at the HTML are paid by the user based on DOE guidelines for ORNL costs.

The HTML User Program – FY2009 Activity

During FY2009, the HTML User Program collaborated with 11 companies, 14 universities, and 3 national laboratories on 41 user projects addressing critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program. There were 107 researchers who visited the HTML for a total of 562 days to conduct experiments.

The HTML User Program FY2009 budget was $5,066,946 and was allocated as follows:

- Capital equipment: $514,025
- Operations: $4,552,921

Users cost-share their HTML user projects through:

1) direct involvement with HTML staff members during the development of the user project;
2) funding their travel to the HTML to perform research;
3) cost of materials provided by the user or the research performed prior to the user project;
4) collaboration with HTML staff members to analyze the data and publish the results.

The HTML also supports the education and preparation of a new generation of scientists and engineers. During FY2009, students and professors from 14 universities participated in the HTML User Program. Four of those students earned their Ph.D. degree and three earned their M.S. degree based in part on research they conducted through the HTML User Program.

Relevance to the VT Program

- The Vehicle Technologies Program funds the operation of the HTML User Program to maintain world-class expertise and instrumentation capabilities for materials characterization to work with industry, universities and national laboratories toward the goals of the Vehicle Technologies Program. The HTML User Program capabilities also support the activities of the Vehicle Technologies Program's subprograms in Lightweight Materials, Propulsion Materials, Energy Storage, and Thermoelectric Conversion at the Oak Ridge National Laboratory.

- This poster presentation highlights ***four*** of the 41 user projects managed by the HTML User Program during FY2009. The user projects in this poster presentation made use of the HTML User Program's Aberration-Corrected scanning/transmission Electron Microscope (ACEM) to address critical barriers such as cost, thermal stability, and lack of understanding of catalyst fundamentals.

Overview

This poster details two HTML User projects using advanced electron microscopy for discoveries in catalytic science…

- **University of Michigan and Ford Research Laboratory**

"Characterization of Alumina-Supported Pt and Pt-Pd Alloy NO Oxidation Catalysts with Advanced Electron Microscopy"

- **Pacific Northwest National Laboratory**

"Morphological and Electronic Structure of Pt-Re Nanoparticles Supported on Carbon under Activation and Reaction Conditions for Aqueous-Phase Reforming of Bioliquid"

…and briefly summarizes findings from two additional user projects in catalyst characterization.

University of Michigan/Ford Research

"Characterization of Alumina-Supported Pt and Pt-Pd Alloy NO Oxidation Catalysts with Advanced Electron Microscopy"

Timeline

- Start date: 5/1/2008
- End date: 9/30/2010
- % complete: 95%

Barriers

- Cost
- Emission control
- Durability

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

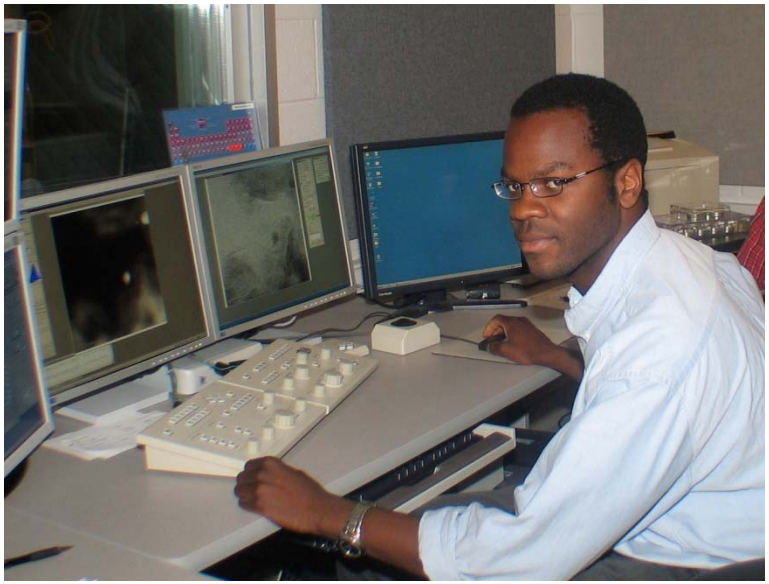
Collaborators

- **Users:**
  University of Michigan:
  Prof. X. Pan, O. Ezekoye
  Ford: A. Drews, G. Graham
- **HTML Staff:** Larry Allard

University of Michigan/Ford Research User Project

Research Problem:

To determine the relative efficacy of Pt/alumina vs. bimetallic Pt-Pd/alumina materials for the catalytic after-treatment of exhaust emissions in lean-burn gasoline and diesel engines.



University of Michigan Ph.D. student Obi Ezekoye at controls of ACEM at HTML's User Program, ORNL.

Technical Approach:

Utilize the unique capabilities at the HTML for characterization of experimental Pt and Pt-Pd on alumina catalytic materials to obtain chemical and structural information at the atomic level, via aberration-corrected electron microscopy techniques, on the nature of catalytic species as a function of preparation techniques and aging treatments.

University of Michigan/Ford Research User Project: Background to the study

- Lean-burn gasoline and diesel engines increase fuel economy over conventional gasoline engines for transportation applications, but the catalytic after-treatment of exhaust, notably NOx and soot, presents unique challenges.
- After-treatment technology has been extended beyond three-way catalysts, to include NOx storage and release (NSR) catalysts, diesel particulate filters, and selective catalytic reduction (SCR) catalysts.
- NO oxidation is a critical step in both the NSR process and soot oxidation, and Pt remains the preferred NO oxidation catalyst.
- Alloying Pt with other metals (such as Pd) is known to inhibit excessive Pt particle coarsening, an important deactivation mechanism for supported Pt catalysts.
- Substitution of Pd for up to 50 at% of the Pt in alumina-supported catalysts reduced particle growth during lean aging with little or no impact on the NO oxidation turn-over frequency.

Composition and preparation of samples

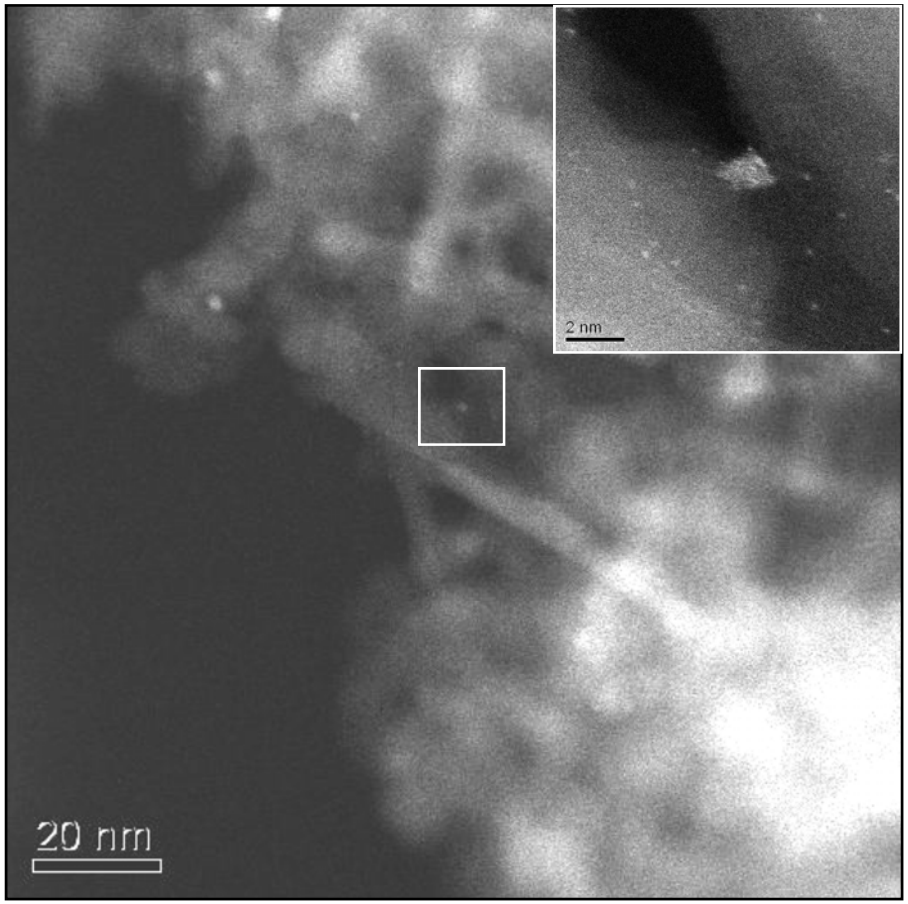
Samples: Pt100-Pd0 and Pt50-Pd50 at nominally 1wt%

Preparation: Ac-Ac (Pt- and Pd-acetylacetonate) and
Pt- and Pd-nitrate solutions by incipient wetness

Aging: 3 hours at 500°C and 900°C in O_2-H_2O-N_2
then reduction 1 hour at 500°C in H_2/N_2

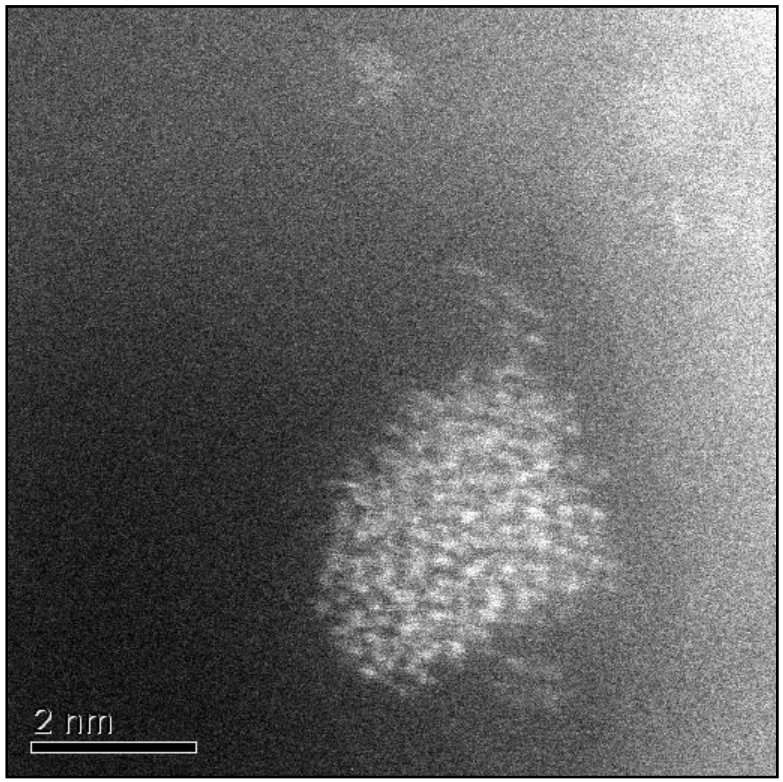
Catalyst Name	Composition (wt%)		Atom Fraction		Equivalent Pt (wt%)
	(Pt)	(Pd)	(Pt)	(Pd)	
Pt100-Pd0 Ac-Ac	0.87	0	100	0	0.87
Pt50-Pd50 Ac-Ac	0.58	0.28	53	47	1.09
Pt100-Pd0 Nitrate	0.87	0	100	0	0.87
Pt50-Pd50 Nitrate	0.58	0.28	53	47	1.09

ACEM imaging: high-angle annular dark-field (HAADF) shows heavy metal species in bright contrast

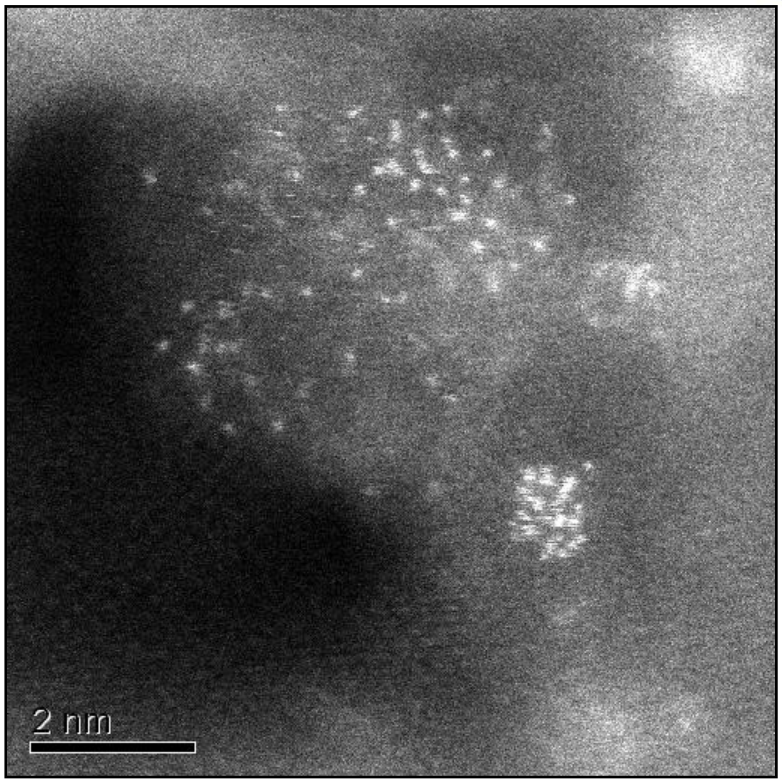


Typical atomic resolution HAADF image of the fresh Pt50-Pd50 Ac-Ac catalyst. Inset shows <2nm particle with single atoms in vicinity.

ACEM imaging:



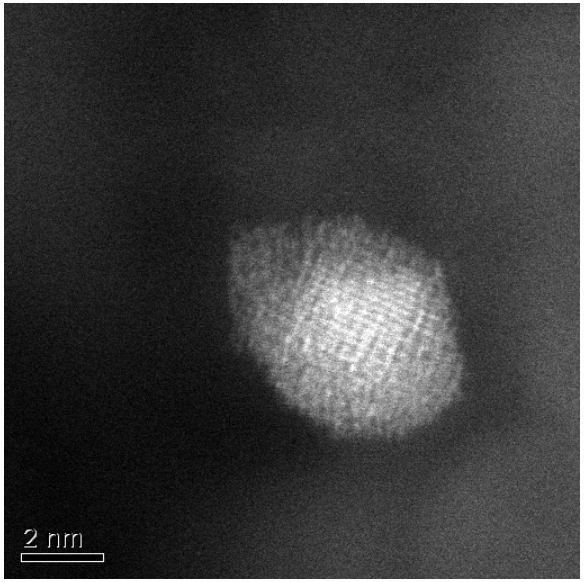
Fresh Pt100-Pt0 Ac-Ac

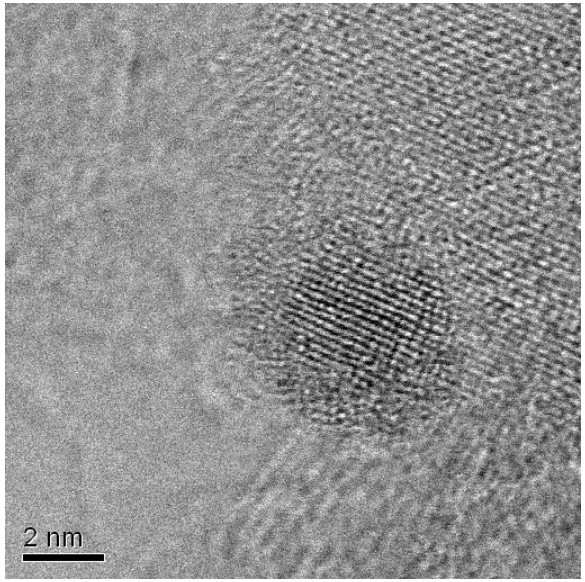


Fresh Pt50-Pd50 Ac-Ac

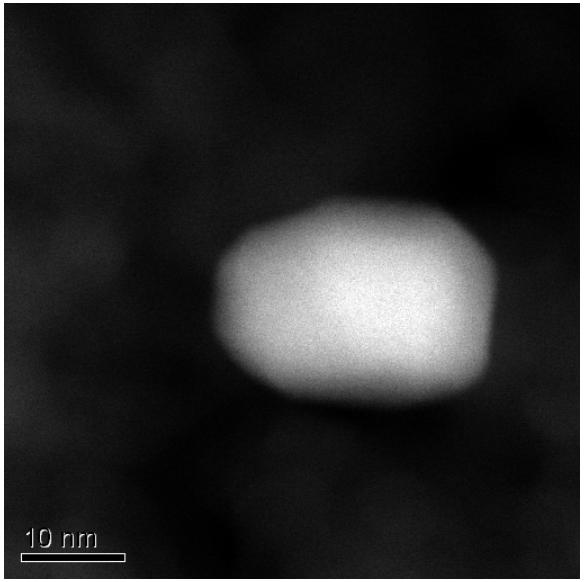
HA-ADF images of typical particles in fresh Pt100-Pd0 (left) and fresh Pt50-Pd50 (right).

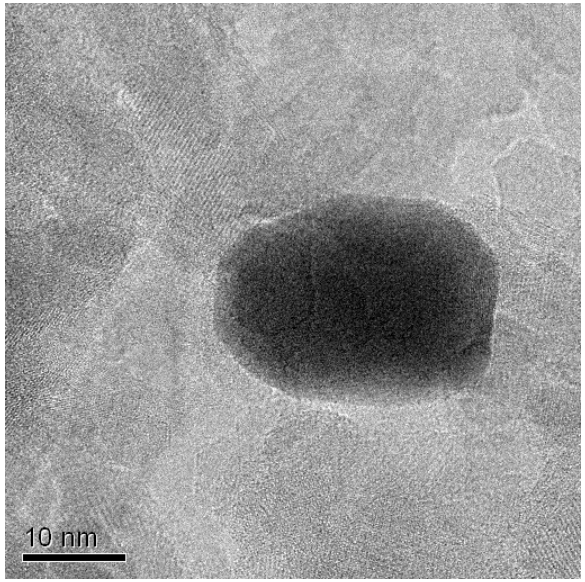
ACEM imaging: typical aging results in Pt50-Pd50 Ac-Ac samples





500°C Aging
particle size ~5nm



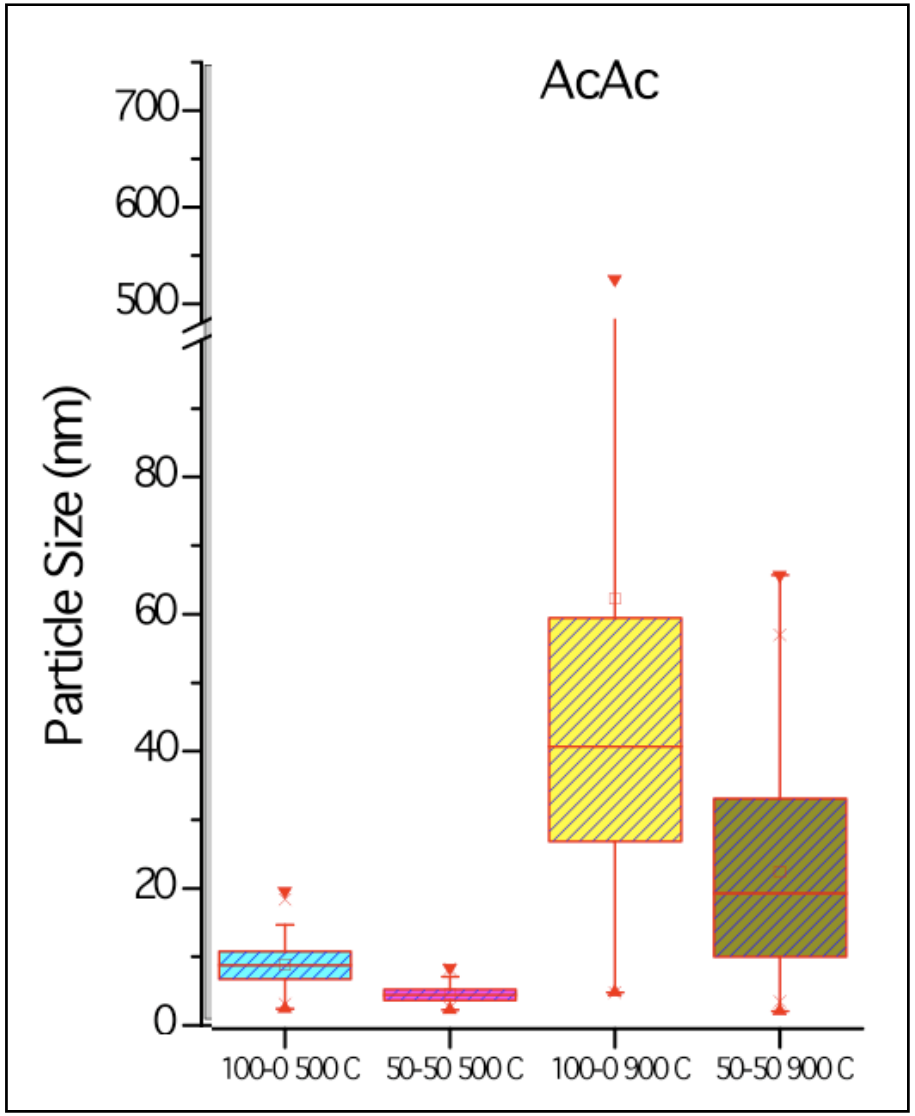


900°C Aging
particle size ~25nm

HA-ADF images

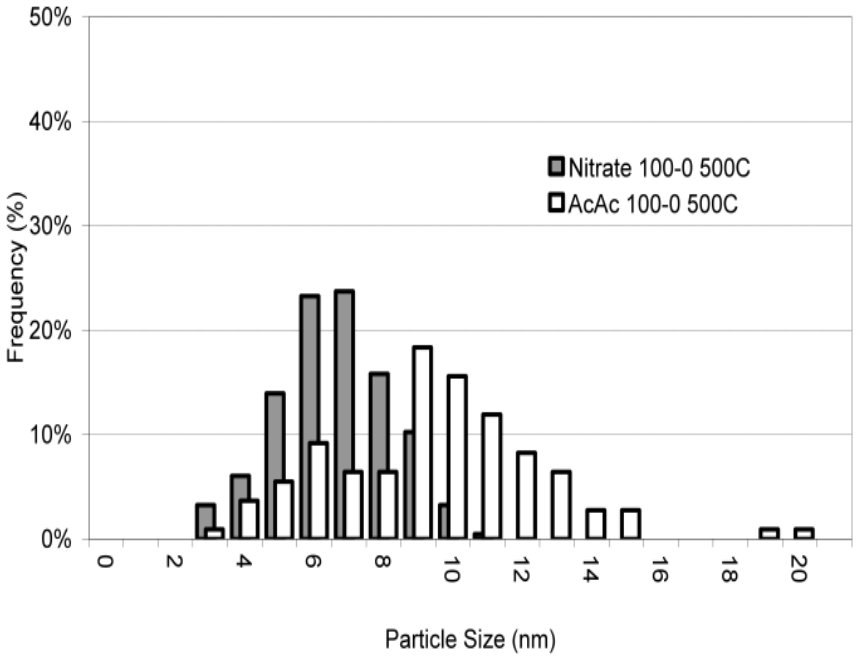
BF images

ACEM imaging:

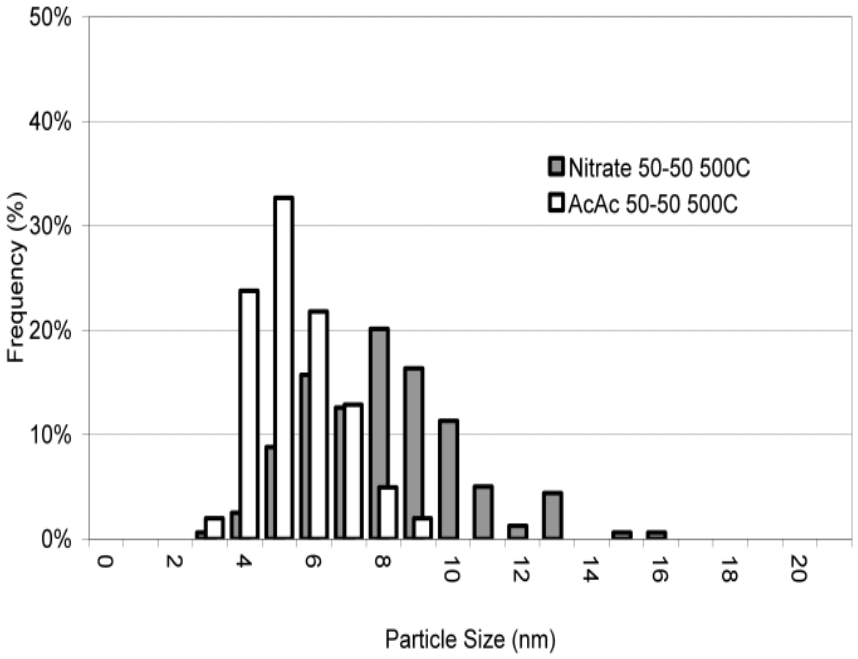


Relative particle sizes in the aged catalysts. The bimetallic catalysts (Pt-Pd) clearly show smaller particle sizes after aging, at both 500°C and 900°C.

Example of 500°C aging results:
Nitrate vs. Ac-Ac preparations



Pt100-Pd0



Pt50-Pd50

What we learned and accomplished:

- Application of advanced electron microscopy techniques to characterization of alumina-supported Pt and Pt-Pd bimetallic catalysts has allowed us to refine our knowledge of the degree of alloying that exists at various stages of aging under lean conditions and thus better understand its relationship to particle coarsening.
- Some direct association between Pt and Pd was observed at the initial stage of bimetallic catalyst synthesis, but there is clearly a strong tendency for alloying to proceed *in situ* during the course of lean aging. This has a positive influence on limiting the growth of anomalously large particles typically found in pure Pt catalysts that have been harshly aged under lean conditions.
- We have also demonstrated that replacement of moderate amounts of Pt with Pd can be done with little or no loss of activity for NO oxidation. Further, standard catalyst precursors and synthesis methods have been shown to suffice.
- The use of Pd to both increase catalyst durability and decrease Pt loading in Pt-based catalysts for lean-burn engine exhaust-gas treatment thus appears even more favorable than before.

Pacific Northwest National Laboratory

"Morphological and Electronic Structure of Pt-Re Nanoparticles Supported on Carbon under Activation and Reaction Conditions for Aqueous-Phase Reforming of Bioliquid"

Pacific Northwest NATIONAL LABORATORY

Timeline

- Start date: 9/11/2009
- End date: 8/31/2011
- % complete: 80%

Barriers

- Cost
- Understanding of catalyst fundamentals

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Collaborators

- **PNNL** Users: Liang Zhang, Yong Wang
- **HTML** Staff: Larry Allard

Pacific Northwest National Laboratory User Project

Pacific Northwest NATIONAL LABORATORY

Research Problem:

To understand the mechanisms by which Re enhances the activity of Pt/activated carbon catalysts for aqueous phase reforming (APR) of oxygenated hydrocarbons for production of hydrogen and biofuels.

Dr. Liang Zhang at controls of ACEM at ORNL

Technical Approach:

Utilize the unique capabilities at the HTML for characterization of experimental Pt and Pt-Re on "real" activated carbon supports and on "model" thin film carbon supports, to obtain chemical and structural information at the atomic level, via aberration-corrected electron microscopy techniques, on the nature of catalytic species as a function of simulated APR reaction conditions.

Background to the study:
Aqueous-Phase Reforming (APR)

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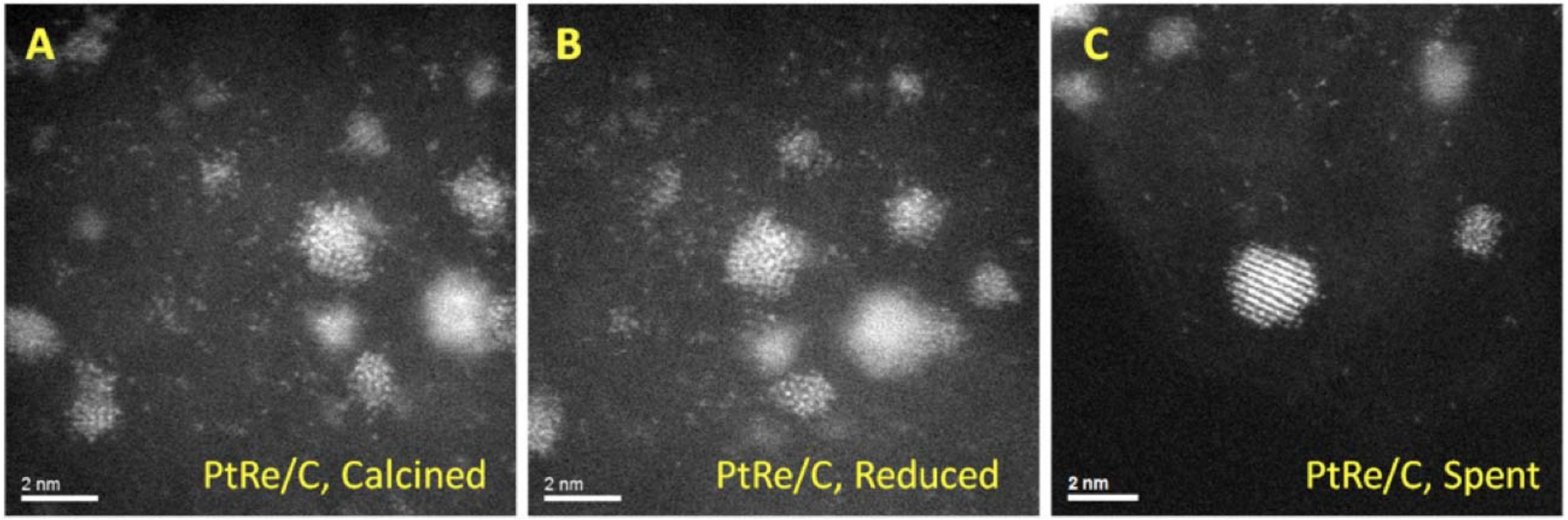
- Production of hydrogen and biofuels via reforming of oxygenated hydrocarbons (sugars, sugar alcohols, polyols, etc.) in the aqueous phase has attracted great interest due to increasing environmental concerns and the national energy security policy.
- Pt-Re/C has proven to be an effective catalyst for the APR process due to its high hydrothermal stability and activity.
- Efforts have been made to understand the effect of Re on activity enhancement. Moreover, definitive evidence is needed to clarify the structure of PtRe nanoparticles and support-particle interaction. Studies to date have been limited to reduced catalysts; no effort has been reported on catalysts under working conditions.
- Our present study has focused on investigation of the structure of a PtRe/C catalyst activated and exposed to hydrothermal environments that are close to APR reaction conditions.

Aqueous-Phase Reforming (APR):

HA-ADF images of "real" PtRe/activated C catalyst



A,B: As-calcined and after reduction treatment; little change in morphology and distribution of nanoparticles, atomic clusters and mononuclear species seen due to anchoring clusters with oxygen-containing functional groups and confining movement of clusters by the unique physical structure of activated carbon (see Fig. D on next slide).

C: After APR reaction, many small clusters disappear, leaving larger, more discrete crystalline nanoparticles with some remaining single atoms. These effects are facilitated by water interaction or leaching by liquid during APR.

Aqueous-Phase Reforming (APR) Catalysts

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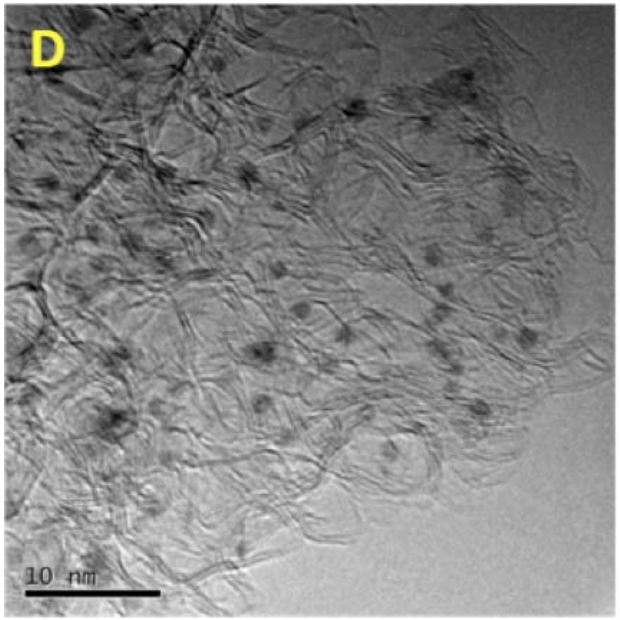
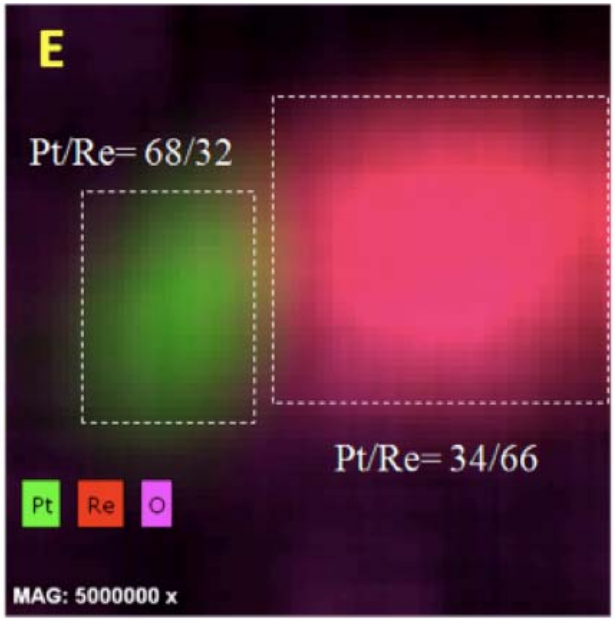
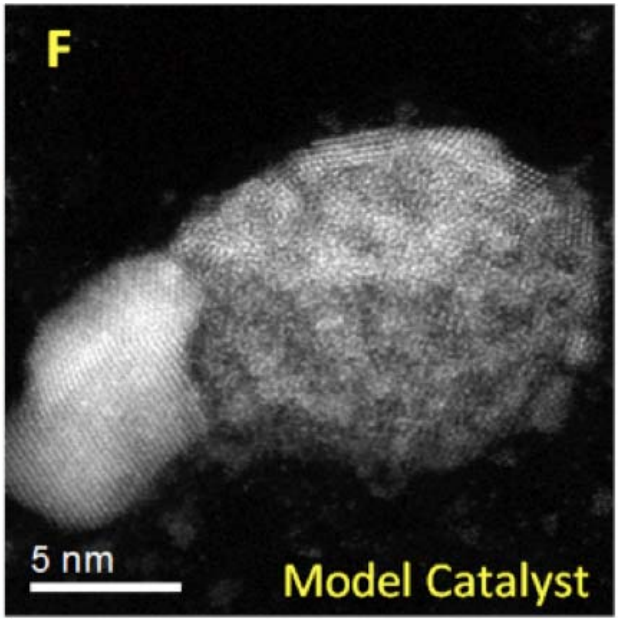
"Real" APR catalyst

"Model" APR catalyst for *in situ* studies







D. PtRe nanoparticles retained in "turbostratic" carbon structure with graphite sheet fragments. EDS showed Pt-rich and Re-rich particles.

E, F: PtRe nanoparticle structure and chemistry studied by *in situ* heating of particles deposited on thin carbon film. Particle shown has left side with high Pt and right side enriched in Re with oxygen. ReOx phase occurs due to water molecules re-adsorbing dissociatively on the Re surface.

What we learned and accomplished:

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- The activated carbon support stabilizes the PtRe dispersion against cluster aggregation and coalescence during reduction treatments.

- After reaction, most of the single atoms or small clusters present in the reduced catalyst disappeared, leaving behind larger nanoparticles, likely due to agglomeration of neighboring clusters facilitated by water interaction or leaching out by liquid. This phenomenon likely leads to the decline in activity over time.

- Both Pt-rich and Re-rich nanoparticles were observed. EDS mapping showed the Re-rich particles were ReOx, suggesting the Pt-Re bond and/or the Pt-O-Re bond might be active sites in the APR reaction.

Summary findings from two additional user projects in catalyst characterization

Ultra-high resolution imaging results from the ACEM have contributed to numerous catalyst studies through the HTML User Program. Short examples of two recent projects follow.

ACEM results significantly support PNNL studies of NOx–trap catalysts, as reported in *Science*.

(User project with J.-H. Kwak, C.H.F. Peden, and colleagues at PNNL)

Coordinatively Unsaturated Al^{3+} Centers as Binding Sites for Active Catalyst Phases of Platinum on γ-Al_2O_3

a Hun Kwak,[1*] Jianzhi Hu,[1] Donghai Mei,[1] Cheol-Woo Yi,[2] Do Heui Kim,[1]
Charles H. F. Peden,[1*] Lawrence F. Allard,[3] Janos Szanyi[1*]

n many heterogeneous catalysts, the interaction of metal particles with their oxide support can lter the electronic properties of the metal and can play a critical role in determining particle norphology and maintaining dispersion. We used a combination of ultrahigh magnetic field, olid-state magic-angle spinning nuclear magnetic resonance spectroscopy, and high-angle annular lark-field scanning transmission electron microscopy coupled with density functional theory alculations to reveal the nature of anchoring sites of a catalytically active phase of platinum on he surface of a γ-Al_2O_3 catalyst support material. The results obtained show that coordinatively nsaturated pentacoordinate Al^{3+} (Al^{3+}_{penta}) centers present on the (100) facets of the γ-Al_2O_3 urface are anchoring Pt. At low loadings, the active catalytic phase is atomically dispersed on the upport surface (Pt/Al^{3+}_{penta} = 1), whereas two-dimensional Pt rafts form at higher coverages.

The ability to control the dispersion and morphology (typical characteristics that determine the performance of catalysts) of oxide-supported metal catalysts is a primary goal f catalyst design and can be enabled by understanding the nature of metal–support surface interactions. Precious metals (e.g., Pt, Pd, and Rh) upported on oxide surfaces are the most widely sed industrial catalyst materials. For these classes f catalysts, dispersion of the precious metal on he oxide support is an especially critical factor ecause of the expense of the metal.

The so-called strong metal-support interaction (SMSI) is often seen as critical to sustaining high catalytic activity under demanding catalyst operation conditions (i.e., high temperature, high water vapor pressure, etc.). Indeed, SMSI has been directly linked to the presence of electronic defects that can be prepared with ease on the surfaces of reducible oxides (e.g., CeO_2 and TiO_2) (*1*). Anchoring the active metal components to these electronic defects has been documented (*2*, *3*), with the strong interaction between the active metal and defects of reducible oxides fundamentally determining the dispersion, morphology, and, therefore, the catalytic activity of metal clusters. For example, the correlation between the number of oxygen defects on the TiO_2 support and the dispersion and morphology of nanosized Au particles has been clearly demonstrated by the results of density functional theory (DFT) calculations of Lopez *et al.* (*2*). Experimentally, Chen and Goodman (*3*) have described the formation of stable, two-dimensional (2D) Au clusters on a defect-rich TiO_2 thin film.

Electronic defects, however, are not present on γ-Al_2O_3, a nonreducible oxide that is one of

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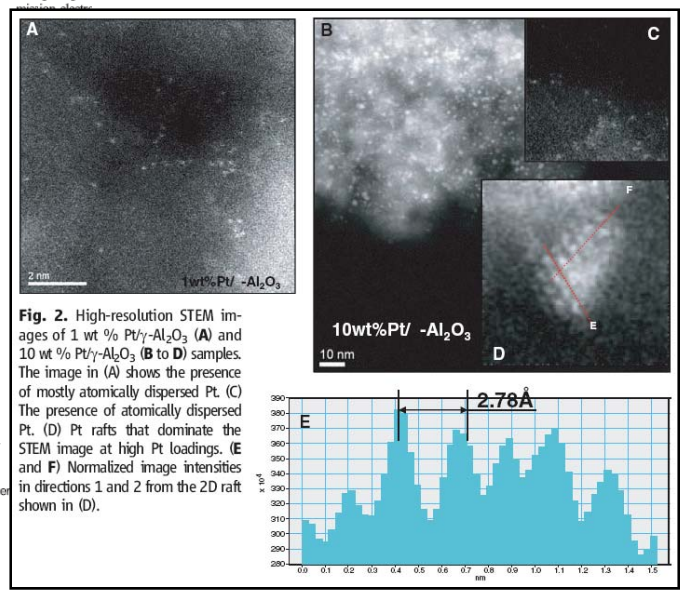
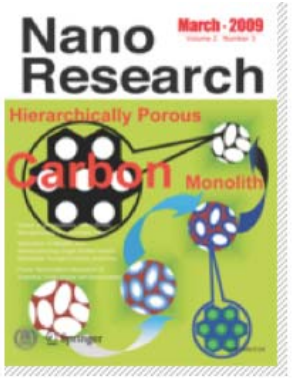


Fig. 2. High-resolution STEM images of 1 wt % Pt/γ-Al_2O_3 (**A**) and 10 wt % Pt/γ-Al_2O_3 (**B** to **D**) samples. The image in (A) shows the presence of mostly atomically dispersed Pt. (C) The presence of atomically dispersed Pt. (D) Pt rafts that dominate the STEM image at high Pt loadings. (**E** and **F**) Normalized image intensities in directions 1 and 2 from the 2D raft shown in (D).

ACEM *in situ* heating research provides insight on surface structure development in Pd nanocrystals.

(User project with Prof. Jimmy Liu and colleagues)



University of Missouri St. Louis

Nano Res (2010) 3: 180–188
DOI 10.1007/s12274-010-1021-5
Research Article

New Insights into the Growth Mechanism and Surface Structure of Palladium Nanocrystals

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ABSTRACT

This paper presents a systematic study of the growth mechanism for Pd nanobars synthesized by reducing Na_2PdCl_4 with *L*-ascorbic acid in an aqueous solution in the presence of bromide ions as a capping agent. Transmission electron microscopy (TEM) and high-resolution TEM analyses revealed that the growth at early stages of the synthesis was dominated by particle coalescence, followed by shape focusing via recrystallization and further growth via atomic addition. We also investigated the detailed surface structure of the nanobars using aberration-corrected scanning TEM and found that the exposed {100} surfaces contained several types of defects such as an adatom island, a vacancy pit, and atomic steps. Upon thermal annealing, the nanobars evolved into a more thermodynamically favored shape with enhanced truncation at the corners.

KEYWORDS

Palladium, nanocrystals, growth, coalescence, surface evolution

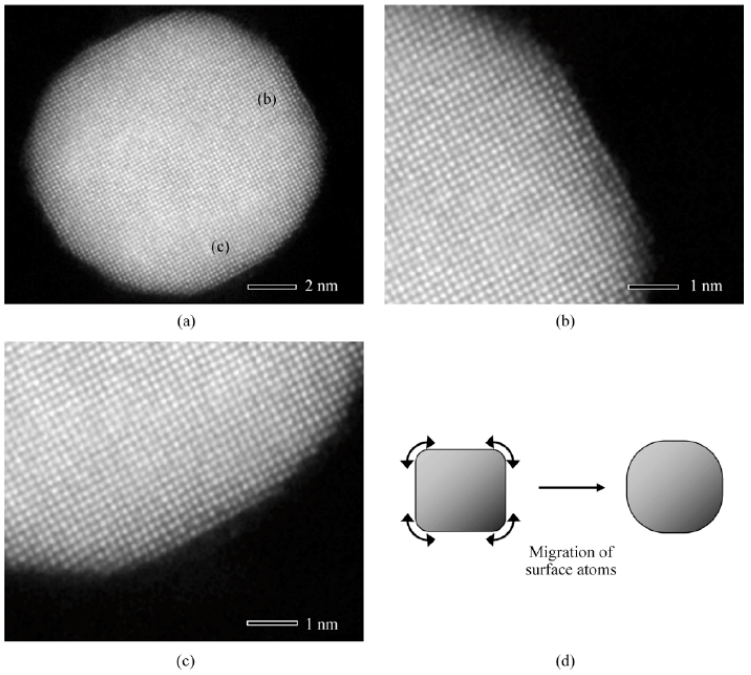

Figure 6 (a) HAADF-STEM image taken from a Pd nanobar supported on a carbon film after *in situ* annealing inside the ele microscope chamber at 500 °C for 1 h. ((b), (c)) Magnified images of the selected regions in (a). Individual Pd atoms are resolv white spots. (d) Schematic illustration of the migration of surface atoms during the annealing process