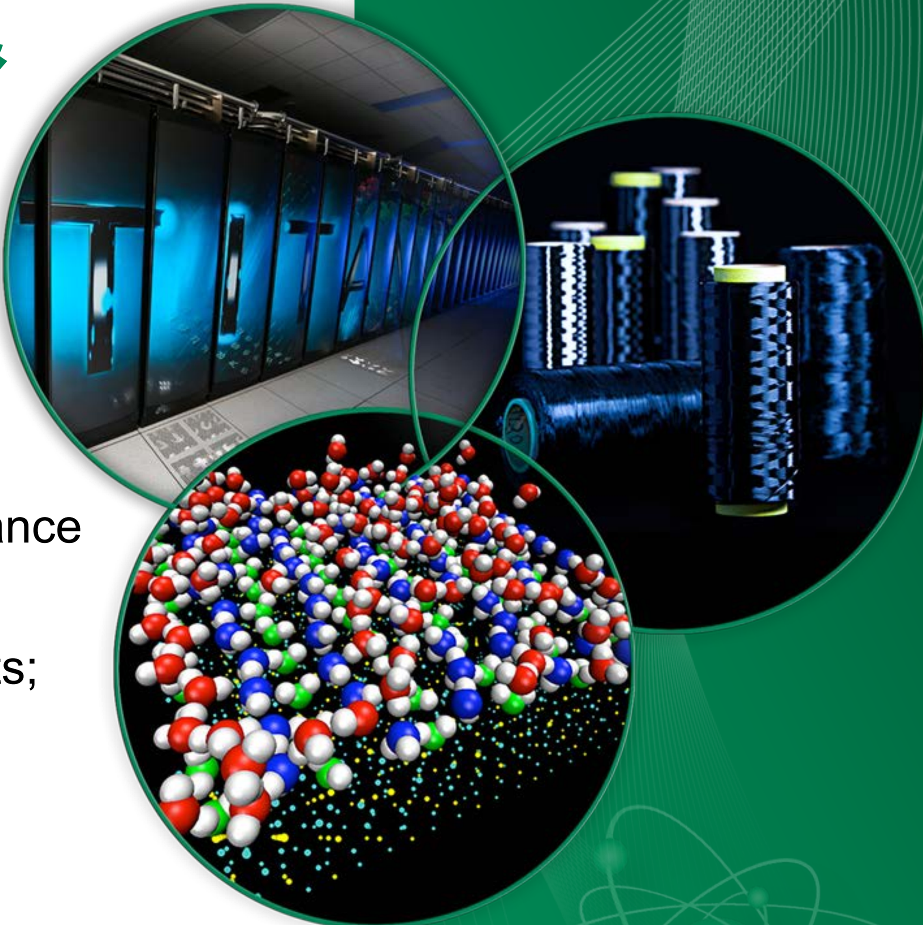
Project ID: PM049

TWO PROJECTS ON Catalyst Characterization: Agreements 9130* & 9105**

2013 DOE Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

May 14, 2013



*Thomas Watkins, Larry Allard, Michael Lance and Harry Meyer; *ORNL*

Krishna Kamasamudram and Alex Yezerets; *Cummins Inc.*

**Larry Allard; *ORNL*

Sponsored by

U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies Program

9130 Overview

Timeline

- Start: June 2002
- End: Sept. 2013
- 97% complete

Budget

- Total Project funding
  - DOE-$2.33M
  - Cummins-$2.43M
- Funding received:
  - FY12 $200k
  - FY13 $130k approved

Barriers* - Propulsion Materials Technology:

- Changing internal combustion engine regimes ➔ Optimize catalysts to minimize emissions
- Long lead times ➔ New formulations take time
- Cost ➔ Precious metal content

Barriers* - Combustion and Emission Control R&D:

- Cost-eff. emission control ➔ Understanding degradation mechanisms
- Durability ➔ Degradation/aging resistant materials needed
- Market perception ➔ Understanding improves public's acceptance

Partner

- Cummins Inc.

* Vehicle Technologies Program, Multi-Year Program Plan 2011-2015, Dec 2010, pp. 2.3-4, 5; 2.5-8.

9105 Overview

Timeline

- Start: Oct. 2007
- End: Sept. 2013
- 94% complete

Budget

- Total Project funding
  - DOE-$1.23M
  - Collaborators-$0.14M
- Funding received:
  - FY12 $98k
  - FY13 $130k approved

Barriers* - Propulsion Materials Technology:

- Changing internal combustion engine regimes ➔ Optimize catalysts to minimize emissions
- Long lead times ➔ New formulations take time
- Cost ➔ Precious metal content

Barriers* - Combustion and Emission Control R&D:

- Cost-eff. emission control ➔ Understanding degradation mechanisms
- Durability ➔ Degradation/aging resistant materials needed

Partners

- Ford Research Lab/U.Michigan
- Protochips Co.

* Vehicle Technologies Program, Multi-Year Program Plan 2011-2015, Dec 2010, pp. 2.3-4, 5; 2.5-8.

Relevance to barriers

- Impact on barriers: Experimental characterization from these projects…
  - Understanding mechanisms (why, when, where and extent) of hydrothermal aging degradation ➔ better strategies which *changes engine combustion regimes*
  - Predictable catalytic behavior ➔ design regimes to improve *durability*
  - Improved strategies minimize loss ➔ saves precious metals ➔ *cost-effective emission control*
  - Materials knowledge is needed now because of the *long lead times* required to put a material/component in place.
  - Net result of above is cleaner diesel which improves *market perception*

Relevance to Vehicle Technologies Goals

- "Advanced Combustion Engine R&D: By 2015, improve the fuel economy of light-duty diesel gasoline vehicles by 25 percent and of light-duty diesel vehicles by 40 percent, compared to the baseline 2009 gasoline vehicle."
- Efficient emission control minimizes fuel penalty.
  - With an efficient and durable SCR and AMOX catalysts, higher NOx conversion efficiencies can be attained, thus minimizing constraints on engine-out NOx emissions and allowing engines to be tuned for optimal fuel efficiency
  - Increases acceptance of clean diesel resulting in reduction in petroleum use
  - "Self-regenerating" catalyst to improve long term performance and reliability
  - First demonstration of "single atom" catalysis (e.g., for CO oxidation) determined mechanisms needed for commercial systems, reducing the amount of precious needed (e.g., 4% to 0.15%)

* Vehicle Technologies Program, Multi-Year Program Plan 2011-2015, Dec 2010, pp. 2.3-2.

Milestones FY12 & FY13

FY12:

- (9130) Begin in-situ ammonia oxidation (AMOX) catalyst characterization of a practically-relevant *zeolite catalyst* subjected to hydrothermal aging at elevated temperatures for lifetime prediction model input using x-ray diffraction or piezospectroscopy.
- (9105) Submit results in 3 refereed publications.

FY13:

- (9130) Continue in-situ evaluation of degradation of commercial AMOX catalysts and a model catalyst as a function of operating conditions (temperature, atmosphere, and time).
- (9105) Submit results in 2 refereed publications.

Technical approach/strategy:

- Experimentally characterize AMOX and SCR materials, supplied by Cummins, from all stages of the catalyst's lifecycle: fresh, de-greened, aged, regenerated, on-engine and off-engine, etc.
- Seek to understand the hydrothermal aging processes and other degradation mechanisms throughout the lifecycle of the catalytic material.
- Develop and utilize the novel in-situ heating/gas reaction techniques.
- Partner with industrial and university research teams.

...addresses barriers:

- This catalytic behavior data *changes internal combustion engine regimes*, minimizing the fuel penalties while meeting emission requirements. This **shared** information also affords *durability* and thereby reduces *cost*, resulting in more *cost-effective emission control*.

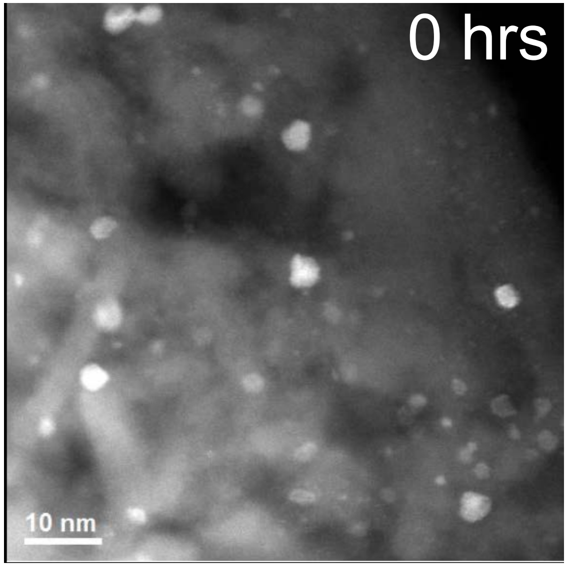
Approach/strategy: Integration within Vehicle Technologies program

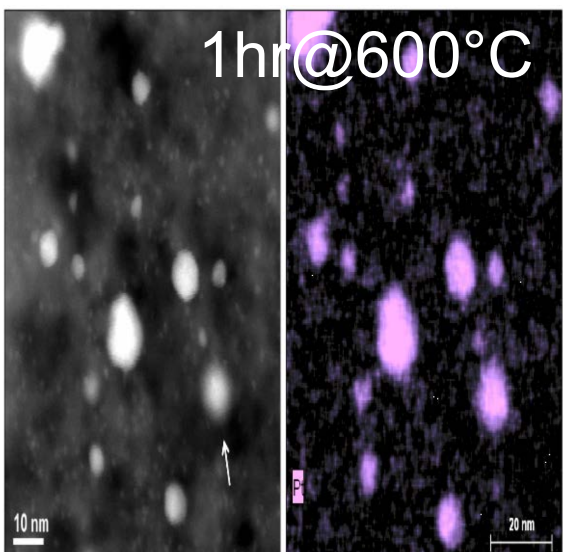
- Utilizes characterization tools acquired and formerly maintained by the High Temperature Materials Laboratory (HTML) Program.
- Developed techniques help both projects.

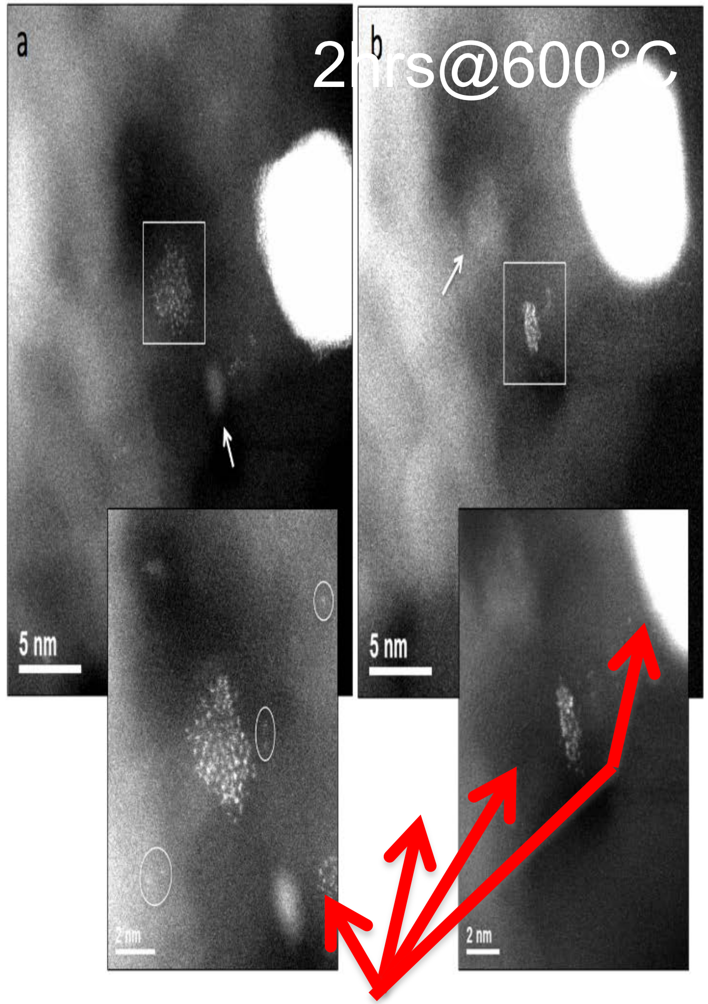
Objectives

- Produce a quantitative understanding of the process/product interdependence leading to catalyst systems with improved final product quality, resulting in emission levels that meet the prevailing emission requirements and in the minimization of the efficiency penalty.

Tech.Acc.: Pt particles/clusters in AMOx catalyst grow with increasing exposure temp in 7v%H_2O

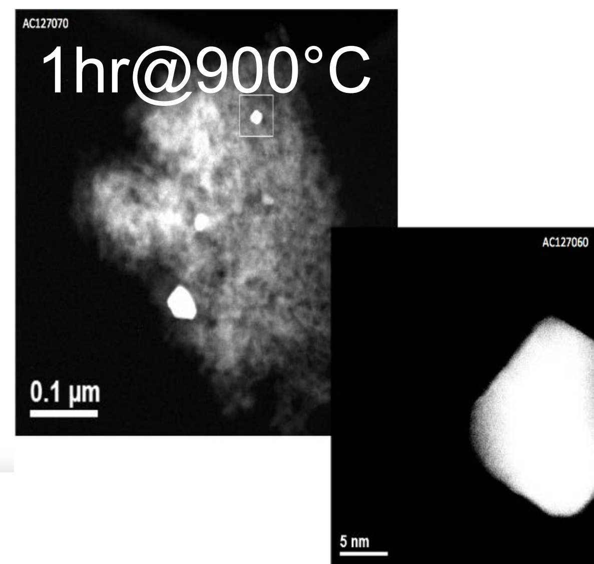






Particle size:
1-4 nm 0 hrs
5-14nm 1 hr@600°C
>20nm 1 hr@900°C
& facetted

Single atoms and clusters of Pt atoms observed

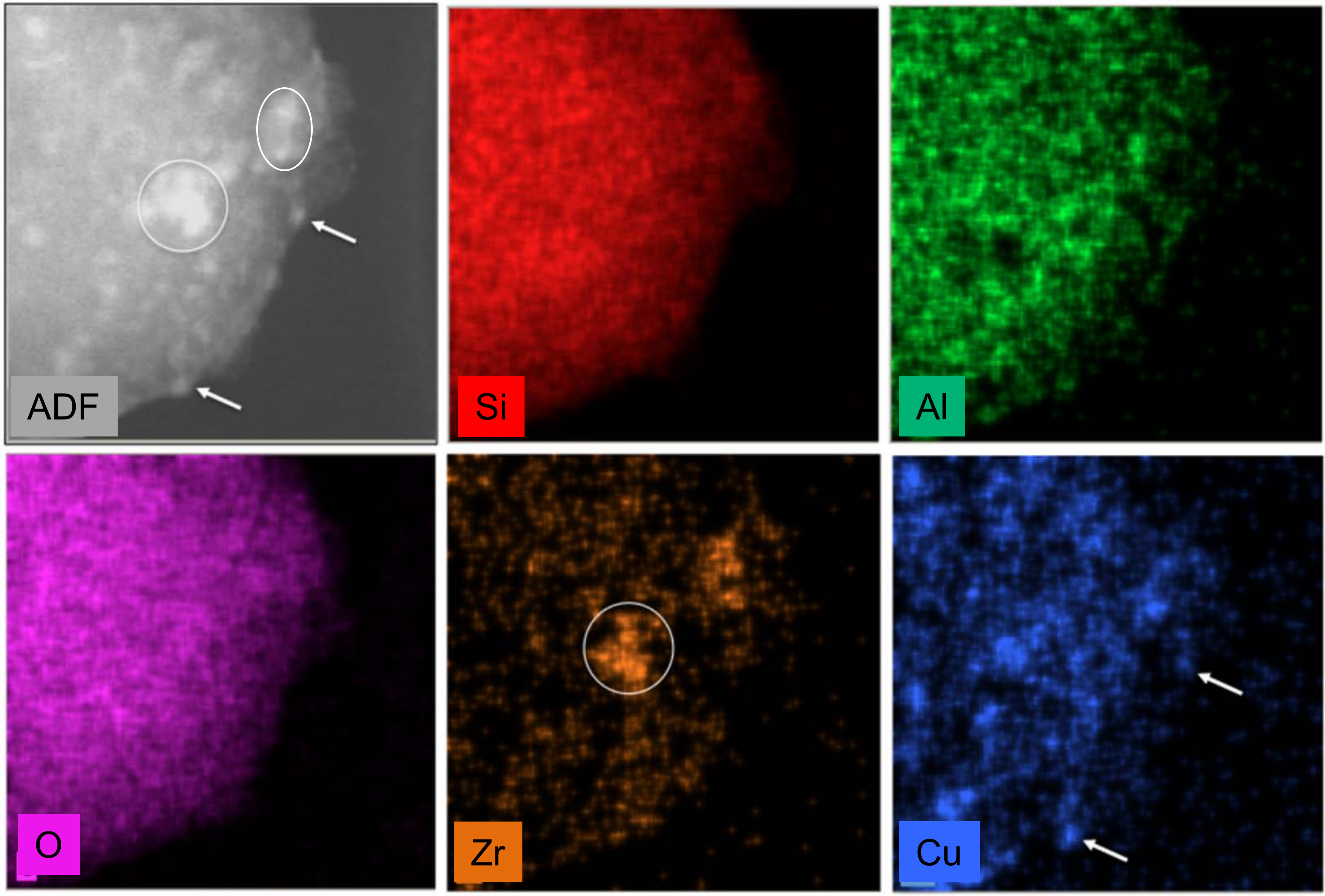


Tech.Acc.: Elemental maps from the particle show the non-homogeneous distribution of Zr and Cu on the surface.

Cu-rich particles on the surface (arrowed), and the circles show significant Zr is present (circled), likely also on the surface.

Cu, active species

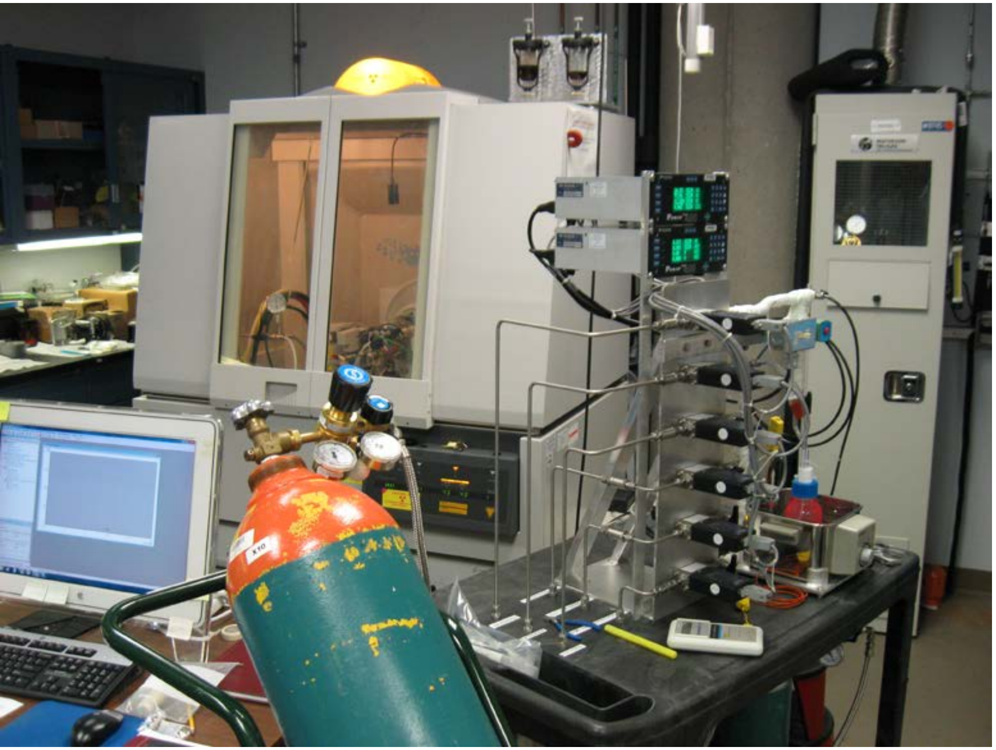
Zr (ZrO_2) may be present to help stabilize the zeolite*

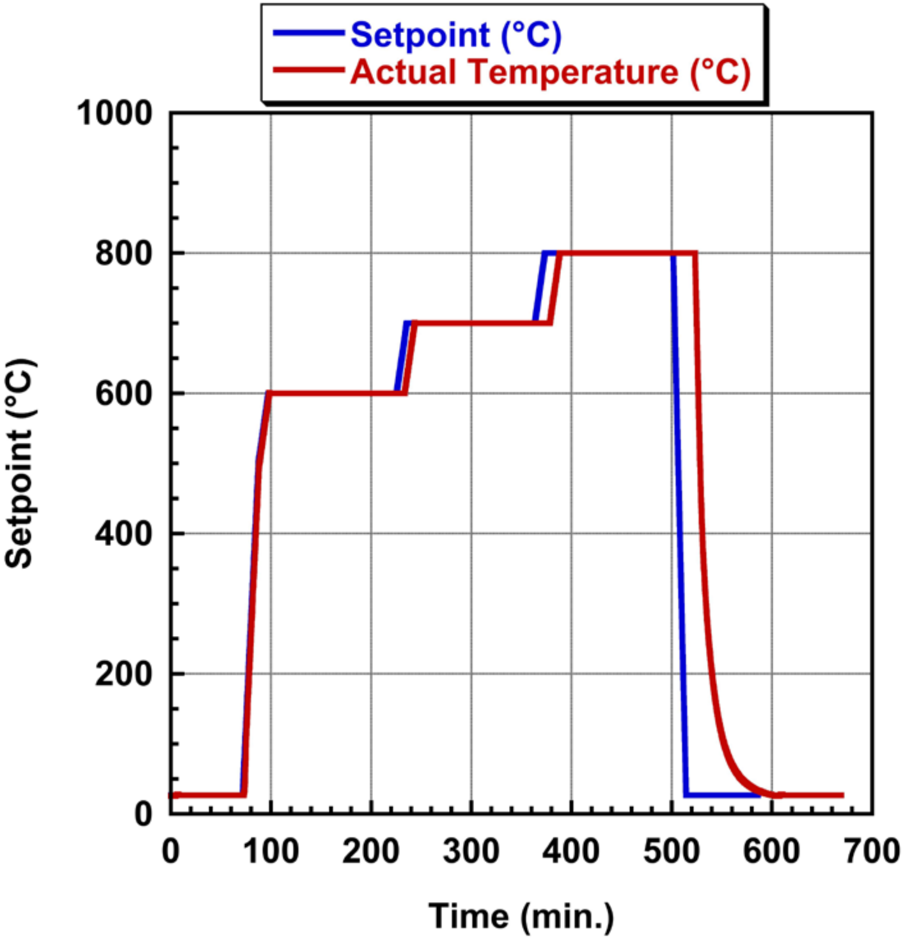


*X. Wei and S.A. Roth, US Patent Application No.2012/0079817

Tech.Acc.: In-situ HT XRD-gas manifold set-up & Hydrothermal aging temperature-time profile used for Cu-C Chabazite powder

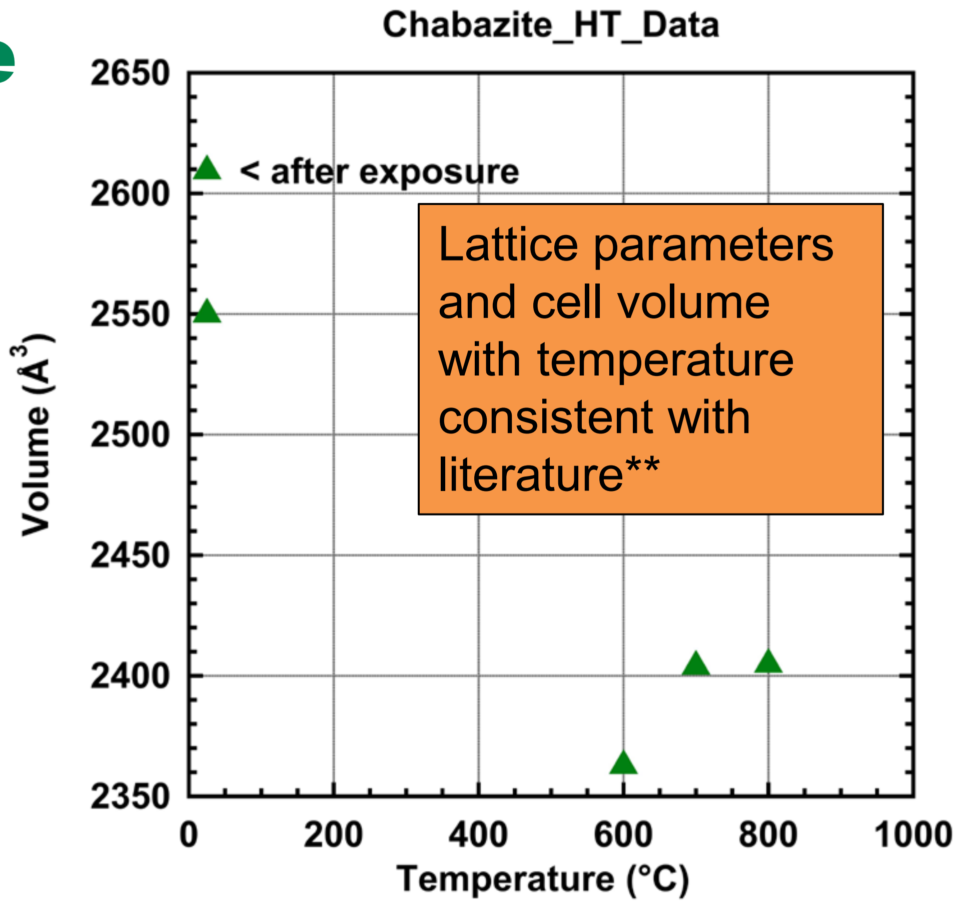
Atmosphere: 80% N_2, 10%O_2, 8%CO_2, 2v%H_2O

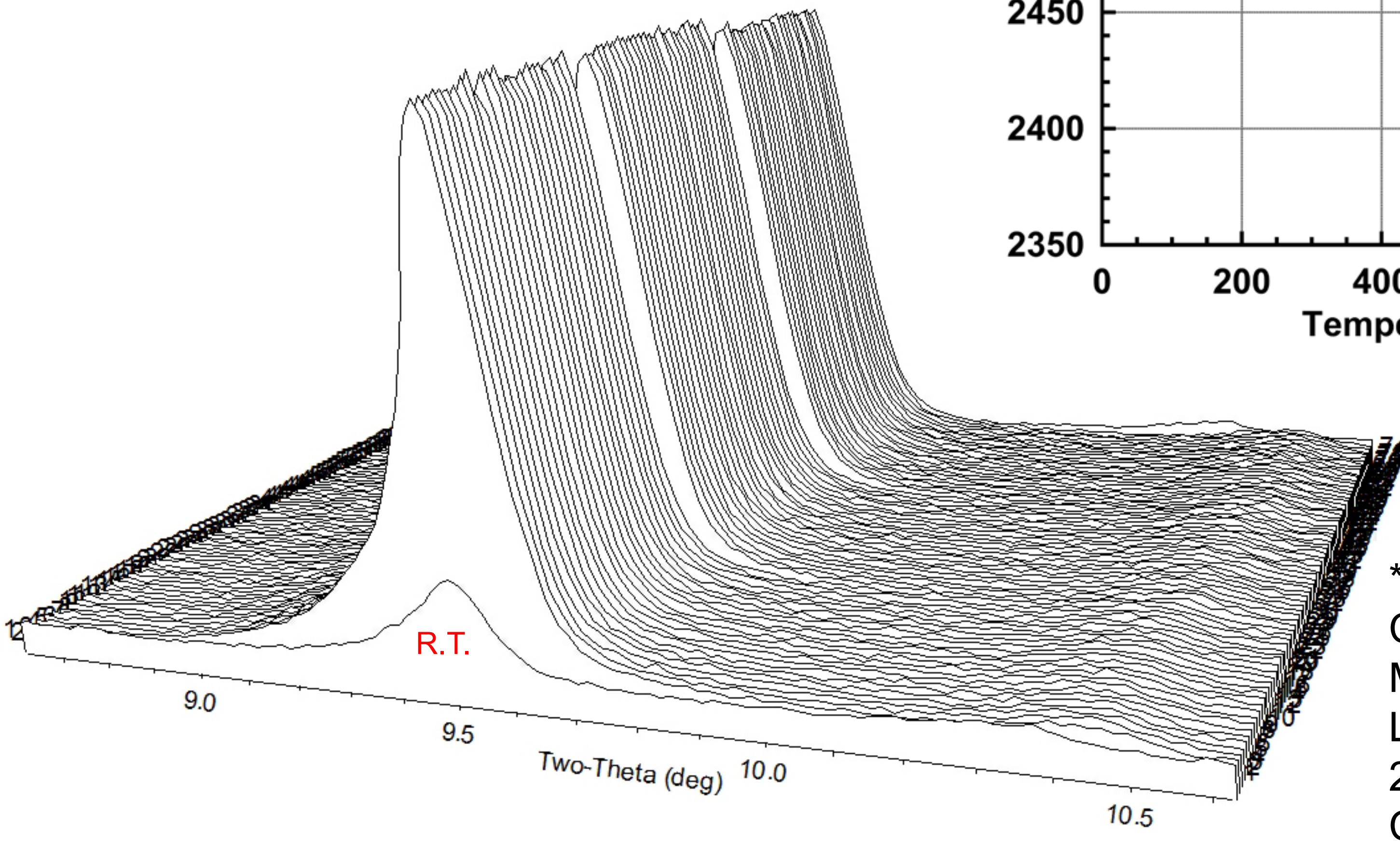




Tech.Acc.: Chabazite exhibits negative CTE*

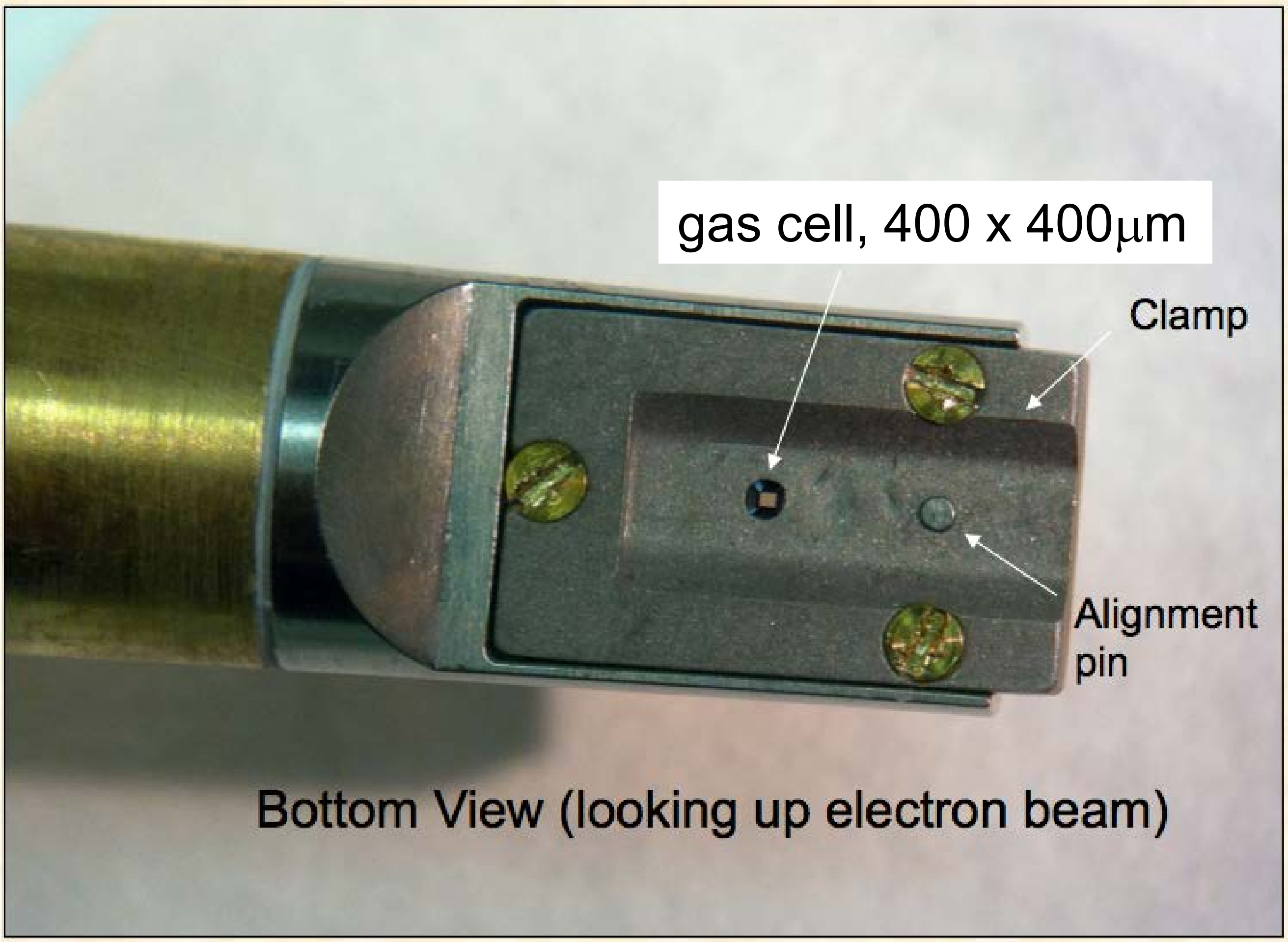
(101) intensity increase at elevated temperatures is curious; perhaps related to the de- & rehydration process.**



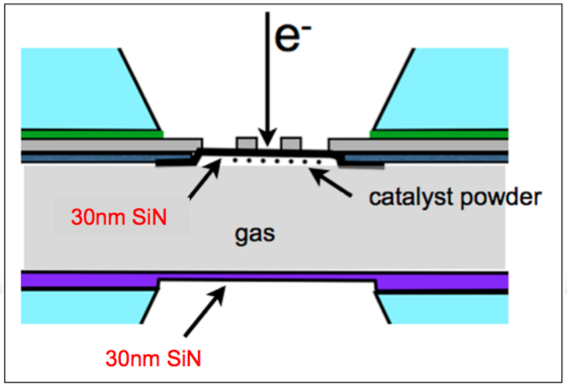


*Woodcock et al., Chem. Mater. 1999; Martínez-Iñesta and Lobo, J. Phys. Chem. B 2005;** Zema et al., Chem. Mater. 2008

Tech.Acc.: Innovative gas-cell specimen holder being developed with Protochips Inc. (Raleigh, NC) allows high-temperature gas reactions up to atmospheric pressure in oxidizing and reducing environments

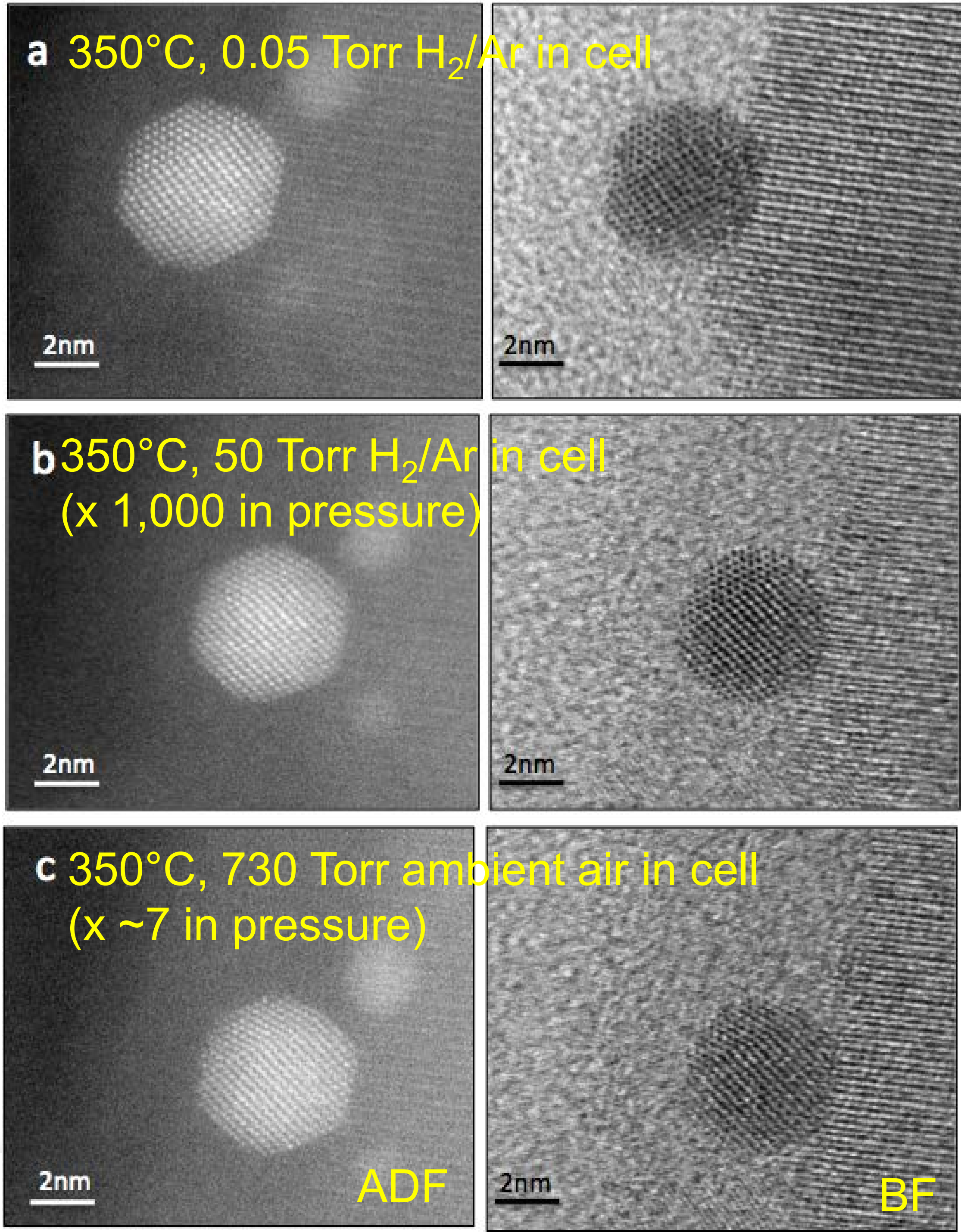


- In-situ TEM work
- RT to >1000°C
- Heat&cool 10^6°C/s
- Oxidizing or reducing atmospheres



Atomic resolution imaging of Rh nanoparticle on $CaTiO_3$ support particle

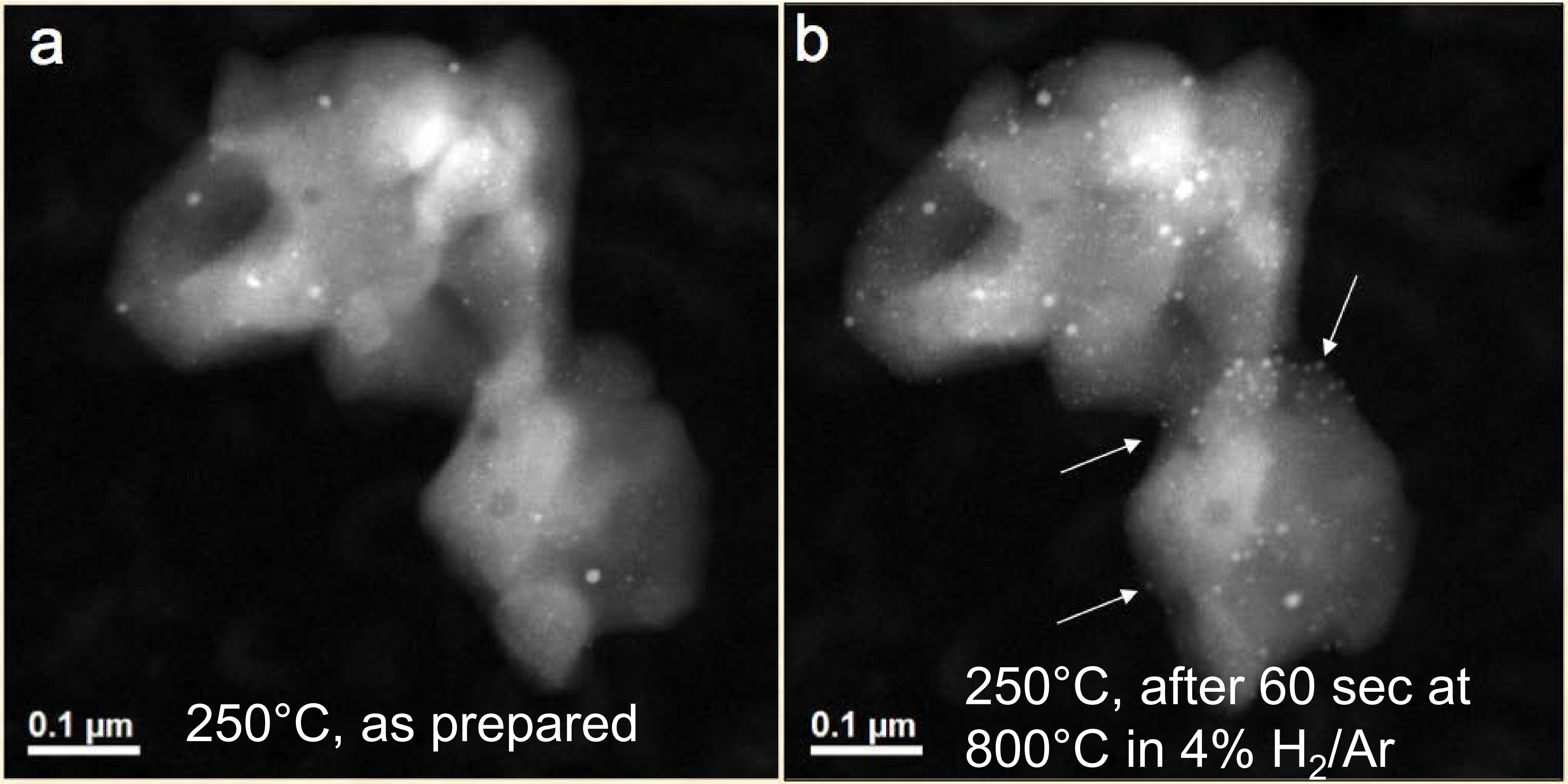
- Particle stable: atomic columns well resolved in all conditions



Tech.Acc.: Pt nanoparticles "extrude" from $CaTiO_3$ lattice onto support surface; oxidation reverses this, but slower

A few nascent Pt nanoparticles are evident.

Many new discrete nanoparticles are present, including a number on the surface (arrows).



Collaborations and coordinations with other institutions: Partners

- Ford Research Lab/U.Michigan provide samples; face to face experimental visits; telecons; publish results
- Protochips Inc. provides all the heating hardware; gas cell reaction holder; gas manifold control system; face to face visits; telecons; publish results

Collaborations and coordinations with other institutions: Tech transfer

Partner: **Cummins Inc**.

- Collaborate and guide the work along
- Supplies samples; share experimental results on samples (e.g. catalyst performance results during aging); exchange of technical information to assist with each others analyses; face to face meetings; telecons
- Information about fundamental material changes, as probed by XRD, microscopy, and other characterization tools available at ORNL, allows Cummins to optimize system operation to minimize or mitigate the overall deactivation, as well as support the development of laboratory diagnostic techniques.

Proposed Future Work (planning for projects to renew)

CRADA, 9130

- Continue to characterize catalytic materials, supplied by Cummins, from all stages of the catalyst's lifecycle: fresh, de-greened, aged, regenerated, on-engine and off-engine, etc.
- Continue in-situ studies of degradation of commercial AMOX catalysts, its SCR and oxidation catalyst components, and a model catalyst, as a function of operating conditions (temperature, atmosphere, and time).
- Initiated in-situ studies of degradation of commercial low-temperature catalysts as a function of operating conditions (temperature, atmosphere, and time).
- Complete in-situ studies of degradation of commercial low-temperature catalysts as a function of operating conditions (temperature, atmosphere, and time).

9105

- Introduce and employ the "Gen 4" gas-reaction holder and new heater device design with improved geometry
- Final calibration of heating devices in gas-cell geometry as a function of gas pressure and composition
- Continue to work with Partners on catalysts for NOx reduction

Summary

- **Relevance:** These in-situ characterizations identify mechanisms of catalytic behavior and degradation of the material systems' performance allowing strategies to be implemented to mitigate degradation which *changes engine combustion regimes*. Predictable behavior allow for better catalysts to be designed which improves *durability*. Improved strategies minimize loss, and save precious metals, *improving cost-effective emission control*.
- **Approach/Strategy:**
  - Partner with industrial (Cummins) and university research teams when such partnerships will benefit both parties.
  - Study catalytic degradation processes using in-situ and ex-situ characterization techniques.
- **Technical Accomplishments:**
  - Introduced MEMS-Based Gas-Cell/Heating stage for in-situ investigations to the microscopy community for catalyst characterizations.
  - Observed that clusters of Pt atoms in pre-particle state then form nanoparticles during hydrotreatment
  - In-situ hydrothermal aging with HTXRD stage with gas-manifold system revealed catalyst is structurally stable under modest temperatures and low water content atmosphere
- **Collaborations and Coordination with Other Institutions:** Assist Cummins and Ford to competitively produce engines which attain the required prevailing emission levels and beyond.
- **Proposed Future Work:** Continue in-situ investigations of the degradation mechanisms of catalytic materials

Technical Backup slides

Background: Exhaust Aftertreatment

- Ammonia containing compounds added to diesel exhaust to reduce NO_x to N_2
  - e.g., $NH_3 + NO + 1/4O_2 \Rightarrow N_2 + 3/2H_2O$
  - Excess ammonia is often needed resulting in NH3 escaping or “slip”
  - This ammonia must be removed by a secondary step.
- NH_3 slip is currently not regulated in US, however for sociability and environmental reasons, Cummins chose to use Ammonia Oxidation (AMOX) Catalyst* device to ensure that ammonia slip to ambient is minimal
- An AMOX catalyst can be used to convert the NH_3 slip to N_2 + H_2O
  - Candidate catalysts: zeolite-based and alumina-supported metal or metal oxide catalysts
  - Temperature and water content play a big role in the functioning and aging of these catalysts

*** Also called Selective catalytic oxidation (SCO) or Ammonia Slip catalyst (ASC)**

What is a zeolite?*

- Classical definition: a crystalline, porous aluminosilicate
- Current definition: porous oxide structures with well-defined pore structures and a high degree of crystallinity
- Large number of structures possible
- Pores/Channels-molecular sieves

* www.personal.utulsa.edu/~geoffrey-price/zeolite/zeo_narr.htm

Chemical interactions of zeolites

- Si-O4 tetrahedra and $(Al\text{-}O4)^{-1}$ tetrahedra
  - Charge compensation with cations in pores
- Uses:
  - Ion exchange as in water softeners
  - Cation=H+, becomes a strong acid-catalytically active
  - Other metal cations-shape selective catalysis

* www.personal.utulsa.edu/~geoffrey-price/zeolite/zeo_narr.htm

Summary: our work supports many entities…