Catalyst Characterization
CRADA No. ORNL-02-0659 with Cummins, Inc.

Principle Investigators:

Thomas Watkins, Larry Allard, Doug Blom, Michael Lance, Chaitanya Narula and Harry Meyer - ORNL
Roger England, Howard Fang and Tom Yonushonis -Cummins, Inc.
Howard Hess - Johnson Matthey
Presenter: Roger England, Catalyst Elements Leader, Cummins, Inc

September 13, 2005

PM_9130

This presentation does not contain any proprietary or confidential information

Catalyst Characterization

21CTP

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.

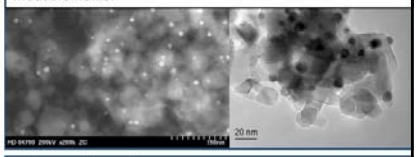
Project Objectives
Developing Tools for State of the Art Characterization on Diesel Catalysts, both from reactor and engine testing, allowing validation of testing techniques.

FY 2005 Focus
Measurement & characterization of the surface features of diesel catalysts, including correlating these attributes directly to fuel economy measurements.

Planned Duration
October 2002 to September 2006

DOE Funding/Industry Cost Share
FY04: $200K/$200K; FY05: $200K/$200K

TEM allows resolution of particles of specific active elements and provides size & distribution statistics, which have been directly correlated to X-ray diffraction and Raman measurements.



Principal Investigators
Thomas Watkins, Oak Ridge National Laboratory
(865) 574-2046; watkinstr@ornl.gov
Roger England, Cummins
(812) 377-7573; Roger.D.England@Cummins.com

Technology Development Manager
Sid Diamond, DOE/OFCVT
(202) 586-8032; sid.diamond@ee.doe.gov

Accomplishments
- Characterized the size and location of light elements on the catalyst surface that had previously not been observed (9/04).
- Measured the particle size and distribution of Pt on the surface of the catalyst non-destructively with Raman and X-ray diffraction and correlated the measurements to TEM data (9/03).

Significant Future Milestones
Characterization of the active elements on the surface of a engine aged catalyst as a function of time to quantify the degradation mechanisms and allow direct comparison of washcoats. (9-06)

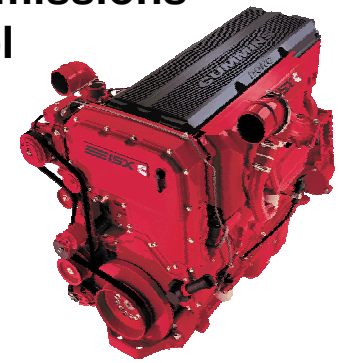
Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
PM_9130	Materials Technology	HV Propulsion Materials	Applied Research	8_15

Objective

- The overall objective of this effort is to produce a quantitative understanding of the processing and in-service effects on NOx adsorber catalyst technology leading to an exhaust aftertreatment system with improved catalyst performance capable of meeting future emission requirements.
- FY05: Evaluation of gradient formation on a macro scale of active elements on a catalyst as a function of catalyst history and operating conditions

The Right Technology Matters … in Emissions Control

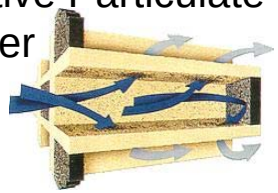
- Integrating critical subsystems
  - Combustion
  - Air handling
  - Fuel systems
  - Electronic controls
  - Aftertreatment



… to deliver best customer value at low emissions

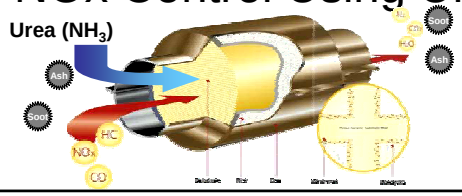
Next Critical Subsystem: Exhaust Aftertreatment

Active Particulate Filter



NOx Adsorber

NOx Control Using Urea SCR



Fleetguard EMISSION Solutions™

Approach

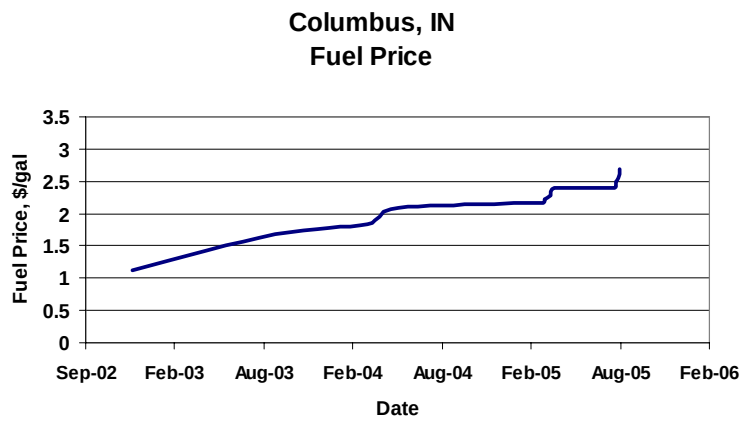
- Experimentally characterize materials, supplied by Cummins, from all stages of the catalyst's lifecycle: raw materials, as-calcined, sulfated, regenerated, etc.
- Determinations include: crystal structure, morphology, phase distribution, particle size and surface species of catalytically active materials.
- Seek the atomic mechanisms and chemistry of adsorption and regeneration processes
- Seek to understand the poisoning processes throughout the lifecycle of the catalytic material.

21 CT Technology Goals addressed by this project

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.
  - Overcome potential fuel penalties from exhaust aftertreatment
  - Enable development of significantly higher fuel efficiency in commercial vehicle engines

Customer Incentives are not Static



Technical Accomplishments / Progress / Results

- Rate of increase of size of Pt particles was not observed to increase along the length of catalyst.
- XRD and TEM crystallite size results did NOT agree.
  - Disagreement can be explained by the overlapping alumina peaks in the XRD pattern.
- Raman spectroscopy was used to monitor sulfation in-situ and calculate activation energies of sulfation.

Results: X-ray diffraction (XRD) peak width related to the crystallite/cluster size

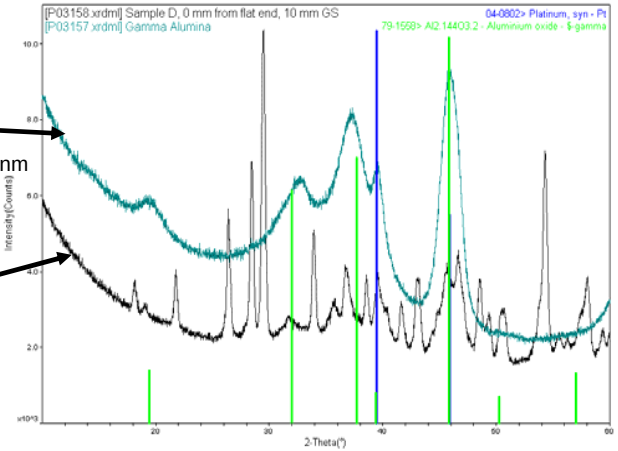
- A crystallite is a region of coherent diffraction.
  - Minimum number of atoms with structured order necessary.
  - Crystallites can be thought of as sub-grains, which are very small perfect single crystals.
- Typically, the crystallite size is smaller than the grain size of a material as observed on the SEM.
- Significant contributions to peak broadening if crystallite size < 0.1 μm.

Model System: Gamma Al_2O_3/Pt on Cordierite.

As-received gamma Al_2O_3 powder

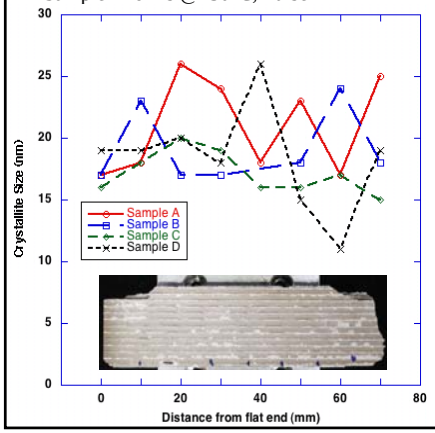
Crystallite size = 3nm

Sample D-6 hrs @ 450°C, Pulse

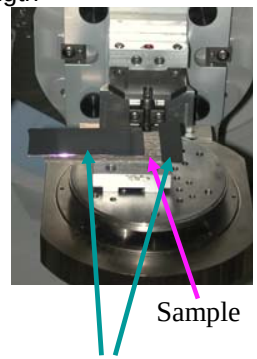


Aged Alumina Crystallites Growth Rate

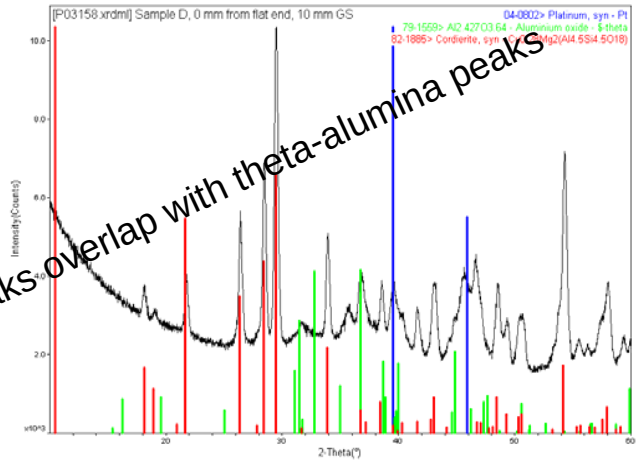
Sample A-Baseline
Sample B-6 hrs @350°C, Pulse
Sample C-6 hrs @350°C, Pulse, Low Volume
Sample D-6 hrs @450°C, Pulse



- Change in crystallite size indicates surface area lost
- No trends observed along length

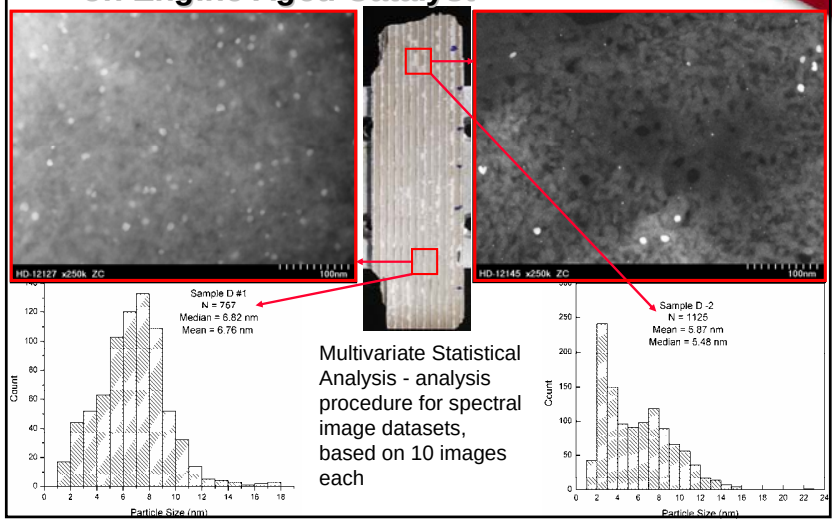


Gamma Alumina to Theta Alumina Transformation Identified



Pt peaks overlap with theta-alumina peaks

Pt Axial Distribution and Size on Engine Aged Catalyst



Multivariate Statistical Analysis - analysis procedure for spectral image datasets, based on 10 images each

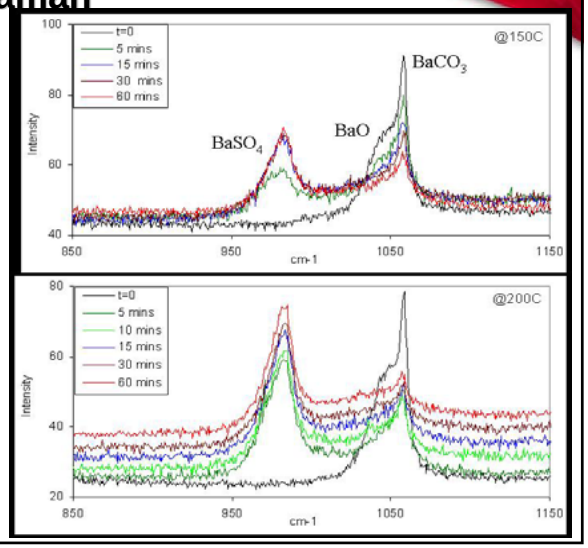
Spectroscopy techniques employed to characterize the adsorbed species

- X-ray Photoelectron Spectroscopy (XPS)
- Raman spectroscopy: Focus
  - Raman spectroscopy measures the characteristic vibrational energy levels of molecules and crystals; very sensitive to any changes in bonding, stoichiometry and phase/symmetry.

Sulfation Measured via Raman

Test conditions were 10 ml/min of 1000 ppm SO_2 in air on $BaO/1\%Pt/Al_2O_3$

Sulfation rate increases as a function of temperature



Sulfation Activation Energies Calculated from Raman Data

O2 Present?	Pt Present?	BaO	BaCO3
No	No	17.8	25.4
No	Yes	11.0	17.9
Yes	No	11.6	15.9
Yes	Yes	7.4	13.1

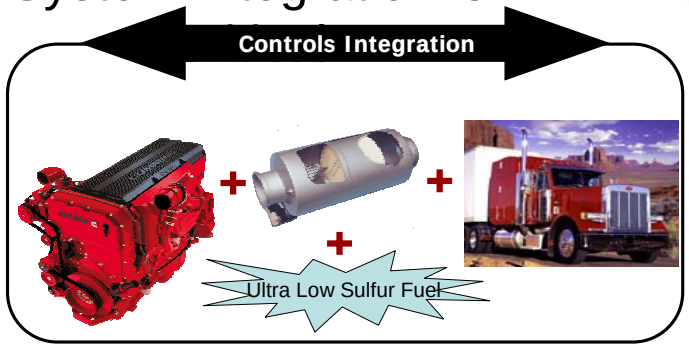
kcal/mol

- Pt reduces the activation energy.
- Oxygen reduces the activation energy.
- Sulfation of BaO is easier than $BaCO_3$

Technology Transfer

- **Timeline: As characterization tools and results come online they are <u>immediately</u> available to Cummins and Johnson Matthey (JM) engineers for application on current and future product.**
- JM joined the project in 2005 after selection as Cummins' supplier partner for aftertreatment technology.
- JM is a leading global supplier of catalyst materials.
- JM has full-time staff on-site at CTC to facilitate technology transfer.

System Integration is

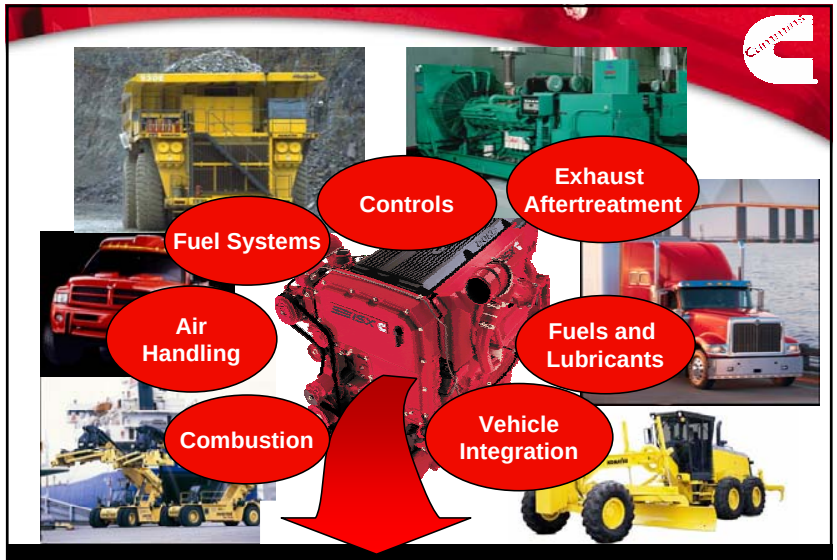


Vehicle, engine, aftertreatment and fuel…

a single system designed to optimize fuel economy, performance, reliability, cost … and emissions

Future Work

- We are populating our tool box.
  - The new microscopy capabilities at the HTML are very promising, we are anxious apply to our catalysts.
  - We need to move to synchrotron radiation to resolve the alumna peaks from the platinum.
  - We are developing technology enablers that will allow us to move into areas of catalyst engine interactions that were previously only theory.
  - The tools that we are developing with the HTML allow us to actually verify our theories, and add rate equations to our models, and use analysis led design to provide the right technology for each engine application and duty cycle.



Industry, universities and national laboratories must work together for our customers to deliver <u>The Right Technology</u>

Publications & Presentations

1. J. Parks, A. Watson, B. Epling, L. Campbell, R. England, N. Currier, A. Yezerets, H. Fang, T. Yonushonis, T. Gallant, T. Watkins, D. Blom, L. Allard, M. Lance, H. Meyer, C. Narula, "NOx Adsorber Catalyst Durability: Light- and Heavy-Duty Perspective," presented by J. Parks at the 9th Diesel Engine Emissions Reduction (DEER) Conference, Newport, Rhode Island, August 28, 2003.

2. T. R. Watkins, L. Allard, D. Blom, M. J. Lance, C. Narula, H. Meyer, R. D. England, H. Fang, and T. Yonushonis, "Development of Materials Analysis Tools for Studying NOx Adsorber Catalysts," (A.) presented at NLCat 2003, Oak Ridge, TN, October 23, 2003; (B.). presented at the 53th Annual Denver Conference, Steamboat Springs, CO, August 2, 2004; (C.) presented at the10th Diesel Engine Emission Reduction (DEER) Conference, Coronado, CA, August 30, 2004.

3. T. R. Watkins, L. Allard, D. Blom, M. J. Lance, H. Meyer, L. Walker, C. Narula, R. D. England, Bill Epling, H. Fang, and T. Yonushonis, "Development of Materials Analysis Tools for Studying NOx Adsorber Catalysts," [Revised] presented at 11th Diesel Engine Emission Reduction (DEER) Conference, Chicago, IL, August 24, 2005.

4. H. L. Fang and M. J. Lance, "Influence of Soot Surface Changes on DPF Regeneration," accepted for publication in J. Soc. Auto. Eng. (2004).

5. Howard L. Fang, Michael J. Lance, and Gayle S. Painter, "Raman Characterization of Pt-support Interactions on Metal Oxides," in preparation.