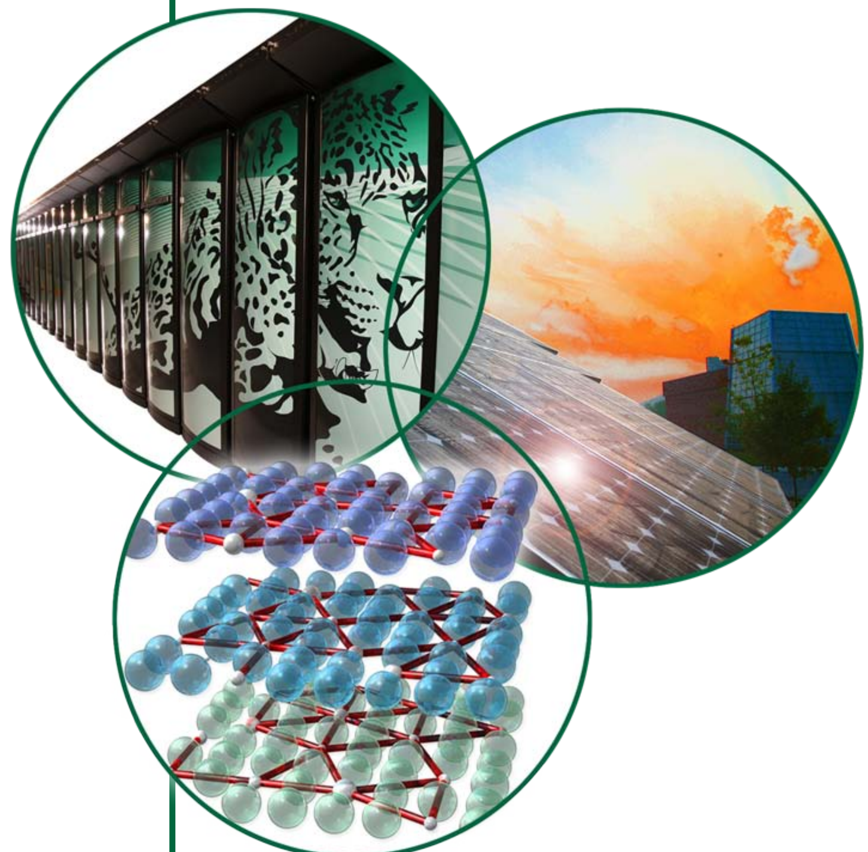
Catalyst Characterization

2010 DOE Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

June 10, 2010



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

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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)

Overview

Timeline

- Start: June 2002
- End: Sept. 2012
- 78% complete

Budget

- Total Project funding
  - DOE-$2.2M
  - Contractor-$2.3M
- Funding received:
  - FY09 $196k
  - FY10 $147k

Barriers* - Advanced Combustion Engine Research: Emission Control System

- Poor durability → materials degradation/aging
- Numerous components
- Costly precious metal content

Partners

- Cummins Inc.
- Johnson Matthey

* FreedomCar and Vehicle Technologies Program, Multi-Year Program Plan 2006-2011, Sept 2006, pp. 3.4-10, 21.

Objective

- The purpose of this effort is to produce a quantitative understanding of the process/product interdependence leading to catalyst systems with improved final product quality, resulting in diesel emission levels that meet the prevailing emission requirements.

Milestones

- **Milestone09: Complete evaluation of feasibility of the advanced tools available at ORNL for quantitative analysis of the materials changes underlying the selective catalytic reduction catalyst performance degradation with age.**

- **Milestone10: Initiate evaluation of feasibility of the advanced tools available at ORNL for quantitative analysis of the materials changes underlying the AMOX catalyst performance degradation with age.**

1 Approach: Technical

- Focus on AMOX materials with the practically-relevant properties
- Experimentally characterize materials, supplied by Cummins, from all stages of the catalyst's lifecycle: fresh, de-greened, aged, regenerated, on-engine and off-engine, 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 thermal and hydrothermal aging processes and other degradation mechanisms throughout the lifecycle of the catalytic material.

2 Approach: Relevance to barriers & Integration

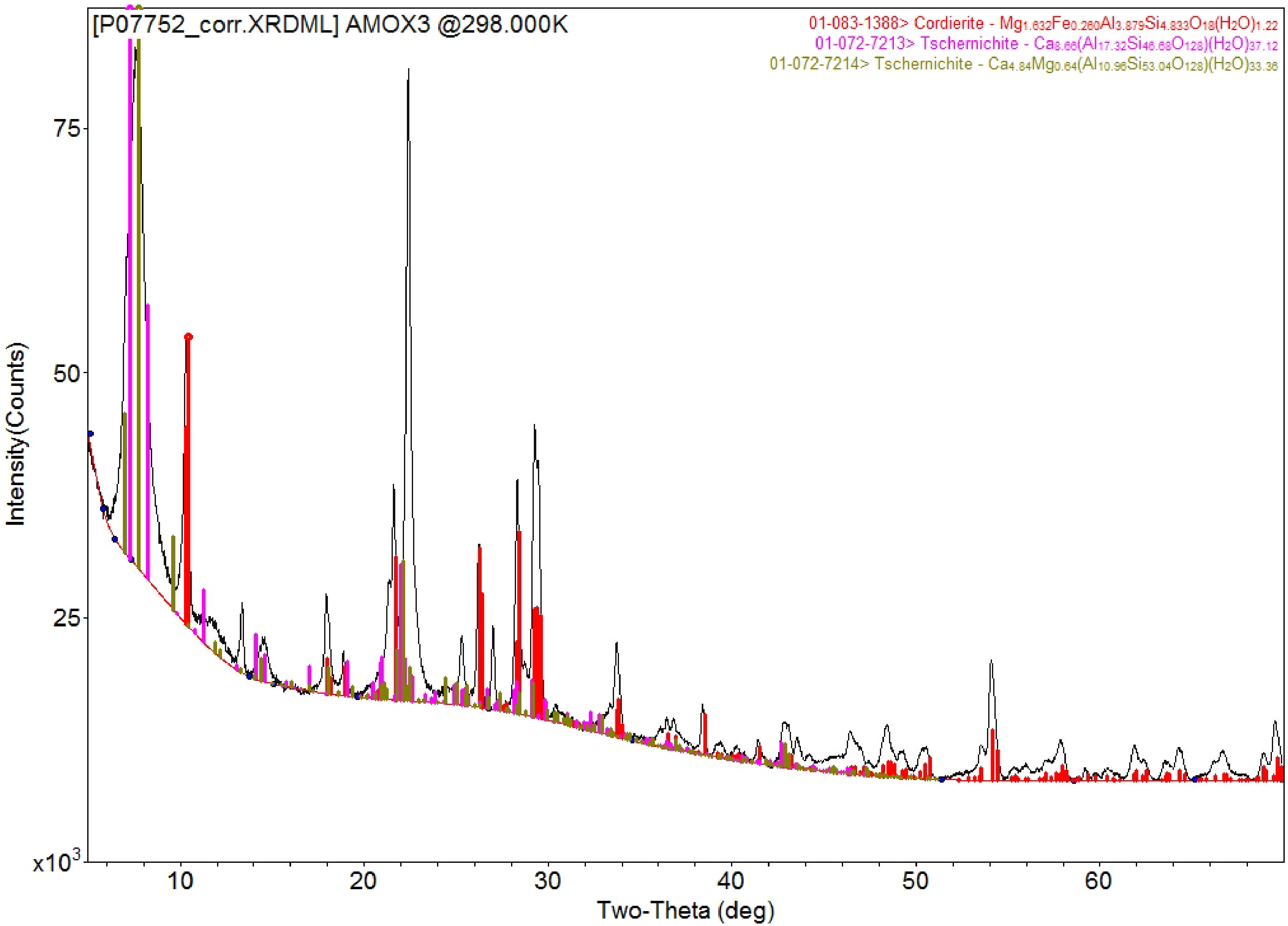
- Impact on barriers: Experimental determination…
  - Of why, when, where and extent of hydrothermal aging degradation on the material system's performance. Understanding mechanisms allows new engine strategies to mitigate aging. Also, better catalysts can be designed.
  - Input for design for fewer, multi-functional components
  - Improved strategies minimize functional loss, save precious metals
- Integration within Vehicle Technology program:
  - Utilizes characterization tools acquired and maintained by the High Temperature Materials Laboratory (HTML) Program

3 Approach: Relevance to Vehicle Technologies Goals

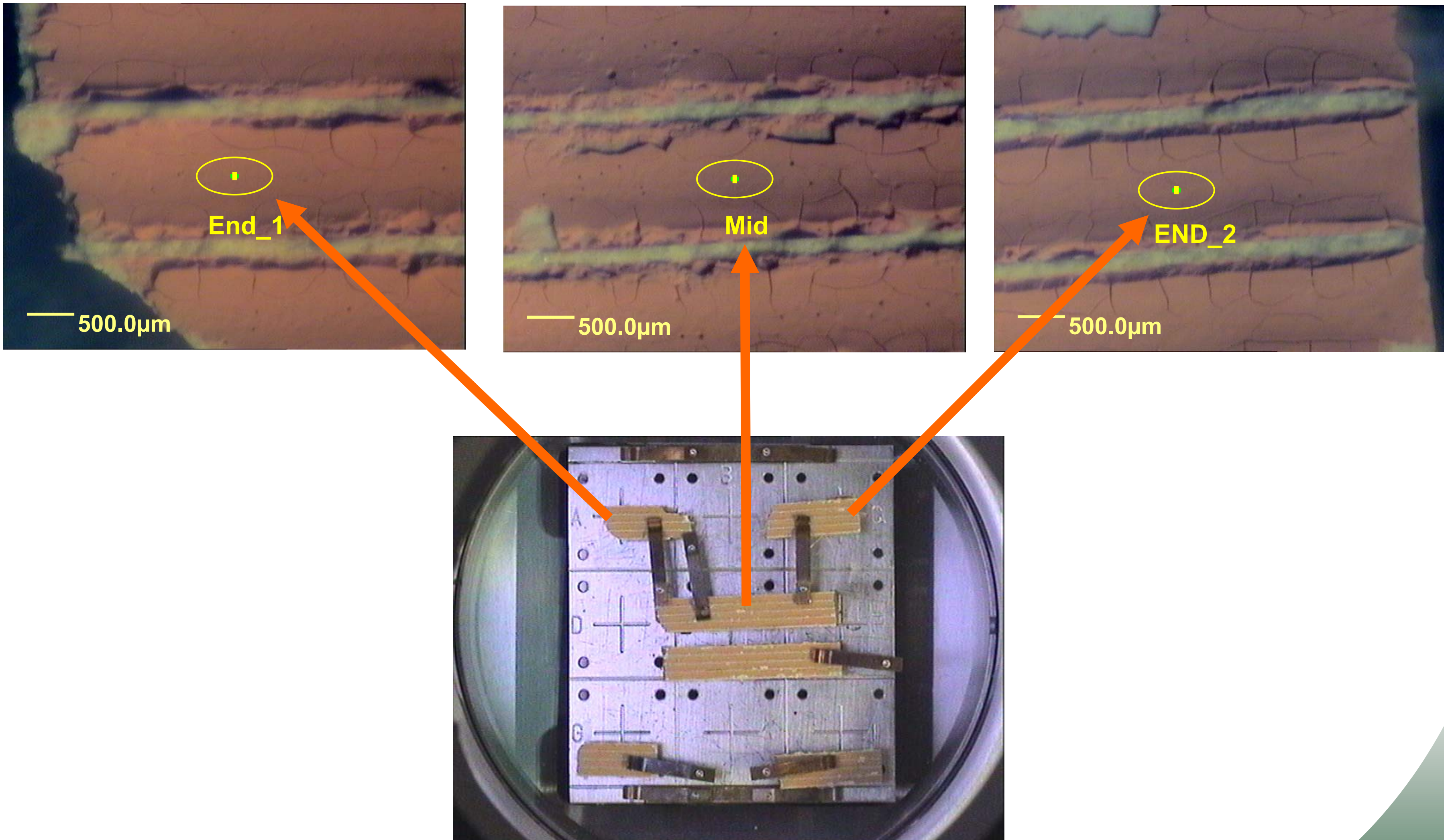
- **Improve commercial vehicle engine efficiency at least 20%**
  - With an efficient and durable AMOX, higher NOx conversion efficiencies can be attained, thus minimizing constrains on engine-out NOx emissions and allowing engines to be tuned for optimal fuel efficiency, cost and durability

- **Achieve engine system cost, durability and emissions targets**
  - See above

X-Ray Diffraction: AMOX catalyst is a Zeolite on a cordierite substrate



X-ray Photoelectron Spectroscopy: Split core layout inside sample chamber

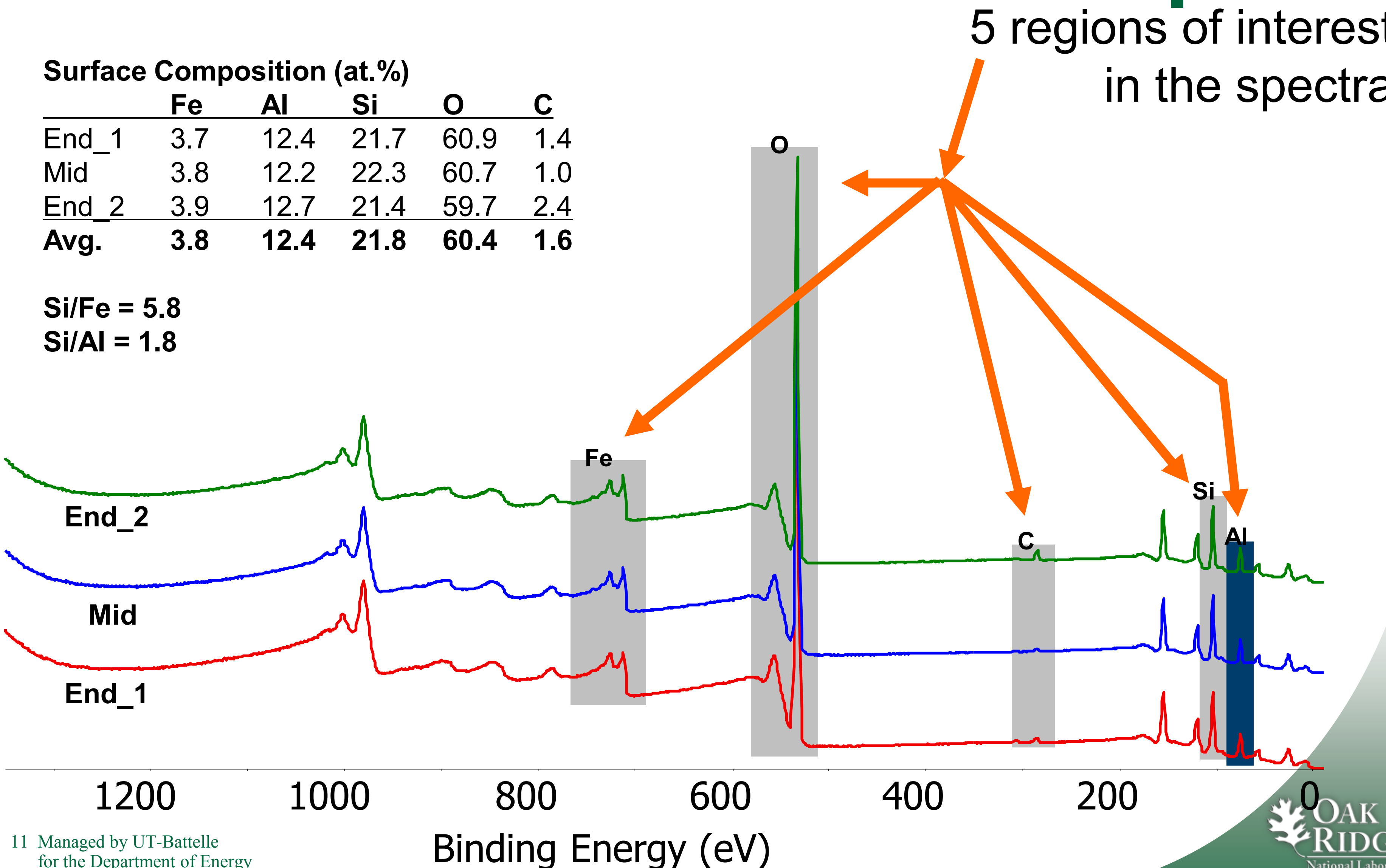


X-ray Photoelectron Spectroscopy: shows composition and valence at the 3 locations of as-received AMOX sample

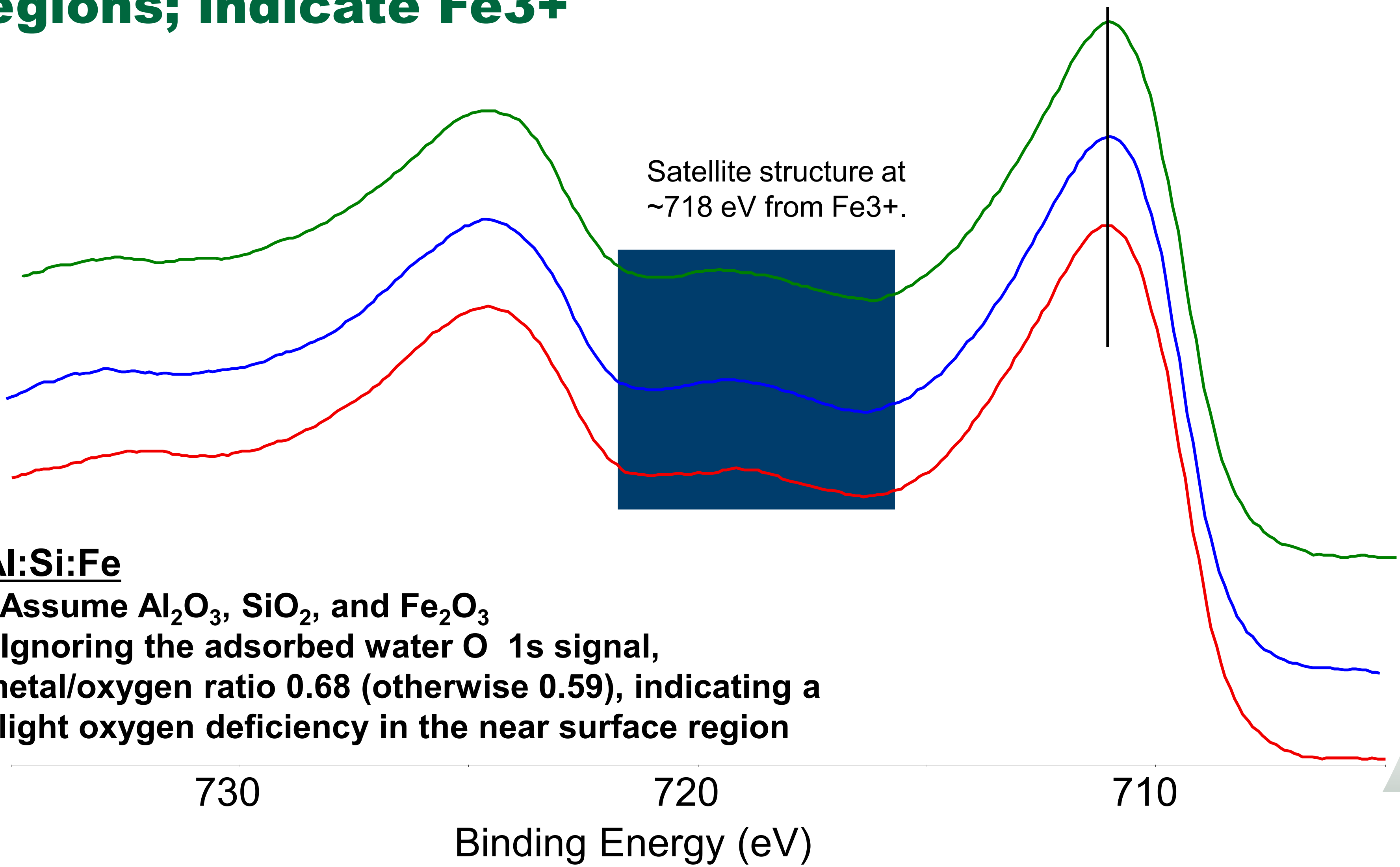
Surface Composition (at.%)

	Fe	Al	Si	O	C
End_1	3.7	12.4	21.7	60.9	1.4
Mid	3.8	12.2	22.3	60.7	1.0
End_2	3.9	12.7	21.4	59.7	2.4
Avg.	**3.8**	**12.4**	**21.8**	**60.4**	**1.6**

Si/Fe = 5.8
Si/Al = 1.8



X-ray Photoelectron Spectroscopy: Fe 2P core level spectra are identical for all 3 sample regions; indicate Fe3+

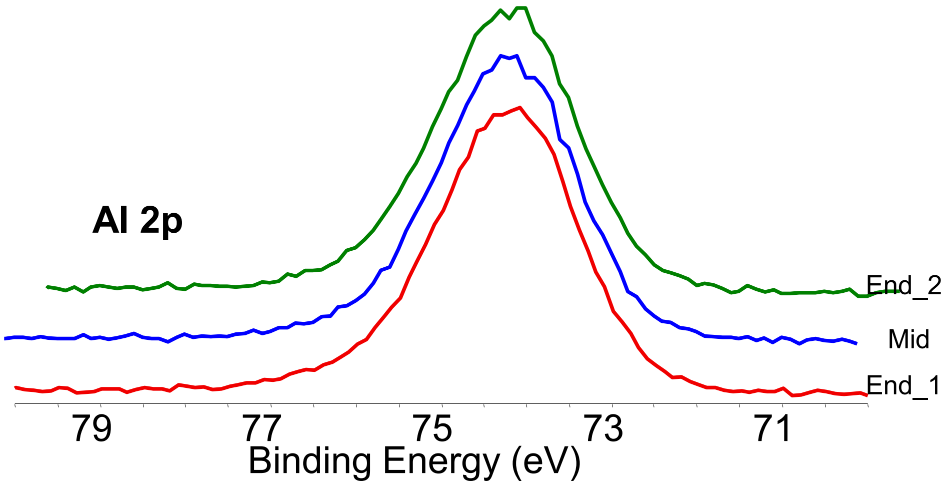


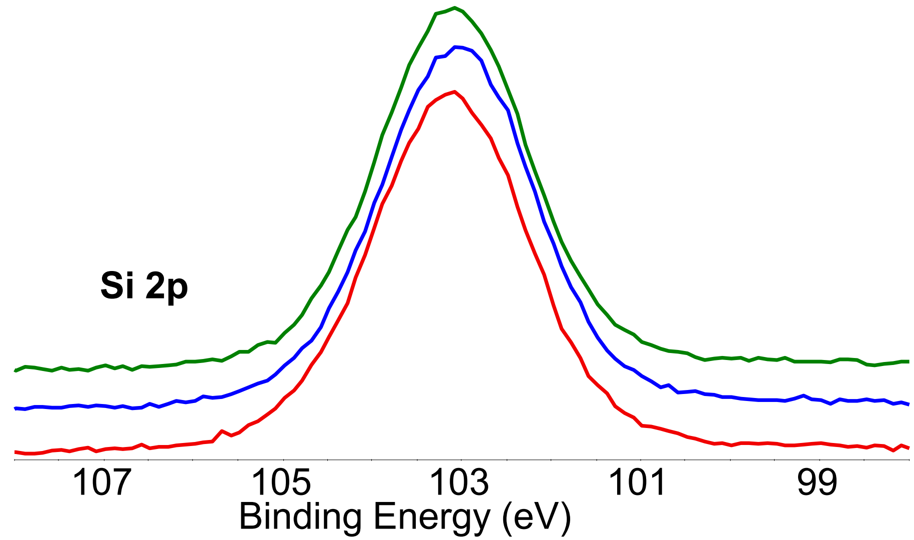
<u>Al:Si:Fe</u>

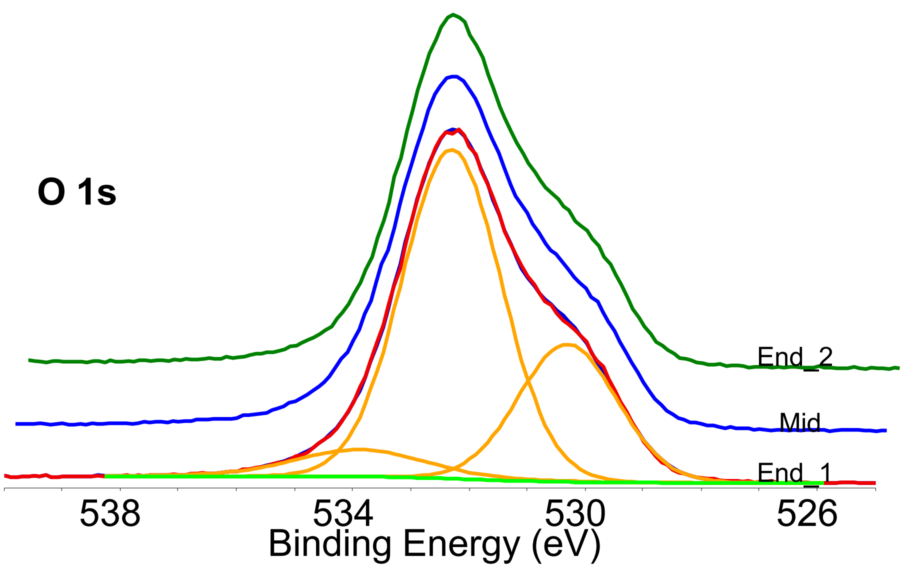
- **Assume Al_2O_3, SiO_2, and Fe_2O_3**
- **Ignoring the adsorbed water O 1s signal, metal/oxygen ratio 0.68 (otherwise 0.59), indicating a slight oxygen deficiency in the near surface region**

- AMOX zeolite shows significantly higher Fe conc. than former SCR samples
- Facilitate detection and characterization of the Fe species by TEM techniques.

X-ray Photoelectron Spectroscopy: Si 2P, Al 2p & O 1s core level spectra also identical for all 3 sample regions; consistent with literature for zeolites



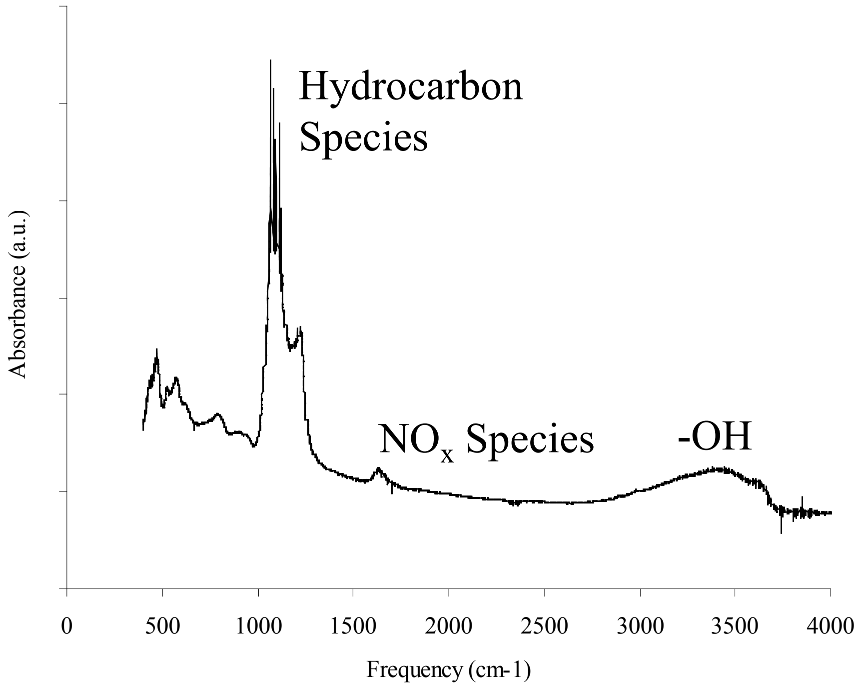




<u>O 1s spectrum</u>

- **Al-O/Si-O bond (~532 eV)**
- **Fe-O bonding (~530 eV)**
- **adsorbed water/-OH (~534 eV).**

Fourier Transform Infrared Spectrum of as-received Fe-Zeolite/AMOX catalyst



Collaborations and coordinations with other institutions

- **Partners**
  - Cummins Inc. (Industry): 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 at least 2X/year
  - Johnson Matthey (Industry): exchange of technical information
- **Tech transfer**
  - Provide guidance for system design, cost (reduce precious metal content, and optimization.
  - Reduce materials and functionality margins for related to catalyst aging.

Future Work

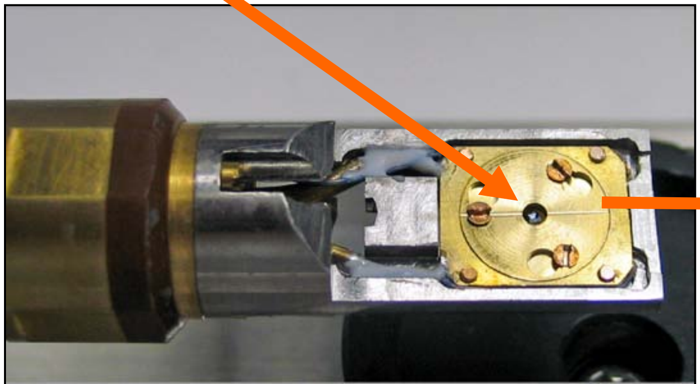
- **Continue ammonia oxidation (AMOX) catalyst characterization of a practically-relevant *zeolite catalyst* subjected to hydrothermal aging for lifetime prediction model input. Utilize new in-situ capabilities.**

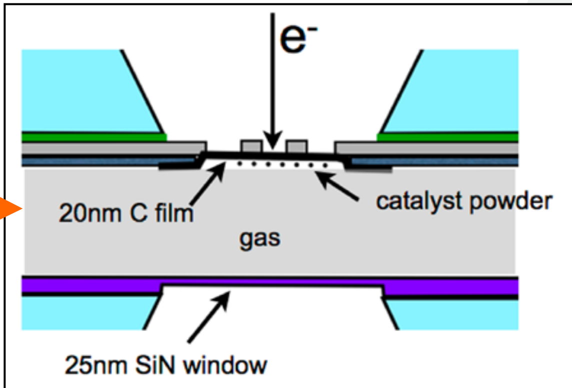
- **Focus on understanding the catalyst degradation mechanisms due to hydrothermal aging using the tools developed under this CRADA (FY10).**

- **Assist Cummins to competitively produce engines which attain the required prevailing emission levels and beyond while maintaining the advantage of the diesel's inherent energy efficiency (FY10 & FY11).**

Summary

- **Through 2009, progress has been slowed considerably due to sample unavailability because of the 2010 product launch focus.**
- **Samples received in January 2010**
- **X-Ray Diffraction, Transmission Electron Microscopy (TEM), Diffuse Reflectance Infra-red Fourier Transform spectroscopy, Fourier Transform Infra-red spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy: will be applied to characterize the new AMOX samples.**
- **Special in-situ capabilities are in place:**
  - **FTIR: High Temperature Cell**
  - **TEM: E-cell reaction holder: heating + gas**





Summary (cont'd)

- **Special in-situ capabilities are in place:**
  - **TEM: elemental mapping with new x-ray detector**
  - **TEM: Energy-loss electron spectroscopy for chemical binding information**
  - **TEM: Our new capability for in-situ heating and gas reaction studies may also be used as the study develops, to provide dynamic/kinetic information on the behavior of the catalyst under selected treatment conditions. Results will be compared to bench tests.**

Acronyms

- ACEM = aberration-corrected electron microscope
- BF = bright-field
- DRIFTS = Diffuse reflectance infra-red Fourier transform spectroscopy
- EDS = Energy dispersive spectroscopy
- EPA = Environmental Protection Agency
- HA-ADF = high-angle annular dark-field
- NMR = Nuclear Magnetic Resonance
- NO_x = Nitrogen and Oxygen containing compounds
- ORNL = Oak Ridge National Laboratory
- SCR = selective catalytic reduction
- STEM = Scanning Transmission Electron Microscopy
- XPS = X-ray photoelectron spectroscopy
- XRD = X-Ray Diffraction

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