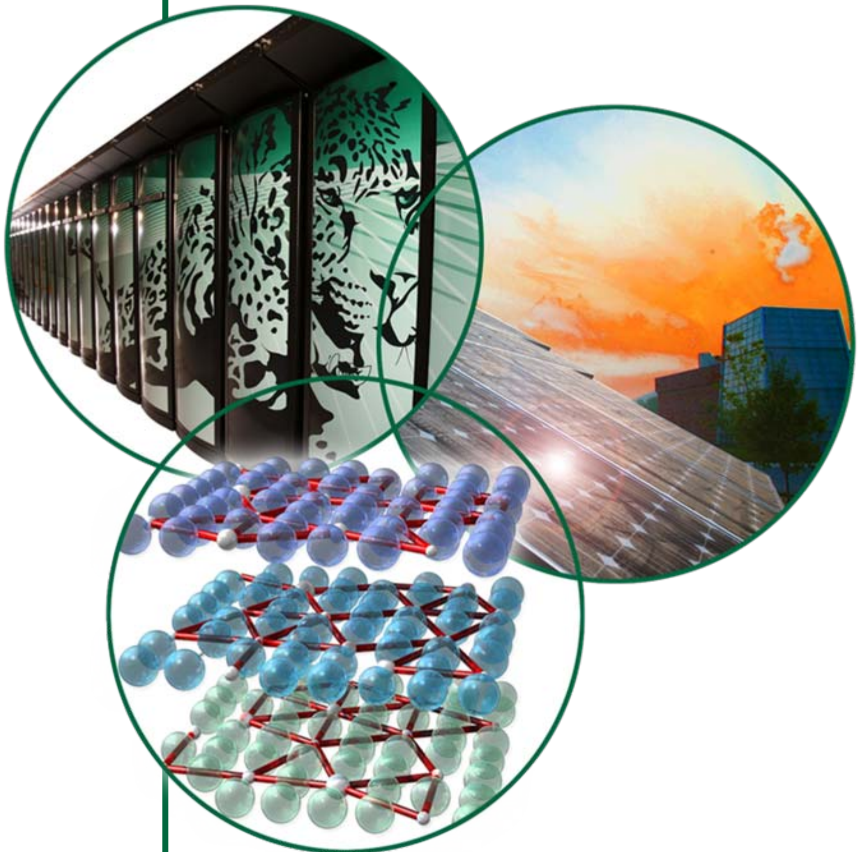
Project ID: pmp_19_watkins

Catalyst Characterization

DOE 2009 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

May 21, 2009



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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

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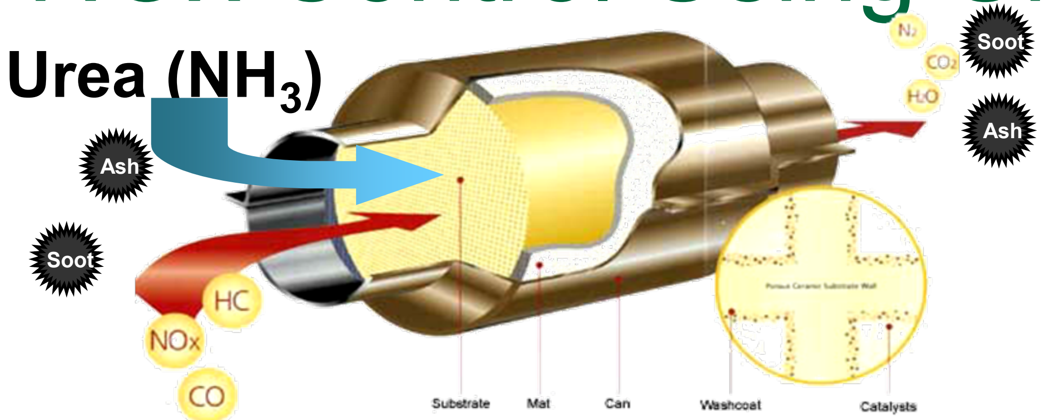
Background: Exhaust Aftertreatment

NOx Control Using Urea SCR



- **FE/Zeolite powder Hydrothermally Aged ex-situ**
  - **H-beta zeolite (plain, no Fe)**
  - **As-received-Fe-Zeolite**
  - **500, 700, or 900°C for 12 hours in a gas was 10 H_2O, 72 N_2 and 18 O_2 v% with a space velocity of ~ 42,000 h^{-1}.**

Emission Solutions

Overview

Timeline

- Start: June 2002
- End: Sept. 2009
- 95% complete (36 mo. renewal in process)

Budget

- Total Project funding
  - DOE-$2.2M
  - Contractor-$2.3M
- Funding received:
  - FY08 $225k
  - FY09 $103k

Barriers*

- Performance
  - Materials degradation/aging
    - Thermal (focus here)
    - Atmospheric
    - Temporal

Targets

- HD diesel engines compliant with 2010 EPA regulations with no fuel penalty

Partner

- 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 2010 emission requirements.

Milestones

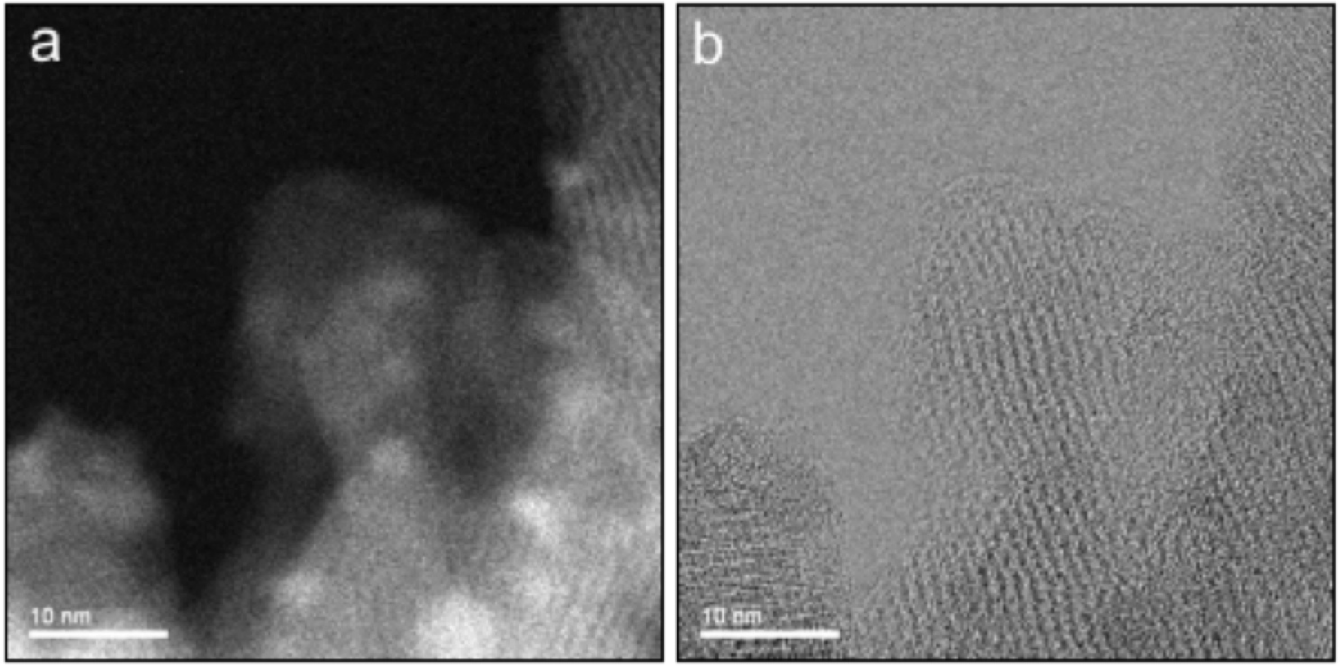
- **Milestone08: Continued evaluation of degradation of commercial zeolite urea SCR catalysts and a model catalyst as a function of operating conditions (temperature, atmosphere, time) in preparation for accelerated aging work.**

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

Approach

- **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.**

No changes observed amongst fresh, 500 and 700°C hydrothermally aged samples using electron microscopy

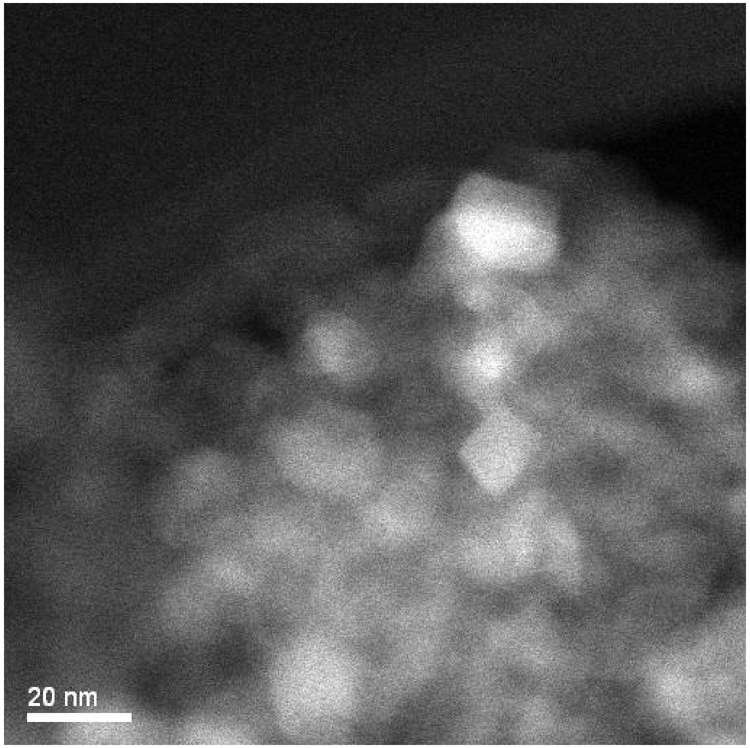


High-Angle Annual Dark Field Image
- No single Fe atoms or discrete clusters observed
- Bright 'patches' of distributed Fe species evident
- Lattice structure evident

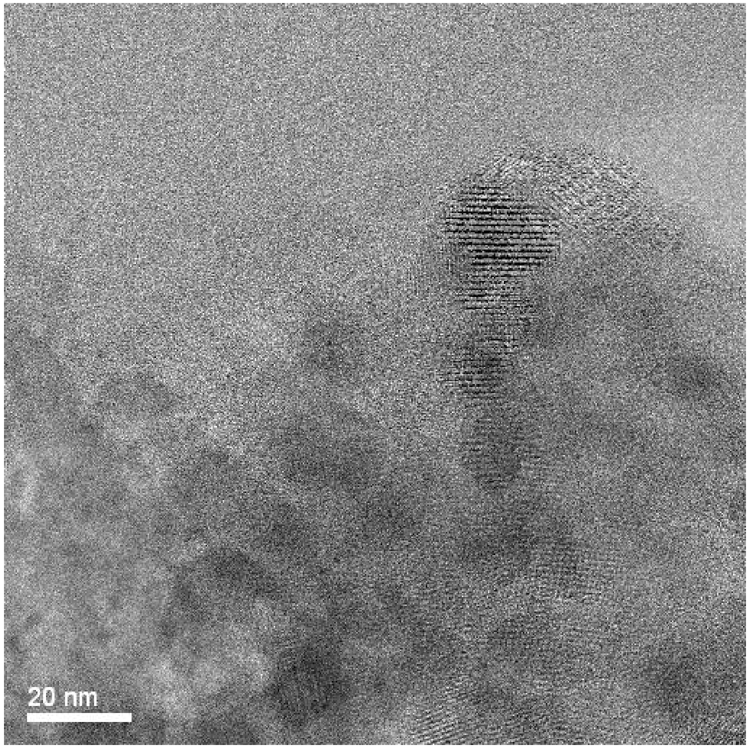
Bright Field Image
- Lattice structure of zeolite evident

Electron microscopy of the hydrothermally aged samples ≤ 700°C was very difficult, even short exposures of the zeolite material to the electron beam resulted in amorphization and often disintegration of the region of interest.

Numerous changes observed in 900°C hydrothermally aged sample using electron microscopy



High-Angle Annual Dark Field Image
- Facetted regions evident
- Lattice structure evident

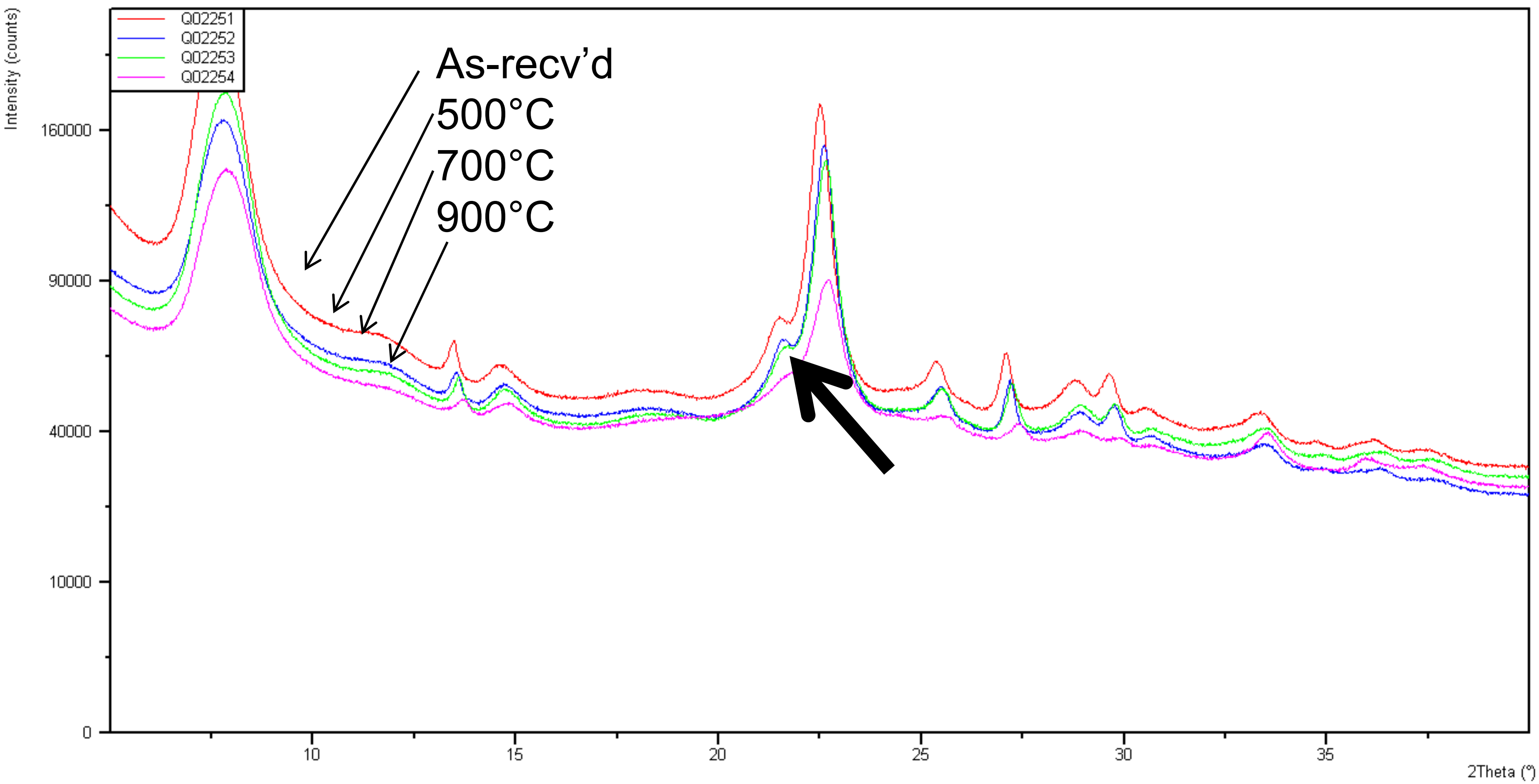


Bright Field Image
•Lattice structure of facetted region evident

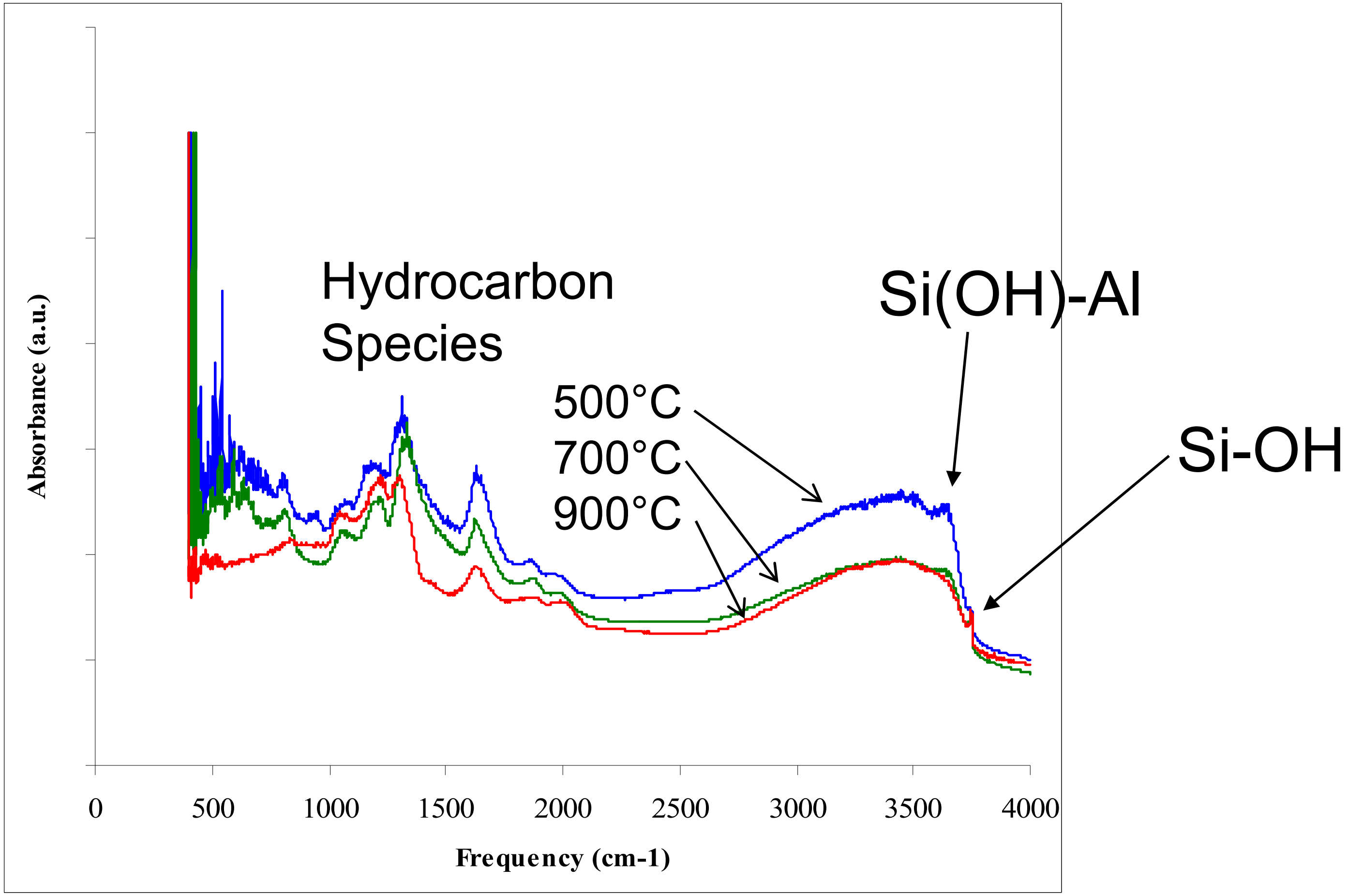
In contrast, hydrothermally aged sample at 900°C was very stable under the electron beam: no material amorphization or disintegration in the region of interest. This indicated that a structural change in the material had occurred.

Changes seen only after 900°C with hydrothermal aging via X-Ray Diffraction

- 900°C HA: 25% decrease in crystallinity relative to as-received sample

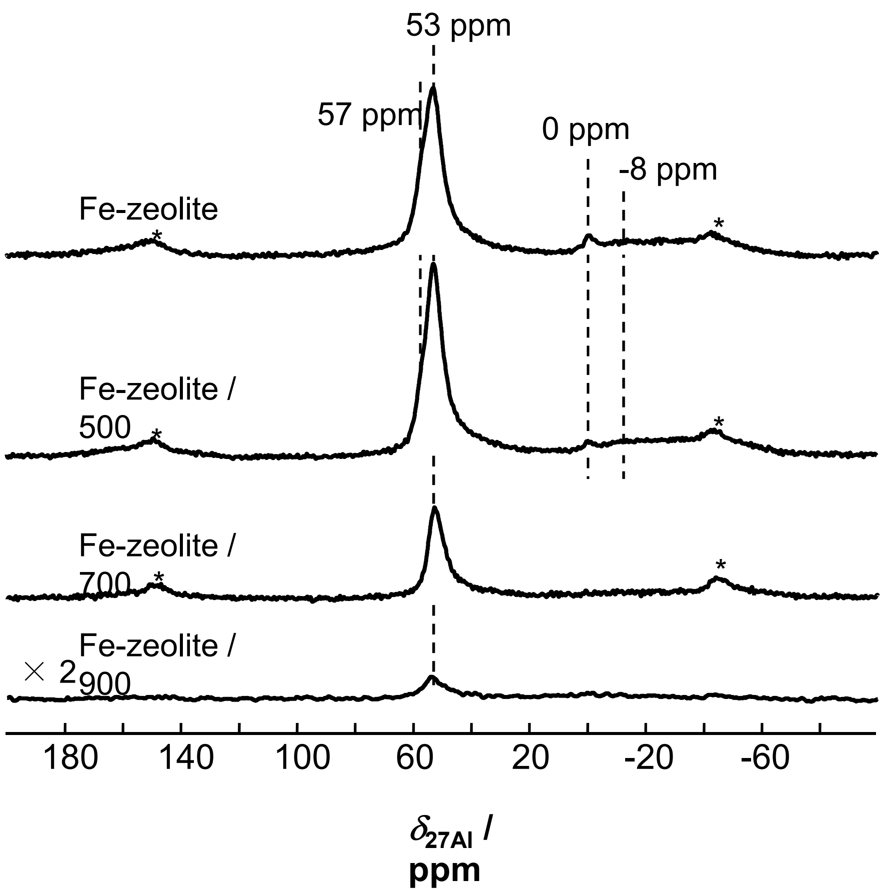


DRIFTS of Fe-Zeolite shows that the lattice is dealuminizing due to hydrothermal aging



- **DRIFTS provides vibrational info from the surface and bulk**
- **Si(OH)-Al peaks decline with increasing hydrothermal aging temperature.**

NMR of Fe-Zeolite also shows that the lattice is dealuminizing due to hydrothermal aging

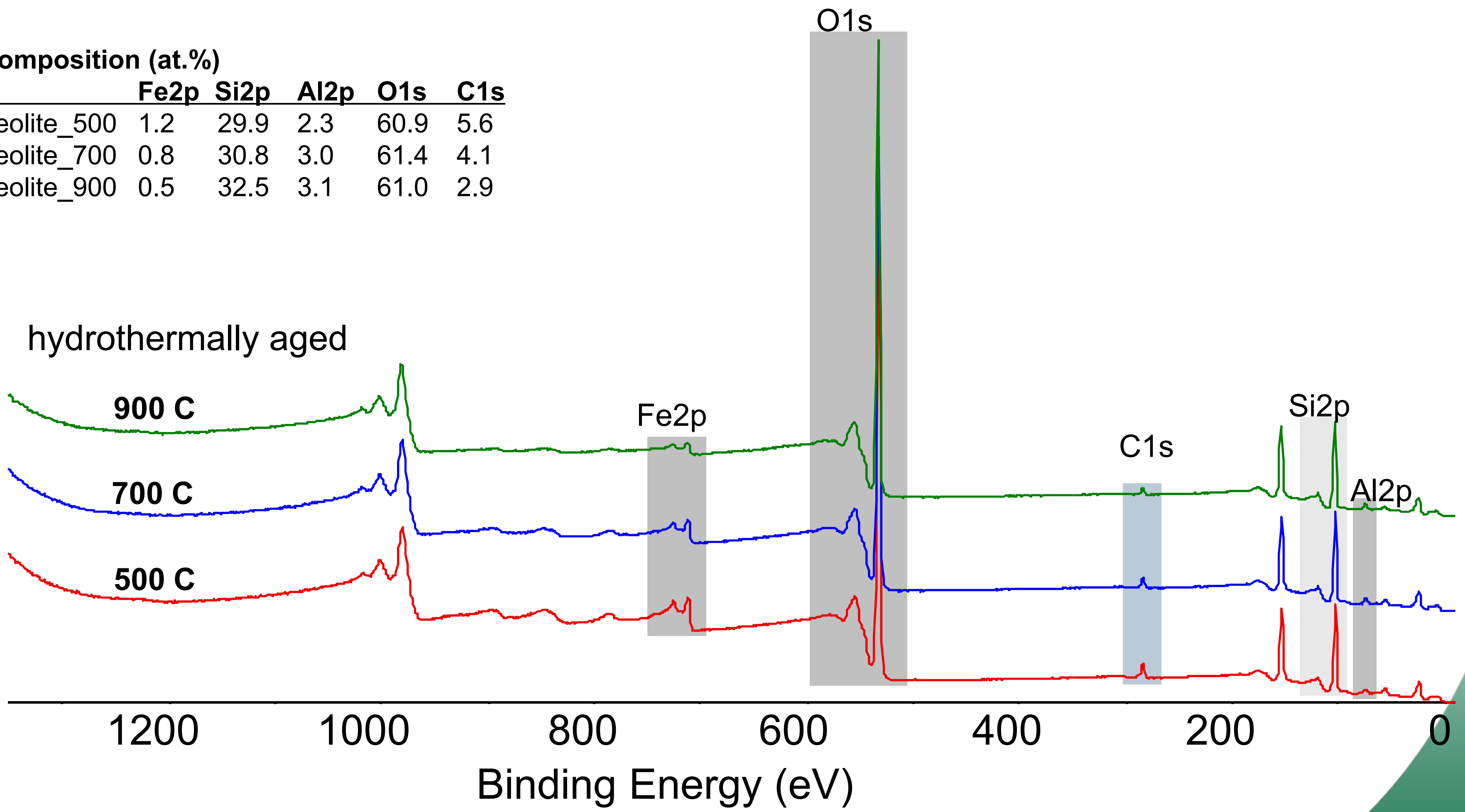


- **Most of the Al are tetrahedral (two different Al tetrahedral sites), and a little bit Al^{3+} and Al_2O_3.**
- **Hydrothermal aging eliminated one tetrahedral site and reduced the other showing that most of the Al is out of the lattice and is probably associated with an Fe center.**

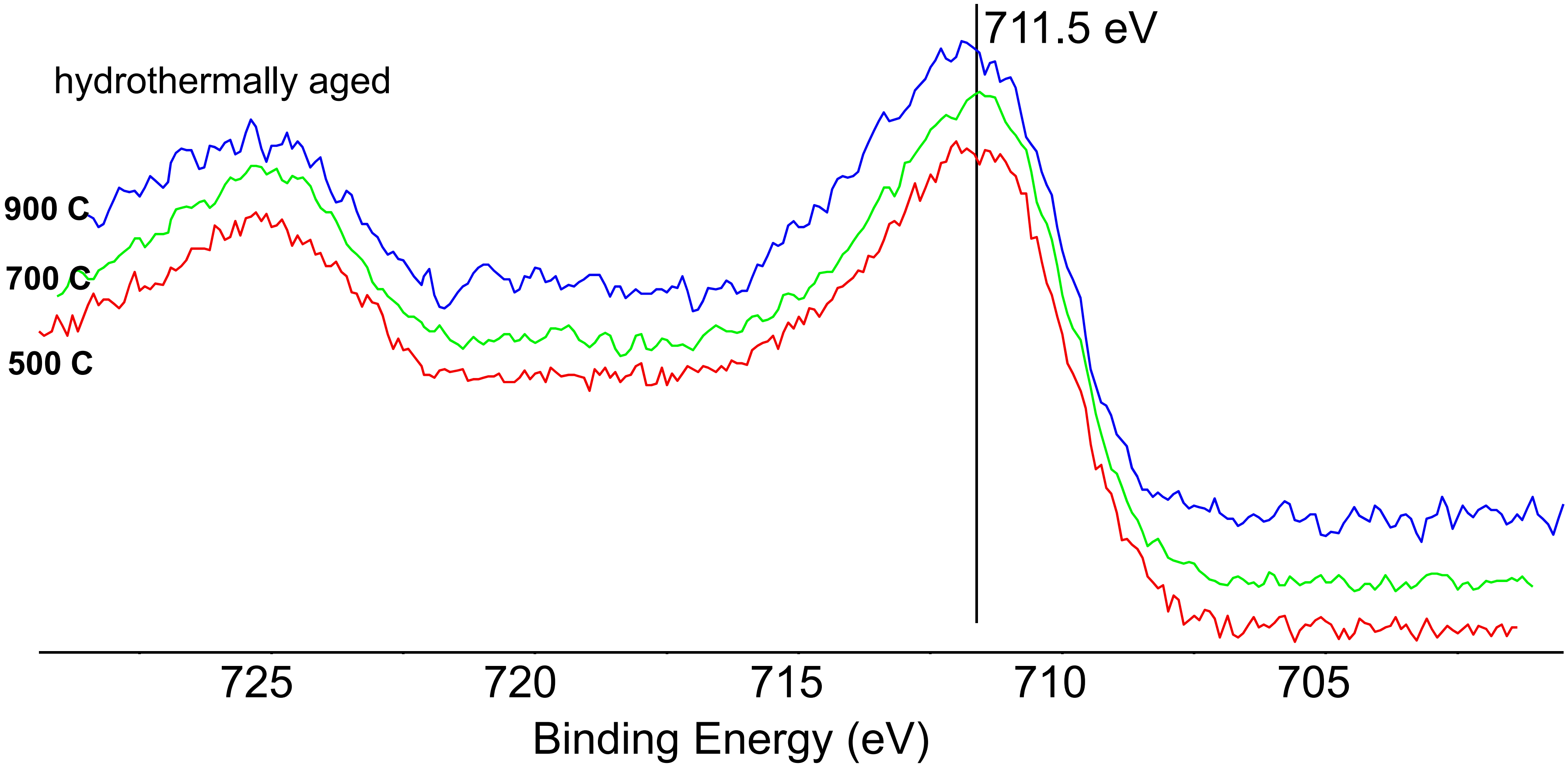
X-ray Photoelectron Spectroscopy show that the overall surface composition of Fe ↓ (i.e., peak area) as temperature ↑.

Composition (at.%)

	Fe2p	Si2p	Al2p	O1s	C1s
Zeolite_500	1.2	29.9	2.3	60.9	5.6
Zeolite_700	0.8	30.8	3.0	61.4	4.1
Zeolite_900	0.5	32.5	3.1	61.0	2.9

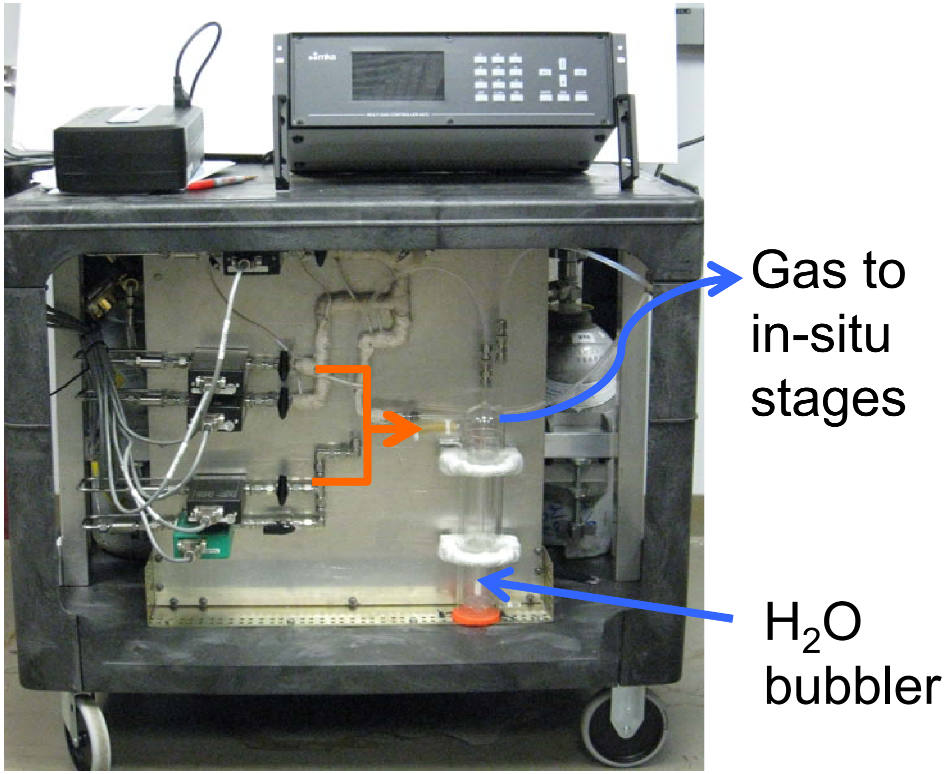


Fe 2p core level XPS spectra shows heating does not drastically change the overall oxidation state of the Fe



- 900°C sample is tending toward a slightly higher binding energy (i.e. more oxidized).

Future work: Expand in-situ studies with new portable gas manifold



- Testing to begin early summer 2009 after safety approvals.

Future Work

- Continue characterization of a commercial zeolite urea SCR catalyst subjected to hydrothermal aging for lifetime prediction model input. Focus on understanding the catalyst degradation mechanisms due to hydrothermal aging using the tools developed under this CRADA.
- Begin ammonia oxidation (AMOX) catalyst characterization.
- Continue to characterize the soot, coke and ash formed on the catalyst from different fuels, including biodiesel.
- Assist Cummins to competitively produce engines which attain the required emission levels for 2010 and beyond while maintaining the advantage of the diesel's inherent energy efficiency.

Summary

- XRD, TEM, DRIFTS, NMR and XPS all showed the effect of hydrothermal aging after 900°C exposure.
- Dealuminization was observed with NMR, DRIFTS and XPS as temperature increased.
- Team consensus is:
  - Spectroscopic techniques + NMR provide important information about hydrothermal degradation of Fe-zeolites
  - XRD and TEM less so
  - Future focus shifting to AMOX catalysts while continuing to support SCR-zeolite work