# Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials

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**This presentation does not contain any proprietary or confidential information**

# Project Overview

- The project is a CRADA between PNNL and Ford Motor Company. DOE funding to PNNL: ~0.4 scientist FTE.
- Project first initiated in February 2007; CRADA agreement signed through January of 2010
- 'Tech transfer' via
  - Kick-off meeting held at PNNL in March, 2007.
  - Regular (approximately bi-monthly) conference calls.
  - Face-to-face meetings are scheduled as opportunities arise (next one during next month's SAE meeting in Detroit).
- This CRADA was not reviewed last summer so there are no peer-reviewer comments to address.

# Purpose of the Work

- Develop an understanding of various aging factors that impact the long-term performance of urea selective catalytic reduction (SCR) materials in diesel vehicle applications.
- Improve the correlation between laboratory and engine aging.
- (Ford activity): Use this fundamental understanding to develop realistic laboratory aging protocols, saving experimental time and cost.

# Barriers

- Lean-NOx emission control technologies, including urea selective catalytic reduction (SCR) are needed to enable wider use of fuel-efficient diesel engines.
- Regulations impose challenging requirements for catalyst activity and durability, with durability especially difficult due to a relative lack of experience with this new technology.
- As such, there is a critical need to develop realistic laboratory aging protocols that effectively simulate engine aging induced catalyst deactivation.  For this, a fundamental understanding of the deactivation mechanisms is essential.

# Approach

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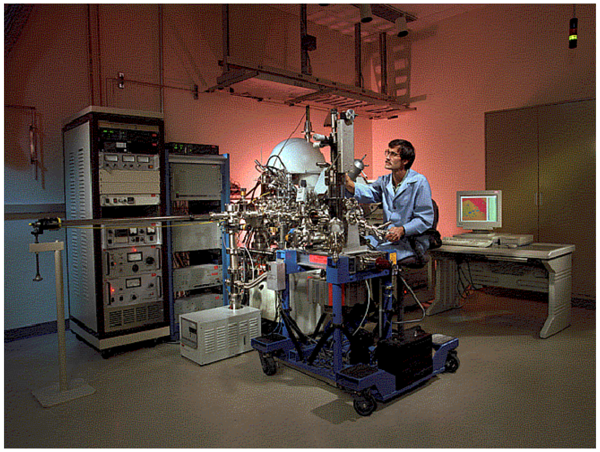
- Ford tasks:
  - Preparation of Fresh and Laboratory Aged Samples.
  - Laboratory and Engine Testing to Correlate Results.
  - Provide Engine-Aged urea SCR catalysts for PNNL Testing
  - Develop refined Laboratory Aging Protocols



- PNNL tasks:
  - Use PNNL/IIC's state-of-the-art tools to characterize sets of laboratory- and engine-aged samples provided by Ford.
  - Correlate urea SCR catalyst materials characterization results with catalytic performance data (provided by Ford), and with changes in catalyst surface chemical properties as a function of wide array of laboratory and engine aging conditions.
  - Use this information for determining important mechanisms for performance degradation of urea SCR catalysts.

# FY 2008 Objectives/Activities

Two primary areas of focus to date:

1. Characterize the nature and thermo-chemical properties of deposits observed on engine-aged urea SCR catalysts.
2. Characterize laboratory- and engine-aged catalysts and correlate the results with Ford performance measurements
   - An initial aging protocol was developed and applied by Ford to monolith-wash coated zeolite-based urea SCR catalysts.
   - Unexpected effects of urea during laboratory aging observed in early Ford studies.
   - Some of the results obtained in this part of the work contain proprietary information regarding catalyst composition and structure.

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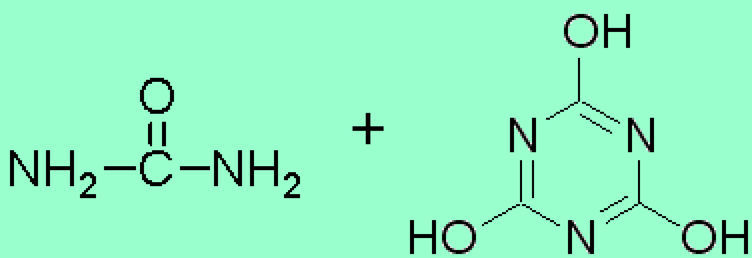
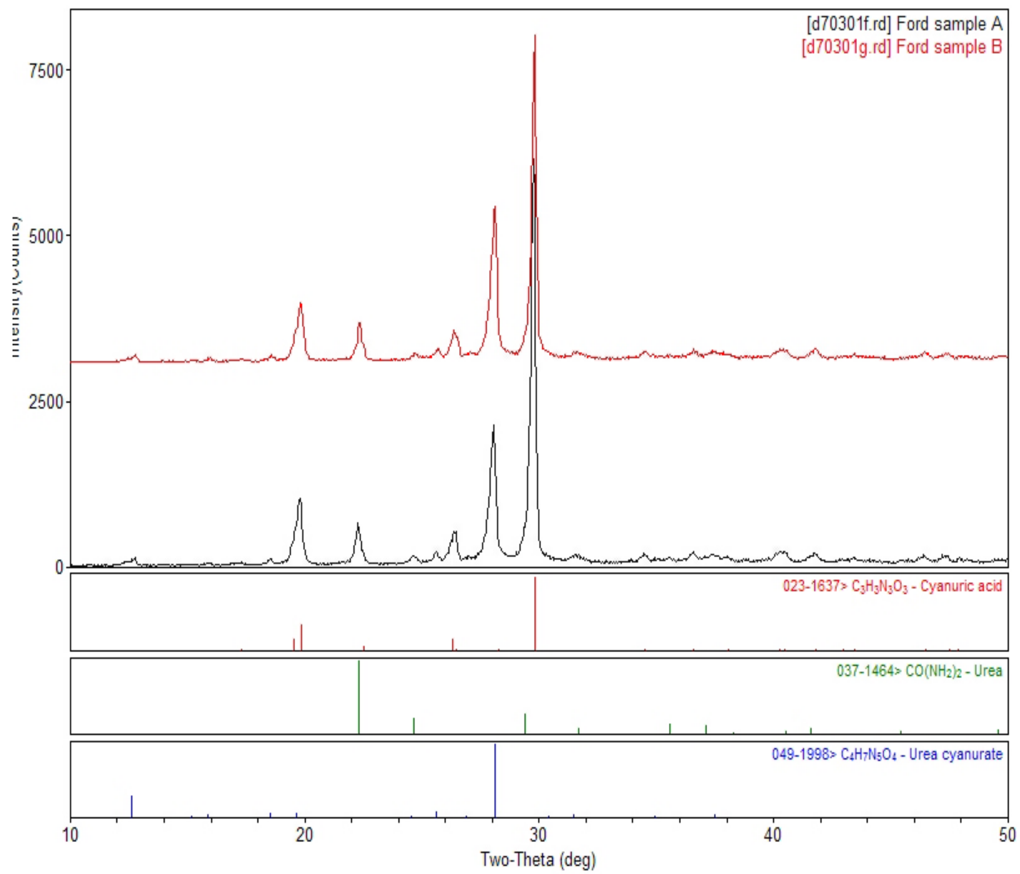
**Ford observed the formation of large deposits upstream and/or on monolith catalysts subsequent to engine tests.**

C. Lambert and coworkers, SAE 2007-01-1582.

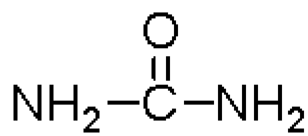



+ **Urea-cyanurate**



# Mechanism of Urea Decomposition

## Urea decomposition




$\rightarrow$ **$NH_3$ + HN=C=O**

**HNCO + $H_2O \rightarrow NH_3 + CO_2$**

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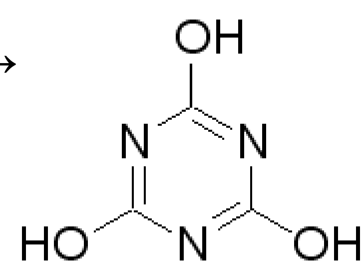
**Urea + $H_2O \rightarrow 2NH_3 + CO_2$**

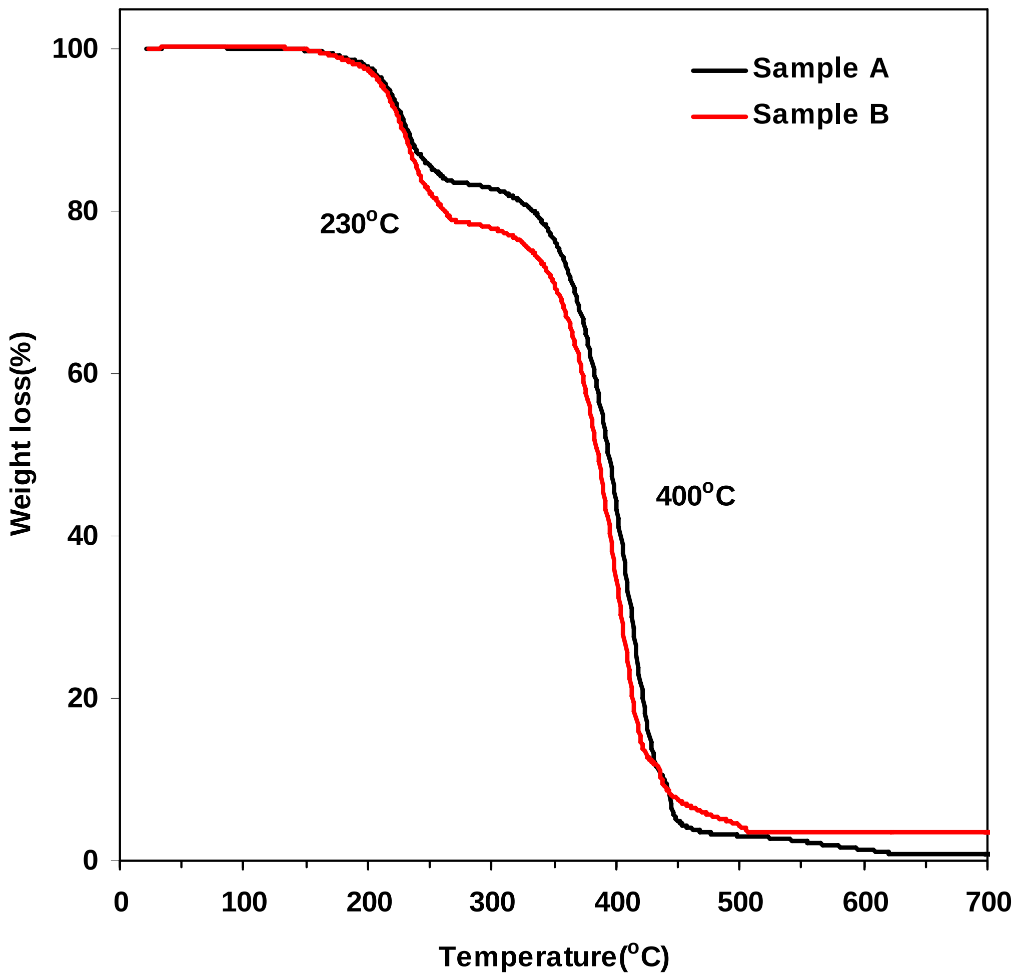
## Cyanuric acid formation

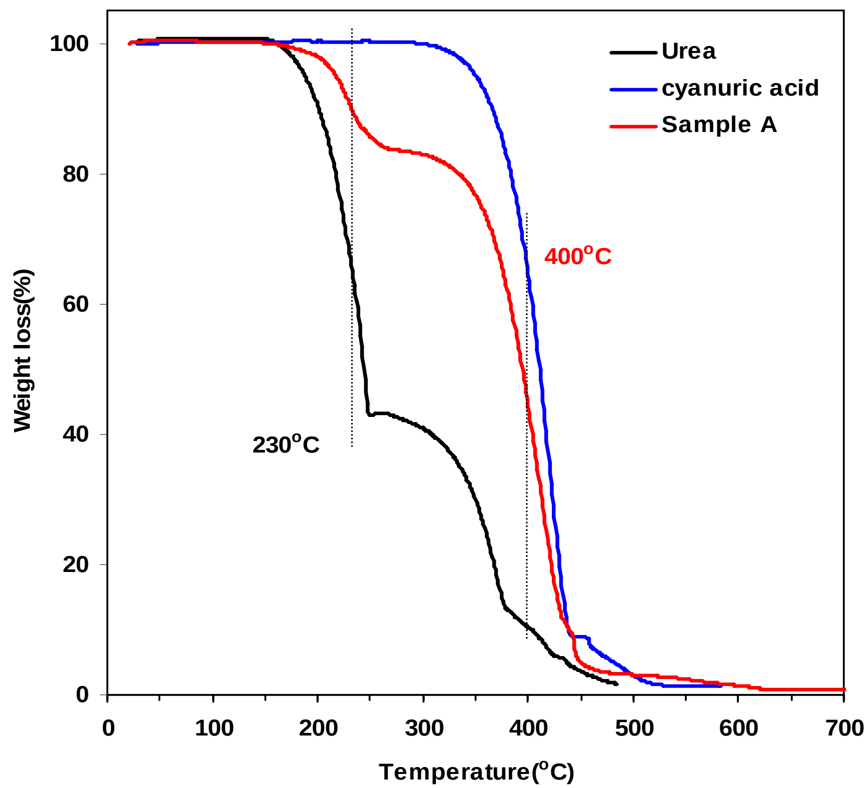
**3 HN=C=O** $\rightarrow$



# Technical Accomplishments/ Progress/Results

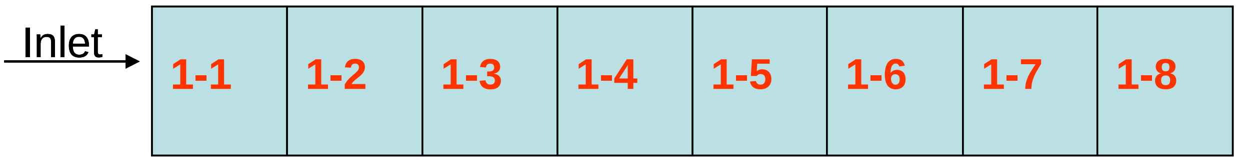
Similar TGA Profiles for two Ford Deposit Samples.

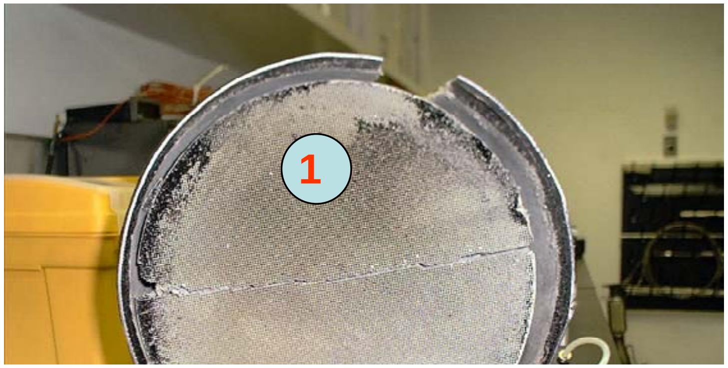


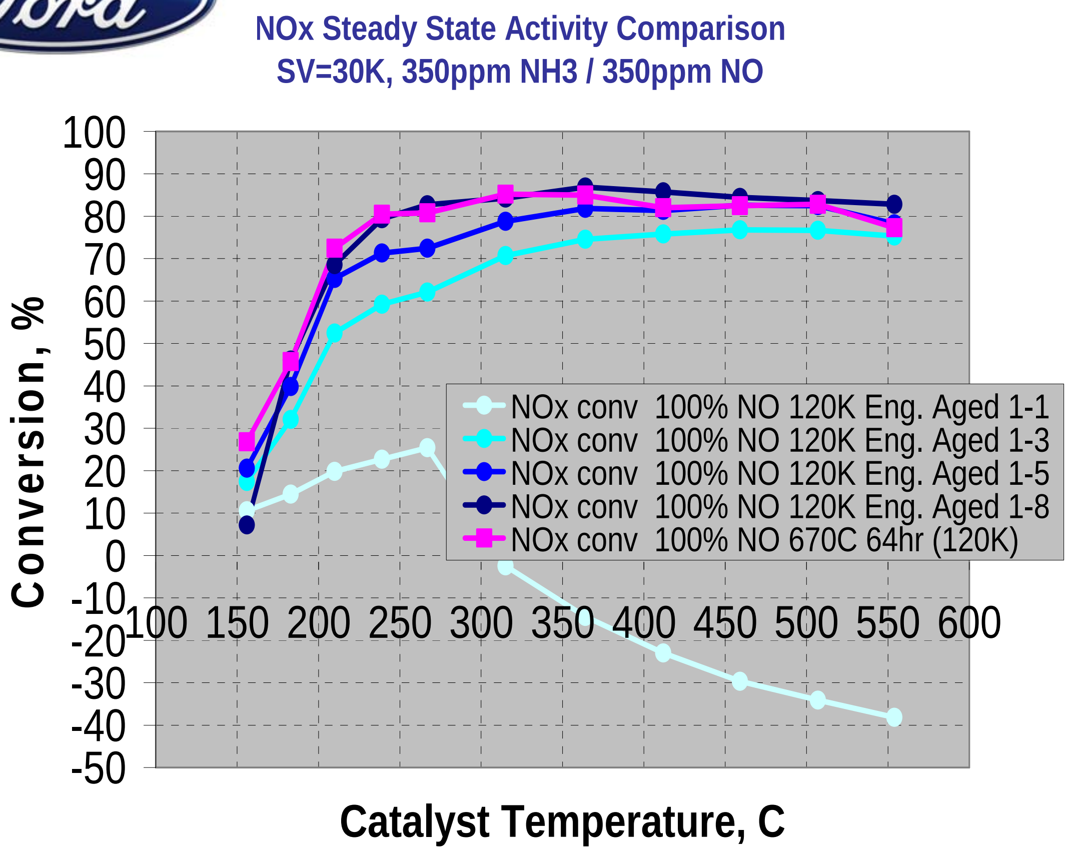



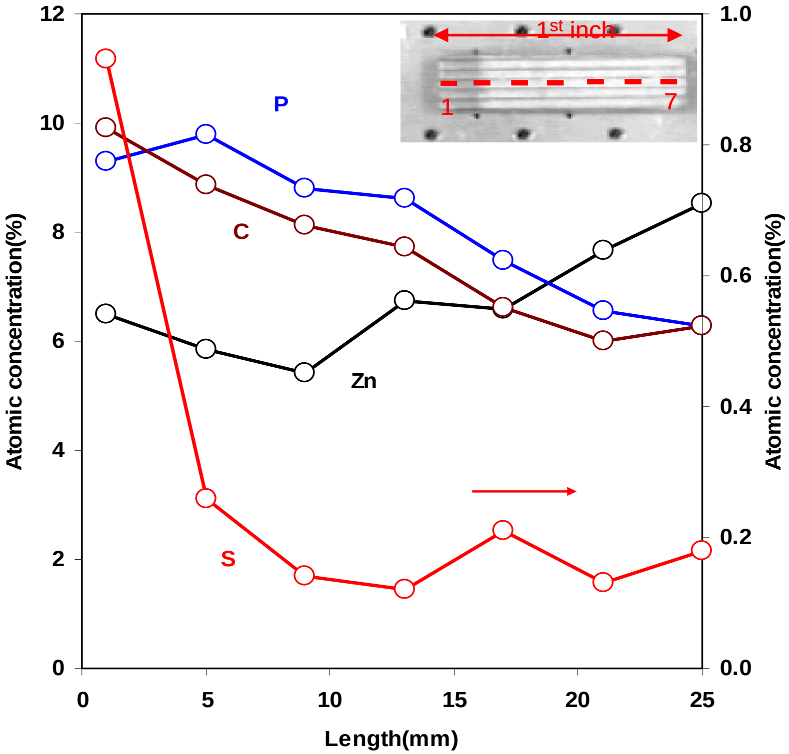

- Urea – two decomposition
  ~230°C and 360°C (???)
  ratio = ~2:1
- Cyanuric acid: ~410°C

# Technical Accomplishments/ Progress/Results



# Technical Accomplishments/ Progress/Results

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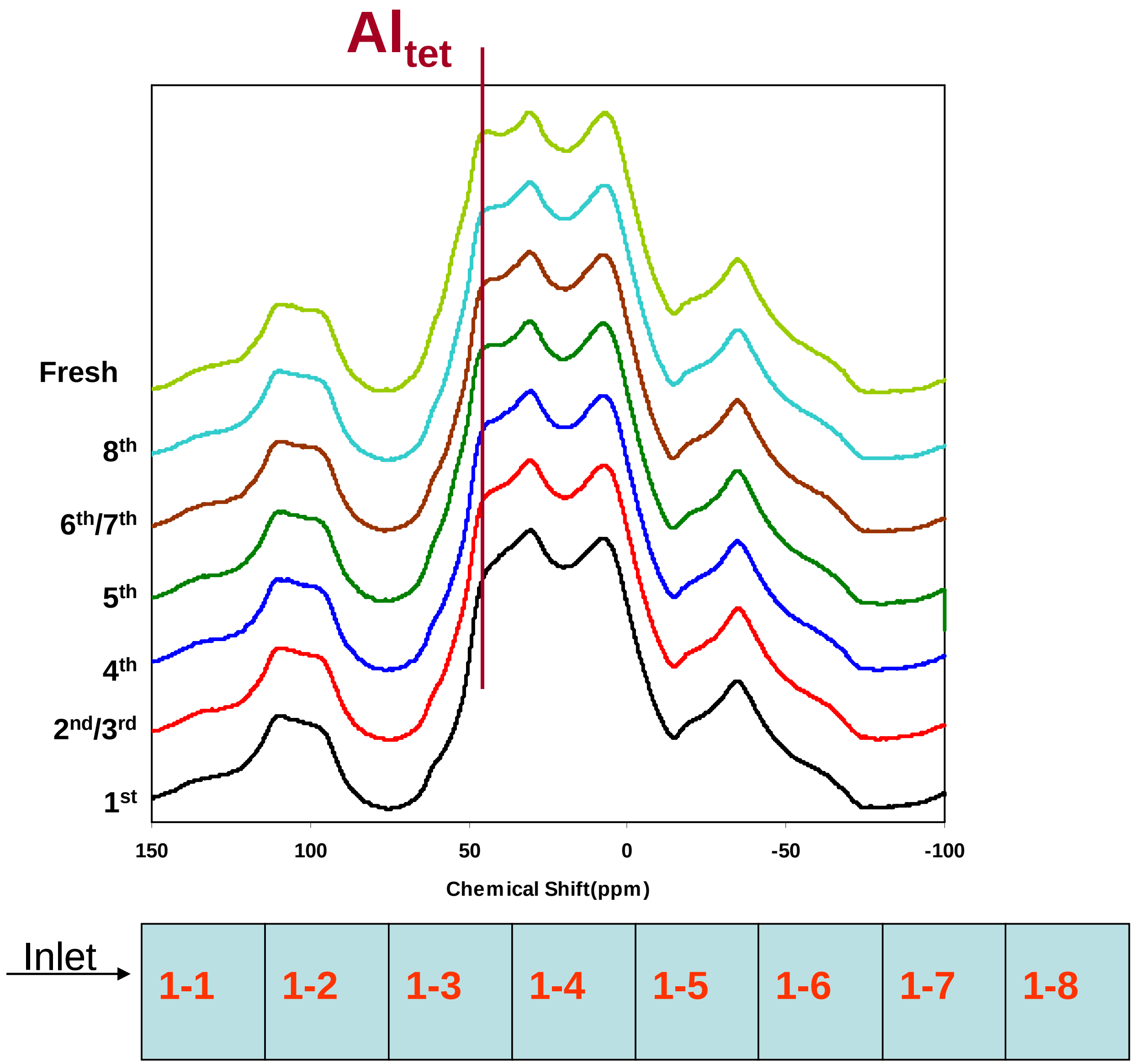


- The front portion of the monolith (1-1) lost more Al$_{tet}$ (i.e., dealumination and/or zeolite structure collapse)
- These results also verified by XRD which showed variable zeolite structure collapse as a function of location in the monolith.

# Technical Accomplishments/ Progress/Results

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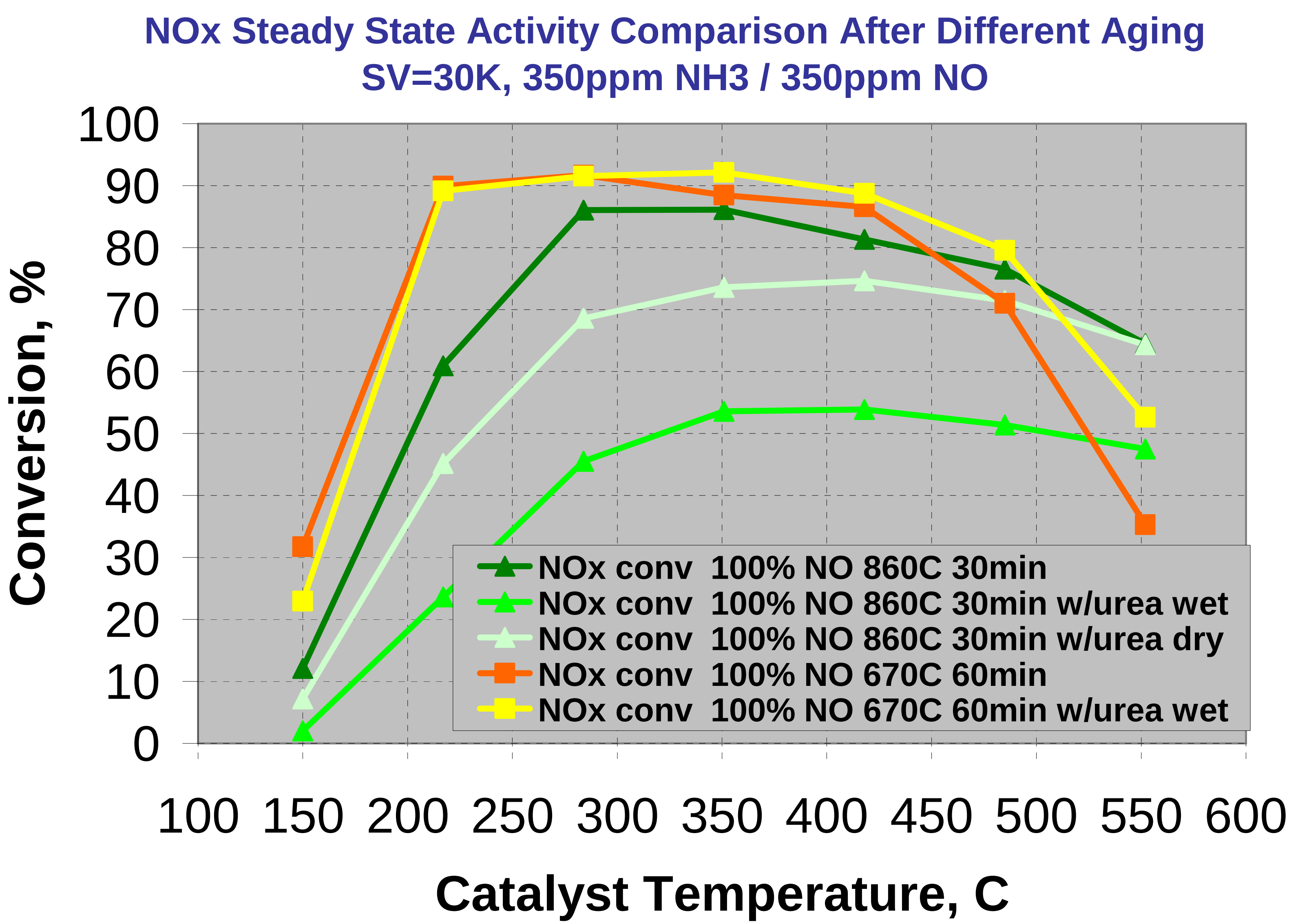
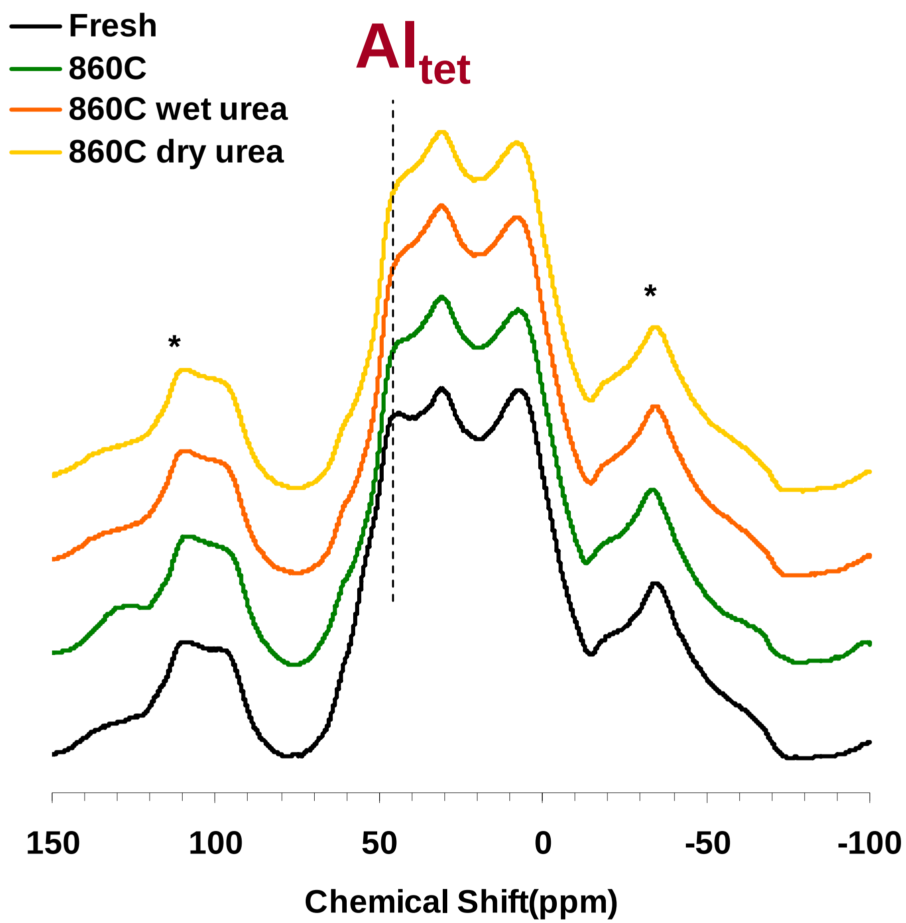



Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, and C.H.F. Peden, Catalysis Today (2008) in press.

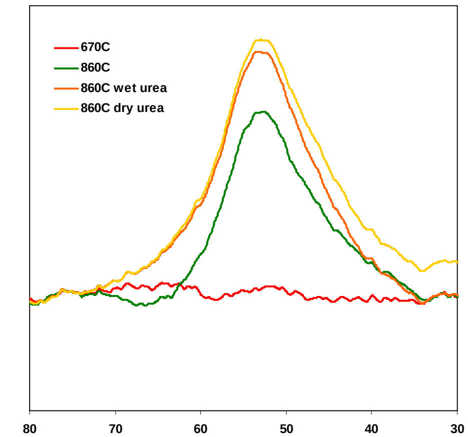
# Technical Accomplishments/ Progress/Results

**Solid-state 27Al NMR Spectroscopy Used to Follow Loss of Al from zeolite framework.**




*: spinning side band

- The spectra from the 670 °C aged samples are very similar to the spectrum from the fresh sample (no evidence for dealumination)
- The 860 °C aged samples show serious loss of tetrahedral aluminum regardless of the process




Relative de-alumination

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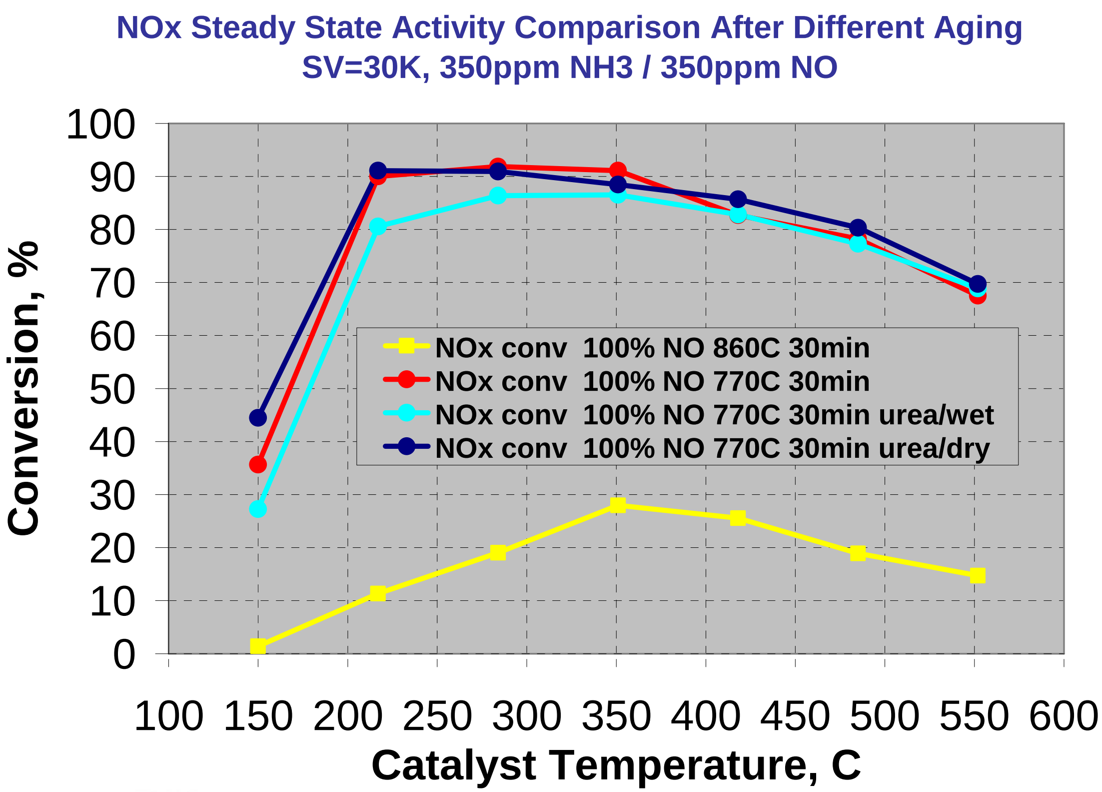
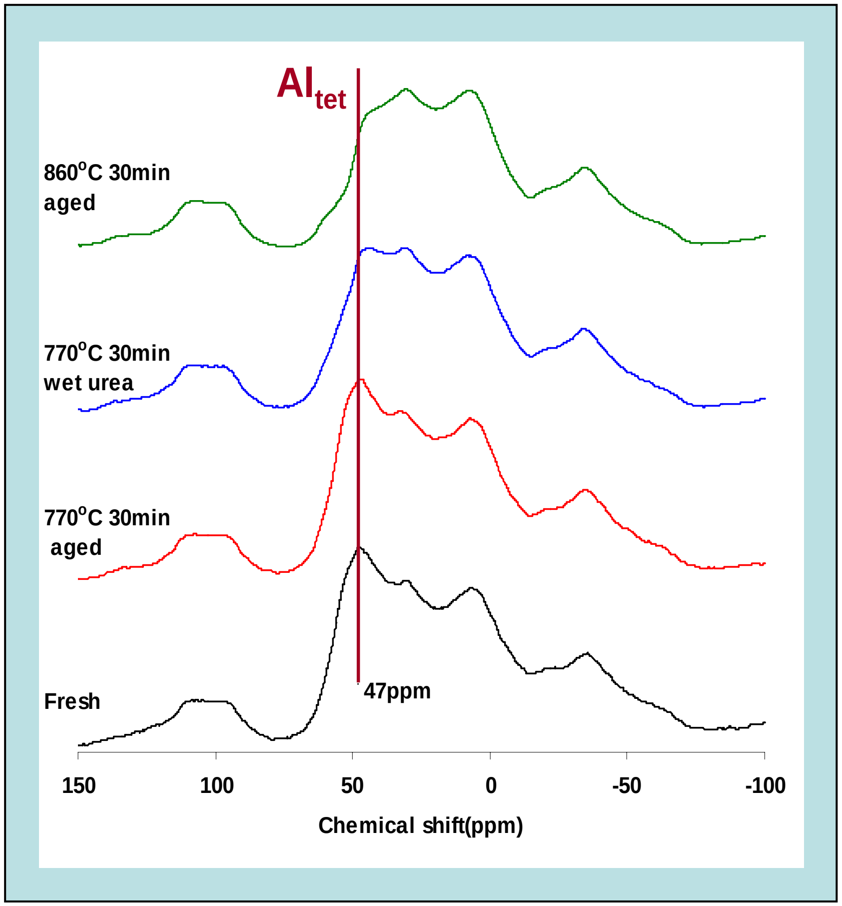
# Technical Accomplishments/ Progress/Results

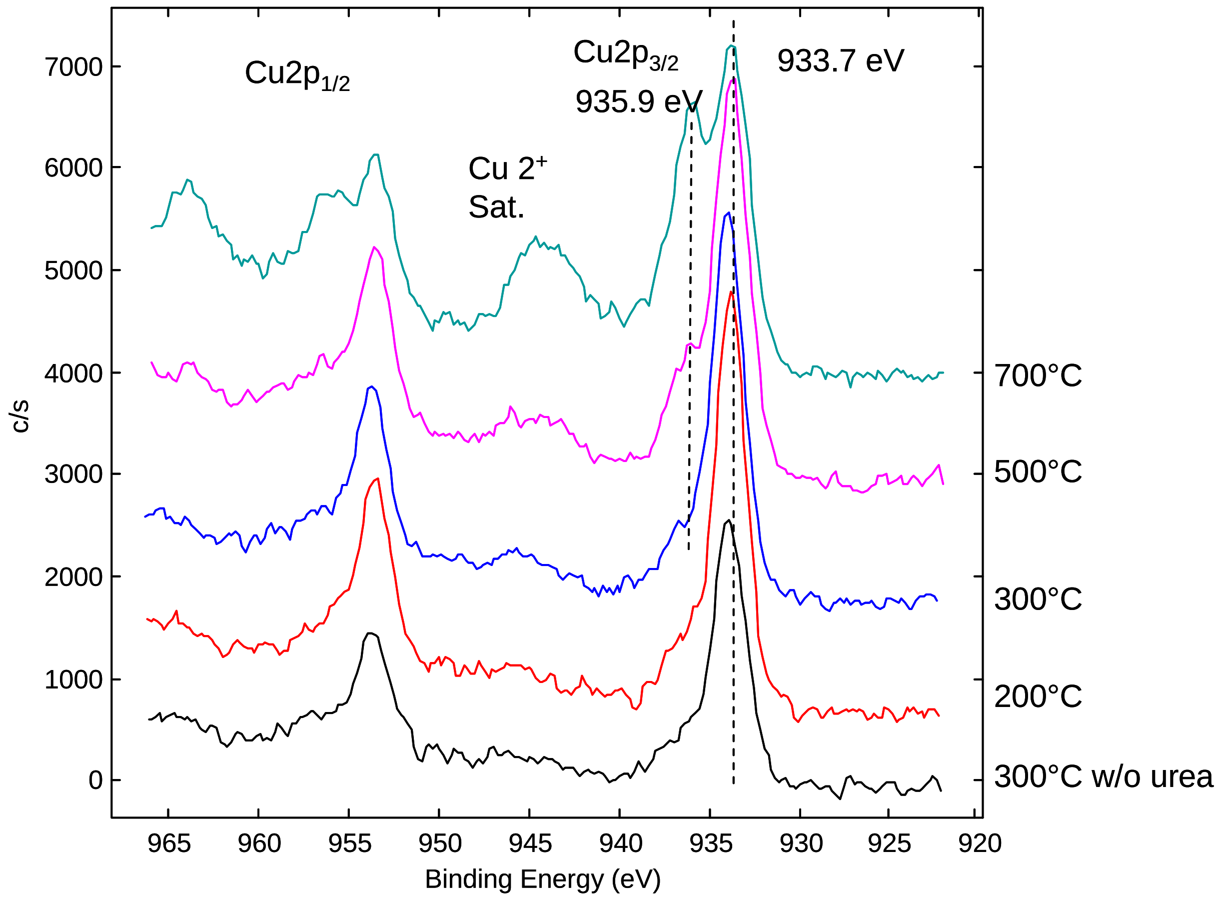
**For laboratory-aged model catalyst, the extent of zeolite dealumination correlates well with reactivity data.**



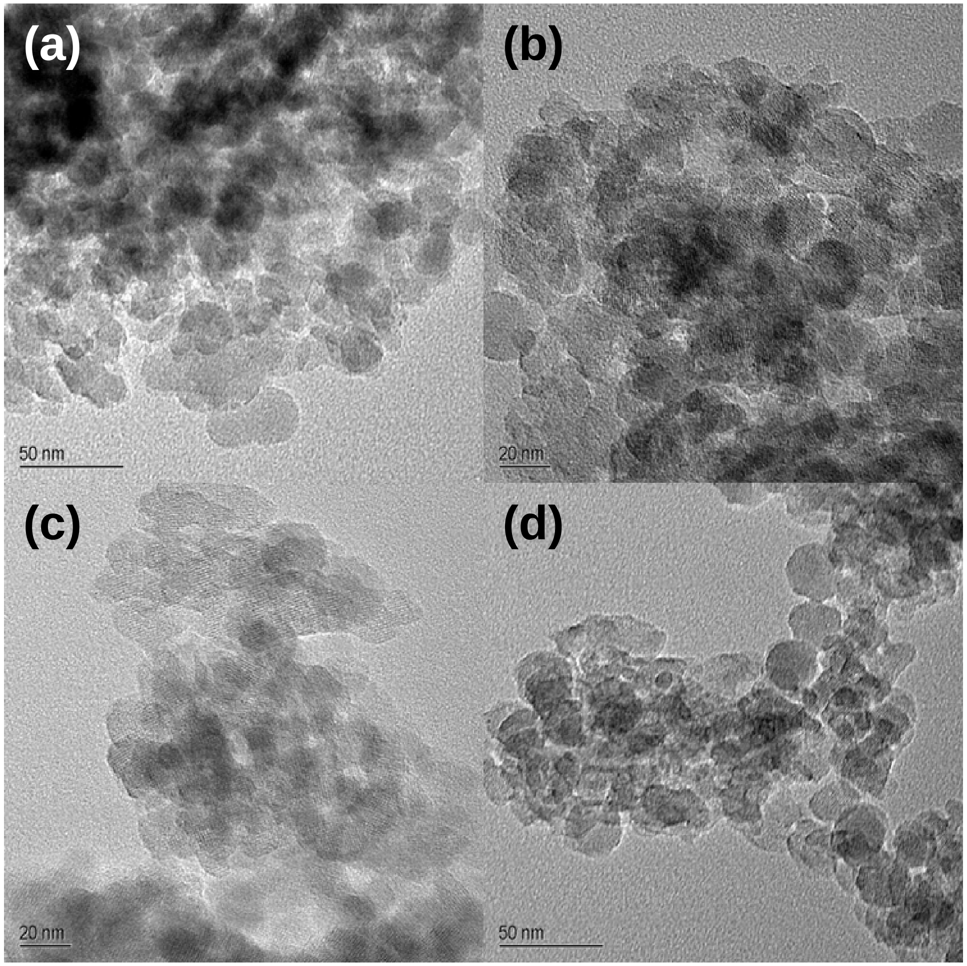
# Technical Accomplishments/ Progress/Results

**Laboratory-aging of Cu-beta zeolite model catalyst shows changes in Cu speciation with urea included in protocol.**




- **Low temperature treatment leads to a single Cu 2p XPS doublet at 933.7 and ~954 eV indicating the presence of only one type of Cu species**
- **A second Cu species, with a Cu $2p_{3/2}$ peak at 935.9eV, appeared and increased in quantity with aging temperature**

**Transmission electron microscopy (TEM) used to study morphological changes in laboratory-aged model catalysts.**




- **No obvious morphological changes during aging up to 700 °C**
- **Little, if any, evidence for Cu sintering**

**(a) 200 °C**
**(b) 300 °C**
**(c) 500 °C**
**(d) 700 °C**

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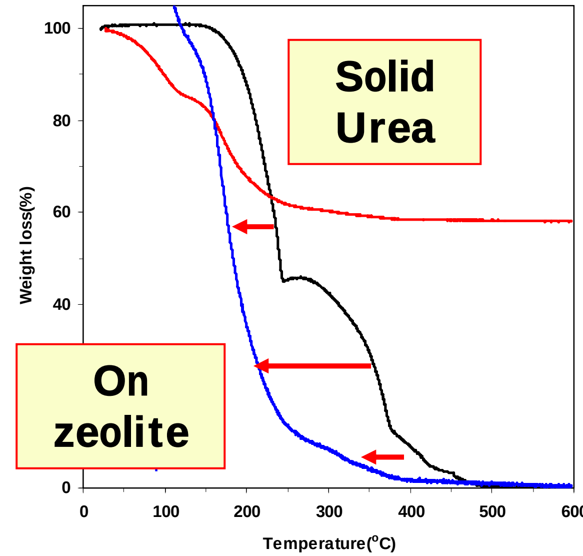
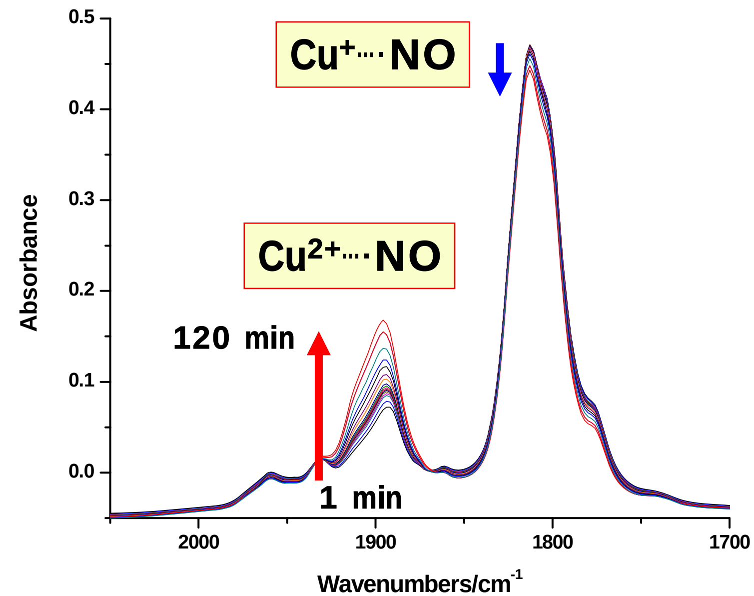
## Principal conclusions of these studies to date:

- Urea deposits collected on monolith catalysts in Ford engine tests are mixtures of urea, cyanuric acid, and a urea-cyanurate complex.
- The combination of urea and high temperature exposure increased the deactivation of realistic proprietary and model Cu/beta-zeolite SCR catalysts beyond that observed by hydrothermal aging alone.
- Volatile isocyanic acid (HNCO) represents one possible source of enhanced degradation for laboratory aging with urea.
- NMR analysis suggests that aging with urea results in relatively more dealumination of the zeolite for the model Cu/zeolite SCR catalyst in this study, with XPS also showing evidence for a second Cu species.
- There are no obvious zeolite morphological changes or Cu sintering observed in TEM as a function of aging temperature up to 700 °C.

# Activities for Next Fiscal Year

- Complete mechanistic studies of catalytic urea decomposition in the presence of water and $CO_2$.
- Identify nature of $Cu^{+2}$ species and its relationship to observed dealumination and deactivation.
- Initiate studies of mechanism of lower and higher temperature deactivation with aging observed in recent Ford experiments.
- Initiate FTIR and $NH_3$ TPD studies of chemical effects of aging with urea (e.g., reaction with HNCO).



# Summary

- PNNL initiated a new CRADA with Ford Motor Company one year ago to study deactivation mechanisms in zeolite-based urea SCR catalysts. A specific goal of this work is to use this fundamental information to develop realistic laboratory aging protocols.
- Technical progress to date included identification of catalyst deposits observed in engine-aged systems, and correlation of catalyst characterization with performance of laboratory aged samples.
- Future work will be studying possible catalyst materials effects of urea with FTIR, and studies of variable low and high temperature deactivation observed in recent Ford experiments.

# Publications, Presentations, Patents

## Publication

- Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, and C.H.F. Peden, "NMR Studies of Cu/Zeolite SCR Catalysts Hydrothermally Aged with Urea", Catalysis Today, in press (2008).

## Presentation

- Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, and C.H.F. Peden, "The Impact of Urea on Hydrothermally Aged Cu/Zeolite SCR Catalysts", presentation at the 20th Meeting of the North American Catalysis Society, Houston, TX, June, 2007.