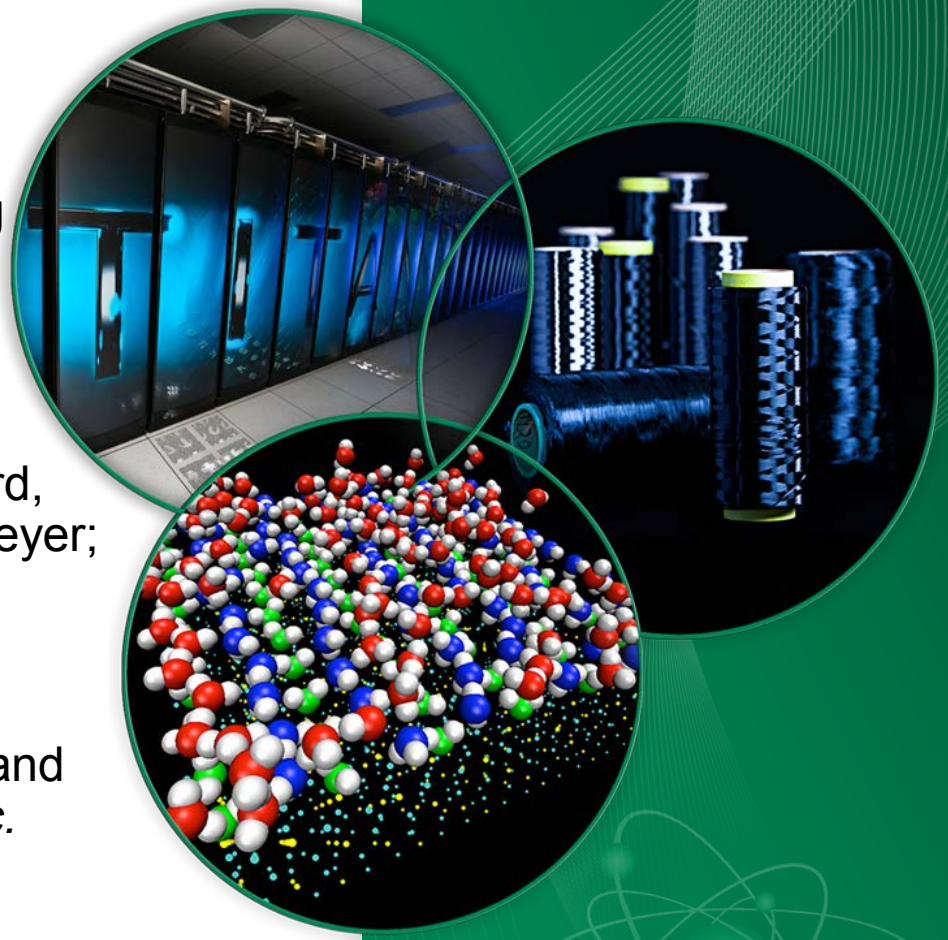
Catalyst Characterization: Agreement 9130

Project ID: PM049

2014 DOE Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

June 20, 2014



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

Krishna Kamasamudram and Alex Yezerets; *Cummins Inc.*

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

Objective

- 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*
  - *The minimization of the fuel penalty*

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.”

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

Project Overview

Timeline

- Start: June 2002
- End: Sept. 2014
- 97.3% complete

Budget

- Total Project funding
  - *DOE-$2.43M*
  - *Cummins-$2.43M*
- Funding received
  - *FY13 $130k*
  - *FY14 $100k*

Barriers

- New challenges to meet future emission regulations
- Aftertreatment system durability
- Cost effective technologies
- Combustion regimes with low exhaust temperatures

Relevance in the next slide

Partner

- Cummins Inc.

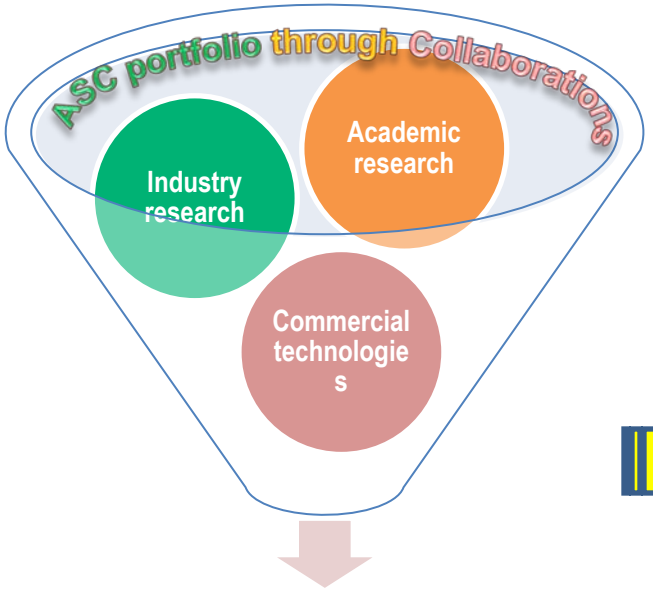
* Vehicle Technologies Program, Multi-Year Program Plan 2011-2015, Dec 2010, pp. 2.3-4, 5; 2.5-8.

Relevance to barriers

- New challenge: N_2O, a green house gas, emissions are capped
  - *ASC is a major contributor of N_2O*
  - *When engines are tuned for high NOx and the application of very efficient aftertreatment systems are expected to increase N_2O*
- Durability of ASC technologies are not well understood
  - *ASC formulations are rapidly evolving*
  - *Durability of formulations have significant impact on emissions reliability*
- Further challenges in meeting emissions due to low exhaust temperatures and low cost systems
  - For example due to reduced PGM use in aftertreatment systems
  - *Low exhaust temperatures higher the risk of NH_3 slip into ASC and tailpipe*
- This project is addressing the barriers by providing fundamental information that is needed now and for future aftertreatment technologies that might result in
  - *Improved aftertreatment strategies*
  - *Fuel efficient and cost effective aftertreatment technologies*

Approach

Cummins



Select ASCs

- Identification of critical studies needed through extensive in-house performance and durability evaluations
- Provide samples and sample preparation methodologies to ORNL

ORNL

- Utilize the expertise to develop advanced characterization methodologies to understand the fundamentals of ASC performance and degradation mechanisms
  - *In situ X-ray diffraction*
  - *FIB, HRTEM technique*
  - *Spectroscopic investigation*


FIB and SEM of Cu-zeolite

Utilizes characterization tools acquired and formerly maintained by the High Temperature Materials Laboratory (HTML) Program at ORNL.

Milestones

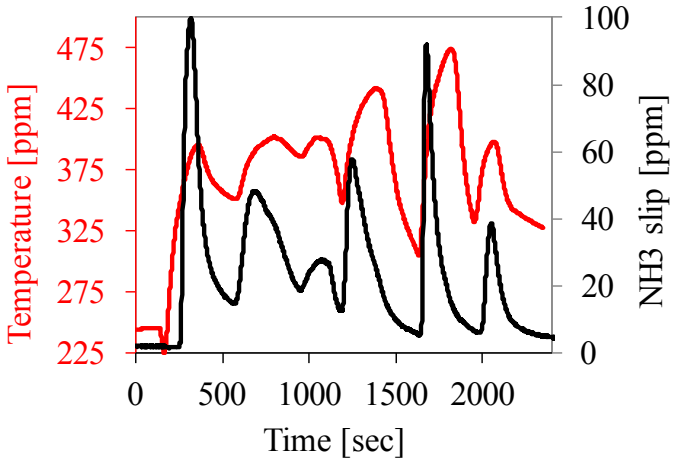
- FY13: Continue in-situ evaluation of degradation of commercial ASCs and a model catalyst as a function of operating conditions (temperature, atmosphere, and time). [Complete]

- FY14: Characterization of the species present in as-received and hydrothermally treated Cu-zeolite catalyst and evaluate the impact of hydrothermal aging on spatial distribution of copper species in zeolite crystallite and Pt particle size/distribution. [On-track]

- FY14: Correlate the materials and the material changes upon hydrothermal aging, identified by ORNL through the above milestone, with activity and selectivity in ammonia oxidation, evaluated at Cummins, on select hydrothermally treated ASCs. [On-track]

Background

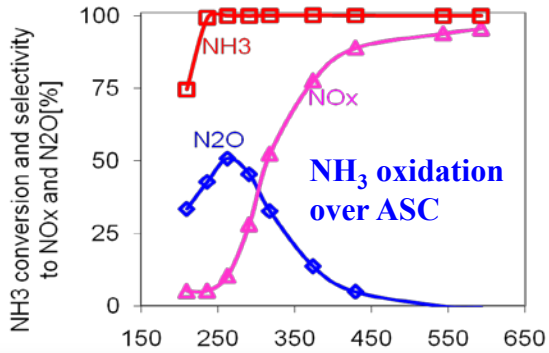
- Minimizing NH_3 slip from SCR catalyst is challenging
  - *e.g., during transient operation, when targeting nearly complete conversion of NOx*
- NH_3 slip from SCR catalyst is oxidized over an ASC, however its selectivity to N_2 is imperfect



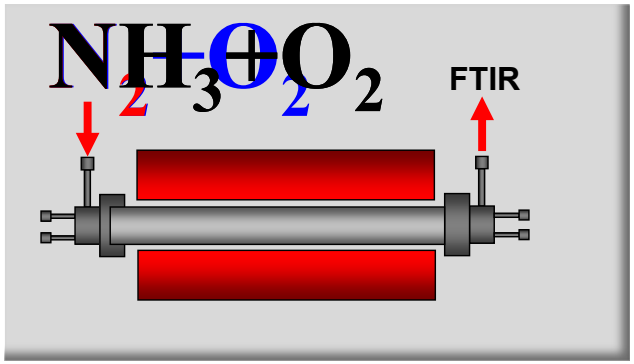
Typical SCR aftertreatment system

Objective

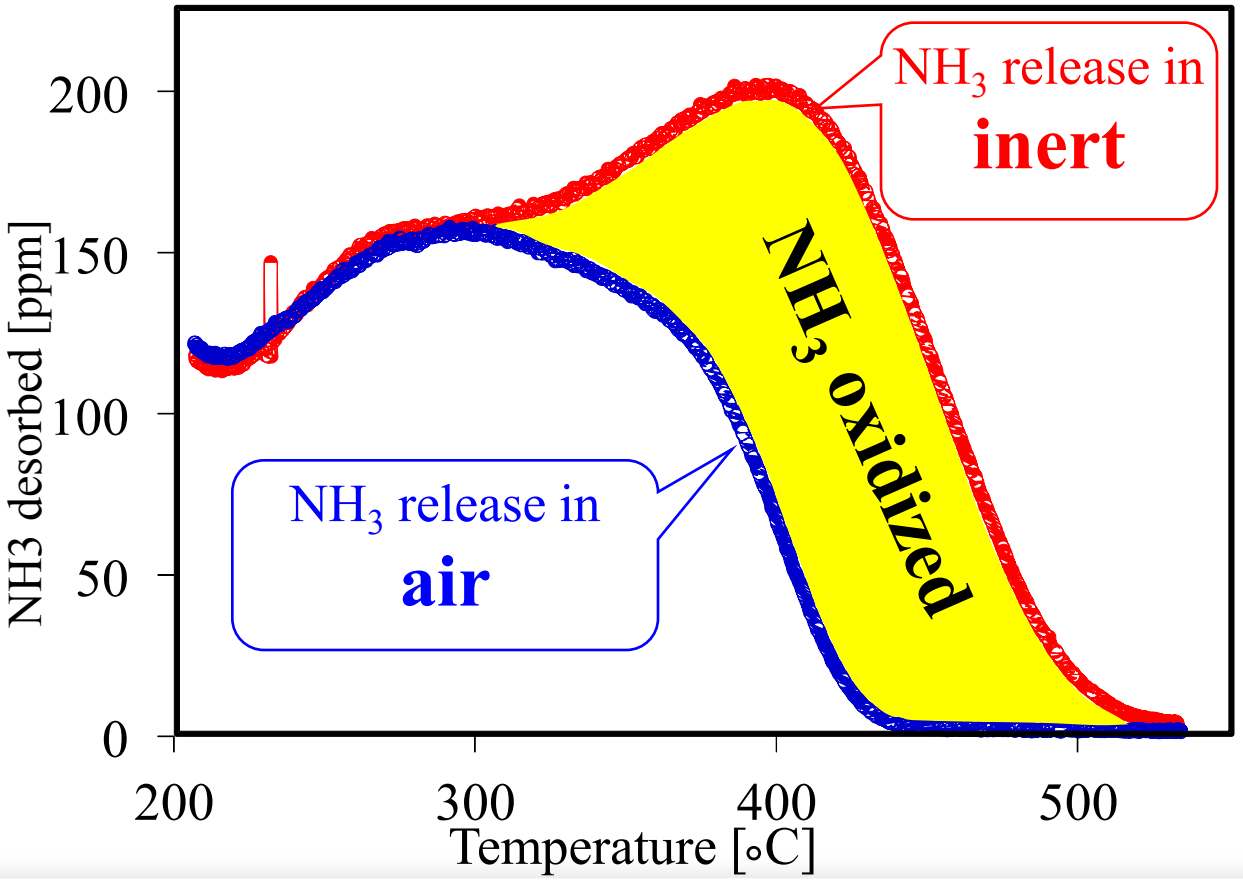
- Demonstrate the benefits of a particular NH_3 release and oxidation properties discovered in Cu-zeolite catalyst, a component in ASC, in minimizing NH_3 slip



NH_3 release under inert and oxidizing conditions

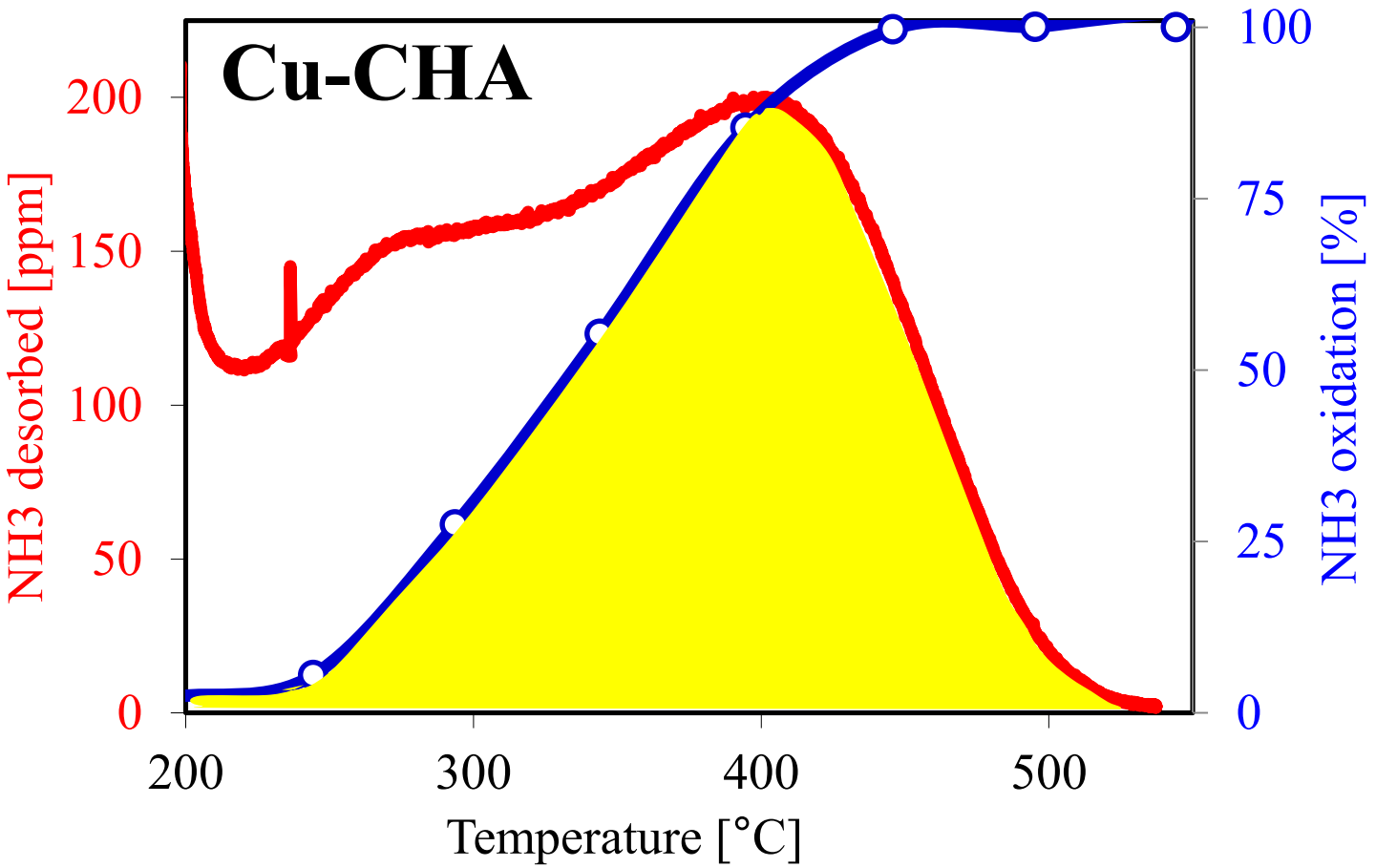


1. NH_3 storage at 200°C
2. NH_3 release under inert
3. NH_3 storage at 200°C
4. NH_3 release under air



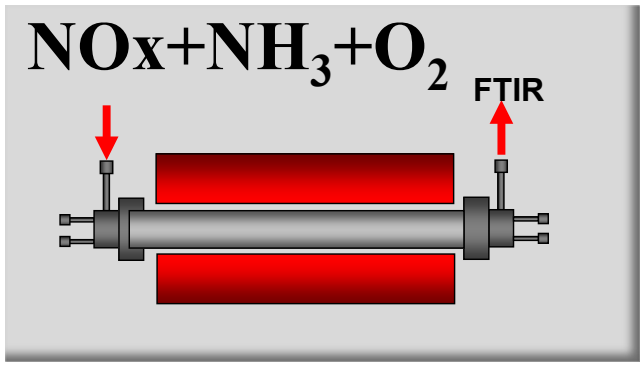
Technical Accomplishments

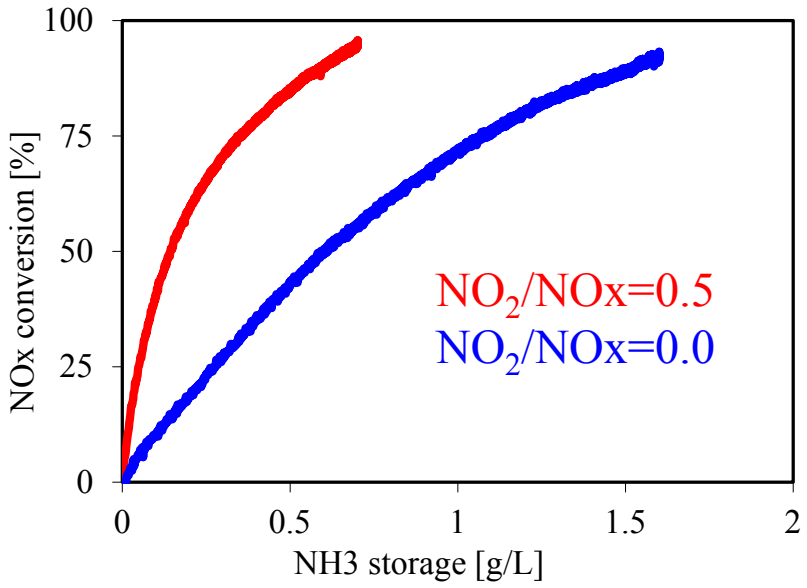
Overlapping NH_3 release and oxidation function



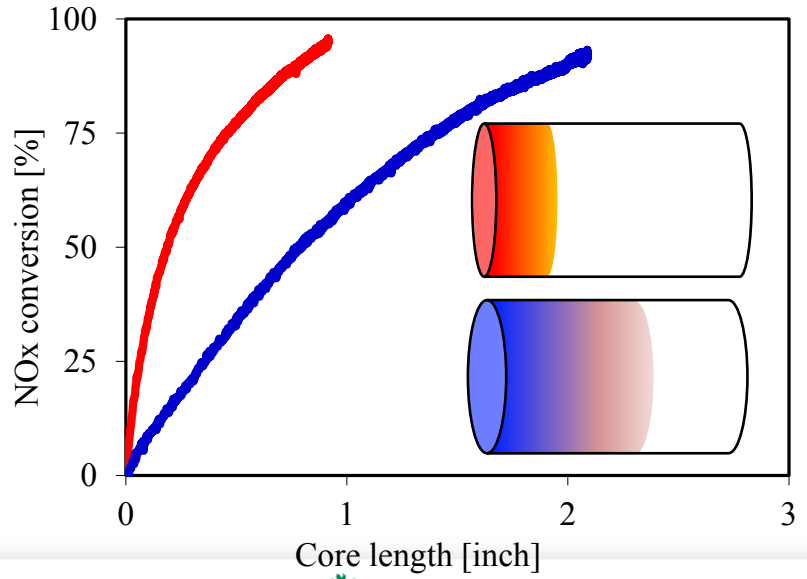
- Substantial amount of NH_3 desorbed above 375°C can be oxidized, and Cu-zeolite is quantitatively selective to N_2

NH_3 storage under practically-relevant operating conditions

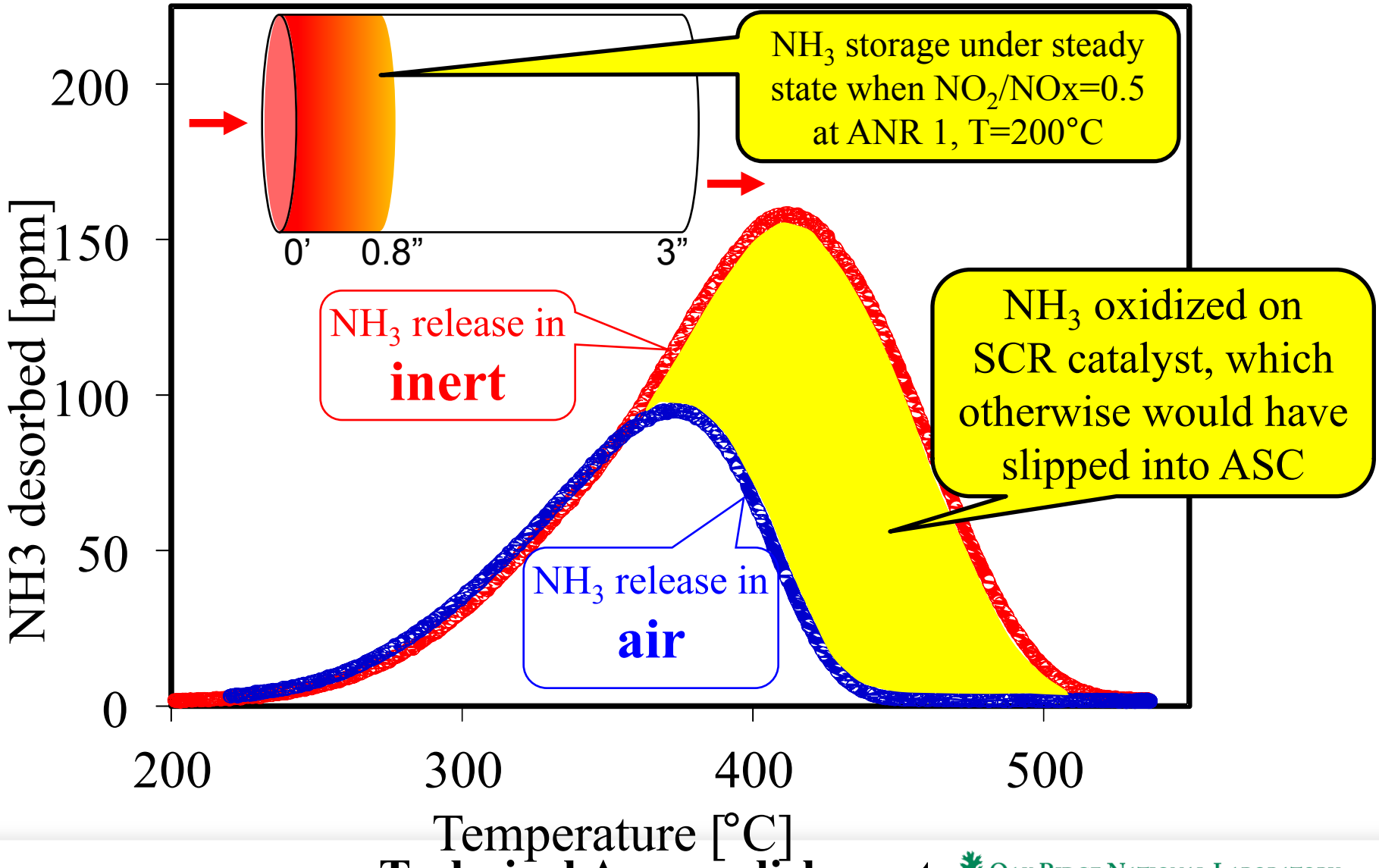




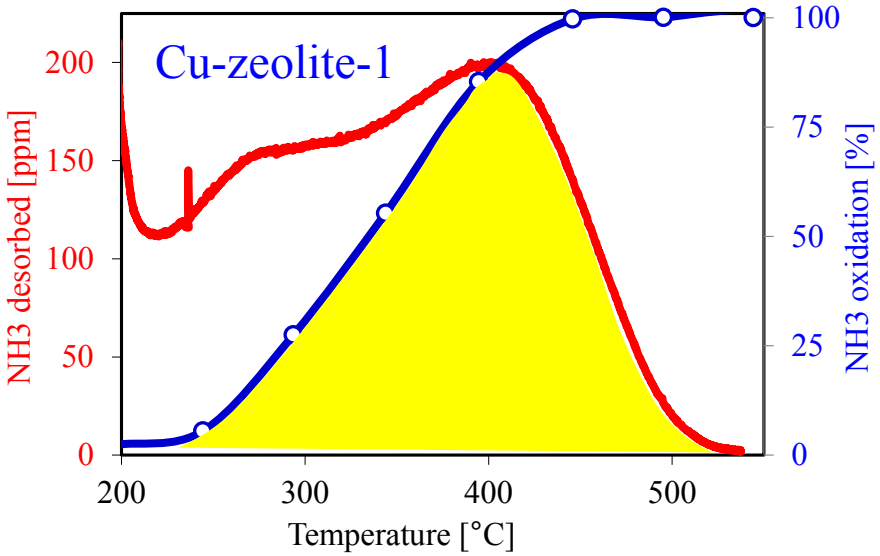
- Under SCR conditions, NH_3 storage is fastest of all processes
- That means, the NH_3 storage can be used as an approximation of the length of the catalyst saturated with NH_3
- Under practically-relevant conditions complete catalyst is virtually never saturated by NH_3

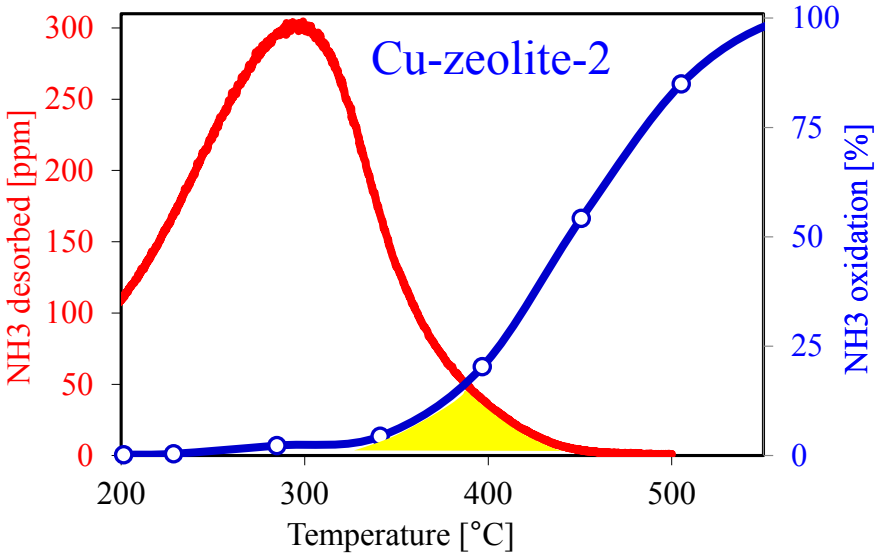


Under partial coverage conditions, strongest sites are responsible for the NH_3 desorption



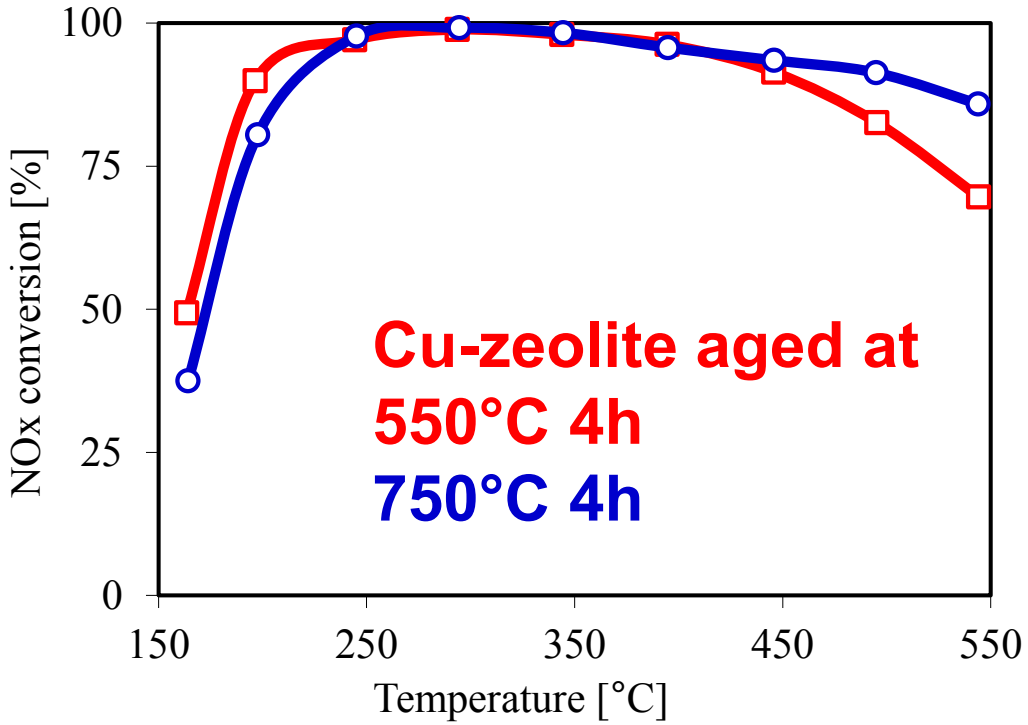
The beneficial overlap between high-temperature NH_3 release and oxidation is not universal to all Cu-CHA formulations





- Points at differences in both redox and acid-base properties between different Cu-CHA materials

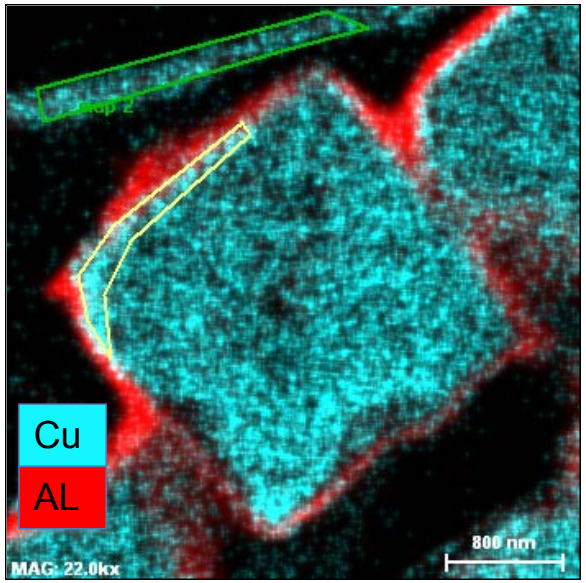
Overlapping NH_3 release and oxidation has minimal impact on the NOx conversion

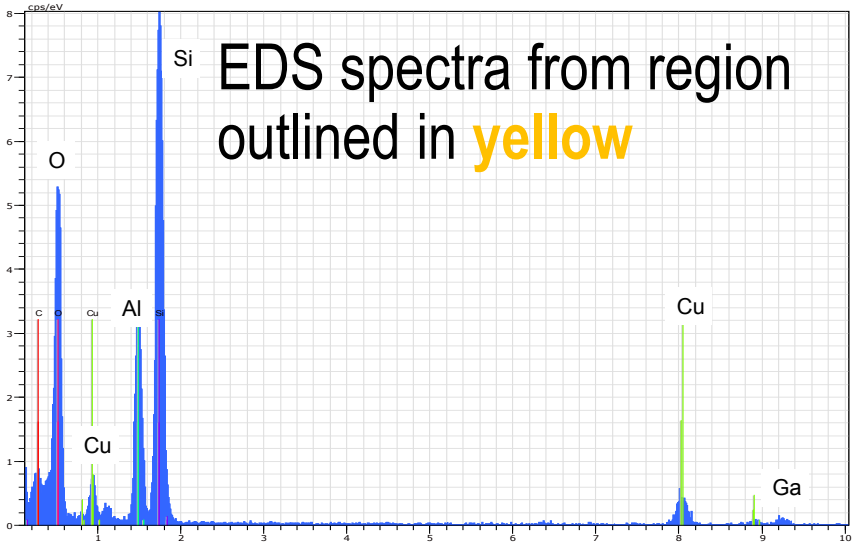


- Despite being very active for NH_3 oxidation, under the SCR conditions the specific Cu-zeolite showed high NOx conversion at elevated temperatures
  - *SCR reactions are much faster than NH_3 oxidation reaction*

Characterization of Cu and Al distribution, two critical functions

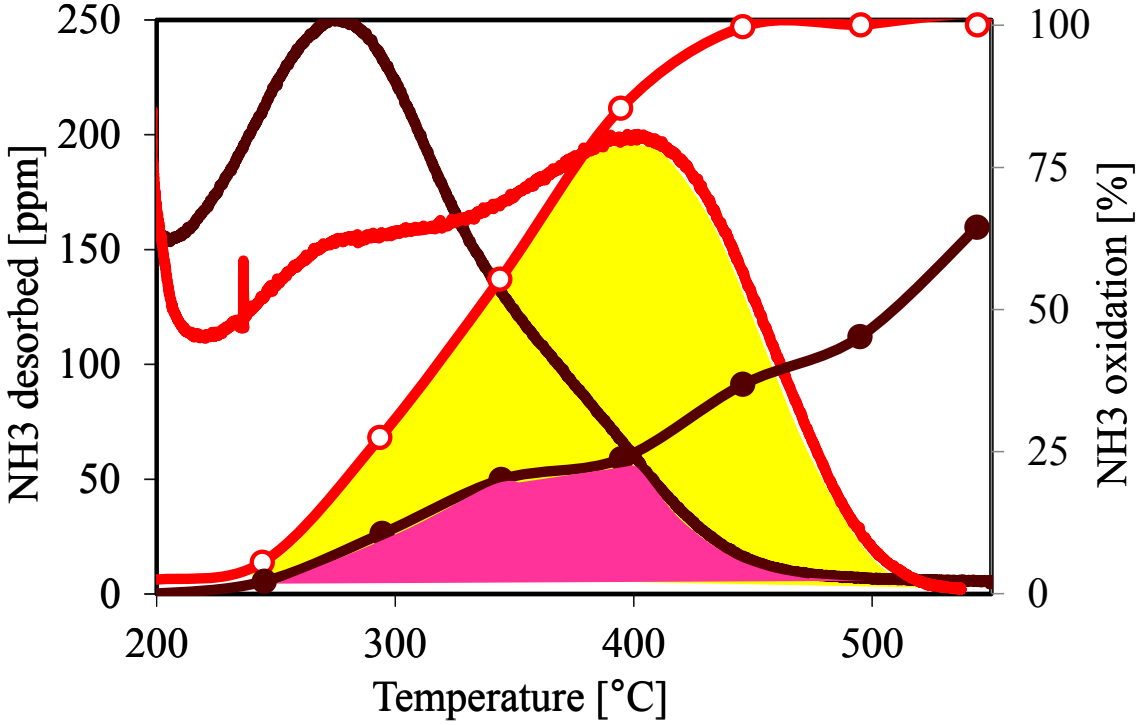
- Cu species distribution in small pore zeolite crystallite was not attempted before
- Amazingly Cu is uniformly distributed in the thick zeolite crystallite
- Cu species seems to be present in higher amount than Al
  - *Similar levels of Cu and Al species were expected*
  - *This characterization technique is under further development*

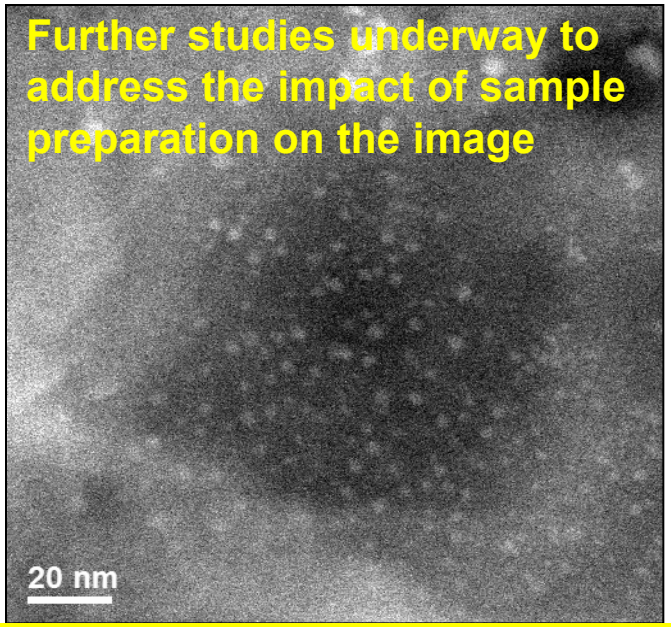




Technical Accomplishments

Impact of hydrothermal treatment on overlapping NH_3 desorption and oxidation

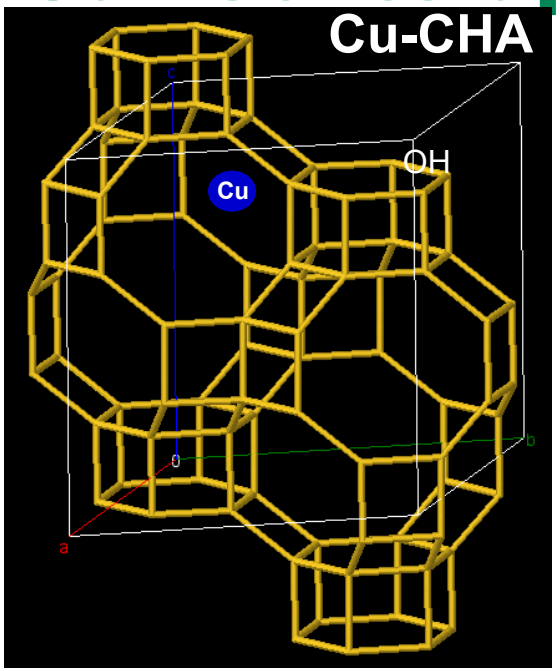


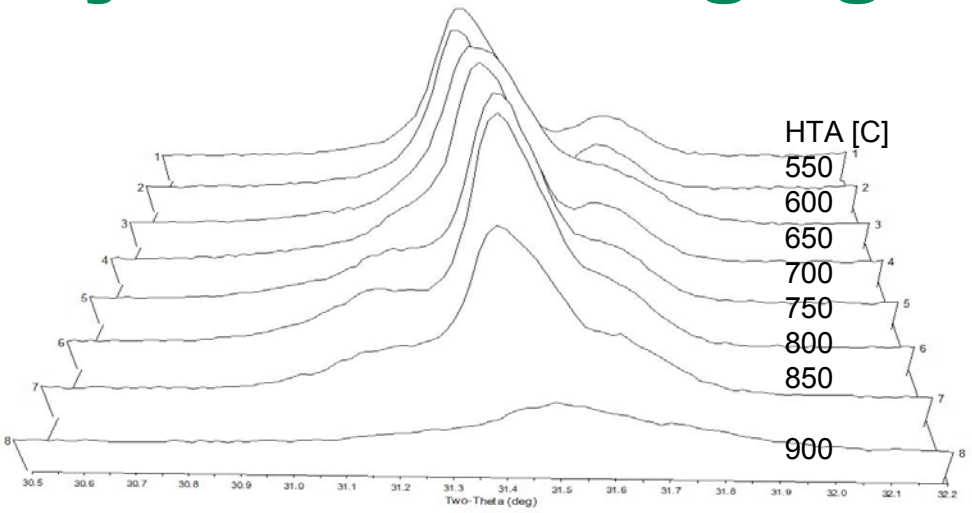


750°C 4h hydrothermal treated Cu-CHA

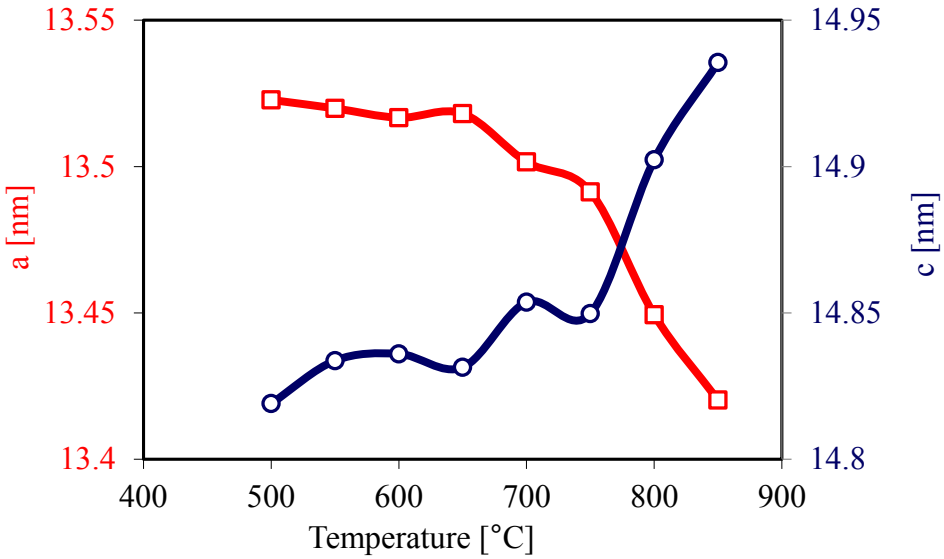
- Hydrothermal treatment decreased the extent of the desirable NH_3 desorption and oxidation overlap
  - *Weak NH_3 adsorption sites increased and strong sites decreased*
  - *NH_3 oxidation is shifting to higher temperatures, due to copper agglomeration*

In situ XRD characterization of changes in Cu-zeolite upon hydrothermal aging



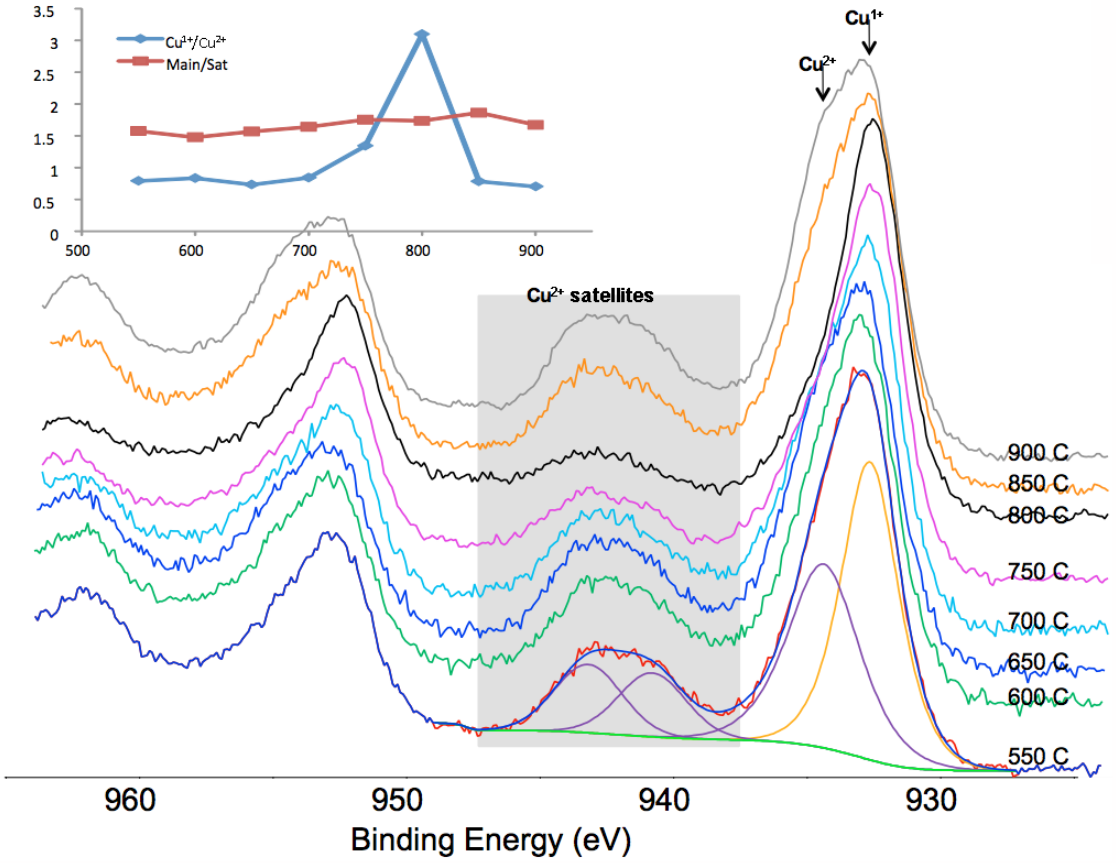


- The changes in lattice parameters (*a* and *c*) were anisotropic
  - *Delamination of zeolite is expected to decrease the cell parameters*
  - *However the anisotropic changes indicates potential reorganization of species **inside** the CHA crystal*



Technical Accomplishments

Impact of hydrothermal aging on the oxidation state of copper species



- Upon hydrothermal aging, up to 800°C, the concentration of partially reduced (Cu^{1+}) species increased

Technical Accomplishments

Response to Reviewer's comments

The repeated criticisms trended into 3 areas:

1. Project longevity: 12 years. Project scope has evolved over the years to address the increasingly stringent emission regulations and rapidly evolving catalyst technologies. Each year both material characterizations and system/parametric studies were performed.

FY2002-3: Focus to meet 2007 emission regulations with studies of engine aged de-sulfated samples containing Pt, TiO2, cordierite.

FY2004-6: Focus to meet 2007 emission regulations with studies of NOx adsorber catalysts in various states (e.g., aged desulfated, aging due to redox pulses, thermal degradation of NOx storage and reduction) in samples containing Pt, Gamma-Al2O3, base metal oxides, cordierite.

FY2007-9: Focus to meet 2010 emission regulations with ex-situ studies of the impact of hyrdothermal degradation/aging of Fe-Zeolites ammonia slip formulations which can be considered as first generation technology.

FY2010-14 Focus to meet the future emission regulations with in-situ and ex-situ characterization studies of hydrothermally aged Cu-Zeolites samples which are an integral part of the second (latest) generation ammonia slip formulations.

The funding level of this project over 12 years is consistent with what is currently possible in area of interest 8 within the recent Funding Opportunity Announcement (FOA) Number: DE-FOA-0000991 over a shorter term. Nevertheless, the project will be complete and **end** this year.

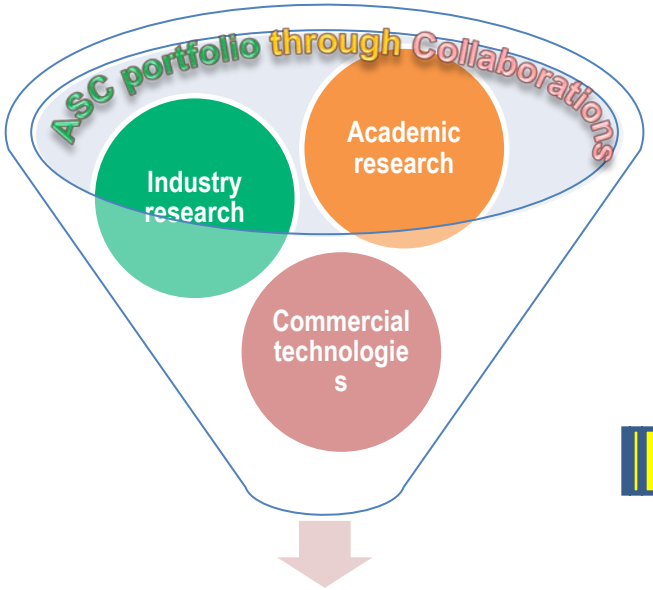
2. Characterization without interpretation: This has been addressed.

3. Service work & Collaboration contribution: In FY13, currently available commercial catalysts, **that are state of the art formulations**, were investigated, and results are made available to the community through the AMR, DOE annual reports and conference presentations and publications (a slide containing presentation / publication information is attached).

Miscellaneous: For Question 2, Reviewer 1: BASF is NOT involved in this project. Also for Question 2, Reviewer 1: To clarify, the in-situ high temperature XRD data shown was collected at ORNL by this research team and not from external sources.

Collaborations and coordination's with other institutions

Cummins



Select ASCs

- Identification of critical studies needed through extensive in-house performance and durability evaluations
- Provide samples and sample preparation methodologies to ORNL

ORNL

- Utilize the expertise to develop advanced characterization methodologies to understand the fundamentals of ASC performance and degradation mechanisms
  - *In-situ X-ray diffraction*
  - *FIB, HRTEM technique*
  - *Spectroscopic investigation*

Telephone conferences, meetings, exchange of samples and reactor data to compliment the characterization studies

Future work and remaining challenges and barriers

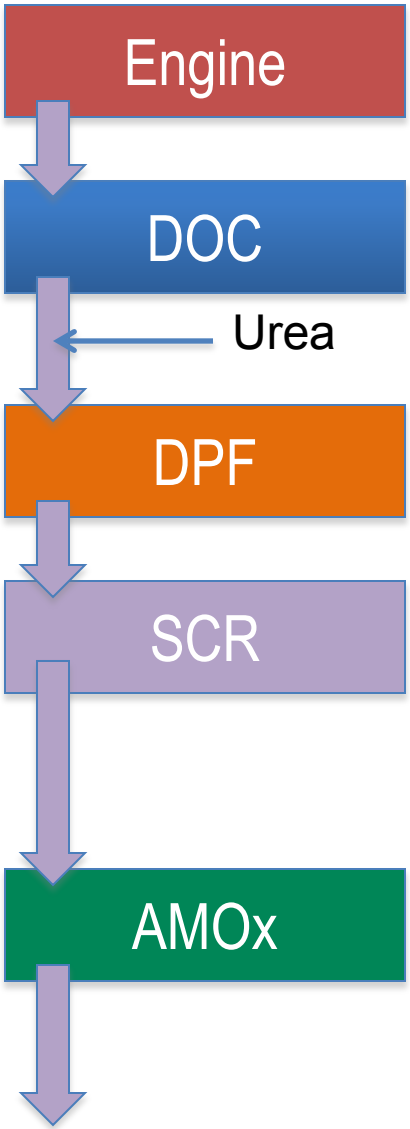
- Complete the characterization of hydrothermally aged samples
- Correlate the characterization and reactor testing results to reactor studies at Cummins, such as temperature programmed desorption evaluation
- Document the findings in the final reports.
- Challenge: Electron microscopy of zeolites is difficult as the electron beam can create the artifacts. Sample preparation techniques and data collection strategies are being developed/evolving

Summary

- The overlapping NH_3 release and oxidation functions, discovered in one of the Cu-CHA formulations, can significantly reduce NH_3 slip from SCR catalyst (**built-in AMOx function**)
  - *Two distinct NH_3 storage sites are present in this Cu-CHA formulation*
  - *The feature is not universal to all Cu-CHA formulations*
- Changes in Cu-zeolite catalyst functions, upon hydrothermal treatement, reduces the extent of the desirable overlap between the NH_3 release and oxidation activity
  - *Hydrothermal treatment leads to*
    - *Increase in the weak storage sites at the expense of the strong storage sites*
    - *Decrease in NH_3 oxidation activity due to re-distribution and sintering of redox sites*
- Characterization by *in situ* XRD, electron microscopy among other techniques at ORNL indicated that upon hydrothermal aging
  - *Anisotropic changes due to potential re-organization of species inside the zeolite crystallite*
  - *Increase in the concentration of reduced copper species concentration*
  - *Sintering of copper species to form copper agglomerates that can be correlated to reactor studies*
- This project is providing fundamental insights needed now and for future aftertreatment technologies that might result in
  - *Improved aftertreatment strategies*
  - *Fuel efficient and cost effective aftertreatment technologies*

Technical Backup slides

Background: Exhaust path though the Aftertreatments



Diesel Oxidation Catalyst (DOC) is heated by the exhaust. Once at temperature, DOC oxidizes or burns off some of the escaping hydrocarbons and in doing so also adds heat to the downstream system.

Diesel Particulate Filter (DPF) or soot filter removes particulate matter. Regen requires a elevated temp. “NOXidation” is possible, wherein the NOx in the exhaust aggressively oxidizes the soot, helping the DPF to function.

Selective Catalytic Reduction (SCR) catalyst which deals with NOx (or a lean NOx trap). Upstream of the DPF, urea is added to the exhaust stream, which then heats up to form ammonia, which reacts on the SCR catalyst to reduce the NOx. So the SCR catalyst oxidizes the NOx to trap it and then with the ammonia reduces the NOx to N2 and O2 on the SCR to regen it. Again this is temperature and gaseous species dependent.

Ammonia Oxidation (AMOx) catalyst which takes care of any unreacted urea/NH3, and which also requires heat but less than others.

Here the AMOx catalyst is a Copper doped Chabazite Zeolite from Johnson-Matthey

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:** Characterize hydrothermally aged samples with X-ray diffraction, spectroscopy, and microscopy. Parametric studies of systems. Correlate findings with to understand degradation mechanisms.
- **Technical Accomplishments:**
  - The overlapping NH_3 release and oxidation functions, observed in one of the Cu-CHA formulations, can significantly reduce NH_3 slip from SCR catalyst
  - Changes in Cu-zeolite catalyst functions, upon hydrothermal treatment, reduces the extent of the desirable overlap between the NH_3 release and oxidation activity
  - In-situ hydrothermal aging with HTXRD stage, XPS revealed catalyst is structurally stable under modest temperatures and low water content atmosphere
  - Above 750°C, HTXRD, NMR indicate zeolite structure begins to change rapidly with Cu exiting the structure
- **Collaboration:** Assist Cummins and the Diesel Engine manufacturers to produce engines which attain the required prevailing emission levels and beyond.
- **Future Work:** Finish investigations of the degradation mechanisms of catalytic materials and write final reports

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