Enhanced High and Low Temperature Performance of NOx Reduction Materials

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ACE026

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Project Overview

Timeline

- 2009 – 2016
- 3-Year Renewal Executed – March 2013

Budget

- Matched 50/50 by Cummins as per CRADA agreement
- DOE funding for FY13 – FY15: $300K each year.

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- Cummins, Inc.
  - w/Johnson Matthey

Barriers - Relevance

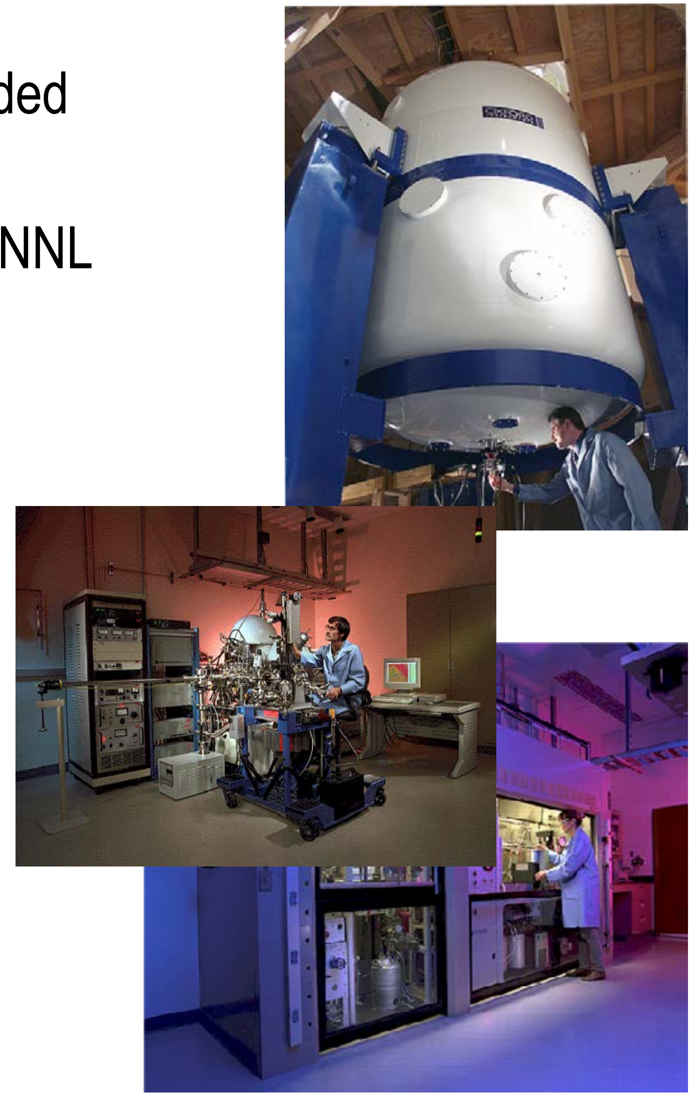
- Petroleum reduction and carbon emissions reduction goals can only be achieved by using new and more efficient powertrains. However, **low exhaust temperatures** of future engines will create major challenges for exhaust aftertreatment technologies.
- In addition NOx reduction systems will also require **improved higher temperature performance** and stability.
  - For example, NOx removal performance during high temperature system maintenance events, including DPF regeneration and catalyst regeneration (e.g., P and S removal). NOx treatment for natural gas engines will also require higher temperature performance.
- It is important to reduce system costs while maintaining, even improving, performance and long-term stability for applications with both petroleum-based fuels and the non-petroleum alternatives.

Goals and Objectives

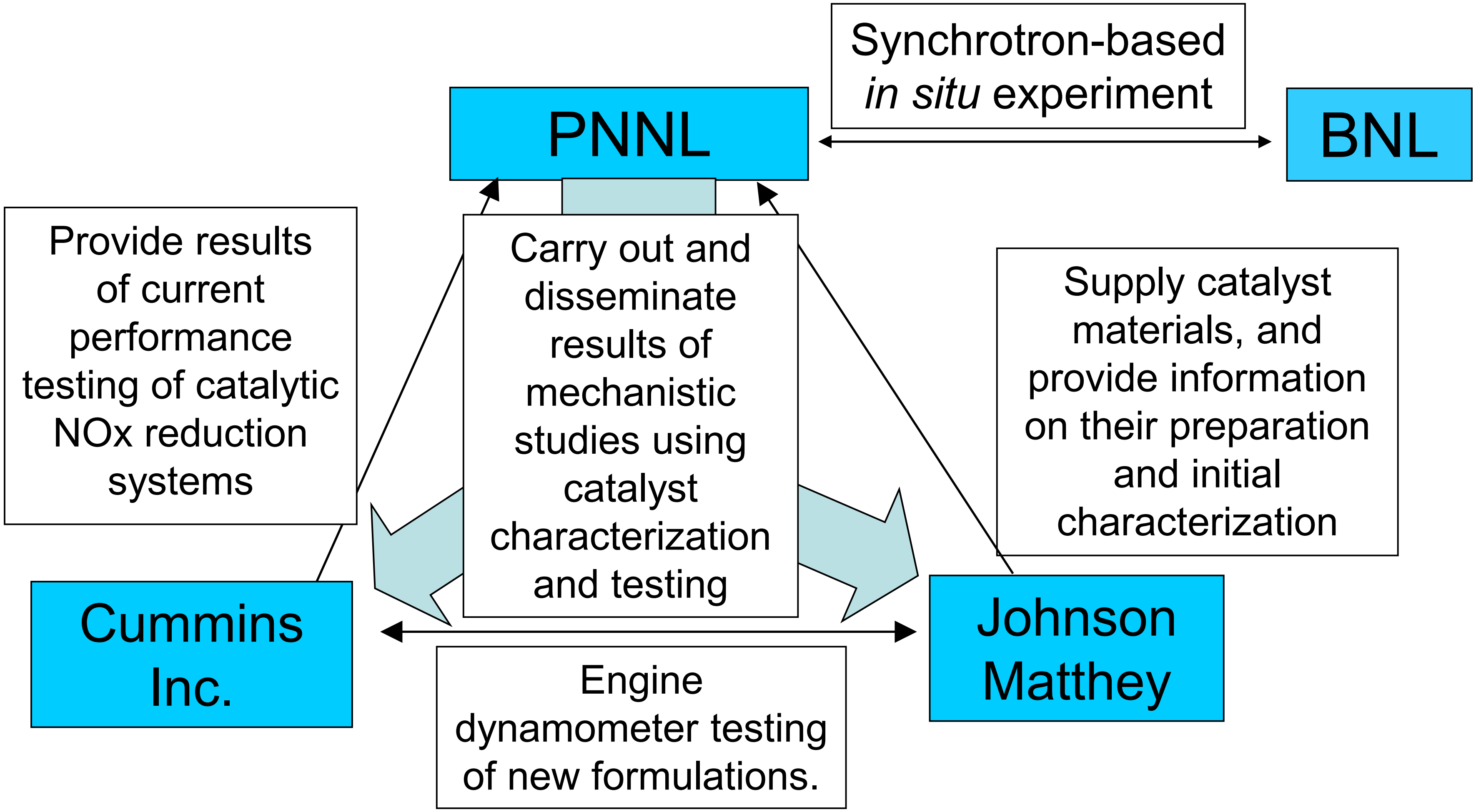
- For NOx after-treatment from lean-burn (including diesel) engines, develop a fundamental understanding of the limitations of candidate next generation materials for operation at **lower** and **higher** temperatures.
- Focus on characterizing and understanding the following specific issues:
  - Limitations on low and high temperature performance;
  - mechanisms for deactivation for candidate materials;
    - significant causes of low and high temperature performance loss;
    - material changes with hydrothermal aging;
    - the sulfur adsorption and regeneration mechanisms for modified and/or alternative catalyst materials.

Approach

- Prepare and Process Catalyst Materials
  - Fully formulated (proprietary) catalysts have been provided by Johnson Matthey.
  - Based on prior PNNL results and published literature, PNNL is preparing model candidate materials:
    - Variations in LNT storage element and support material;
    - Identification of optimum synthesis procedures for preparing reproducible SCR catalysts.
  - These materials are studied:
    - Fresh, as-received (AR) and degreened
    - Thermally-aged and/or variably sulfated
  - Utilize expertise and state-of-the-art catalyst characterization and testing facilities at PNNL's IIC to address mechanisms and structure/function
    - XRD, XPS, NMR, TEM/EDX and SEM/EDX
    - NH_3 and NO_2 TPD, H_2 TPRX
    - Synchrotron based techniques (*in situ* time-resolved XRD)
    - Lab reaction system



Collaborations/Interactions



- Conference calls are held typically once every month or two to discuss the results.
- The most recent annual face-to-face CRADA Review was held in Columbus, IN (December, 2014).

Collaborations/Interactions

Vehicle Technologies Office

Synchrotron-based
in situ experiment

BNL

Results obtained on similar model catalyst formulations in more fundamental CLEERS-funded studies are essential for this program's success.

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Current Year Studies

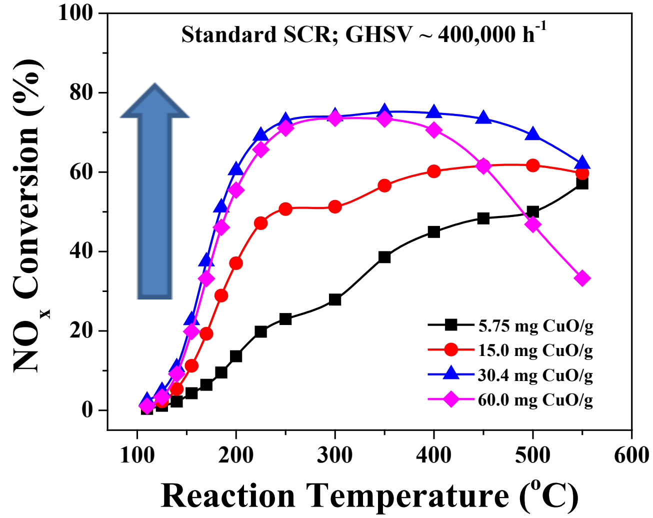
- **Realistic and model catalyst studies of low and high temperature performance of CHA-based SCR catalysts**
  - Characterization and reactivity of Cu/SAPO-34 as a function of Cu loading – effects on low and high temperature performance.
  - Hydrothermal stability of newly synthesized Fe/SSZ-13 catalysts (prepared in CLEERS program).
  - Effects of alkali and alkaline earth cocations on reactivity and hydrothermal stability of Cu/SSZ-13 catalysts.

- Model catalysts synthesized to address the following issues this year:
  - Model Cu/SSZ-13 catalysts:
    - Have addressed some specific issues with engine- and vehicle-tested catalyst materials.
    - Effects from Cu loading on hydrothermal stability.
    - Effects from cocations (alkali and alkaline-earth cations, e.g., Na^+, K^+, Ca^{2+}) to Cu ion location, reactivity and hydrothermal stability.
  - Fe/SSZ-13 catalysts:
    - Fe loading effects on hydrothermal stability.
    - Fe catalysts show considerably lower "light-off" temperatures during "fast SCR" reaction in contrast to Cu/SSZ-13.
    - Comparison between Fe/SSZ-13 and commercialized Fe/beta.
  - Cu,Fe/SSZ-13 catalysts.
    - Synergy between Cu and Fe ions in improving light-off and operation temperature window.

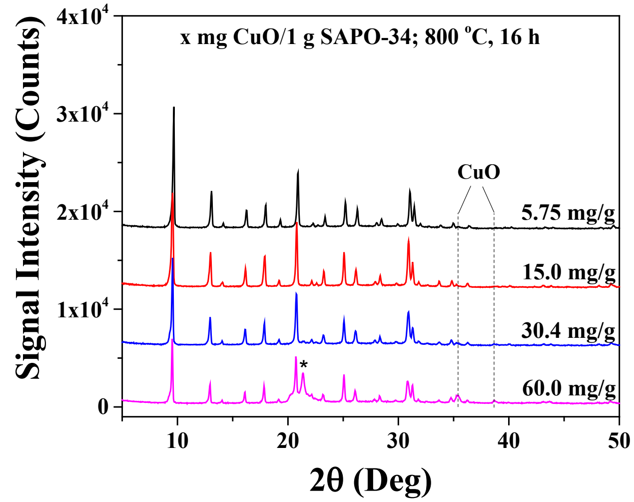
Cu/SAPO-34 Catalysts: effects from Cu loading and hydrothermal aging

Standard SCR

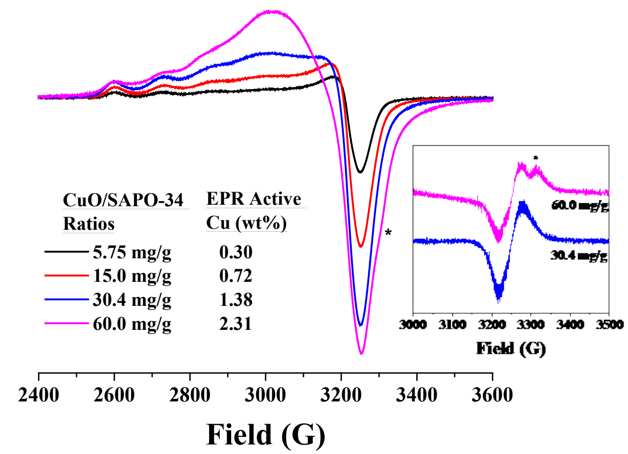
NOx Conversion



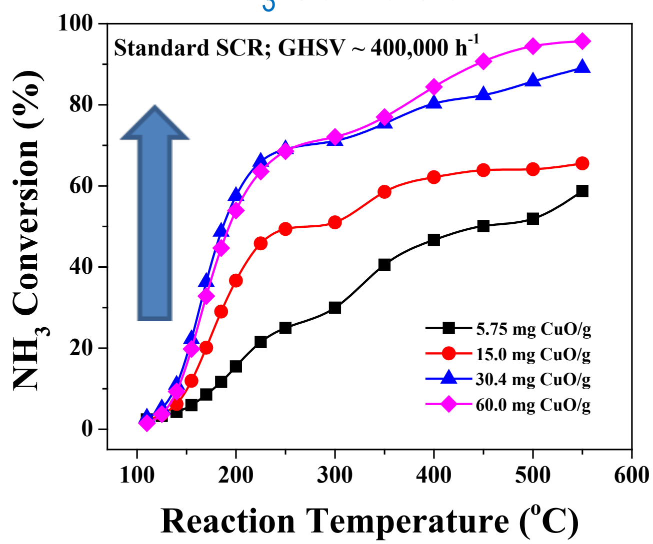
XRD



EPR



NH_3 Conversion



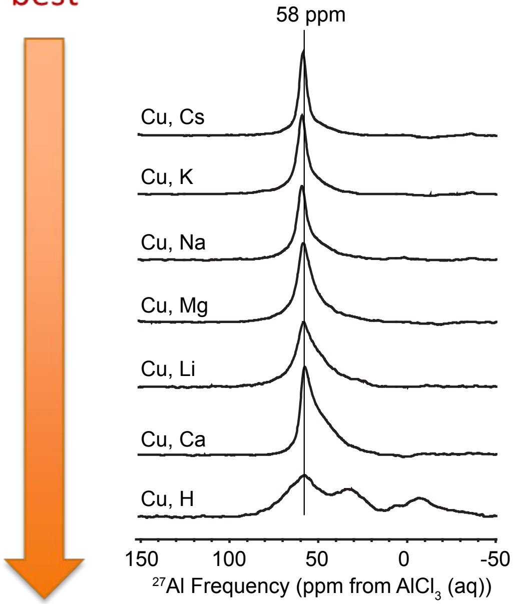
- Cu loading of ~1.0-1.5 wt.% gives the most optimized catalyst performance.
- Excessive Cu loading is a much more severe factor than hydrothermal aging time and temperature for the destruction of the SAPO-34 structure.
- Chemical poisoning more important than structure degradation to explain deactivation of Cu/SAPO-34.

F. Gao, E.D. Walter, N.W. Washton, J. Szanyi, C.H.F. Peden, Appl. Catal. B 162 (2105) 501-514.

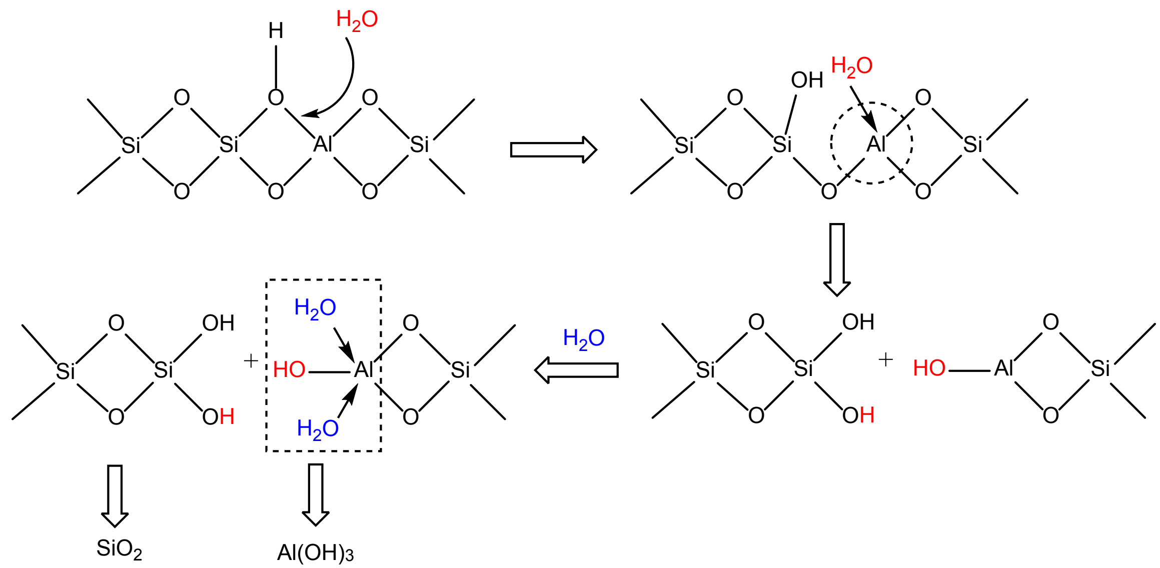
Cu/SSZ-13 Catalysts: effects from alkali and alkaline earth cocations

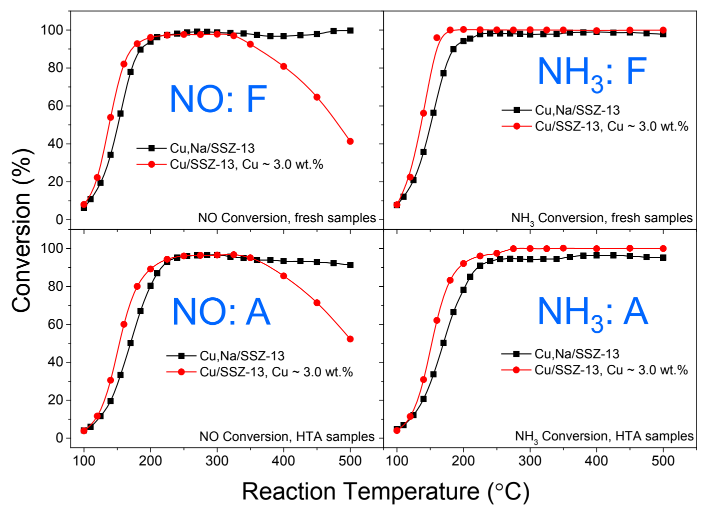
Na/SSZ-13 → NH_4/SSZ-13 → M/SSZ-13 → Cu,M/SSZ-13

best



worst



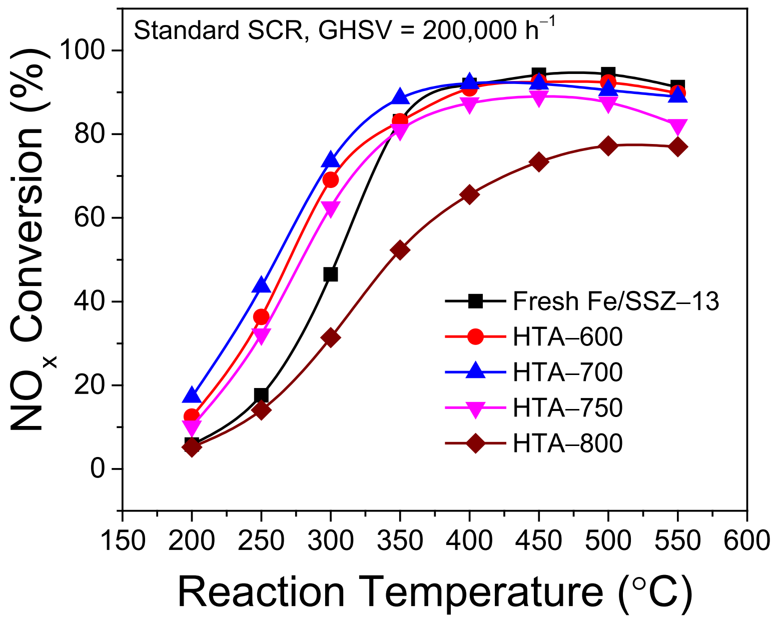


- The introduction of certain amounts of cocations tunes both Brønsted acid site density and Cu-ion location.
- This allows both low-temperature activity and hydrothermal stability to be enhanced.

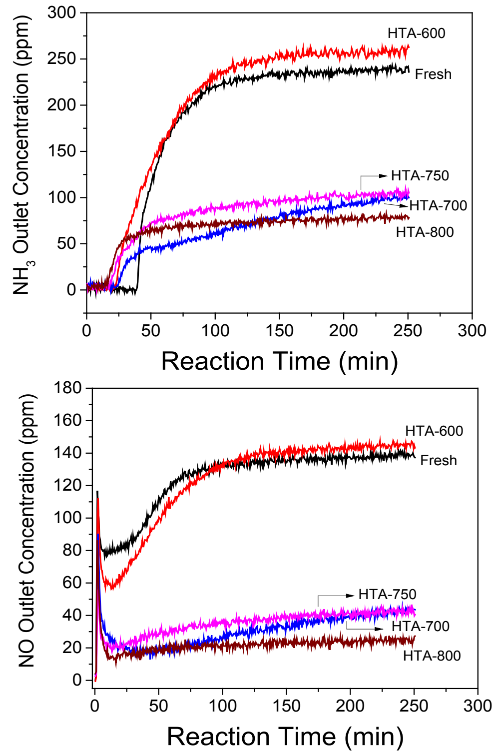
F. Gao, M. Kollar, N.M. Washton, Y.L. Wang, J. Szanyi, C.H.F. Peden, in preparation.

Fe/SSZ-13 Catalysts: effects from hydrothermal aging

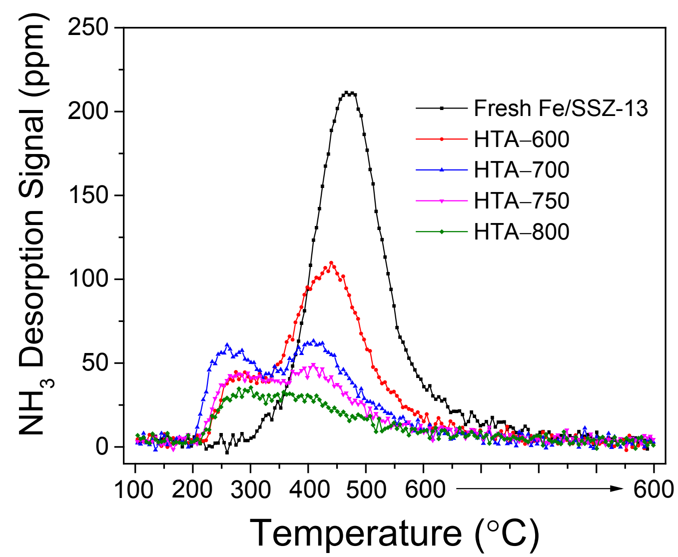
Standard SCR



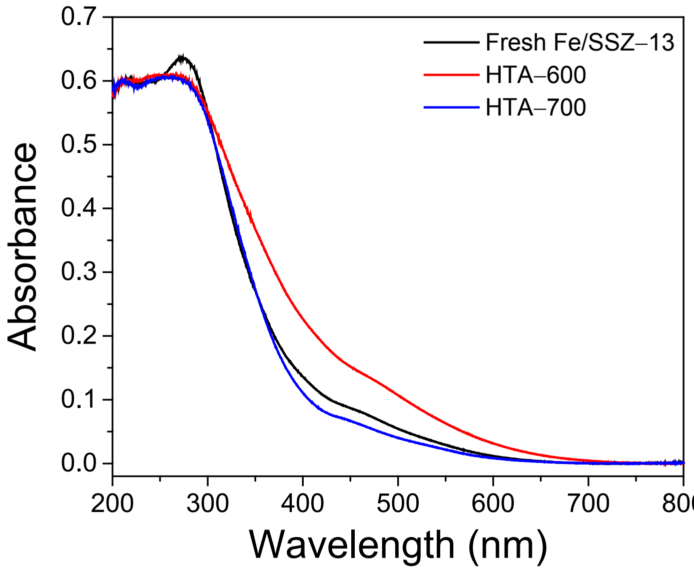
Fast SCR at 200 °C



NH_3-TPD



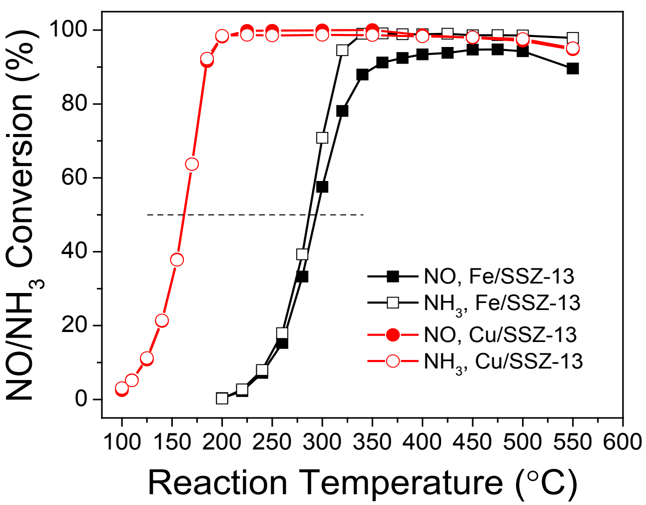
UV-Vis



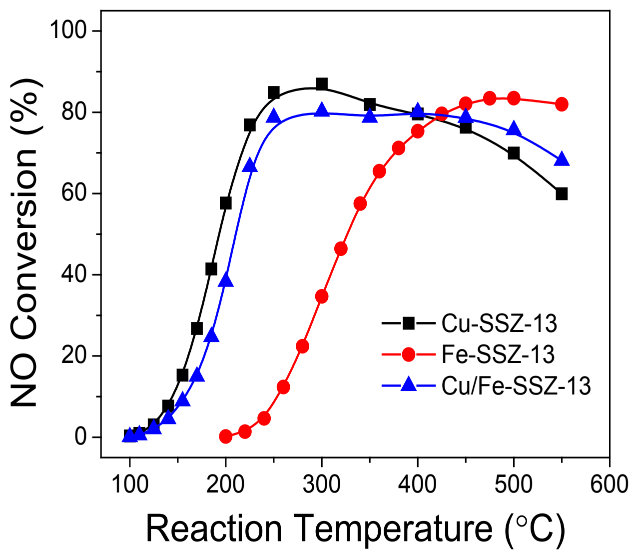
- Redistribution of Fe ions during hydrothermal aging. This enhances low-temperature performance. FeOx clustering, followed by FeAlOx formation.
- Decrease Brønsted acidity eliminates NH_4NO_3 inhibition and enhances fast SCR performance.

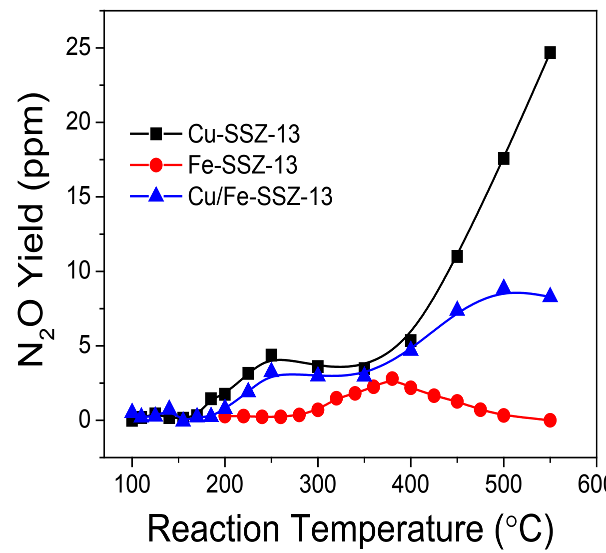
Comparison and synergy between Cu/CHA and Fe/CHA catalysts

Standard SCR



Standard SCR, aged Cu/CHA + Fe/CHA mixture





- Poor low-temperature standard SCR performance for Fe/CHA due to NH_3 inhibition.
- Combination of Cu/CHA and Fe/CHA broadens the operational window.
- Synergy between the two catalysts in eliminating N_2O formation.

F. Gao, Y.L. Wang, M. Kollar, N.M. Washton, J. Szanyi, C.H.F. Peden. *Catalysis Today* (2015) doi:10.1016/j.cattod.2015.01.025.

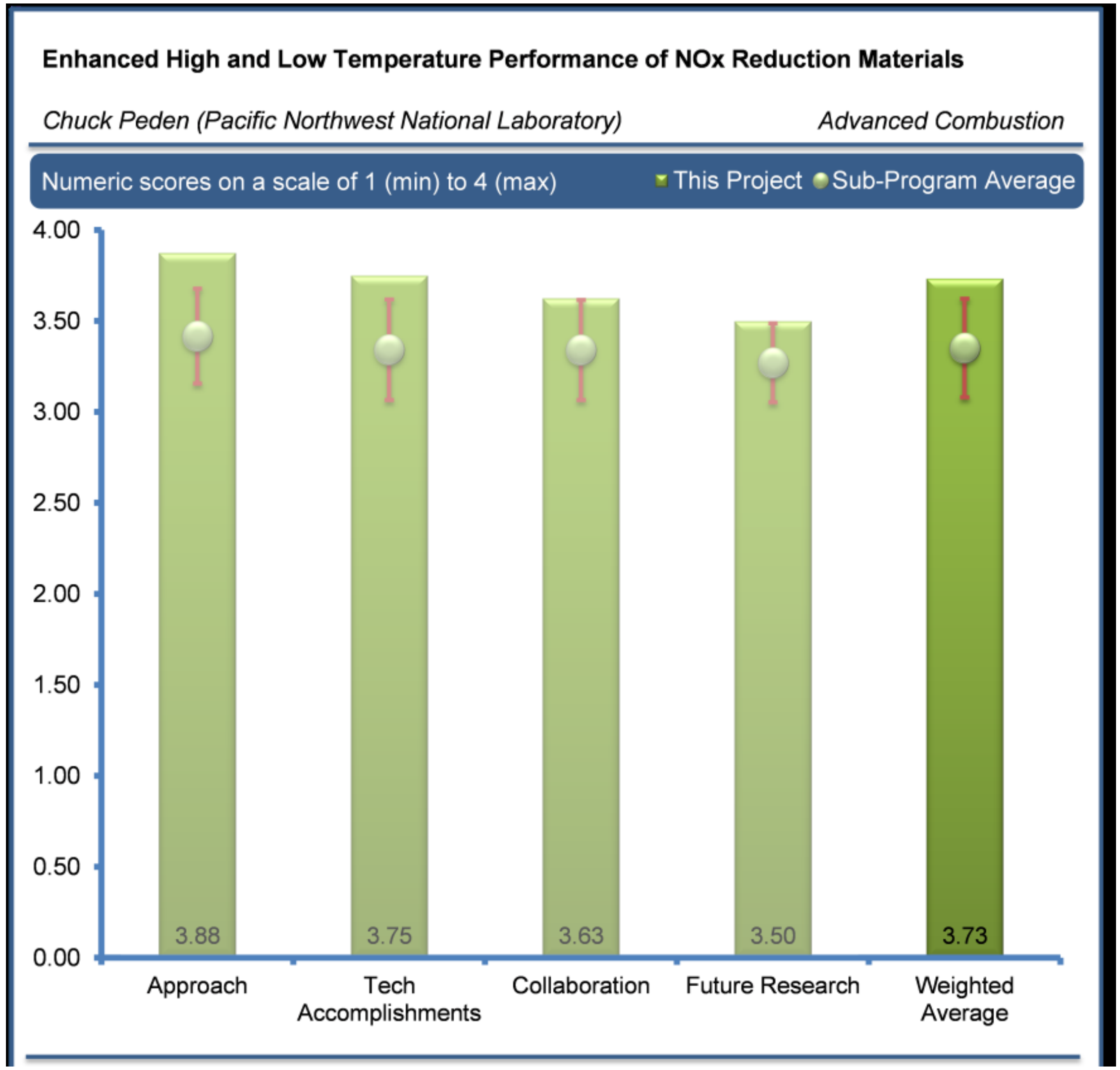
Planned Future Work

- Studies will continue to be especially focused on mechanisms/limitations for both low and high temperature performance with an emphasis on catalyst durability.
  - NO_2/NOx ratio effects and the removal of NH_4NO_3 poisoning by control of zeolite acidity.
  - Effects from hydrocarbons and sulfur to low temperature reactions.
- Detailed characterization (EPR, Mössbauer, TPR, x-ray absorption, etc.) of Cu and Fe species in Cu-Fe/SSZ-13 and Cu-Fe/SAPO-34 catalysts as a function of metal loading.
- Theoretical support for these studies is obtained in collaboration with Purdue, Notre Dame and Washington State University as part of a NSF-DOE funded program.

Response to previous (2014) AMR reviewer's comments

Above average scores and numerous positive comments:

We are gratified that the reviewers recognize this area as important, and that our approach, that takes advantage of a considerable history in studying the properties of the current generation of NSR and especially SCR catalysts, is a good and useful one. We also noted that the reviewers supported our reduced emphasis on NSR catalysts proposed for this year in favor of more attention to SCR studies. **There were no specific negative comments or suggestions that seem to require a response here.**



Summary

- A critical need for future NOx emission control technologies will be significantly **improved lower and higher temperature performance** and stability.
- PNNL and Cummins are carrying out collaborative research aimed at addressing these critical performance issues in LNT and SCR catalysts. This CRADA is also focused on catalyst deactivation due to thermal degradation and/or sulfur poisoning.
- Additional leverage is being provided by studies of SCR catalysts carried out at Purdue, Notre Dame and Washington State University as part of a newly NSF/DOE-funded project (Alex Yezerets, Cummins, and Chuck Peden, PNNL, are co-PIs).
- Technical highlights from this project included:
  - Model Cu/SAPO-34, Fe/SSZ-13, and Cu/SSZ-13 with various Cu/Al and Si/Al ratios have been prepared for a number of studies of low- and high-temperature performance of CHA-based SCR catalysts.
  - These studies led, in part, to the identification of SCR catalyst materials with significantly lower "light-off" temperatures and NH_4NO_3 resistance than the first-generation Cu/SSZ-13.
- Primary focus of future work for this next year will be on limitations of low- and high-temperature performance of CHA-based SCR catalysts.