Enhanced High and Low Temperature Performance of NOx Reduction Materials

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ACE026

Project Overview

Timeline

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

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

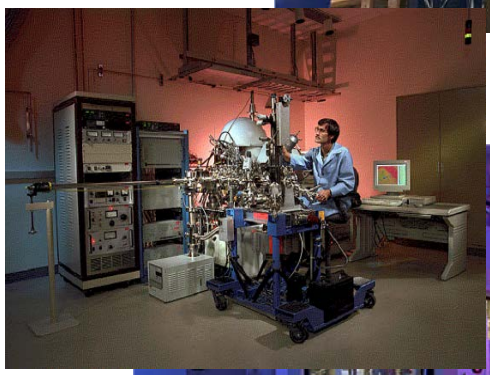
- Petroleum reduction and carbon emissions reduction goals can only be achieved by using new and more efficient powertrains. However, **low exhaust temperatures** of future engines will create major challenges for exhaust aftertreatment technologies.
- In addition, NOx reduction systems will also require **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).
  - 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.

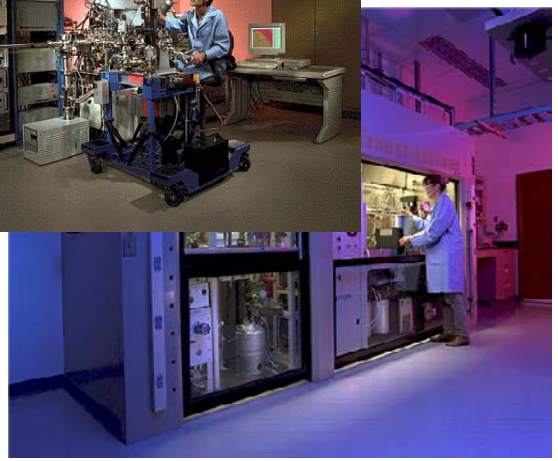
Goals and Objectives

- For NOx after-treatment from lean-burn (including diesel) engines, develop a fundamental understanding of the limitations of catalytic systems for operation at **lower** and **higher** temperatures, and provide guidelines for breaking such limitations.
- 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 state-of-the-art 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, EPR, Mössbauer, TEM/EDS and SEM/EDS
    - NH_3 and NO_2 TPD, H_2 TPR
    - Synchrotron based techniques (*in situ* time-resolved XRD)
    - Lab reaction systems





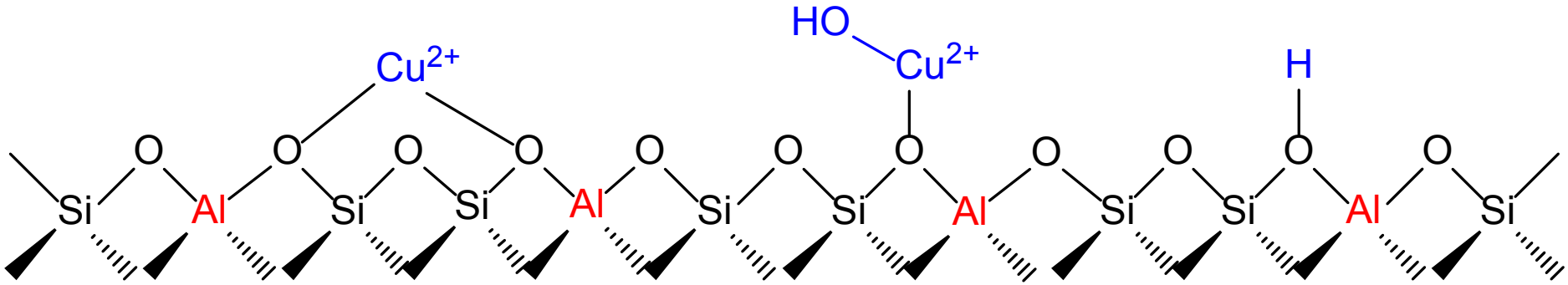
Current Year Studies

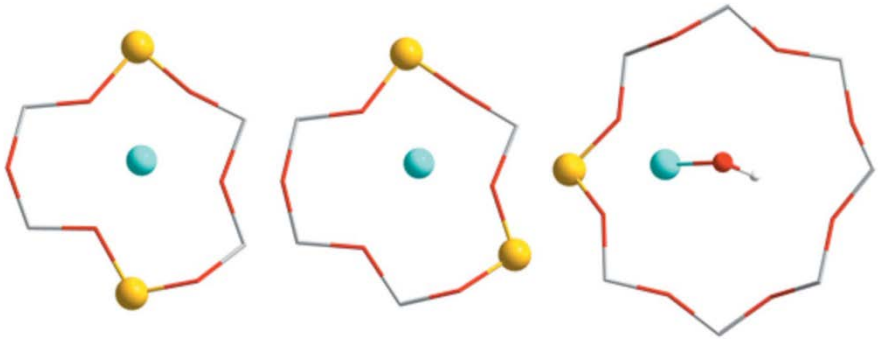
- **Realistic and model catalyst studies of low and high temperature performance of CHA-based SCR catalysts**
  - Guidelines for rational design of Cu/SSZ-13 and Cu/SAPO-34 catalysts used in standard SCR.
  - Key rate-limiting factors for fast SCR catalyzed by Fe/zeolites.
  - Cu and Fe co-cationed Cu,Fe/SSZ-13 catalysts: research on the synergy between different active sites.

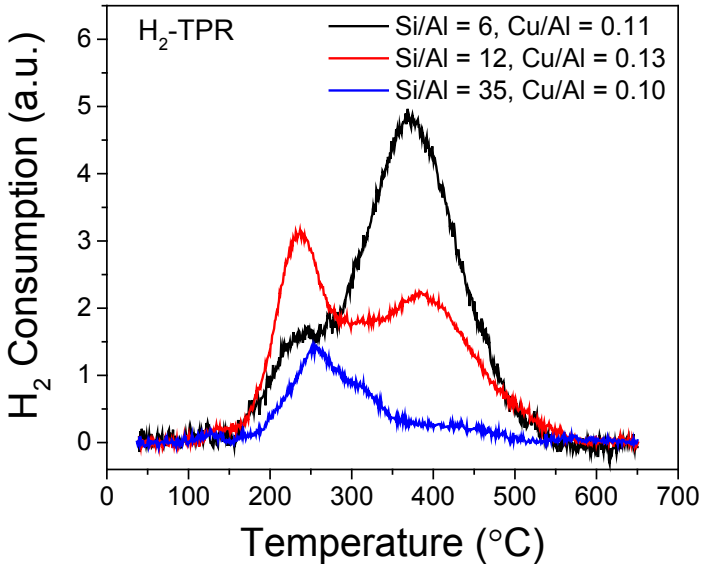
Technical Accomplishments

- Model catalysts synthesized to address the following issues this year:
  - Model Cu/SSZ-13 and Cu/SAPO-34 catalysts:
    - From studying kinetics of the target and side reactions, suggested Cu loadings are derived.
    - Effects from cocations (e.g., Na^+): synthesis of hydrothermally stable SCR catalysts with excellent selectivity at any temperature.
  - Fe/SSZ-13 and Fe/beta catalysts:
    - Understanding key limitations for low- and high-temperature NOx conversion efficiency.
  - Cu,Fe/SSZ-13 and Cu,Fe/beta catalysts.
    - Synergy between Cu and Fe ions in improving light-off and operation temperature window.

Cu/CHA Catalysts: determination of optimized compositions from rational design



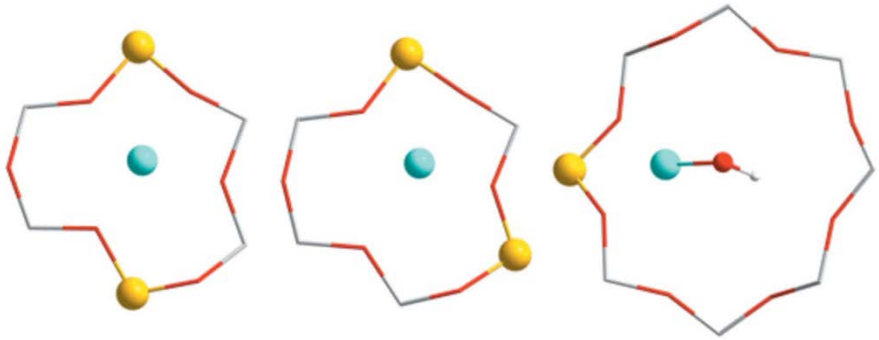




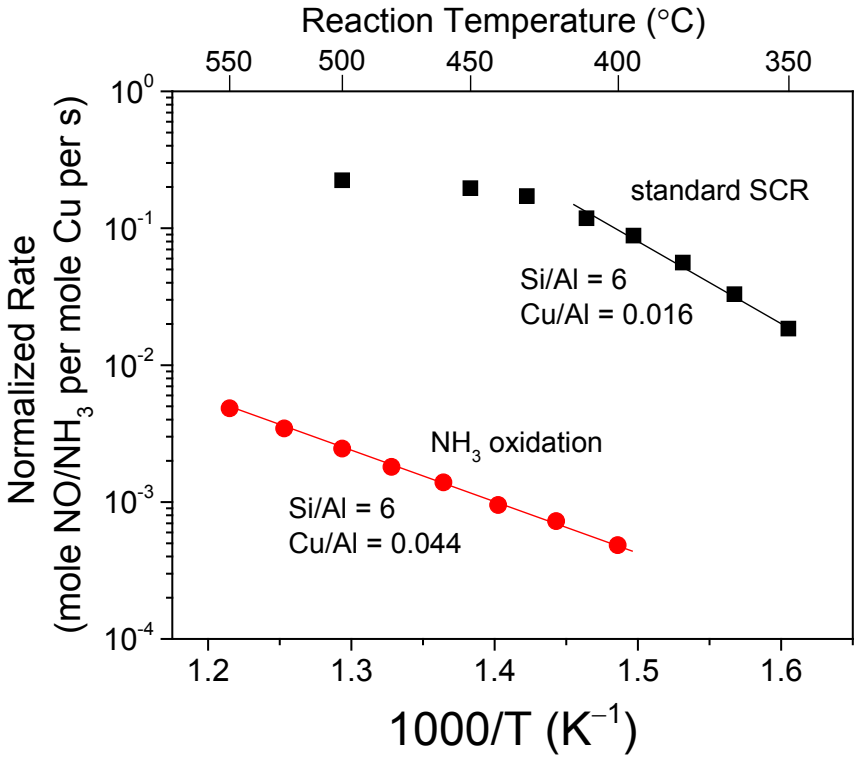
- Two relevant Cu-ion active sites in Cu/CHA determined from a combination of spectroscopy and theory.
- Model catalysts designed with only one of the Cu-ion active sites by varying Si/Al ratios and Cu contents.
- Reaction kinetics utilized to study SCR selectivity of these sites.

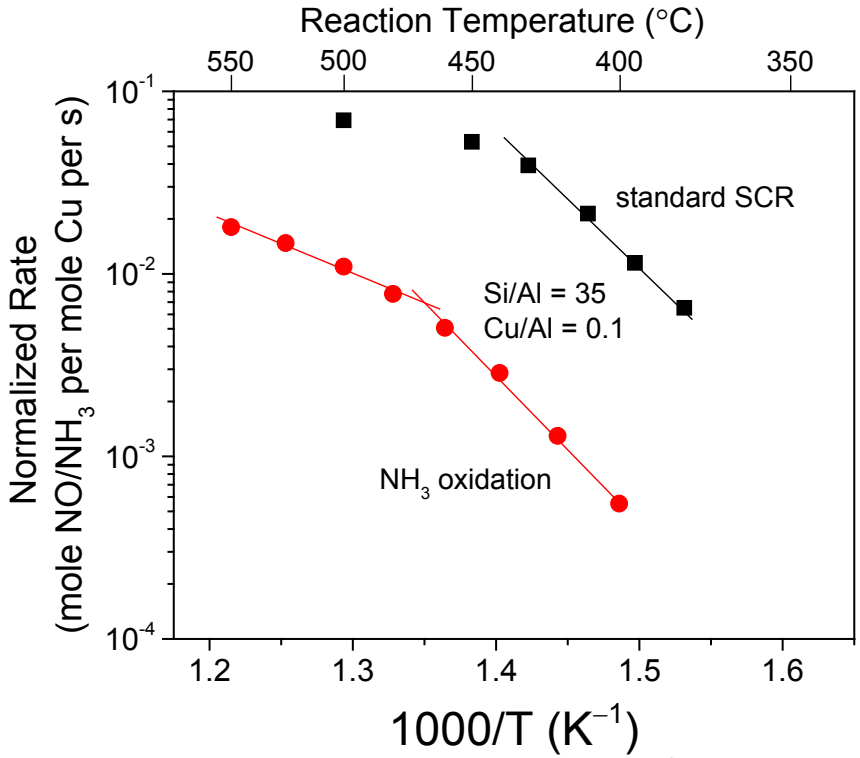
Andersen, et al., *IUCrJ*, 1 (2014) 382-386.
Gao, et al., J. Catal., 331 (2015) 25-38.

Cu/CHA Catalysts: determination of optimized compositions from rational design



- Target reaction: $4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$.
- Side reaction: $4NH_3 + 3O_2 = 2N_2 + H_2O$.





- Below ~300 °C, selectivity is never an issue. Above ~400 °C, only Cu^{2+}-2Al maintains excellent selectivity.

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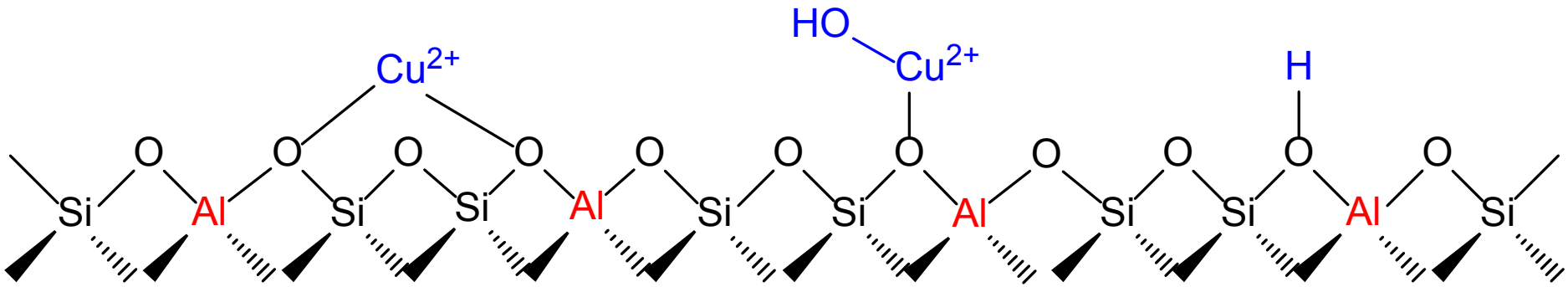
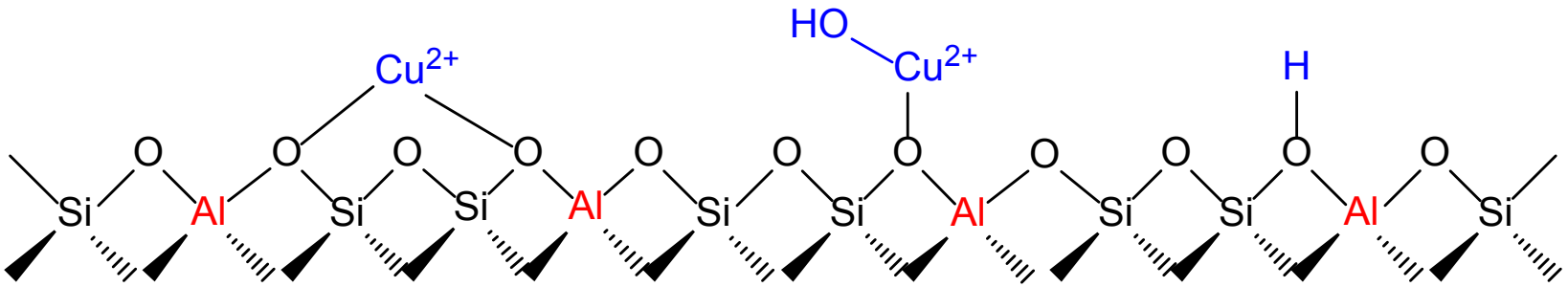
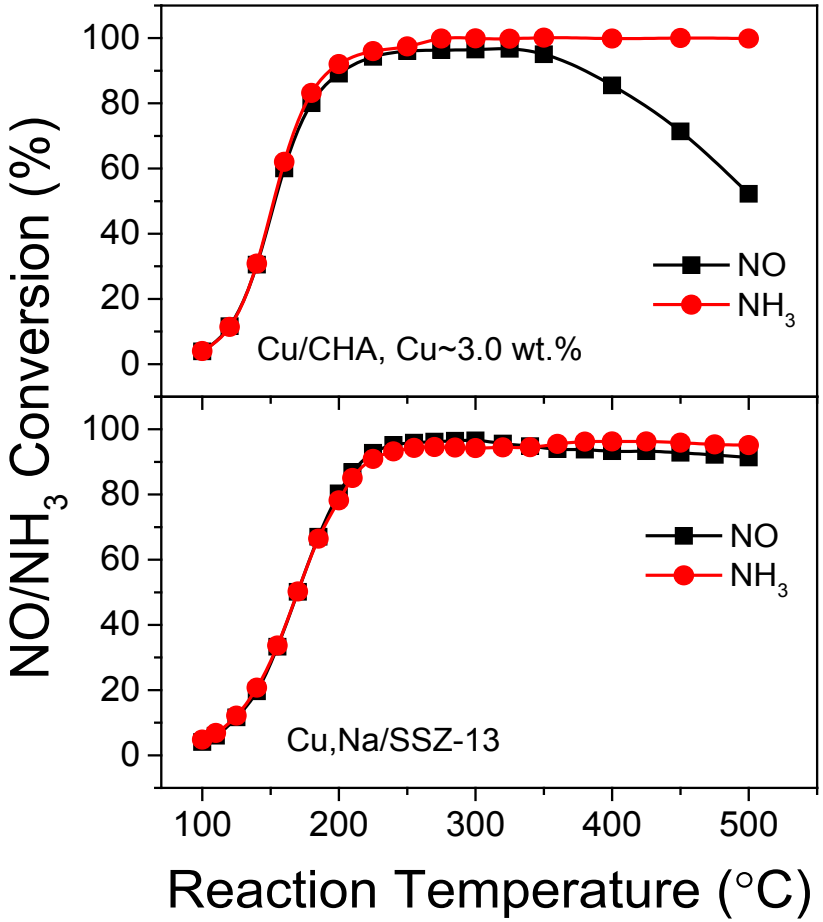
Cu/CHA Catalysts: determination of optimized compositions from rational design



- To meet hydrothermal stability requirements for applications, recommended Si/Al ratios between ~12 and ~20.
- Maximize Cu^{2+}-2Al, but optimize $Cu(OH)^{+}$ and H^{+} ratios.
- Cu^{2+}-2Al maintains integrity and activity even after severe hydrothermal aging.
- $Cu(OH)^{+}$ tend to migrate and agglomerate to form unwanted CuOx in aging.
- Brønsted acid sites tend to hydrolyze and lose NH_3 storage capacity in aging.
- Recommended Cu/Al ratio 0.2-0.3.
- For Cu/SAPO-34, Cu/Si ratio should be much lower – lower acidity, lower strongly bound Cu^{2+}.

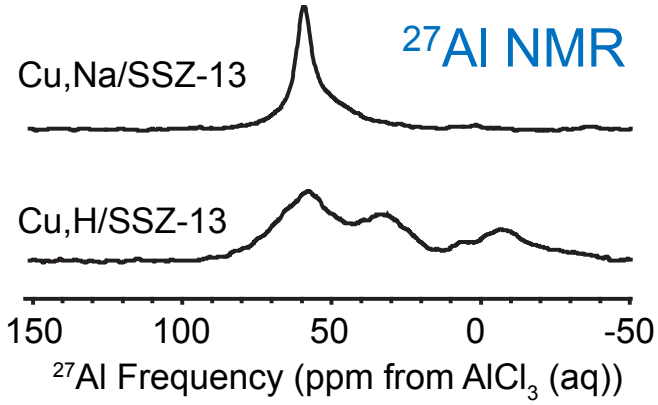
Case study: Cu/SSZ-13 with excellent high-temperature selectivity and stability.





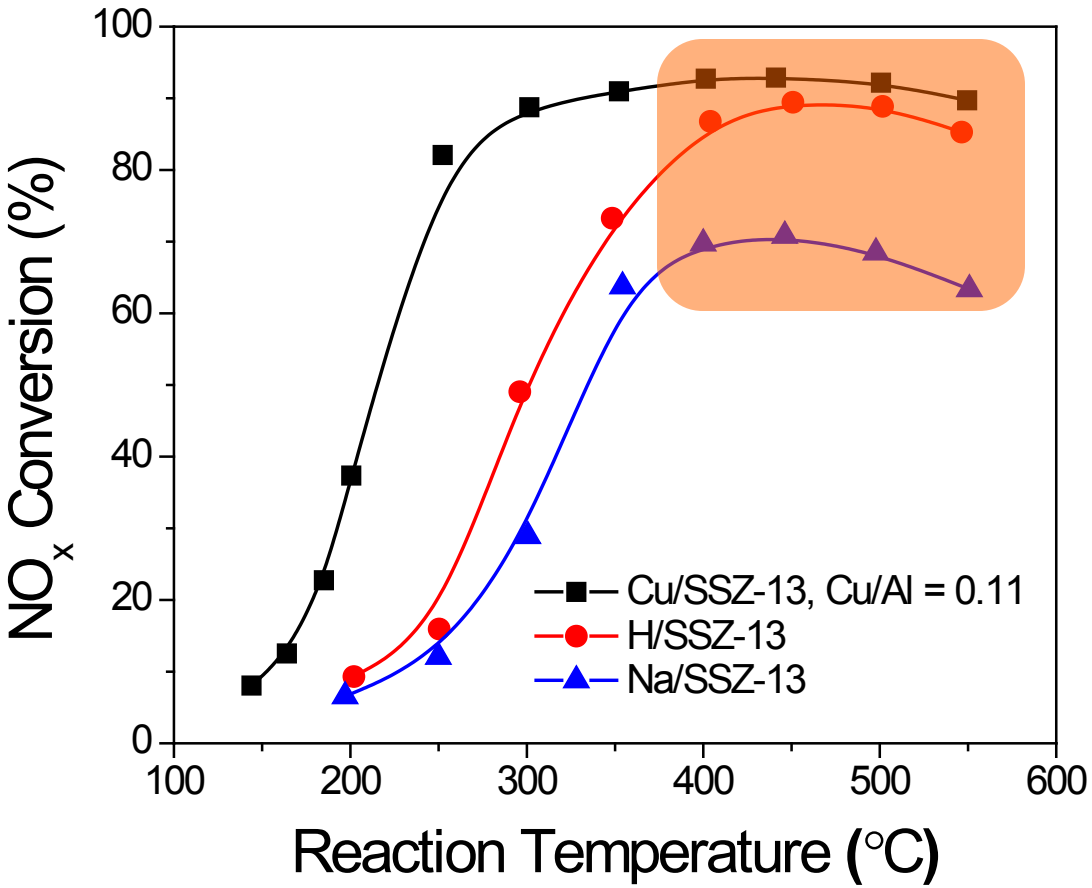
Cu/CHA,
Si/Al = 12.5
Cu ~ 3.0%

Cu,Na/CHA
Si/Al = 6
Cu ~ 1.0%
Na ~ 1.8%



F. Gao, Y.L. Wang, N.M. Washton, M. Kollar, J. Szanyi, C.H.F. Peden, ACS Catal. 5 (2015) 6780–6791.

Fast SCR: limitations for low- and high-temperature NOx conversion efficiency on Fe/zeolites

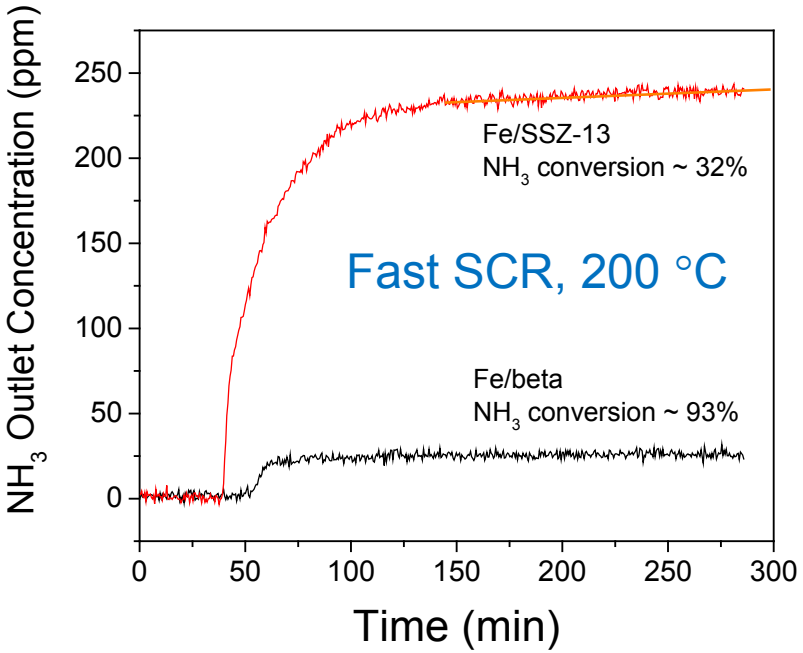


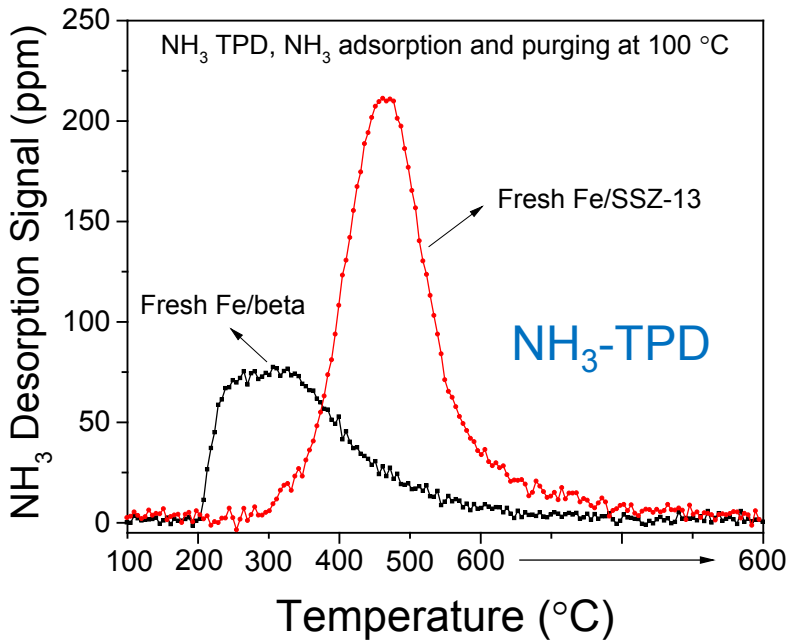
Light-off curves in fast SCR on Cu/, H/ and Na/SSZ-13 at Si/Al = 6. Reactant feed contains 175 ppm NO, 175 ppm NO_2, 350 ppm NH_3, 14% O_2, 2.5% H_2O balanced with N_2 at a GHSV of 800,000 h^{-1}.

- Target reaction: $NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O$.
- Above ~400 °C, this reaction is efficiently carried out in zeolite cages; Cu and Fe sites are only unnecessary luxuriousness.
- NH_3 storage capacity is still required for high-temperature NOx conversion.

A. M. Beale, F. Gao, I. Lezcano-Gonzalez, C. H. F. Peden, J. Szanyi, ***Chem. Soc. Rev.,*** 2015, 44, 7371-7405.

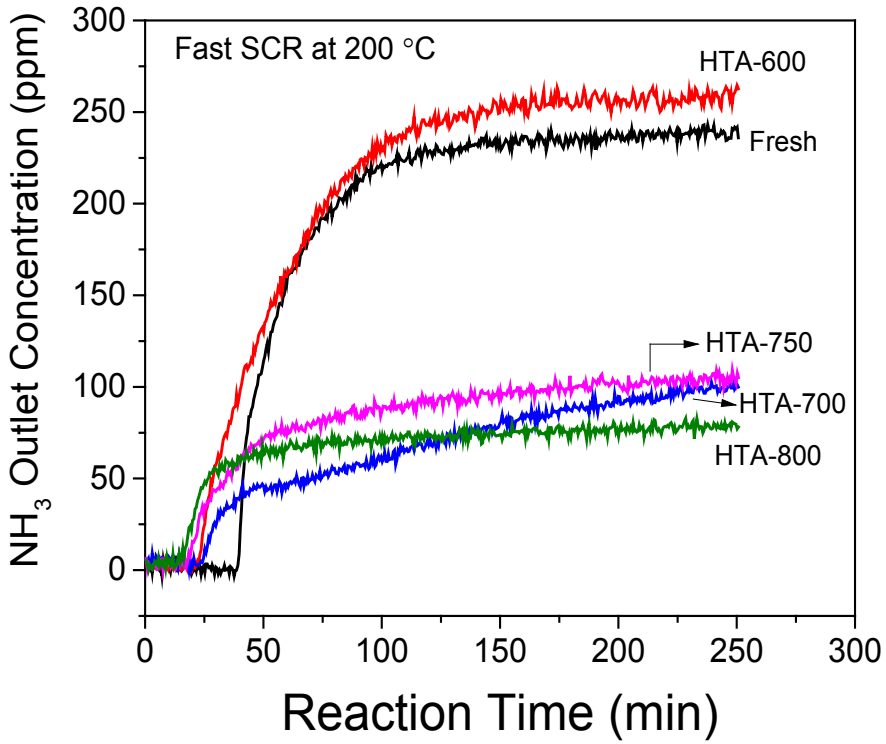
Fast SCR: limitations for low- and high-temperature NOx conversion efficiency on Fe/zeolites

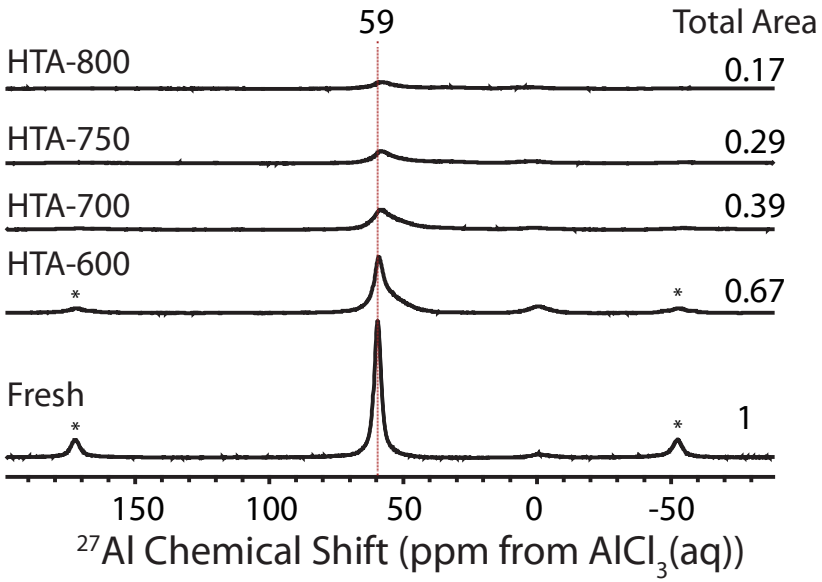




- Fe/SSZ-13 and Fe/beta prepared with both Si/Al ≈ 12 and Fe/Al ≈ 0.2.
- At 200 °C, Fe/beta much more active than Fe/SSZ-13 (not the case for standard SCR).
- Two possible reasons: (1) active Fe sites very different; (2) NH_4NO_3 inhibition very different, i.e., much stronger on Fe/SSZ-13.
- NH_3 binding much stronger on Fe/SSZ-13.

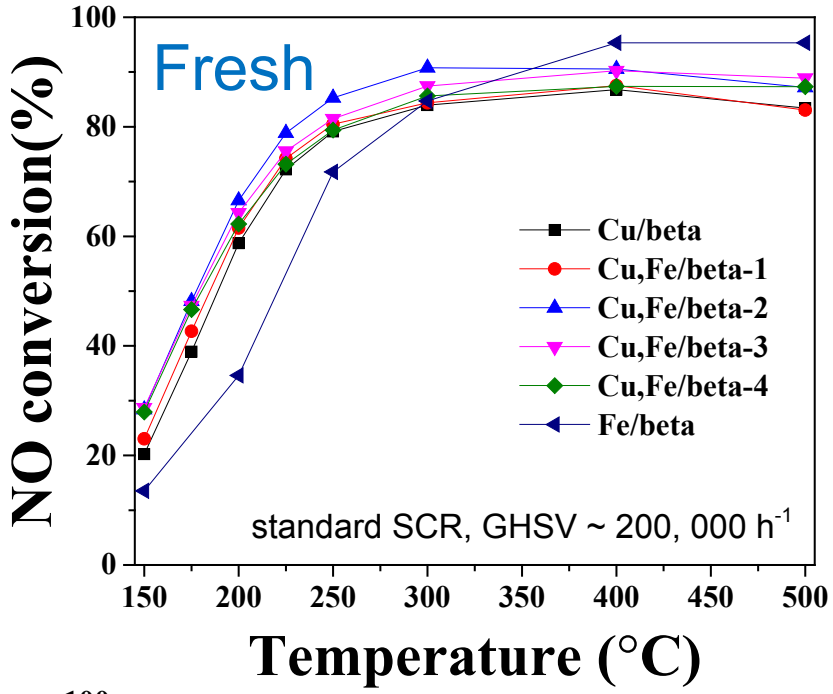
Fast SCR: limitations for low- and high-temperature NOx conversion efficiency on Fe/zeolites

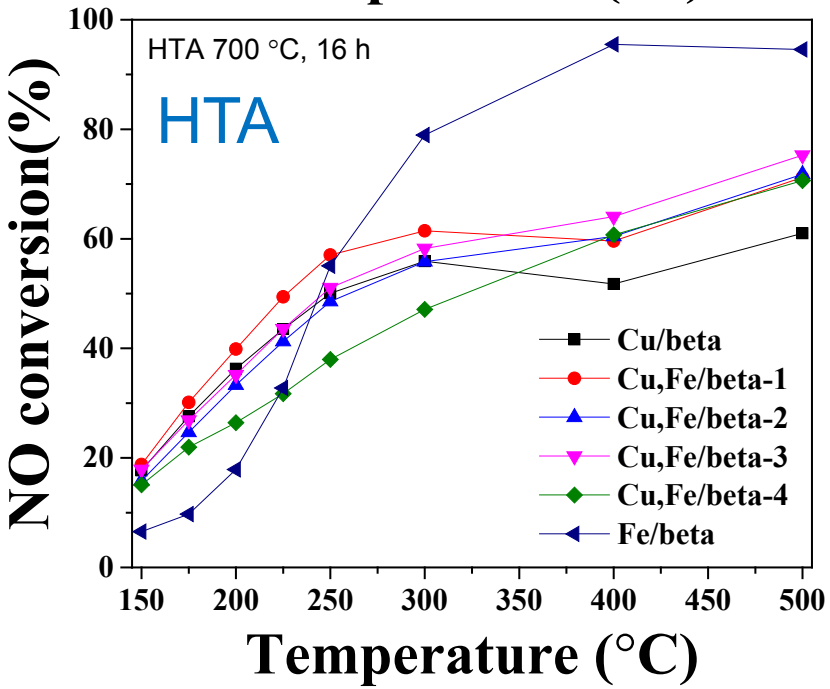




- After hydrothermal aging, performance for Fe/SSZ-13 greatly enhanced.
- Fe-ion density does not play a critical role.
- NH_4NO_3 inhibition much more crucial in determining low-temperature performance.
- $2NO_2 + H_2O = HNO_2 + HNO_3$; $NH_3 + HNO_3 = NH_4NO_3$

Cu,Fe co-cationed catalysts: initial results on Cu,Fe/beta





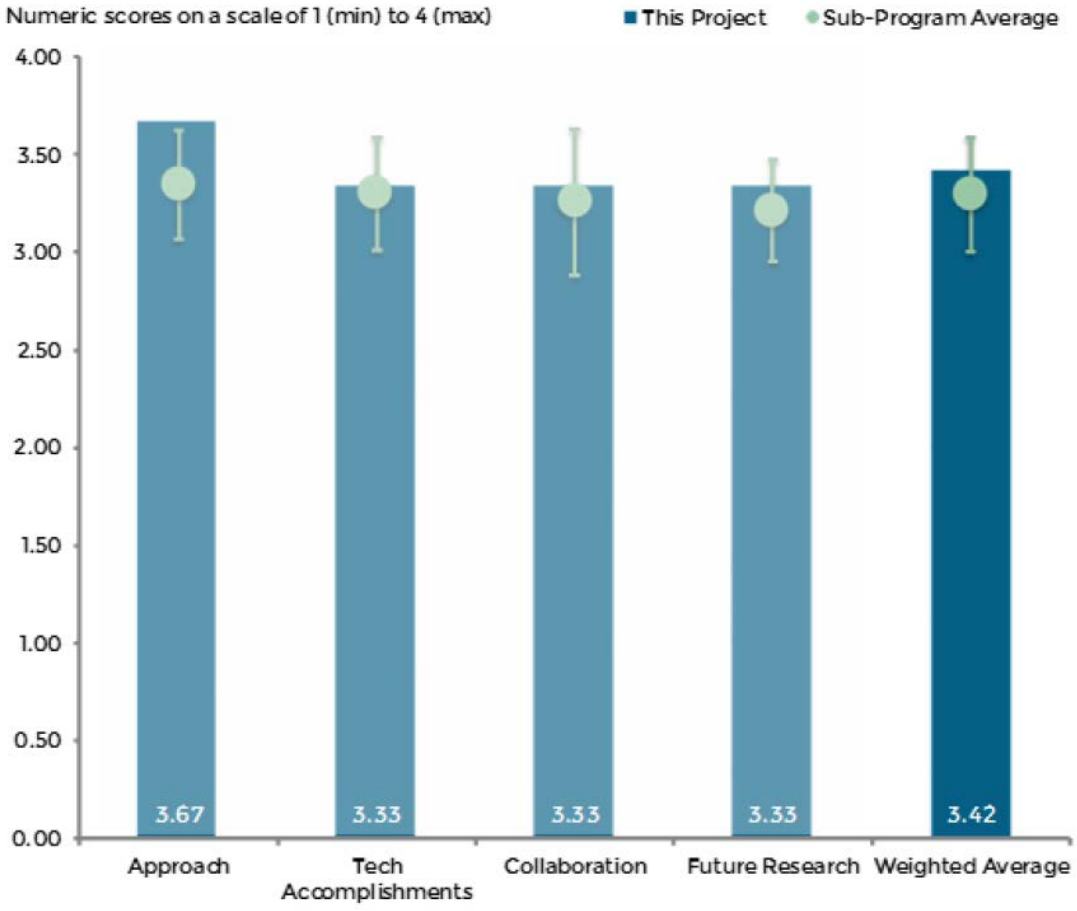
- For fresh co-cationed catalysts, there is indeed some enhancement in low-temperature NOx conversion efficiency.
- However high-temperature performance not satisfactory after hydrothermal aging.
- Work has also initiated on Cu,Fe/SSZ-13.

Response to previous (2015) 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.



Response to previous (2015) AMR reviewer's comments

- Expanding the operating temperature window is an important area for improving SCR catalyst performance, especially after realistic aging.

  We fully agree with the reviewer. We have made efforts to better understand the key limiting factors in low- and high-temperature NOx conversion efficiency. We have specifically designed catalysts using alkali cocations and Fe cocations to address this issue.

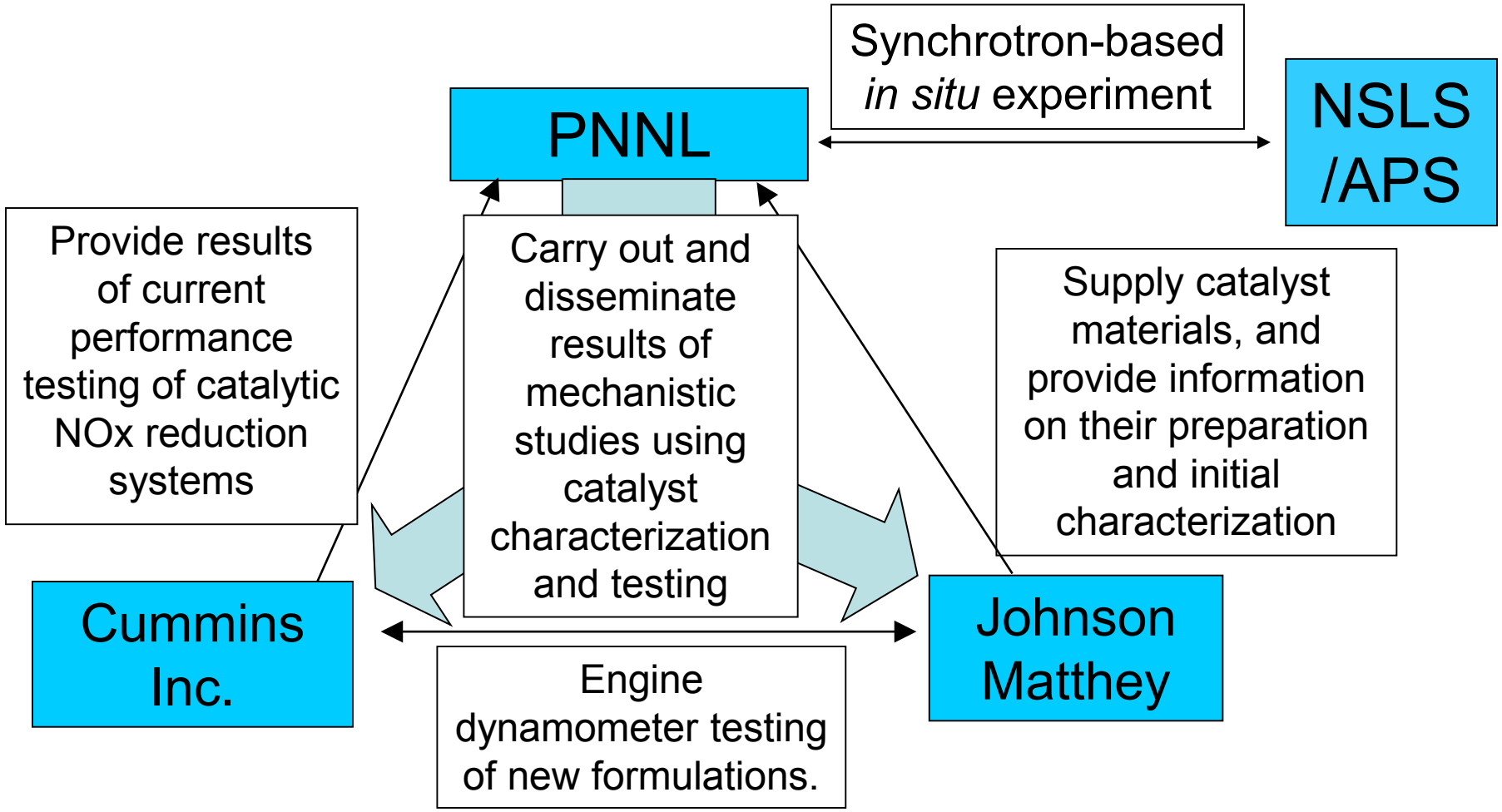
- It is not clear that LT performance has been improved. There are no results on structure/LT performance.

  We have proven that both Cu^{2+}-2Al and $[Cu(OH)]^{+}$-1Al sites are SCR active. Therefore, increasing Cu loading boosts low-T NOx conversion. However one must balance low- and high-T performance. A high Cu-loaded catalyst will lose more high-T performance after aging.

- The project team is not using JM and maybe even Cummins to their full potential.

  We want to clarify that we indeed work on "field" catalysts provided by Cummins (manufactured by JM). However the knowledge gained is considered proprietary per our CRADA agreement.

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 (October, 2015).

Planned Future Work

- The CRADA has been finished on March 31st, 2016.
- A final report has been finished.
- Transfer the remaining Cu,Fe/SSZ-13 work under PNNL CLEERS.

Summary

- A critical need for future NOx emission control technologies will be significantly improved with **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.
- Additional leverage is being provided by studies of SCR catalysts carried out at Purdue, Notre Dame and Washington State University as part of a NSF/DOE-funded project (Alex Yezerets, Cummins, and Chuck Peden, PNNL, are co-PIs).
- Technical highlights from this project included:
  - Guidelines for the preparation of Cu/CHA catalysts with optimized performance.
  - Identification of the key limiting factors in fast SCR catalyzed with Fe/zeolites.
- This project has been successfully finished in March 2016. All key milestones have been accomplished. From 2014 to 2106, 14 journal publications, 1 patent application and 17 presentations (including 3 keynote lectures) have been delivered.