

Enhanced High and Low Temperature Performance of NOx Reduction Materials

Feng Gao, George Muntean,
Janos Szányi, Chuck Peden
Institute for Integrated Catalysis
Pacific Northwest National Laboratory

Neal Currier, Ashok Kumar,
Krishna Kamasamudram, Junhui
Li, John Luo, Alex Yezerets
Cummins Inc.



Mario Castagnola, Hai-Ying Chen,
Howard Hess
Johnson Matthey



Program Managers: **Ken Howden and Gurpreet Singh**

The work was funded by the U.S. Department of Energy (DOE) Office of FreedomCar and Vehicle Technologies.

June 19, 2014

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

ACE026

Timeline

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

Budget

- Matched 50/50 by Cummins as per CRADA agreement
- DOE funding for FY13: \$300K; Same for FY14 – \$300K.

Barriers

- Discussed on next slide

Partners

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



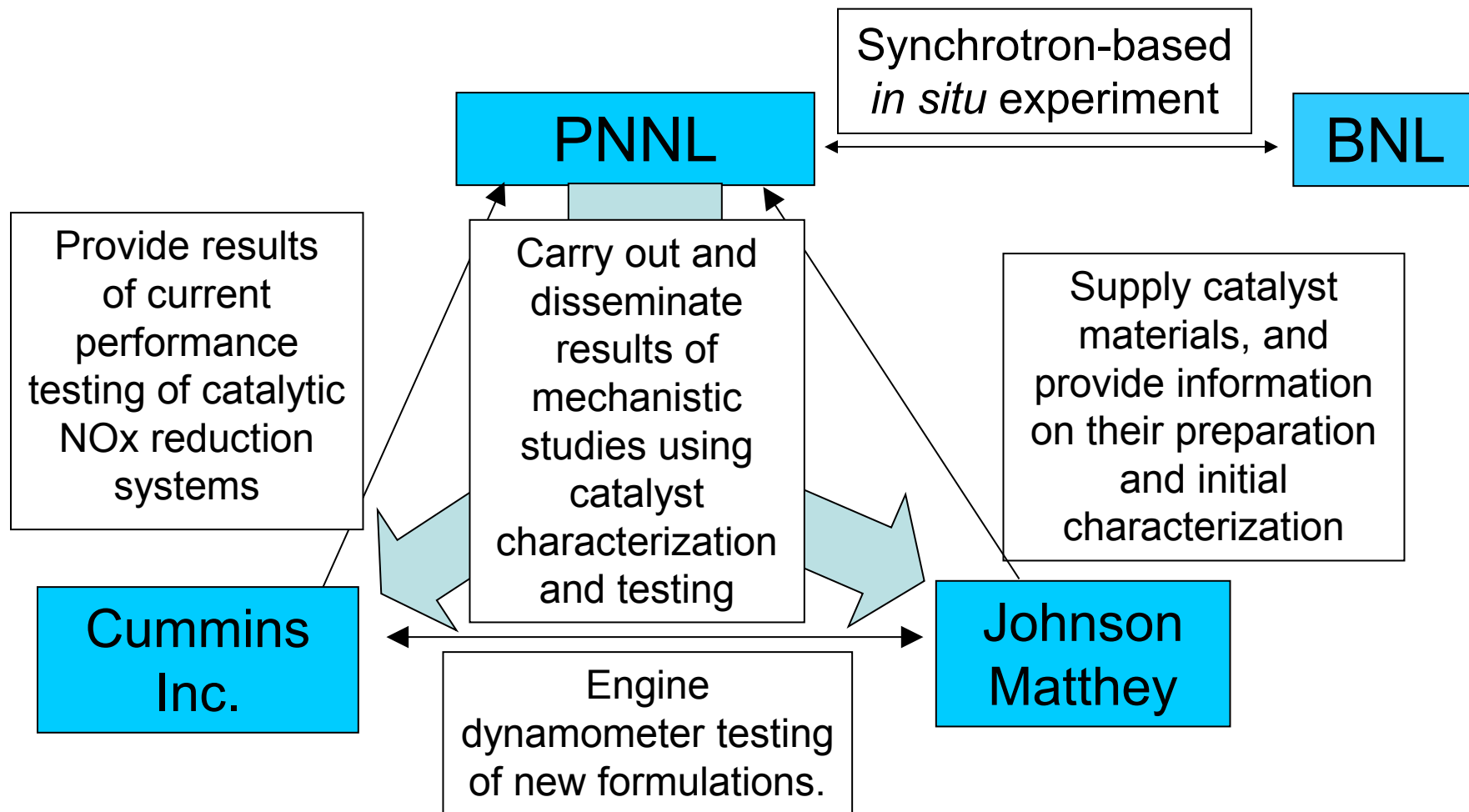
- As noted in a recent USDRIVE-sponsored workshop, low exhaust temperatures of future engines will create major challenges for exhaust aftertreatment technologies.
- In addition NO_x reduction systems will also require **improved higher temperature performance** and stability.
 - For example, NO_x removal performance during high temperature system maintenance events, including DPF regeneration. NO_x treatment for natural gas engines will also require higher temperature performance.
- It is important to reduce system costs by, for example, **minimizing the precious metal content** while maintaining, even improving, performance and long-term stability.

- For NO_x 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:
 - determination of factors that limit low and high temperature performance;
 - mechanisms for deactivation for candidate materials;
 - determination of significant causes of low and high temperature performance loss;
 - characterization of material changes with hydrothermal aging
 - the sulfur adsorption and regeneration mechanisms for modified and/or alternative catalyst materials.



- **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
 - NO₂ TPD, H₂ TPRX
 - Synchrotron based techniques (*in situ* time-resolved XRD)
 - Lab reaction system





- Conference calls were 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 (September, 2013).

Synchrotron-based

in situ experiment

BNL

Provisional
of
per
testing
NOx
S

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

n
n

Cu

of new formulations.

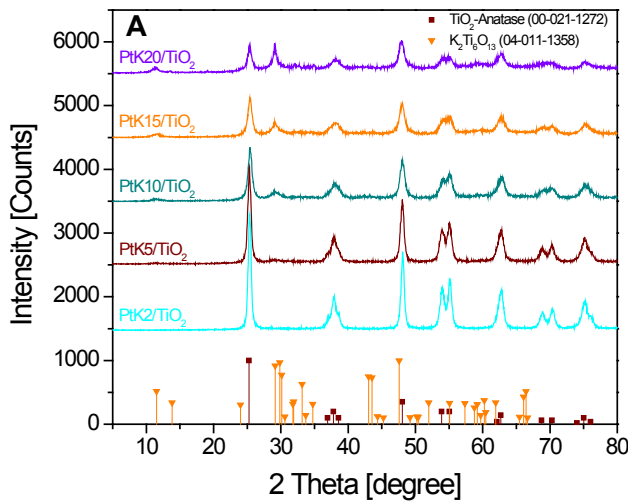
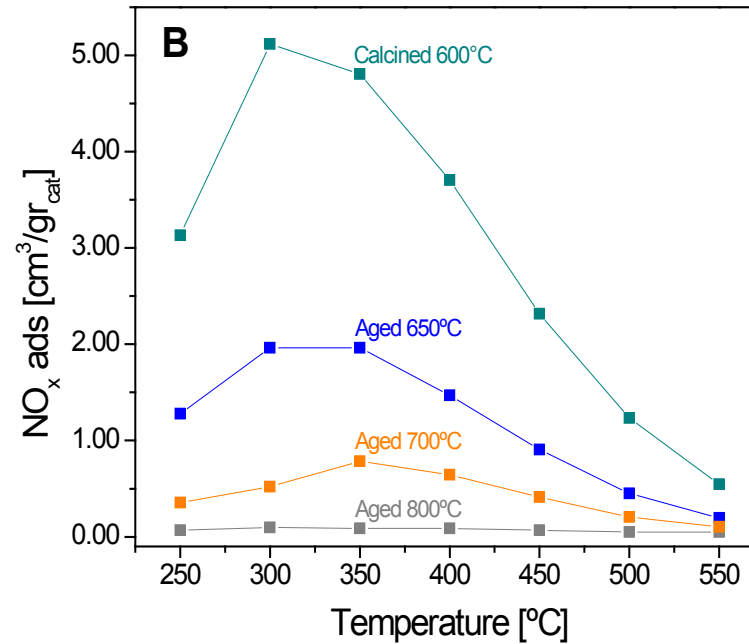
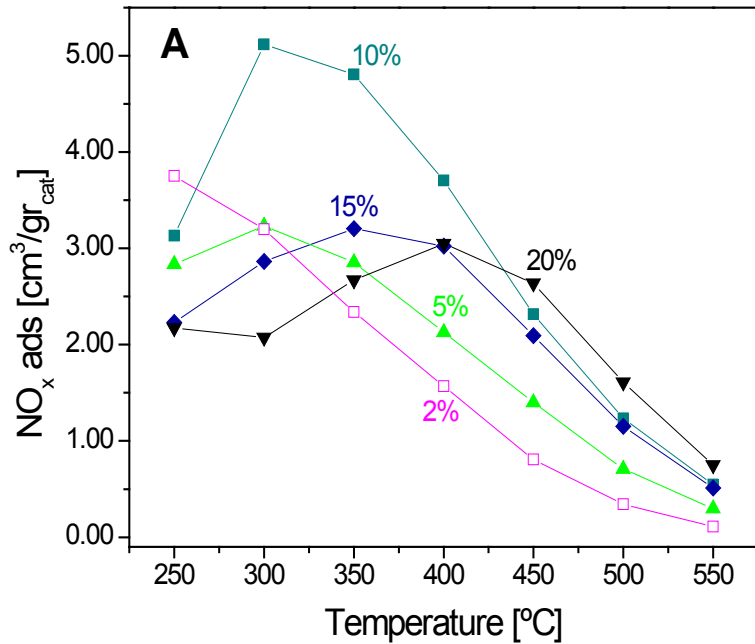
- Conference calls were held typically once every month or two to discuss the results.
- The next annual face-to-face CRADA Review will be held in Columbus, IN (either April or September, 2013).

- **High temperature LNT catalysts prepared by PNNL – Lower emphasis this year due to changing Cummins priorities**
 - Studies of the effects of storage elements and various supports on the NO_x storage activity, are being carried out as part of PNNL's CLEERS activities.
 - Detailed studies of the deactivation mechanisms in these high temperature NO_x storage materials. These studies involve activity testing, thermal treatments, variable desulfation processing, and extensive catalyst characterization.
- **Realistic and model catalyst studies of low and high temperature performance of new SCR catalysts**
 - Optimum preparation of model Cu/SAPO-34 catalysts.
 - Characterization and reactivity of Cu/SAPO-34 as a function of Cu loading – effects on low and high temperature performance.
 - New studies of Fe/SSZ-13 catalysts for low temperature reactivity.
 - Role of CHA acidity in low and high temperature reactivity.

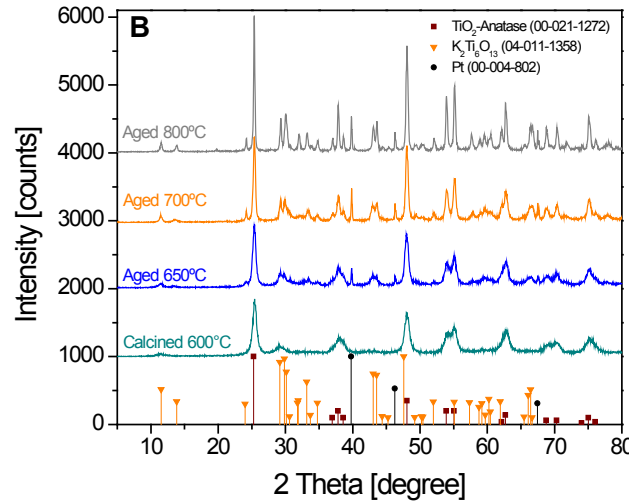
- ▶ Catalysts first studied in this program:
 - ▶ K/Pt/Al₂O₃ (2%, 5%, 10%, 15%, 20%, weight):
 - Higher temp window (maximum ~400-450 °C) than Ba-based catalysts.
 - Poor stability due to Pt sintering and K migration.
 - ▶ K/Pt/MgAlO_x (2%, 5%, 10%, 15%, 20%, weight):
 - Max performance at T > 500 °C.
 - Activity loss due to Pt sintering is reversible; K migration still a problem.
- ▶ Catalysts studied in last year (based on recent literature reports):
 - ▶ K/Pt/TiO₂ (2%, 5%, 10%, 15%, 20%, weight):
 - **TiO₂ Supports** (P-25, Hombicat)
 - **Pt/Al₂O₃** (1%): Impregnation of Al₂O₃ (150 m²/g) with Pt(NH₃)₄(NO₃)₂, 500°C calcination for 4hrs
 - **K loading**: Impregnation of Pt/Al₂O₃ with K₂CO₃ of different K loadings, 600°C calcination for 4hrs
 - ▶ Pt/K₂Ti₆O₁₃: ~80 m²/gm; Pt loading as above.
 - ▶ K(10%)/Pt/K₂Ti₆O₁₃: K and Pt loading as above.
- ▶ Deactivation issues (e.g., thermal aging) are being addressed as part of this CRADA. Two issues currently being addressed:
 - Mobility of K species
 - Reactivity of K with other catalyst components

Brief highlights of recent results for titanate-supported LNTs.

TiO₂-supported K LNTs deactivate irreversibly due to formation of K-titanates (K₂Ti₆O₁₃)



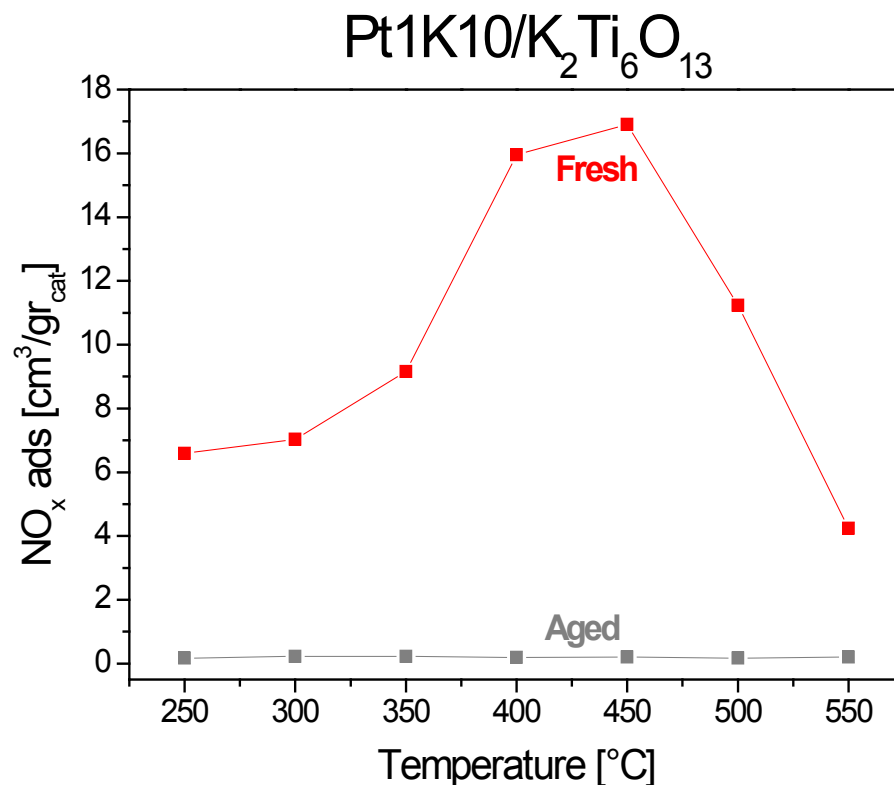
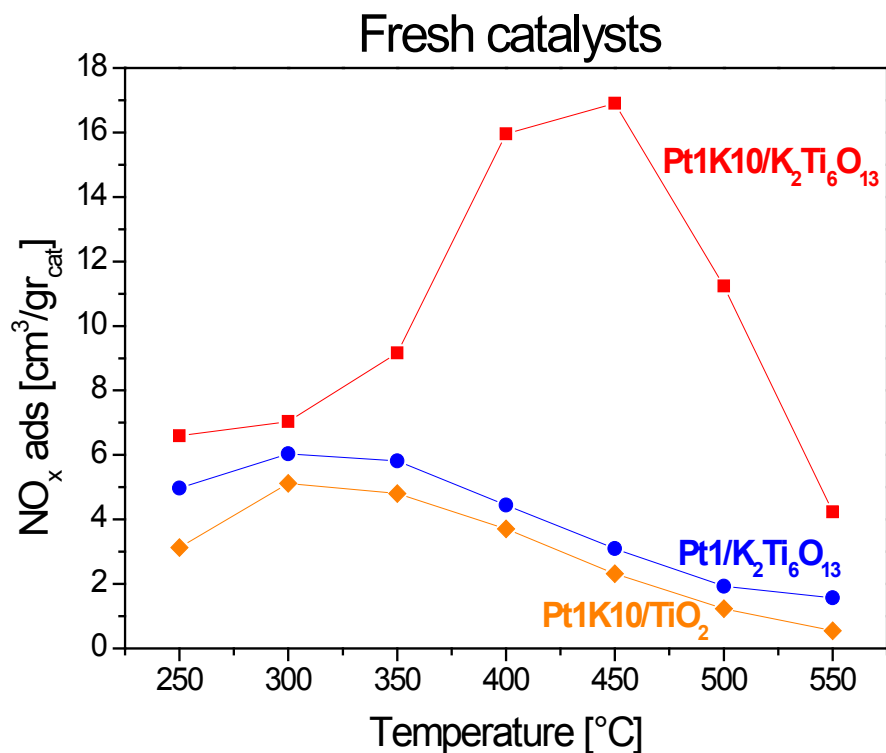
XRD of freshly calcined Pt-K(x)/TiO₂ catalysts (x= 2, 5, 10, 15, 20 wt%)



XRD of Pt-K(10)/TiO₂ catalysts aged at 650, 700, 800°C for 4 h.

- Lower T performance.
- Pt-K(10)/TiO₂ activity drops even after 650 °C aging.
- K₂Ti₆O₁₃ even evident for freshly degreened (600 °C) Pt-K(10)/TiO₂ catalyst.
- What about K₂Ti₆O₁₃ as a support material?

Initial results were promising but $K_2Ti_6O_{13}$ supports still suffered from aging



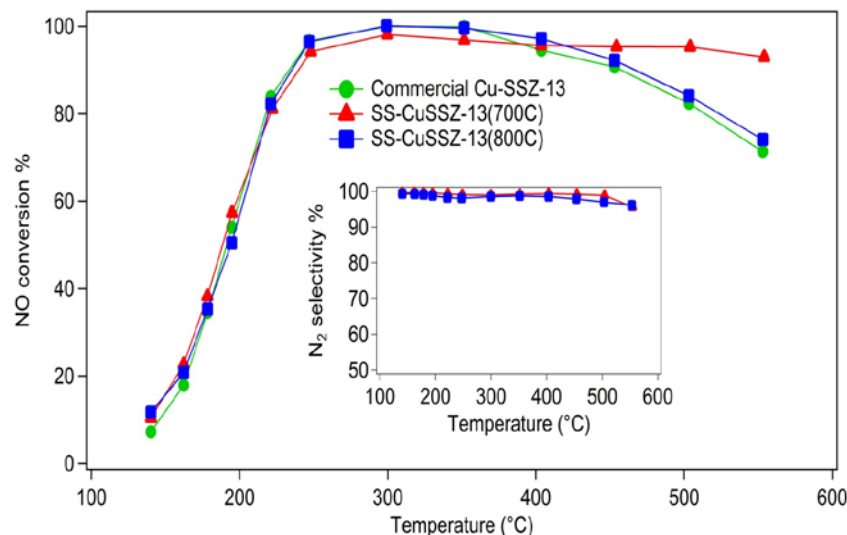
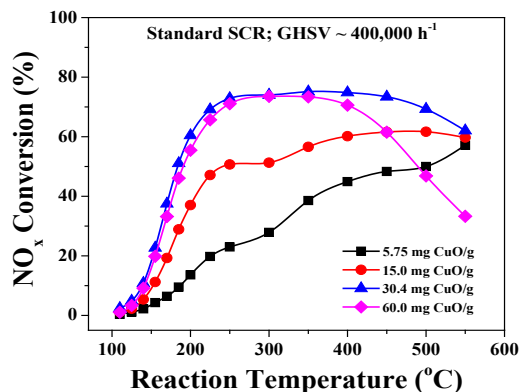
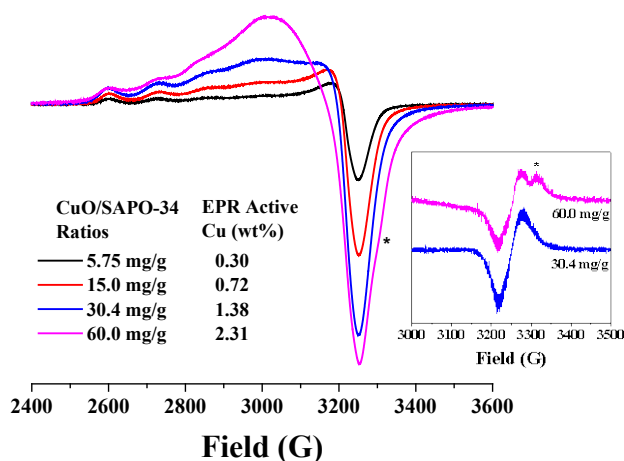
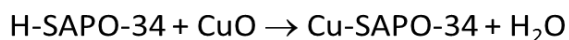
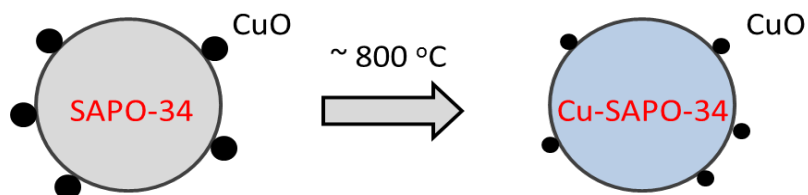
- Pt-K(10)/ TiO_2 and Pt/ $K_2Ti_6O_{13}$ show very similar NO_x storage properties while the further addition of K to the Pt/ $K_2Ti_6O_{13}$ catalyst significantly increased stored NOx amounts and shifts the maximum storage temperature from 300-350 to 450°C
- All the samples show a severe loss of the storage property after the aging treatment

Work was carried out by Laura Righini, visiting graduate student from Politecnico Milano

- ▶ Synthesis of Cu-Fe/SSZ-13 and Cu/SAPO-34 model catalysts to address both fundamental and applied scientific questions in NH₃-SCR.
 - ▶ Formation of Cu/SAPO-34 *without* aqueous ion exchange:
 - **Solid-state ion exchange** with nanosized CuO at high temperatures. (with Bill Epling, we've shown this is also a good method for preparing Cu/SSZ-13)
 - **One-pot synthesis:** addition of Cu salts to the synthesis gels.
 - ▶ Synthesis of SSZ-13 with various Si/Al ratios (6, 12, 35):
 - Model catalysts with a vast variety of Si/Al and Cu/Al ratio combinations to address sitting and nature of catalytically active Cu ion sites.
 - Brønsted acid site density (affecting both Cu ion location and NH₃ storage) is varied using the same approach.
 - ▶ Synthesis of Fe/SSZ-13 using improved solution ion exchange methods:
 - Ion exchange using HCl solution, Fe powder and SSZ-13: *in situ* formation of Fe⁺² for exchange.
 - Ion exchange with FeCl₂ in the presence of NH₄Cl: prevent Fe⁺² hydrolysis.

- ▶ Synthesized catalysts used to address the following issues this year:
 - ▶ Model Cu/SAPO-34 catalysts:
 - Have addressed some specific issues with engine- and vehicle-tested catalyst materials.
 - Differences between SAPO-34 and SSZ-13. For example:
 - Hydrothermal stability.
 - Acidity and NH_3 storage.
 - Nature and location of Cu species.
 - ▶ Fe/SSZ-13 catalysts:
 - Fe catalysts show considerably lower “light-off” temperatures during “fast SCR” reaction in contrast to Cu/SSZ-13.
 - What fundamental differences between Fe- and Cu-based CHA catalysts account for this and other differences?
 - ▶ SSZ-13 with various Si/Al ratios (6, 12, 35):
 - Can initial Cu location and coordination effect low-temperature behavior?
 - How does Brønsted acidity and, correspondingly, NH_3 storage effect low-temperature “light-off”?

Simple “dry” method in Cu/CHA synthesis: solid-state ion exchange

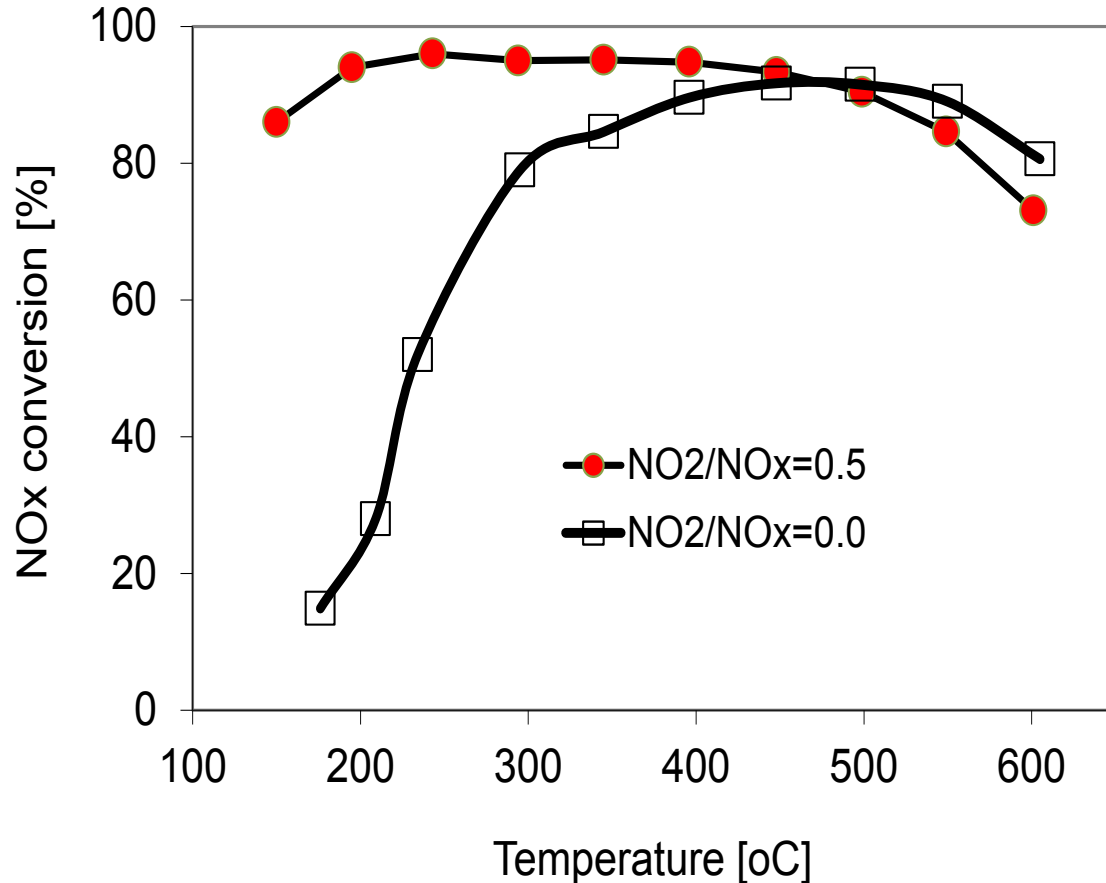


D Wang, F Gao, CHF Peden, K. Kamasamudram, WS Epling, ChemCatChem. (2014) in press.

- Developed a simple, readily adaptable method for the synthesis of Cu/CHA catalysts.
- Catalysts prepared in this way show performance comparable and, in many cases, superior to other methods.

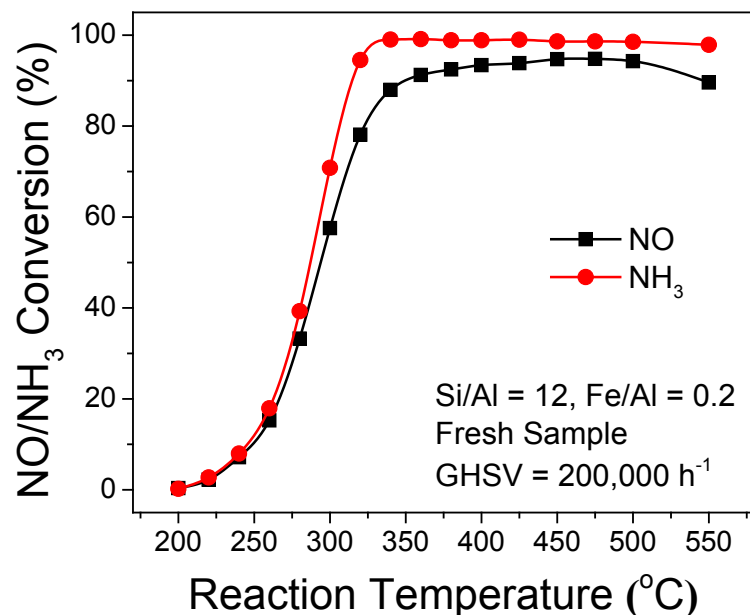
F Gao, ED Walter, NM Washton, J Szanyi, and CHF Peden, Catal. Lett. (2014) submitted.

K Kamasamudram, N Currier, T Szailer
and A Yezerets, SAE 2010-01-1182.

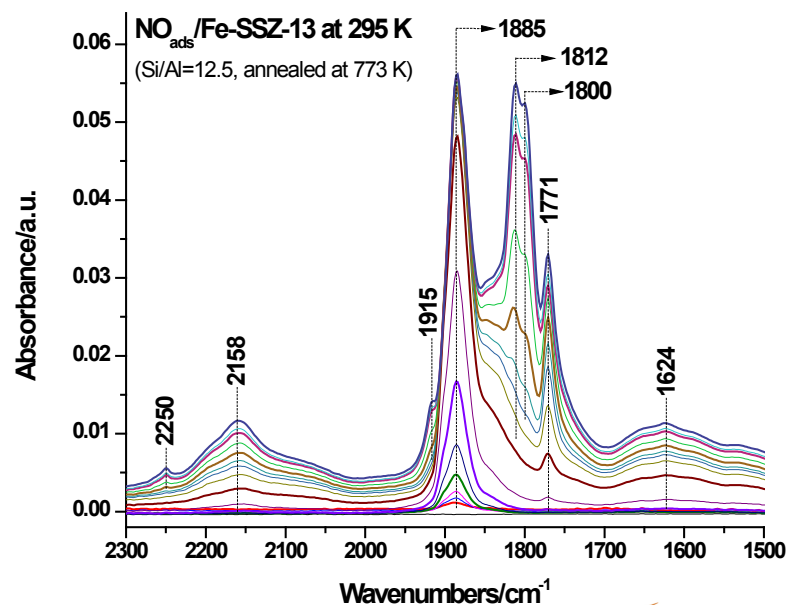
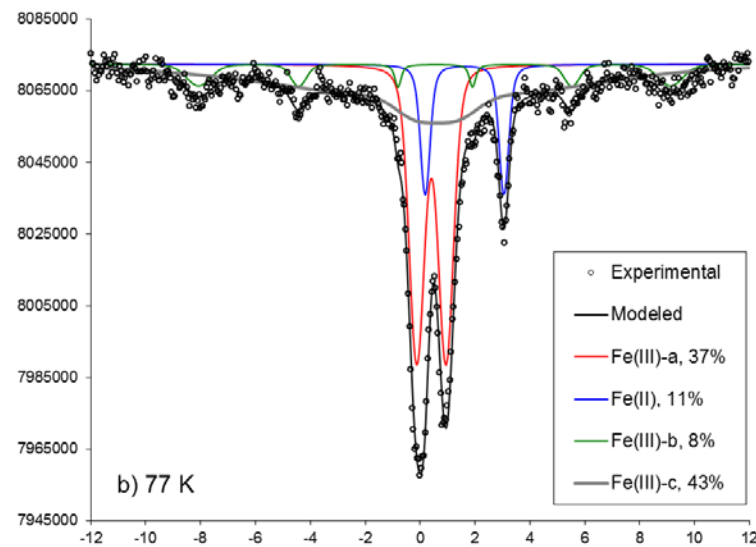


- Even $> 80\%$ conversions at $150\text{ }^\circ\text{C}$ for optimum NO_2/NO_x ratios of 0.5 (i.e., “fast SCR”).
- However, deactivation at these temperatures may be caused by formation of ammonium nitrate that decomposes at $T > 200\text{ }^\circ\text{C}$.

Model Fe/SSZ-13 catalysts have been synthesized for comparative (vs. Cu/SSZ-13) fundamental studies of these properties.

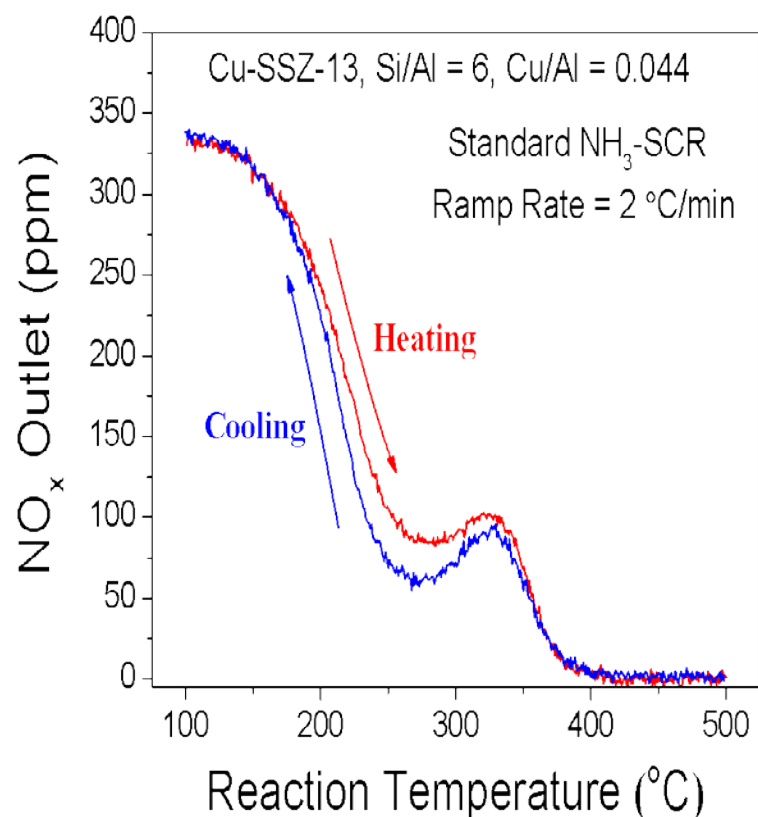


- Stable and high SCR activity/selectivity above 350 °C.
- Possible active Fe species: $[\text{Fe}(\text{OH})_2]^+$ and $[\text{HO-Fe-O-Fe-OH}]^{2+}$ in a fresh, hydrated sample. Fe^{2+} and $[\text{Fe-O}_2\text{-Fe}]^{2+}$ after dehydration.
- FTIR NO titration confirms Fe species in exchange sites.

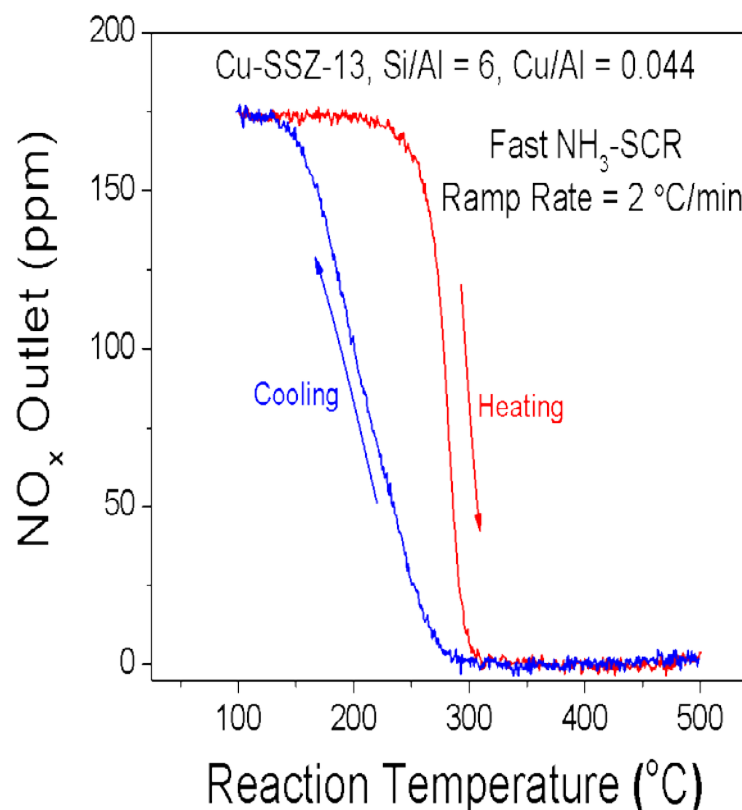


F Gao, J Szanyi and CHF Peden, in preparation.

$\text{NO}_2/\text{NO}_x = 0$



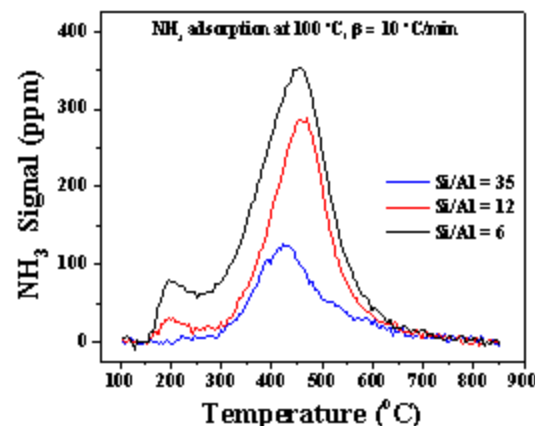
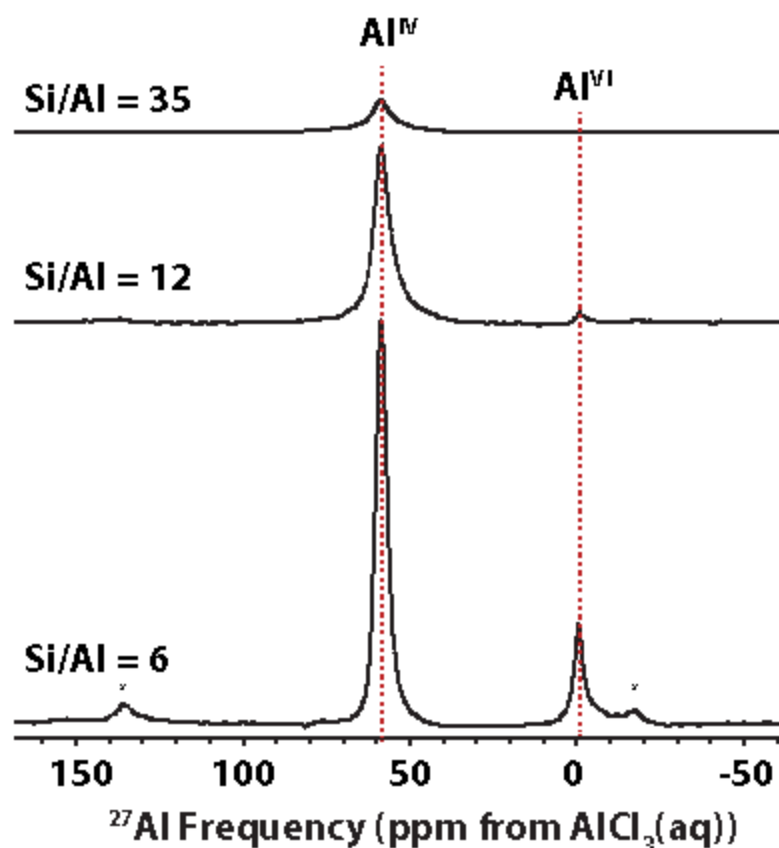
$\text{NO}_2/\text{NO}_x = 0.5$



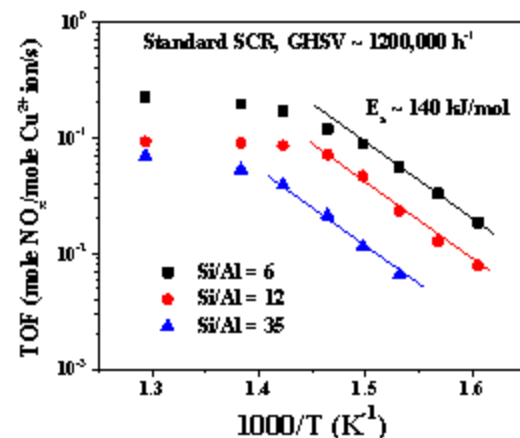
Hysteresis in NH₃-SCR "light-off" curves (heating versus cooling) is likely due to formation of ammonium nitrate for "fast" SCR conditions:

- Can zeolite acidity effect this behavior?

Brønsted acid site density change by changing Si/Al ratios: Cu-SSZ-13



NH_3 TPD



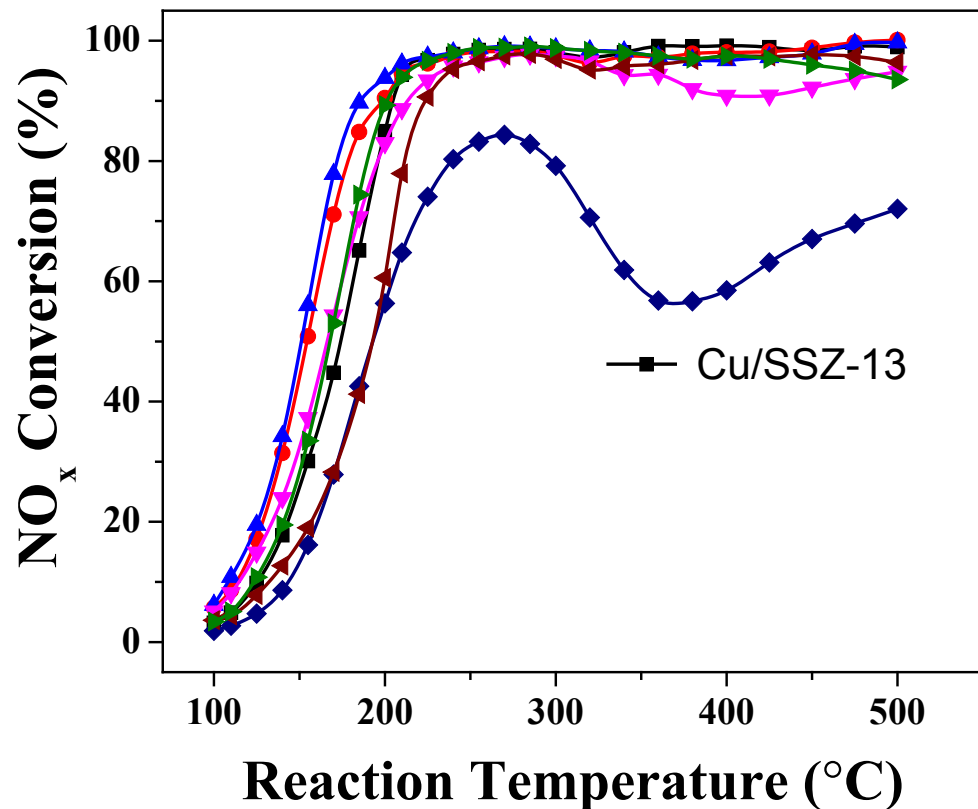
'Standard'
 NH_3 SCR at
 $T > 350$ $^{\circ}\text{C}$

- High quality SSZ-13 materials with minimal extra-frame Al (NMR and NH_3 -TPD).
- Confirmation of the significant role of Brønsted acidity at high reaction temperatures (> 350 $^{\circ}\text{C}$).
- Current studies probing low temperature behavior, including Cu-site coordination.

F Gao, M. Kollar, ED Walter, NM Washton, J Szanyi, and CHF Peden, J. Catal. (2014) submitted.

New Low-Temperature Catalyst Formulations Identified

Standard SCR, $\text{NH}_3 = \text{NO} = 350 \text{ ppm}$, $\text{H}_2\text{O} = 2.5 \%$, $\text{O}_2 = 14\%$, $\text{GHSV} = 100,000 \text{ h}^{-1}$



Sample	T ₅₀ (°C)
Cu/SSZ-13	174
Red Circles	154
Blue Triangles	151
Pink Inverted Triangles	166
Brown Triangles	193
Dark Blue Diamonds	193
Green Triangles	168

Gao, F.; Wang, Y.; Kollar, M.; Szanyi, J.; Peden, C.H.F. "Catalysts for Low Temperature Selective Catalytic Reduction of NO_x with Ammonia", invention disclosure filed 2/8/2014.

1. NO_x Adsorption Materials:

- Not planning any work this next year.

2. CHA-based SCR catalysts:

- Detailed characterization (EPR, TPR, x-ray absorption, etc.) of Cu and Fe species as a function of loading – in collaboration with Purdue, Notre Dame and Washington State University.
- Studies will be especially focused on mechanisms/limitations for low temperature performance. Some specific questions:
 - Why is “fast” SCR fast for Fe and not Cu?
 - Can control of zeolite acidity for Fe/CHA and Cu/CHA minimize deactivation during “fast” SCR?
 - Can sulfur especially effect this low temperature behavior?
- Mechanism for low-temperature performance in newly disclosed Cu/zeolite catalysts.

- 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:
 - K addition to a Pt/K₂Ti₆O₁₃ LNT significantly enhances NOx storage at high temperatures. However, this material still suffers from serious deactivation during aging.
 - Model Cu/SAPO-34, Fe/SSZ-13, and SSZ-13 with various 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 than 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. No studies of LNT catalysts are planned for this next year.