NOx Abatement Research and Development

CRADA with Navistar Incorporated

(successor to International Truck and Engine Corporation)

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U.S. DEPARTMENT OF ENERGY

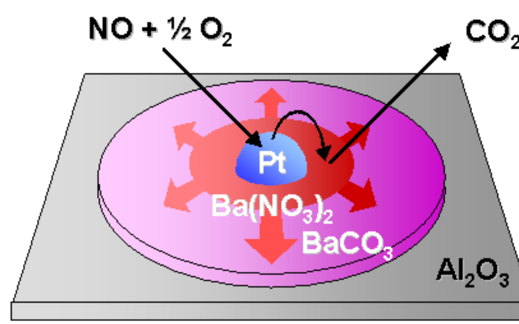
OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

NOx Abatement R&D – Navistar CRADA
Project Overview

CRADA Timeline:

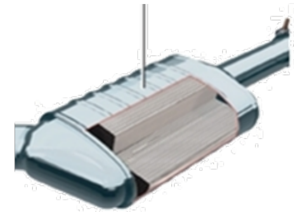
2000-2006

LNT

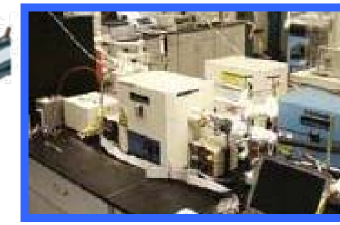


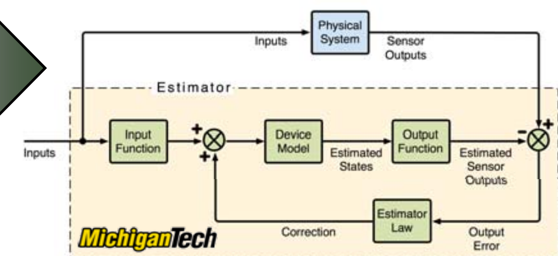
2006-2007

SCR



Bench Reactor





2008-present

Budget

- 2000-2006 budget
  - ~$400k/year
- Funding for FY08
  - $125k
- Funding for FY09
  - $125k

Barriers

- Meet 2010 emissions standards
- Maintain high efficiency
- Control SCR performance
  - Minimize NOx and NH_3 emissions

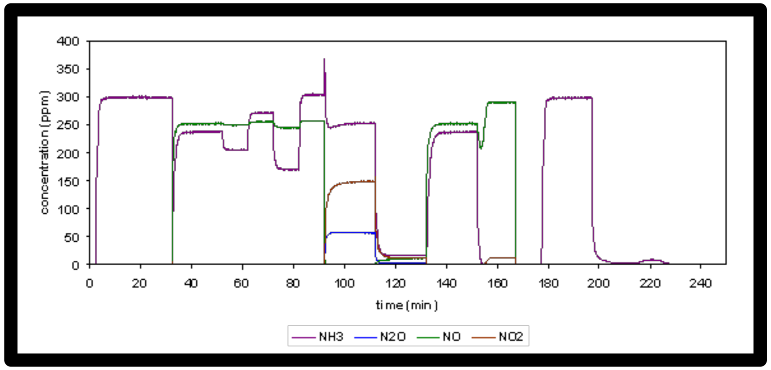
Partners

- Navistar Incorporated
- Michigan Technological University

NOx Abatement R&D – Navistar CRADA
Objectives

- Enable maximum fuel economy while meeting emissions regulations
  – Modeling and understanding emissions control devices critical to efficient operation

- Obtain accurate temperature dependent data under transient operation
  – Performance data and rate parameters
  – Define key catalyst characteristics and storage capacity



- Evaluate sensors for on-board diagnostic (OBD)

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Milestones

- FY 08 (<u>Completed</u> September 30, 2008)
  - Evaluate at least two LNT samples in bench flow reactor to establish relationship between space velocity, temperature, and product selectivity

- FY 09 (<u>On Target</u> for September 30, 2009 completion)
  - Evaluate NH_3 storage and reactivity on fresh and aged fully-formulated urea SCR catalysts

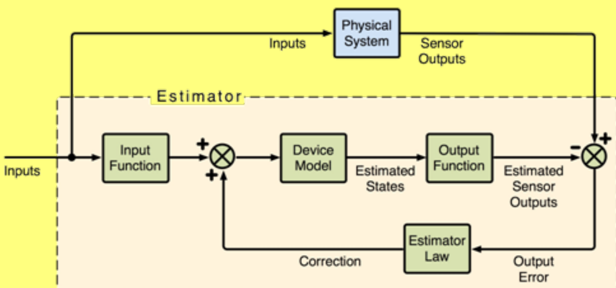
NOx Abatement R&D – Navistar CRADA

Approach

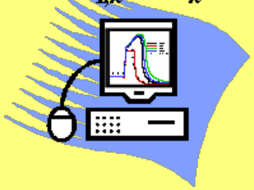
Catalyst Supplier

- ORNL provides unique capabilities and expertise not available at Navistar
- Michigan Tech models results with input from ORNL
- Navistar implements control model for device operation

INTERNATIONAL
A NAVISTAR COMPANY



$$k_{1,k} = k_k T \exp\left[-\frac{E_k}{RT}\right]$$



MichiganTech

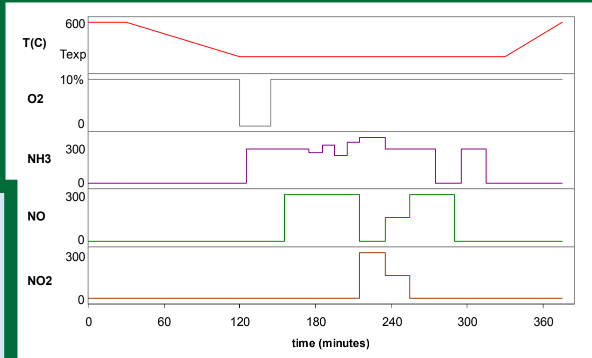
FEERC
Fuels, Engines, and Emissions Research Center

CLEERS

OAK RIDGE National Laboratory

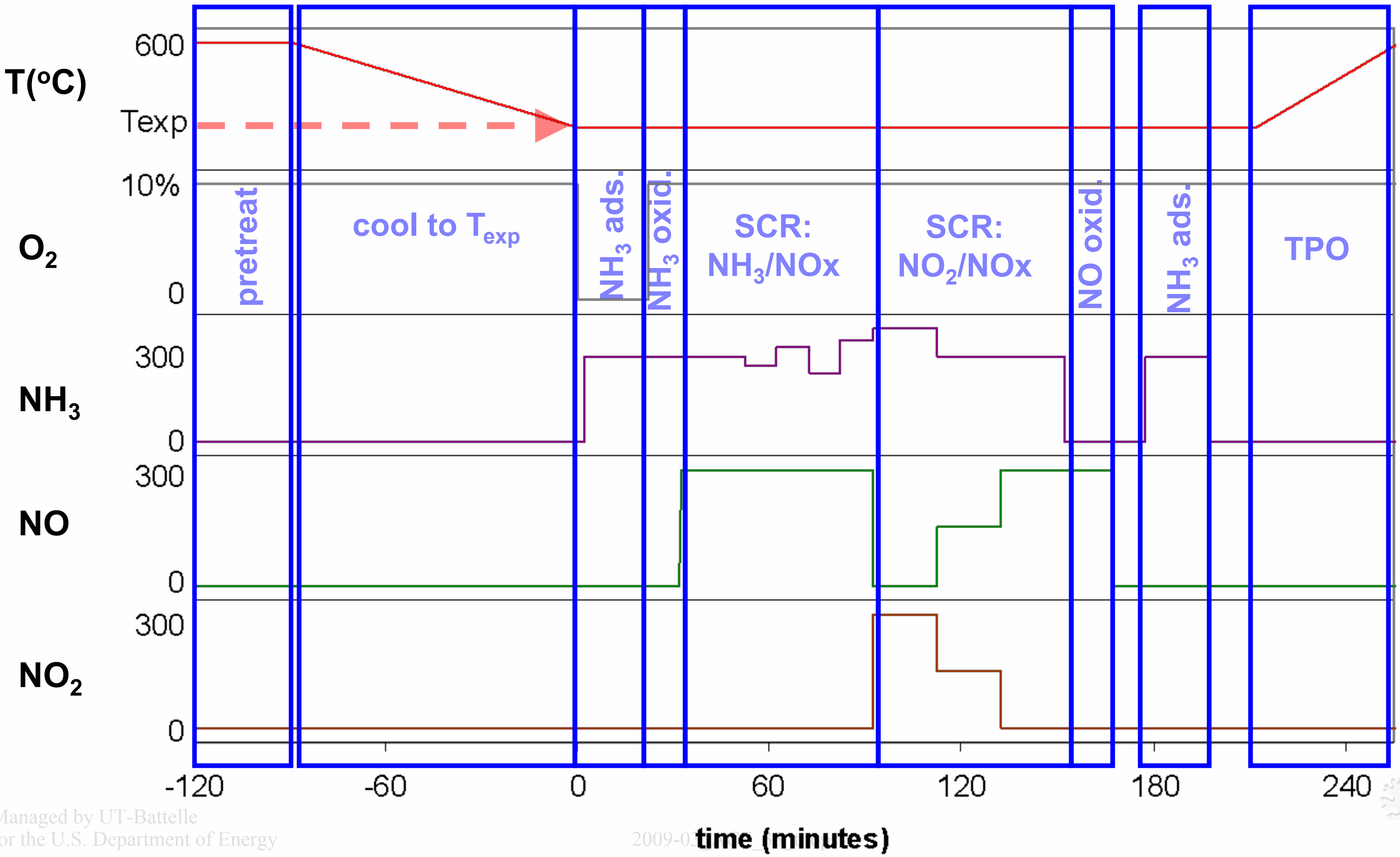
NOx Abatement R&D – Navistar CRADA
Technical Accomplishments

- Established SCR test protocol that provides critical transient and steady-state conditions for a given temperature
- Evaluated fresh zeolite-based SCR catalyst using protocol at nine temperatures and two space velocities as of March 2009
- Evaluated NOx sensor while operating protocol
- Automated bench reactor to allow unattended operation
  - Meets ORNL's stringent safety regulations



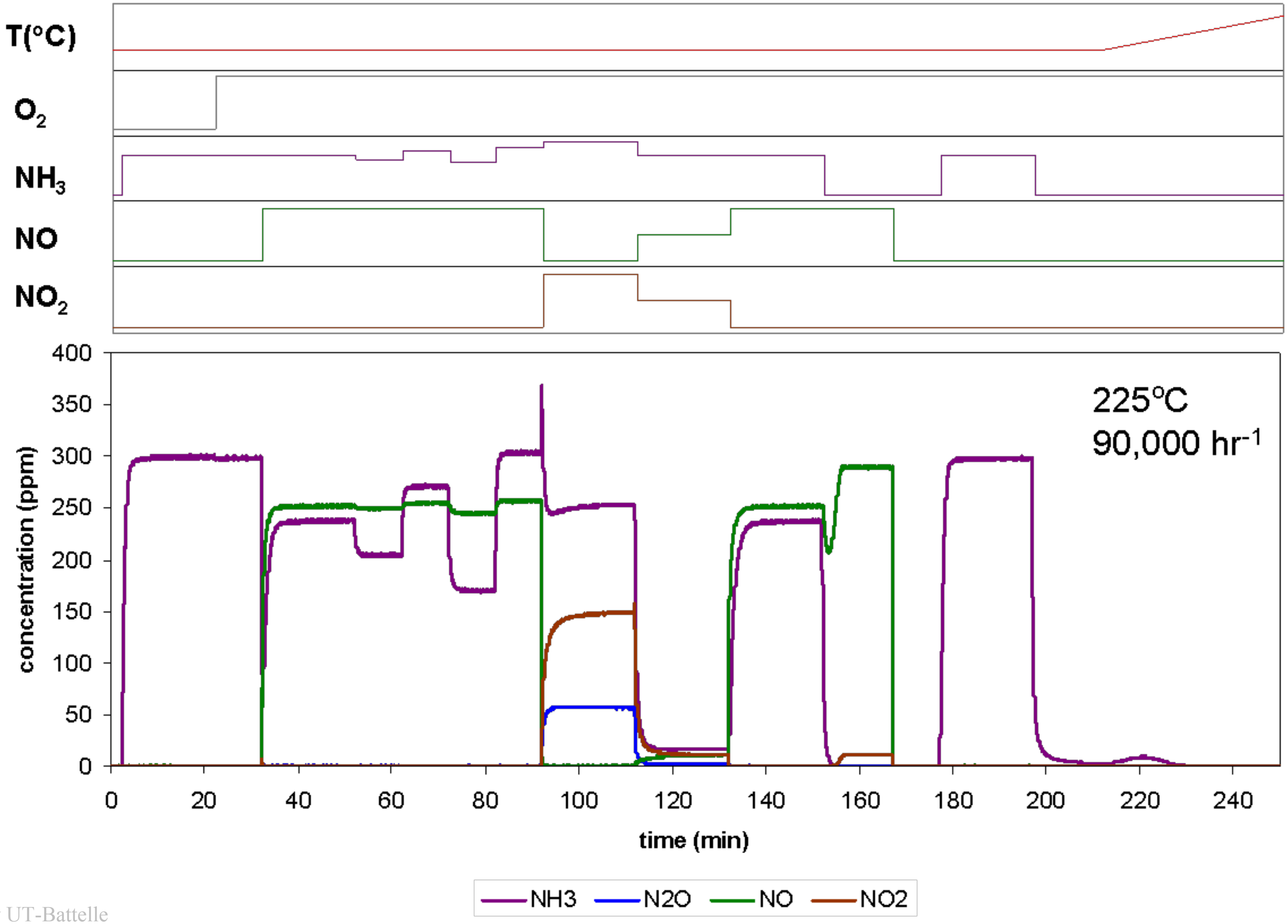
Evaluation Protocol Developed for SCR

- CLEERS SCR focus-group has developed a <u>steady-state</u> SCR protocol
- Accurate models also require transient data; especially for system control
- CRADA-developed protocol provides both transient & steady-state model parameters



Protocol reveals characteristic transient chemistry of catalyst

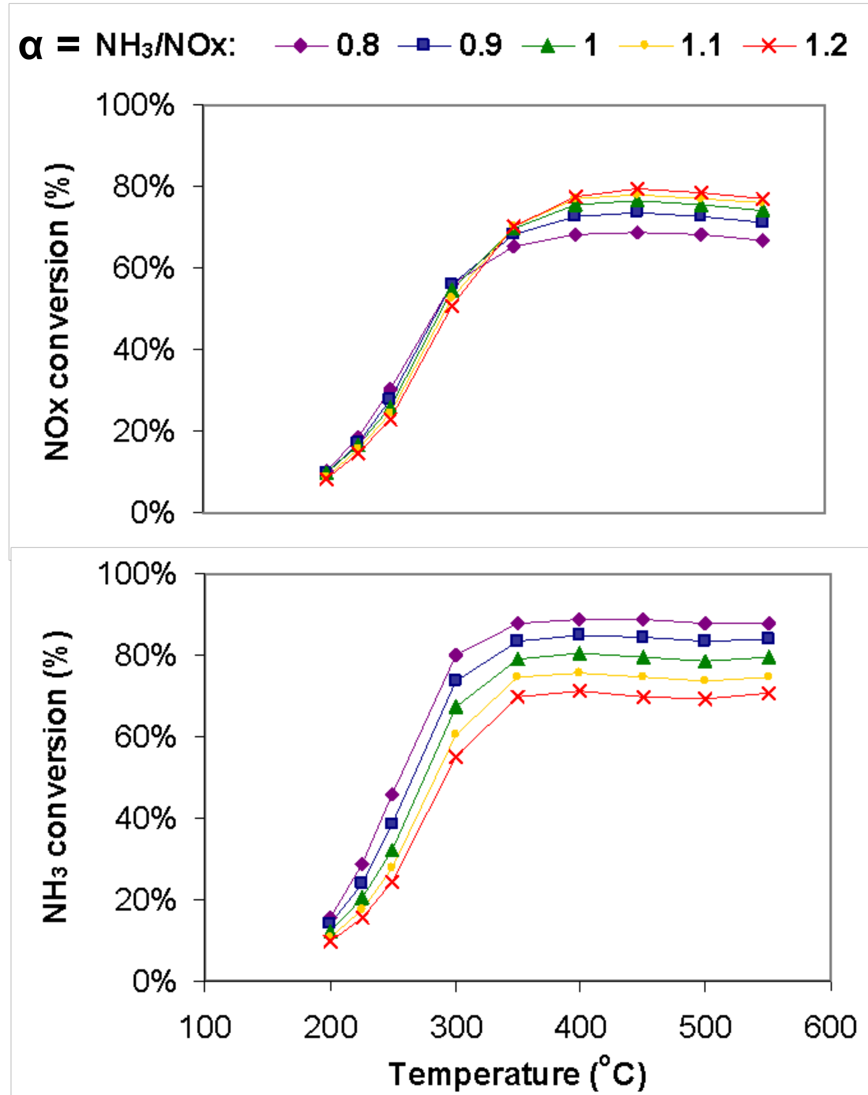
- Planned protocol evaluated at 150-600°C, 30k-120k h^{-1}, inlet NOx: 150-500 ppm



Steady-State Results

Varying NH_3/NOx (α-ratio) and T demonstrate operating range of catalyst

- Generally, expected trends observed
  - With increasing temperature:
    - NOx and NH_3 conversion increase
  - With increasing NH_3 dose (α-ratio):
    - NOx conversion increases
    - NH_3 conversion decreases

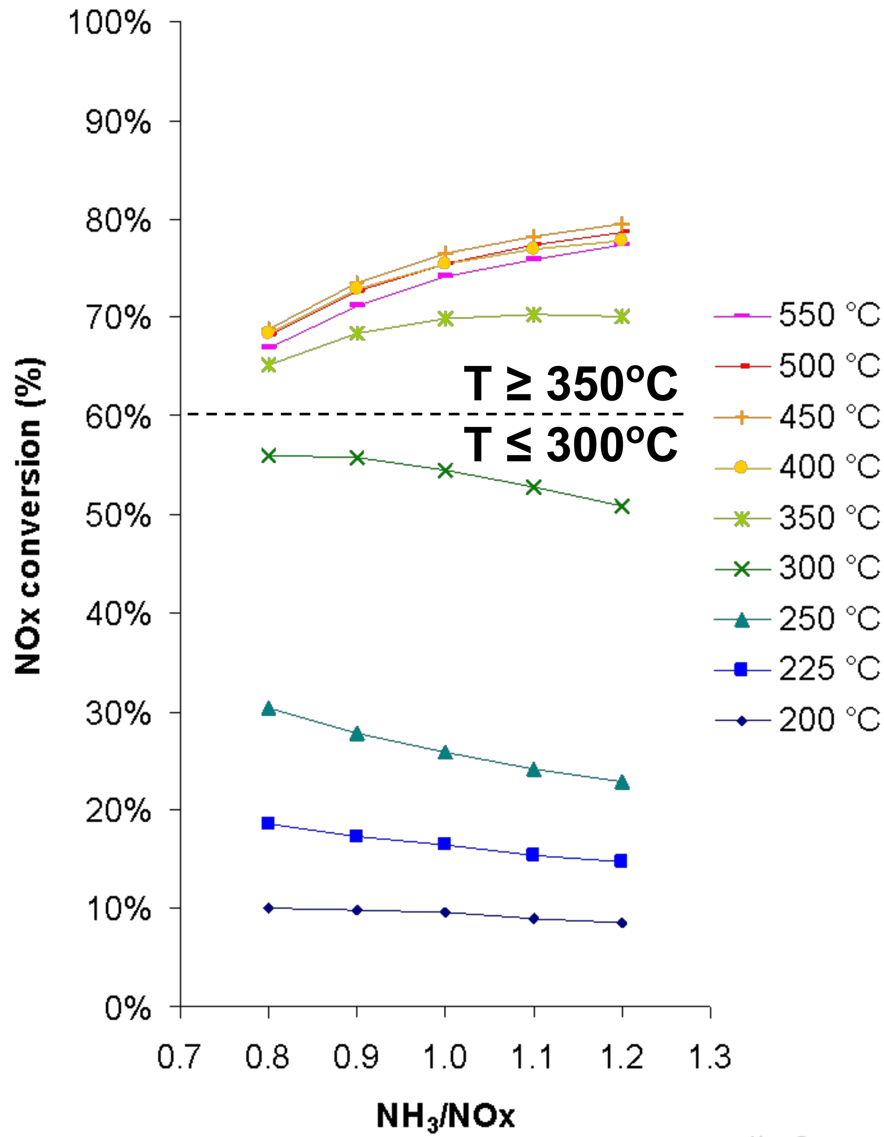


Experiment conditions:

- SV = 90,000 hr^{-1}
- NO_2/NOx = 0
- α = NH_3/NOx = 0.8, 0.9, 1.0, 1.1, 1.2
- Total NOx = 300 ppm
- 10% O_2, 5% CO_2, 5% H_2O

NH_3 inhibits NO-SCR reaction at low T

- Re-plotting data as a function of NH_3/NOx ratio reveals NH_3 inhibition
- For T ≤ 300°C, increasing NH_3 decreases NOx conversion
  - Indicates inhibition of NO-SCR reaction by excess NH_3 at low T
- Trend previously reported for zeolite-SCR
  - M. Wallin et al., J. Catal. 218 (2003) 354
  - A. Grossale et al., Catal. Today 136 (2008) 18
- Temperature of inhibition is catalyst dependent



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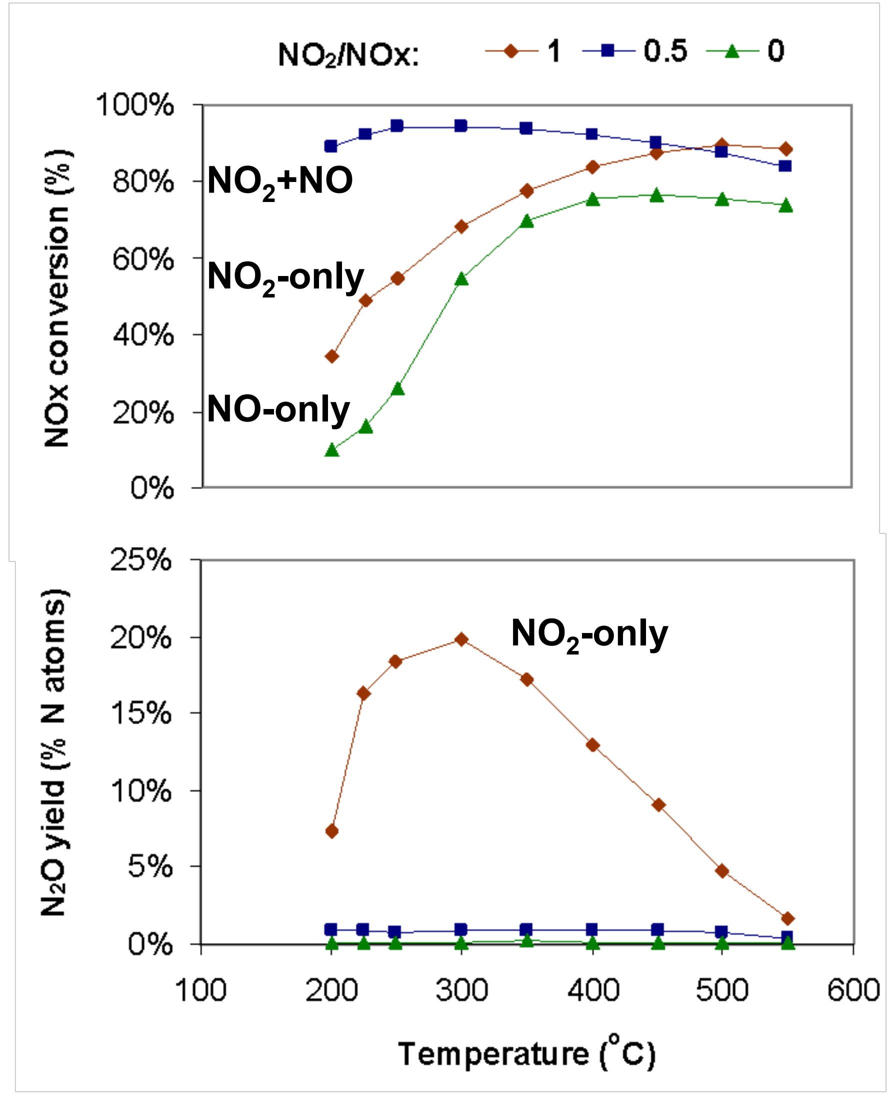
- NH_3/NOx = 0.8, 0.9, 1.0, 1.1, 1.2
- Total NOx = 300 ppm
- 10% O_2, 5% CO_2, 5% H_2O

NO_2 more reactive than NO at all T

- As expected, 1:1 mixture of $NO+NO_2$ gives best performance
  - "Fast SCR" reaction
- However, NO_2 more reactive than NO at all temperatures
  - "Slow SCR" reaction not observed with NO_2
  - NO-only is "slowest" reaction
  - Characteristic of zeolite catalyst

A. Grossale et al. Catal. Today 136 (2008) 18

- NO_2-SCR reaction only contributor to N_2O formation

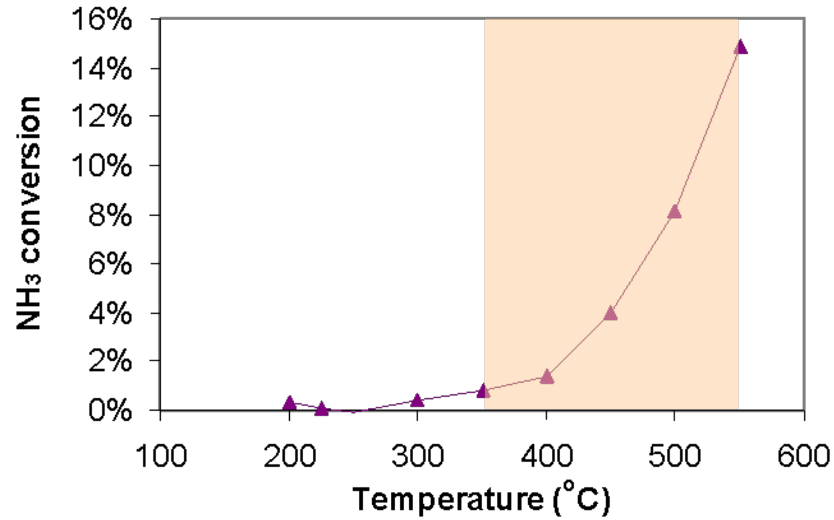


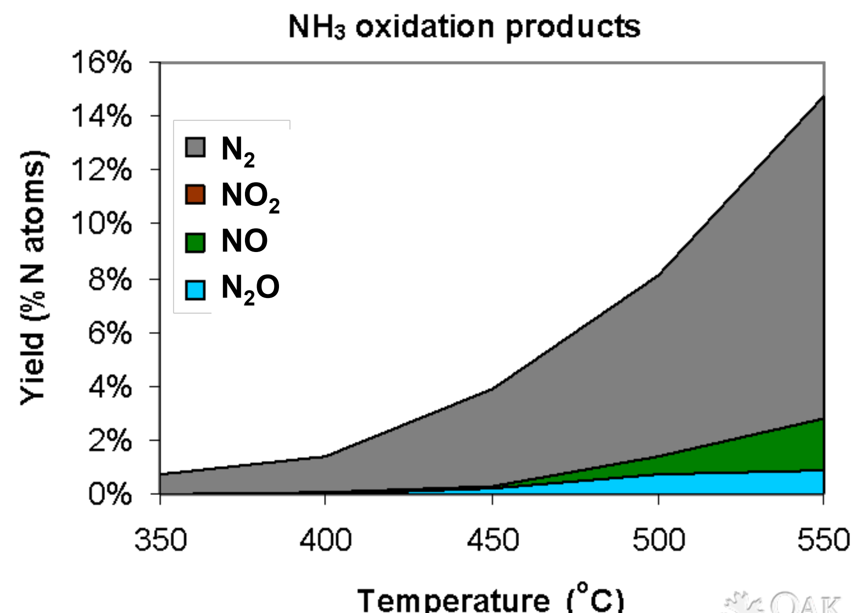
Experiment conditions

- $SV = 90{,}000\ hr^{-1}$
- NO_2/NOx = 0, 0.5, 1.0
- NH_3/NOx = stoichiometric
- Total NOx = 300 ppm
- 10% O_2, 5% CO_2, 5% H_2O

NH_3 oxidation observed above 350°C

- NH_3 oxidation increases rapidly above 350°C
- Catalyst selective for N_2 production from NH_3 oxidation
  - Typically oxidized to NO over precious metals
- Model must account for losses of NH_3 to direct oxidation
  - but not for additional NO formation



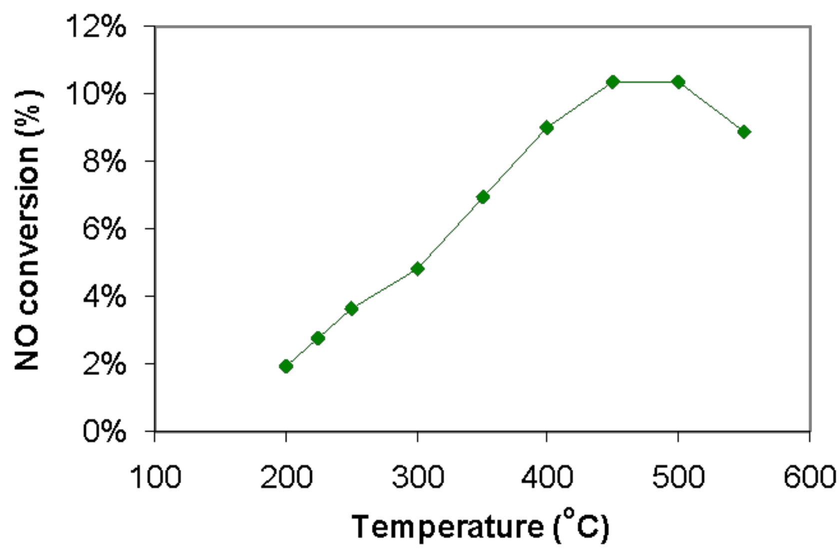


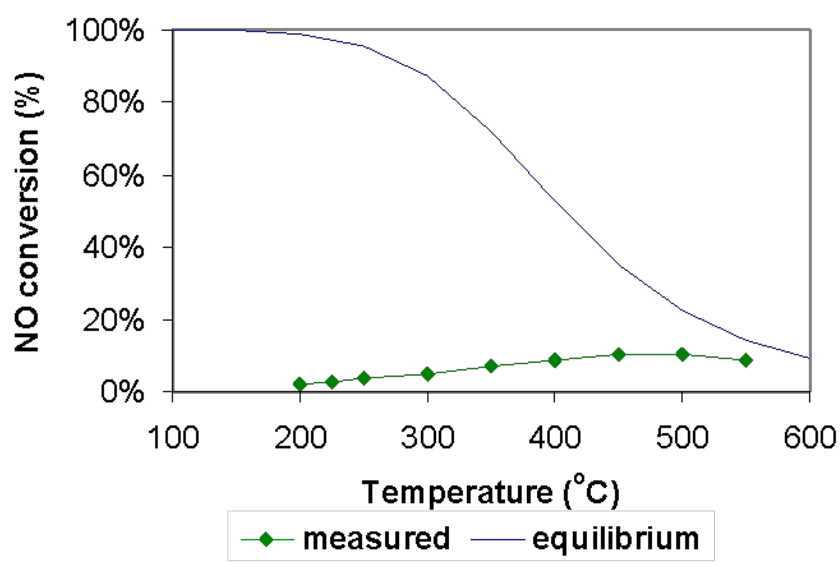
Experiment conditions

- SV = 90,000 hr^{-1}
- 300 ppm NH_3, 10% O_2, 5% CO_2, 5% H_2O

NO-oxidation peaks at 450-500°C

- NO oxidation increases with temperature up to 450°C
- Conversion decreases above 500°C
  - NOx concentrations approach equilibrium values ∴ reaction slows





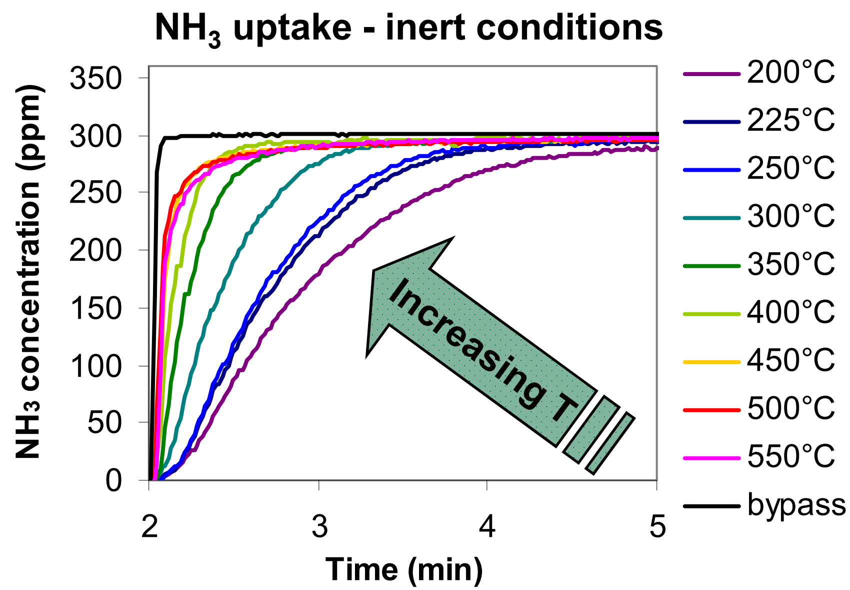
Experiment conditions

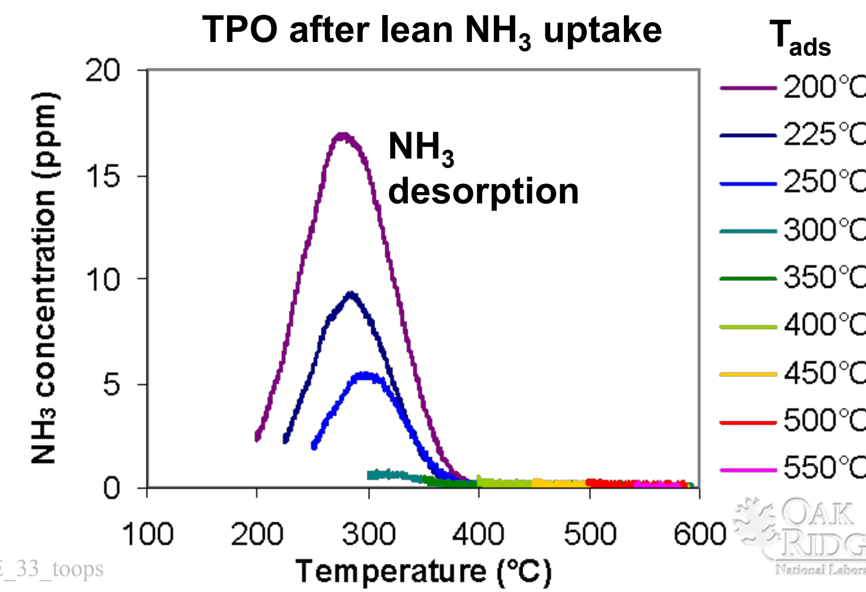
- $SV = 90,000\ hr^{-1}$
- 300 ppm NO, 10% O_2, 5% CO_2, 5% H_2O

Transient Results

All surface NH_3 oxidizes or desorbs at temperatures above 400°C

- NH_3 storage capacity probed at two points:
  1. NH_3 uptake during step change at inlet
     - Absence of O_2
     - NH_3 stored at all temperatures
     - Storage decreases as T increases
  2. Temperature Programmed Oxidation (TPO) performed after lean NH_3 storage
     - Single desorption peak centered near 300°C
     - All NH_3 released/oxidized by 400°C
- All NH_3 stored at T ≥ 400°C oxidized by O_2 or desorbed when NH_3 flow stops



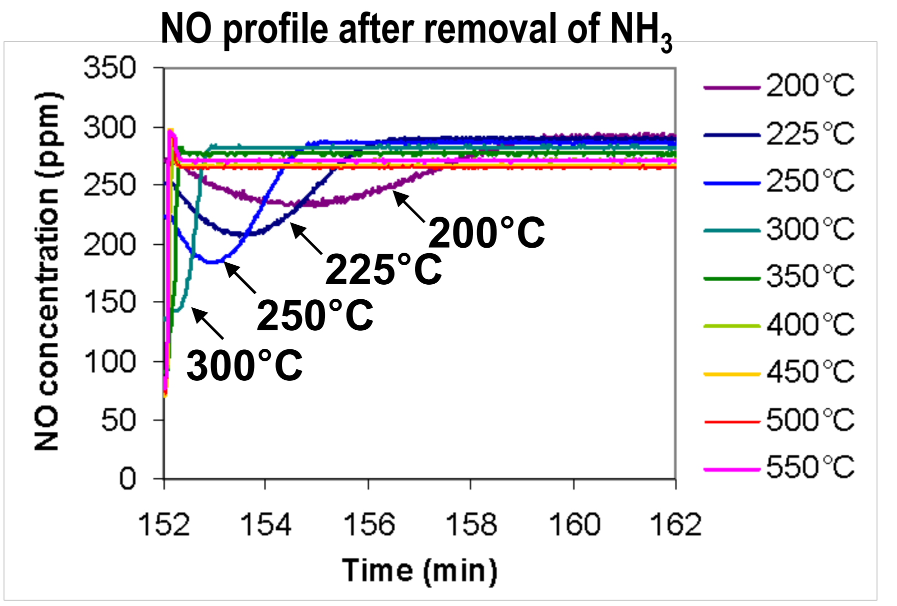


Experiment conditions

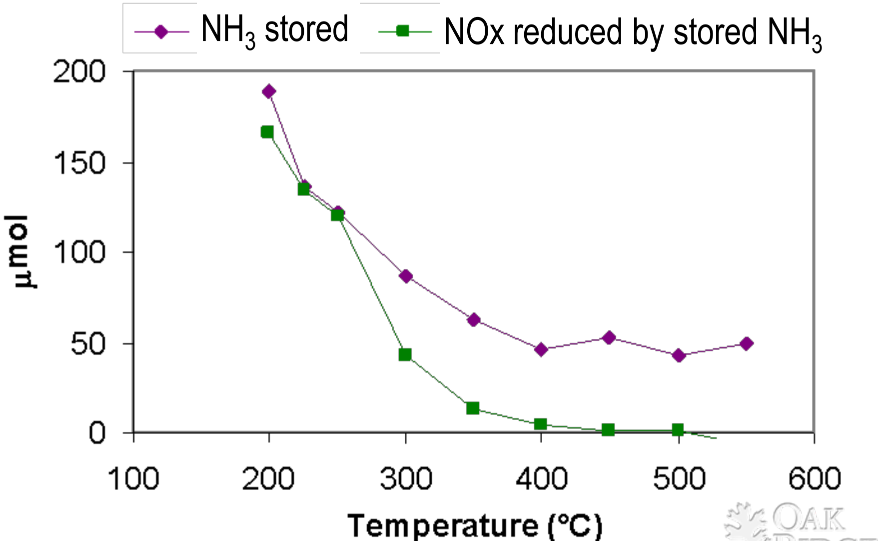
- SV = 90,000 hr^{-1}
- NH_3 Ads: 300 ppm NH_3, 0-10% O_2, 5% CO_2, 5% H_2O
- TPO: 10% O_2, 5% CO_2, 5% H_2O, 5°C/min ramp

Stored NH_3 not available for subsequent NO_x reduction above 350°C

- NO oxidation step provides another measure of NH_3 storage capacity
  - NO feed constant at 300 ppm after NH_3 turned off
  - Dips in NO concentration due to conversion by stored NH_3
  - Rate of stored NH_3 consumption (depth of dip in NO) increases with T



- Comparison to NOx uptake under inert conditions confirms oxidation or desorption of previously stored NH_3



Experiment conditions

- SV = 90,000 hr^{-1}
- 300 ppm NO, 10% O_2, 5% CO_2, 5% H_2O

Optimization of protocol necessary

- Current research plan requires ~300 hours of catalyst evaluation
  - Planned protocol evaluated at 150-600°C, 30k-120k h^{-1}, inlet NOx: 150-500 ppm
  - Eight weeks of normal workday operation

- Protocol must be optimized to aid new catalyst transitions
  - Identify most critical experiments through model parameter sensitivity analysis
  - Experiments with low sensitivity are removed from the matrix

- Work through CLEERS to relate complete and optimized protocol

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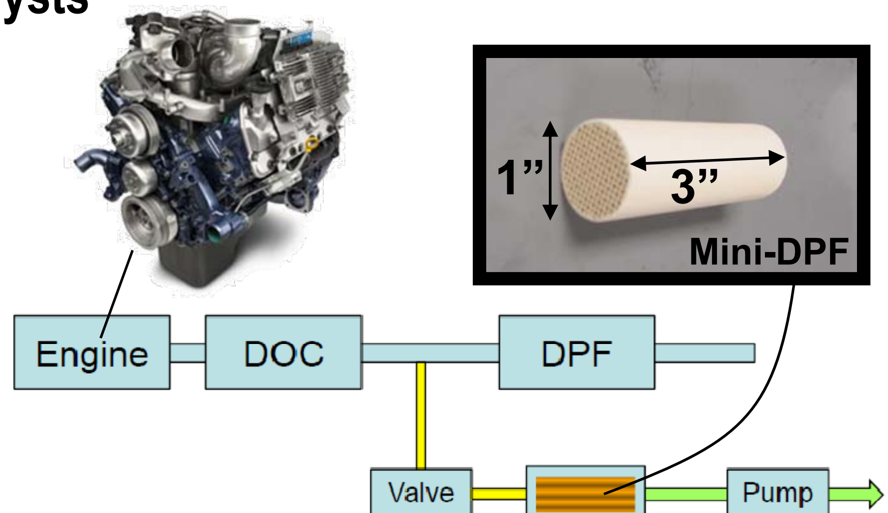
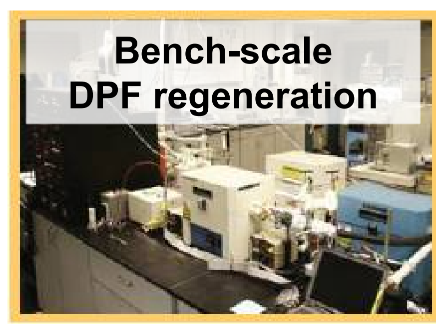
Future Plans

- Fully execute protocol under all conditions and space velocities
  - Vary total NOx level and increase space velocity up to 120k h^{-1}
- Complete model development and protocol optimization
- Evaluate model parameters with aged catalysts

- New direction for FY10:
  DOC and DPF regeneration kinetics
  - DPF regeneration has large impact on fuel economy
  - Soot to be collected on production or production-intent Navistar engines
  - Explore effects of advanced combustion modes
    - Hydrocarbons generated and effect on soot oxidation





NOx Abatement R&D – Navistar CRADA
Summary

- Established evaluation protocol providing both steady-state and transient chemistry
  - Benefits experimental and modeling community in addition to Navistar
  - Optimized protocol will economize experiments
  - Starting point for validated CLEERS SCR protocol for transient behavior
- Several key SCR-chemistry findings
  - Stored NH_3 reactivity identified specifically for reactivity to NOx reduction
  - NH_3 identified as an inhibiting species at low temperatures
  - Temperature dependent NH_3 storage identified
- Detailed transient and steady-state data generated for CRADA partner and model
  - Additionally benefits systems level modeling efforts (PSAT)
  - Current plans are to publish model and data