CLEERS Coordination & Joint Development of Benchmark Kinetics for LNT & SCR

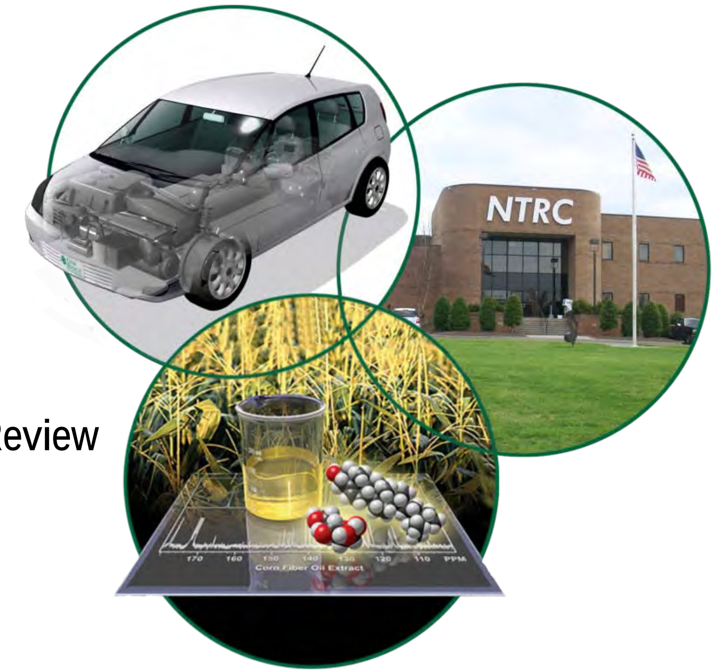
Agreements:

- Coordination of Cross-Cut Lean Exhaust Emission Reduction Simulation (8745)
  Stuart Daw, Vitaly Prikhodko, Charles Finney
- Joint Development of Benchmark Kinetics for LNT & SCR (8746)
  Jae-Soon Choi, Josh Pihl, Bill Partridge, Miyoung Kim, Kalyana Chakravarthy, Todd Toops Michael Lance, Stuart Daw

PI: Stuart Daw

Presenter: Jae-Soon Choi

Oak Ridge National Laboratory



Project ID: ace_022

Vehicle Technologies Program Annual Merit Review
May 11, 2011, Washington, DC

DOE Managers: Ken Howden, Gurpreet Singh

U.S. DEPARTMENT OF ENERGY

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

Overview

Timeline

- Project start date:
  - CLEERS Coordination (8745) FY00
  - LNT & SCR Kinetics (8746) FY00
- Project end date & percent complete:
  - All ongoing

Budget

- Project funding for FY10/FY11
  - CLEERS Coordination (8745): $200K/$200K
  - LNT & SCR Kinetics (8746): $500K/$500K
- Funding request for FY12
  - Similar to FY11

Barriers

- Fuel penalty
  - Regeneration & desulfation of emission controls require extra fuel consumption
- Cost of aftertreatment
  - High cost inhibits market acceptance of diesel & lean-gasoline
- Durability
  - At present, large built-in margin required

Partners

- Close collaboration w/ CLEERS Focus Groups & DOE Advanced Engine Crosscut Team
  - > 20 institutions
  - Nat'l labs: SNL, PNNL
  - Industry: GM, Ford, Cummins, DDC, Navistar, Delphi, Umicore …

Project objectives-Relevance

Enable robust & energy efficient lean emission control technologies
by
Coordinating & conducting emissions controls simulation research

Current development of lean-burn aftertreatment is highly empirical & requires fundamental insights to significantly improve system performance & reduce cost

- Identify and prioritize R&D needs within industry, and coordinate DOE research efforts (CLEERS Coordination)
- Develop detailed technical data required to simulate energy efficient emission controls (CLEERS Research)
  - Experiments: specialized measurements under relevant conditions to provide new insights into key LNT and SCR chemistry and kinetics
  - Modeling: consolidate new insights into LNT and SCR models that relate device and catalyst properties to fuel efficiency and emissions performance

Research targets chosen based on the latest CLEERS poll & reviewer comments
SCR: surface chemistry and properties of advanced catalysts; impacts of aging and fouling on catalyst function
LNT: NH_3 & N_2O mechanisms for both CLEERS reference and new generation LNTs

Milestones

- FY2010 milestones completed
  - ✓ 8745: Organized 2010 CLEERS public workshop
  - ✓ 8746: Publish joint results with PNNL on SCR catalyst kinetics
- FY2011 milestones on track
  - ✓ 8745: Organized 2011 CLEERS public workshop
  - – 8746: Develop model for ammonia generation in LNTs

Approach: Prioritize/Coordinate/Perform/Disseminate Lean Exhaust Emissions Research

Coordination

DOE Advanced Engine Cross-Cut Team

Caterpillar, Cummins, Chrysler, Detroit Diesel, DOE-VTP, Ford, General Motors, Navistar, U.S. Army TARDEC, U.S. EPA, Volvo

CLEERS Planning Committee

- Wei Li (GM),
- Stuart Daw (ORNL)
- Louise Olsson (Chalmers)
- Chris Rutland (UW)
- Kevin Sisken (DDC)

Technology Focus Groups

- DPF/DOC, LNT, SCR
- Monthly teleconferences
- Selected membership

Website (www.cleers.org)

- General information
- Meeting announcements
- Shared data

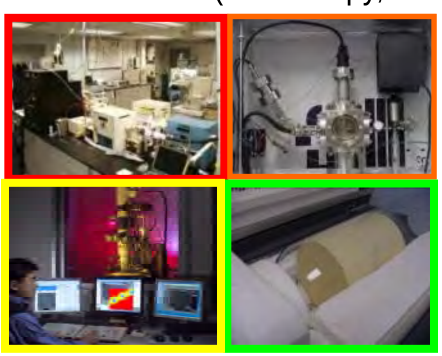
Workshops

- Public
- Annual in Detroit area
- Presentations on website

R&D

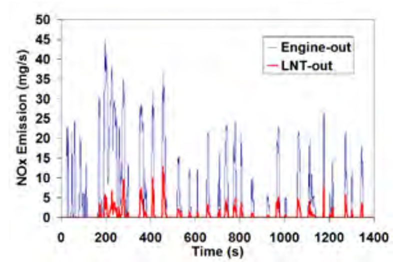
Experiments

- Bench/micro/DRIFTS reactors
- Specialized diagnostics (SpaciMS)
- Characterization (Microscopy, TPR)



Modeling/Simulation

- Microkinetic-based model
- Global model



New insights, data & models relevant to development of robust, energy-efficient, & cost-effective emission controls

Collaboration w/ PNNL, SNL, ICT Prague, Chalmers, U Kentucky

Technical Accomplishments

- CLEERS coordination
  - Organized 14th (2011) CLEERS Workshop
  - Coordinated monthly Focus Group teleconferences
  - Conducted new R&D priority survey
  - Leveraged ORNL, PNNL, SNL unique capabilities
  - Continued refining protocol for transient SCR catalyst characterization and utilizing results for systems simulations

- SCR research
  - Exercised transient SCR protocol on commercial copper zeolite catalyst
  - Transferred protocol data to PNNL for SCR model development and validation
  - Hydrothermally aged core samples to study impacts on catalyst function through protocol experiments and modeling (collaboration with PNNL)

Technical Accomplishments (cont'd)

- LNT research
  - Clarified correlations between NH_3 & N_2O selectivities with experiments & modeling of CLEERS LNT
    - Evaluated impact of reductant type (H_2, CO, C_3H_6, C_3H_8) on selectivity
    - Studied transient chemistry of NH_3 decomposition, oxidation & adsorption
    - Enhanced global model in collaboration with ICT Prague, Chalmers
    - Continued micro-kinetic modeling with SNL (lean/rich cycling, sulfation)
  - Started benchmarking CLEERS reference against a new generation lean GDI LNT

Technical Highlights

CLEERS Coordination

ORNL continued established coordination roles

- CLEERS website
- Monthly teleconferences
  - Group telecon (20-30 domestic + int'l participants)
  - Presentations of very recent technical results
  - Host rotates among DPF, LNT, SCR Focus Groups
- Workshop #13, April 20-22, 2010, UM Dearborn
  - 90 attendees (OEMs, suppliers, software companies, nat'l labs, universities)
  - Industry panel on systems simulations
- Workshop #14, April 19-21, 2011, UM Dearborn
  - About 90 attendees (OEMs, suppliers, software companies, nat'l labs, universities
  - Industry panel on aftertreatment kinetic parameter evaluation from engine dynamometer and vehicle measurements
- Revised SCR transient catalyst lab protocol
  - Presented and discussed at public workshop and telecons
- Simulated comparisons of gasoline and diesel hybrids with lean NO_x control
  - Demonstrated and published

2010 CLEERS Workshop

We have continued to utilize CLEERS aftertreatment models for systems simulations

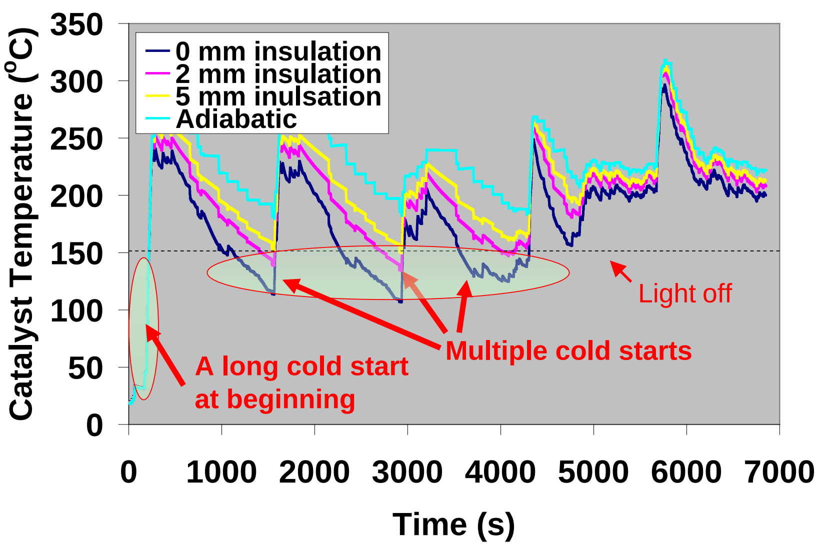
Example study of insulation effect on SCR NO_x control for diesel PHEV

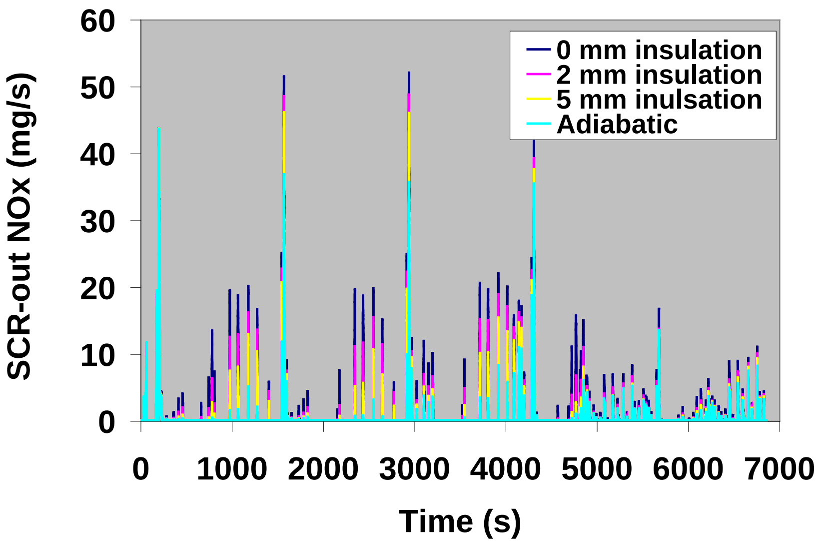
- 5 UDDS cycles beginning with cold start
- 2.4-L urea-SCR (Cu-ZSM-5 catalyst) for NO_x control
- Varying level of mineral fiber catalyst insulation
- Non-optimized urea control

Observations:

- Insulation keeps SCR catalyst warm enough to reduce impact of cold starts
- Higher temperatures may accelerate aging
- Insulation reduces NO_x and NH_3

Insulation (mm)	NOx (g/mile)	NH_3 (g/mile)
0	0.159	0.068
2	0.117	0.048
5	0.095	0.035
Adiabatic	0.068	0.010





We recently completed an updated survey of CLEERS R&D priorities

Questionnaire sent to DOE AEC Team and collaborators

- 8 OEMs
- 6 emissions control suppliers
- 5 energy companies
- 2 non-DOE federal agencies

Survey structure

- 3 response categories: HD diesel, LD diesel, gasoline
- 3 survey areas: Technology priorities, CLEERS activities, databases
- Multiple topics rated as having High, Medium, or Low concern/value

Preliminary Highlights (report will be issued after CC Team review):

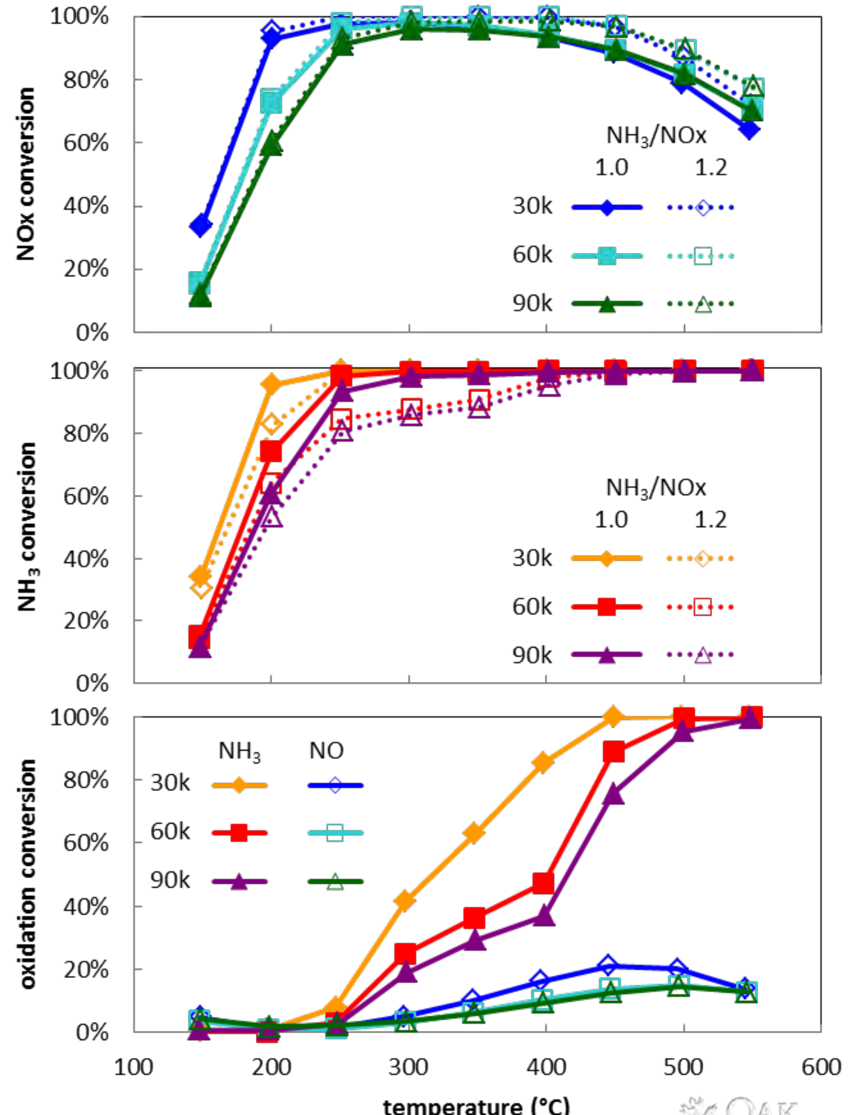
- 25 responses returned
- Greatest emissions control technology R&D needs:
  - Understanding urea SCR catalyst properties and chemistry
  - Particulate filter measurement, sensing, and diagnostics
  - Understanding oxidation catalyst properties and chemistry
  - Reducing LNT PGM levels
  - Systems simulations of LNT-DPF and SCR-DPF combined devices

Technical Highlights

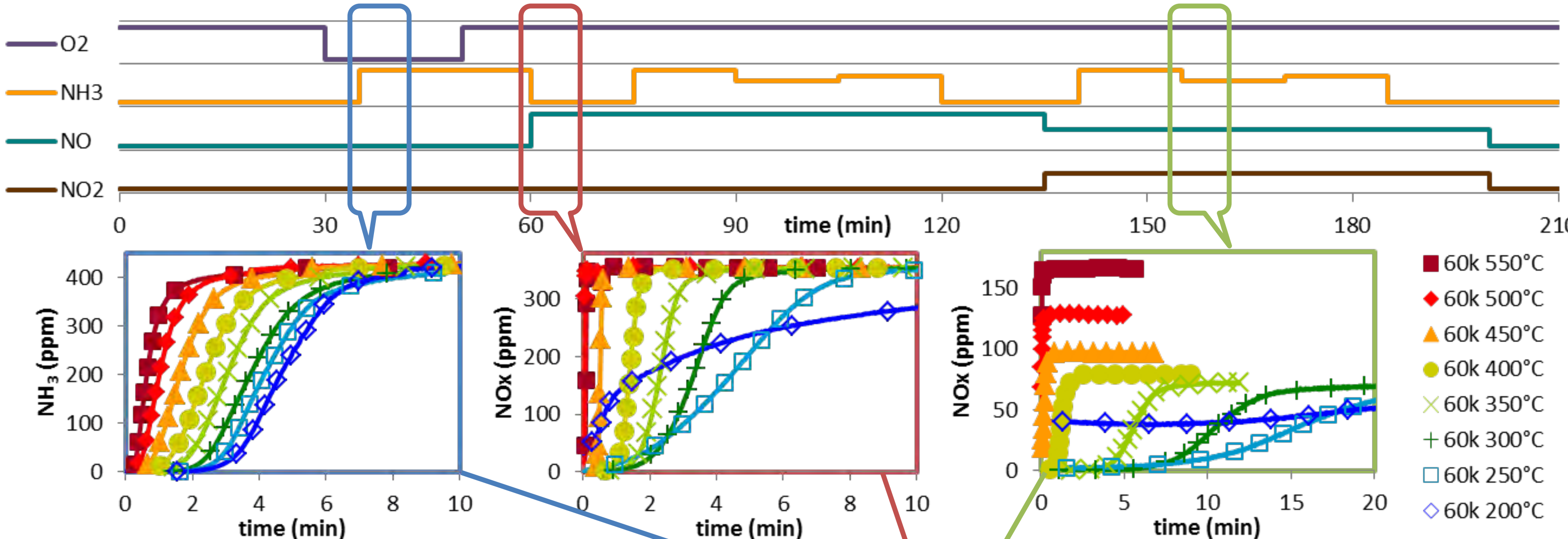
SCR

Protocol data show wide operating window for fresh commercial Cu zeolite

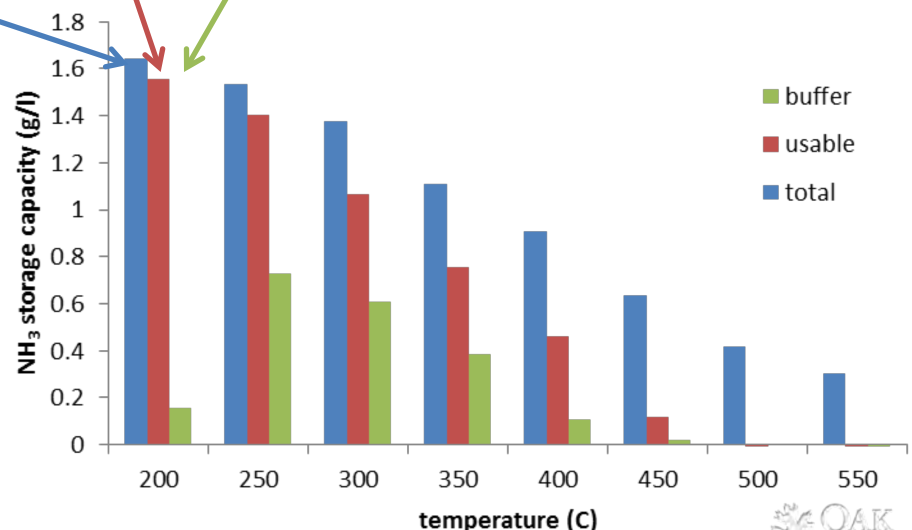
- Cu zeolite from Ford Super Duty Turbodiesel
- High NO_x conversions at T>=250°C
  - Up to 90k hr^{-1}
  - Without NO_2 in feed
- High T performance limited by NH_3 oxidation
  - 100% NH_3 conversion for SCR NH_3/NO_x = 1
  - NH_3 overdosing improves NO_x conversion
  - Substantial NH_3 + O_2 oxidation at T>=300°C
- High NO oxidation activity reduces need for NO_2 in feed
- Data transferred to PNNL for model calibration and validation
  - Baseline for aging and fouling studies
- Steady state protocol points provide:
  - Performance characterization
  - Data for model calibration
  - Insights into performance limitations



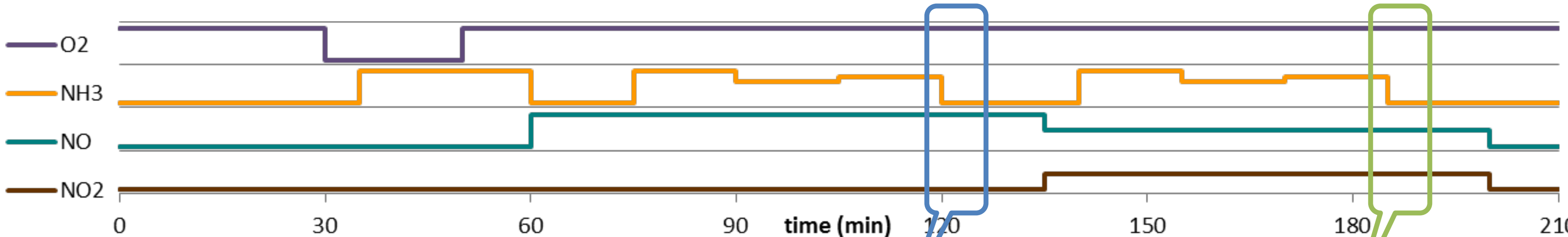
New protocol transients quantify details of NH_3 storage capacities



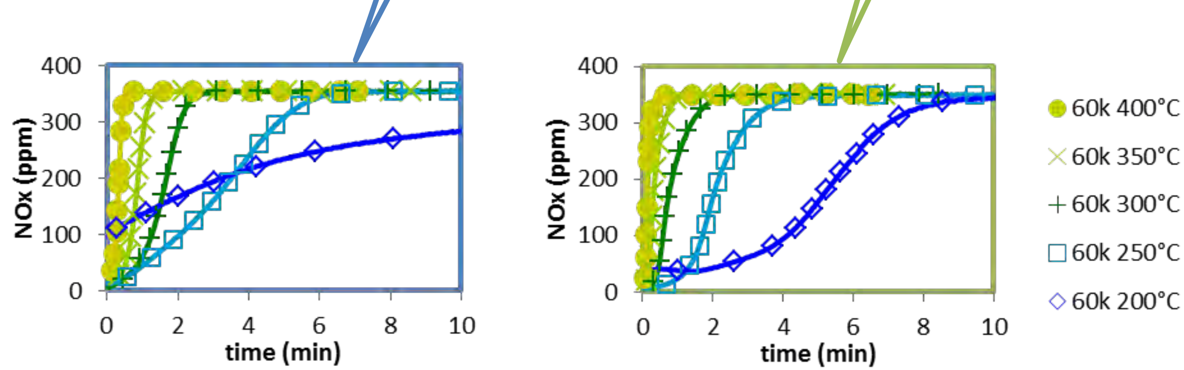
- Example capacities:
  - Total: NH_3 uptake without O_2
  - Usable: NH_3 storage under O_2
    - < Total due to NH_3 oxidation
  - Buffer: ability to handle transient NH_3 overdose/underdose
- Available NH_3 storage capacity changes with current conditions & operating history

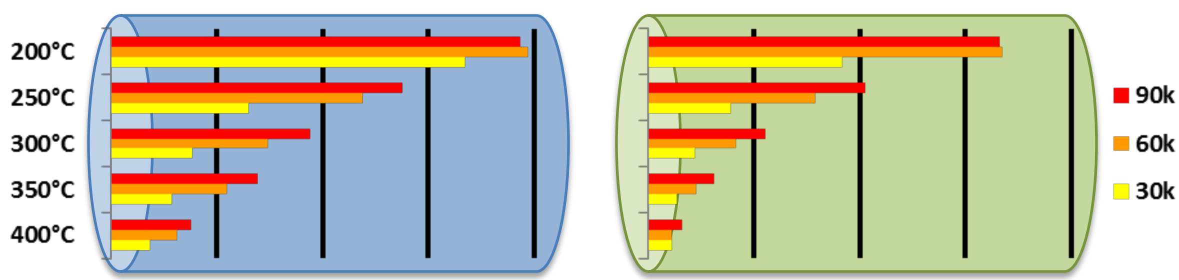


SCR surface NH_3 inventory provides insights into catalyst utilization



- Fractional catalyst utilization estimated from NH_3 coverage:
  - Turn NH_3 off, leave NO_x on at end of SCR steps
  - Integrate NO_x reduced by stored NH_3
  - Divide by Usable NH_3 capacity at same T
- Utilization decreases with:
  - higher T
  - lower SV
  - NO_2 in feed
- NH_3 coverage yields insights into catalyst function





NH_3 coverage (catalyst utilization)
$NO_2/NOx = 0.0$
$NH_3/NOx = 1.0$

Standard SCR

NH_3 coverage (catalyst utilization)
$NO_2/NOx = 0.5$
$NH_3/NOx = 1.0$

Fast SCR

Technical Highlights

LNT

Elucidate NH_3 & N_2O mechanisms via lab experiments & modeling

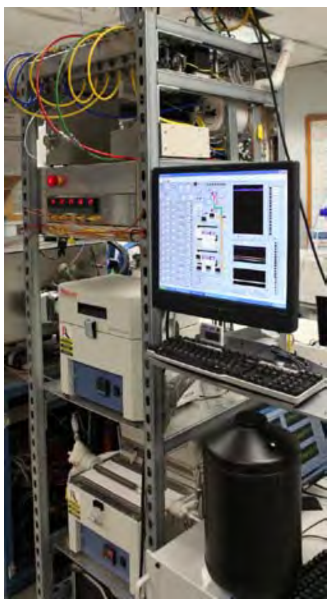
Understand dependence on reaction conditions

- Sweep reductant type

  H_2, CO, H_2/CO, C_3H_6, C_3H_8, H_2/HC

- Sweep temperature

  150-550 °C



Automated bench reactor

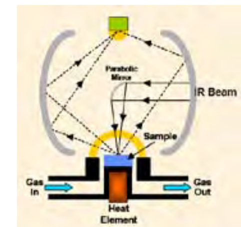
Improved understanding & models

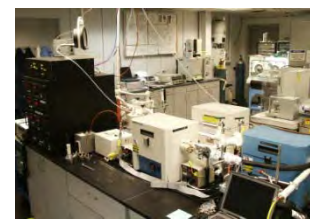
Relevant to implementations (slip control, LNT-SCR in cost efficient manner)

Transient surface chemistry

- NH_3 adsorption, oxidation, decomposition
- Gas & surface species

DRIFTS





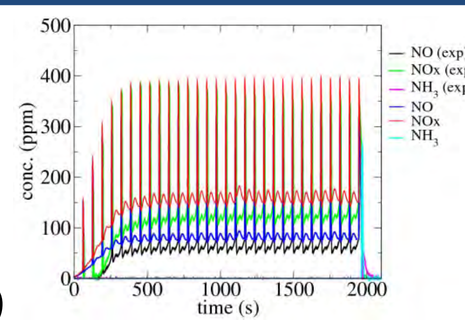
Bench reactor

Simulation

- Incorporate new findings
- Extend reaction kinetics model

  Currently limited NH_3 & N_2O capabilities

  (intermediate: NH_3 + NO_x; not tracking N_2O)

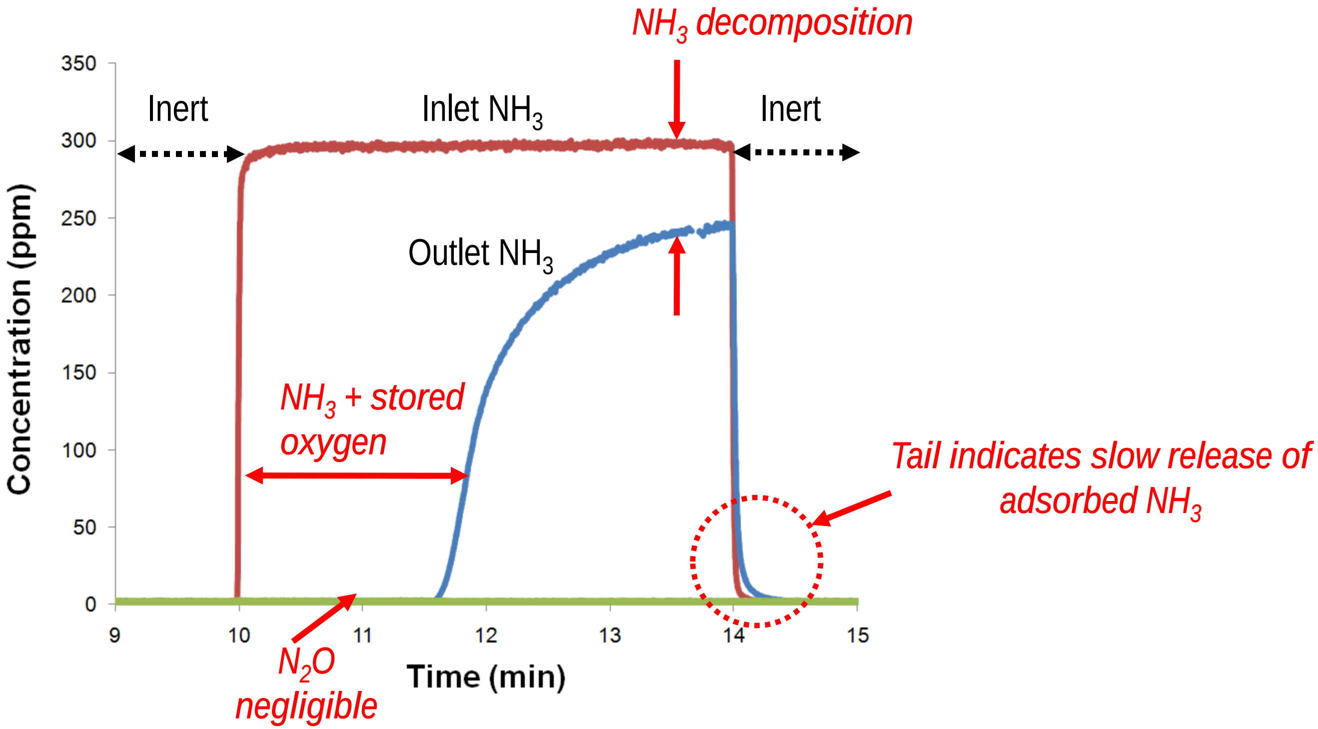


Model

Various NH_3 surface interactions influence LNT selectivity

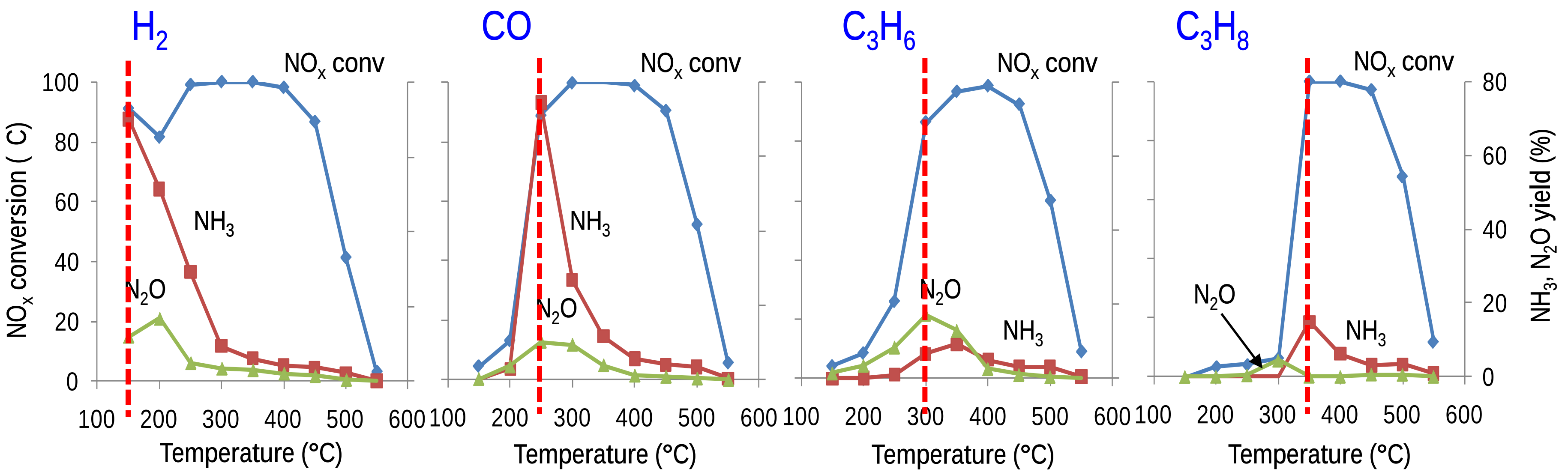
Transient response experiment at 300 °C

NH_3 input to CLEERS LNT pre-oxidized with O_2; no surface NO_x

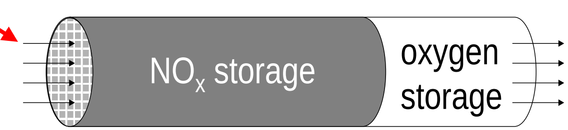


- NH_3 reduction of stored oxygen (CeO_2): very efficient (plug-like front)
- NH_3 reduction of CeO_2 not a major contributor to N_2O (vs. NH_3 reduction of surface NO_x)
- NH_3 decomposition ($2NH_3 > N_2 + 3H_2$): higher rates under transient conditions
- NH_3 adsorption & desorption

Reductant type affects spatial distribution of NH_3 chemistry controlling NH_3 & N_2O yields



- Light-off temperature is highly dependent on reductant type: $H_2 < CO < C_3H_6 < C_3H_8$
  - At light-off : near max conv. reached using whole LNT
  - Above light-off : max conv. using partial length of LNT

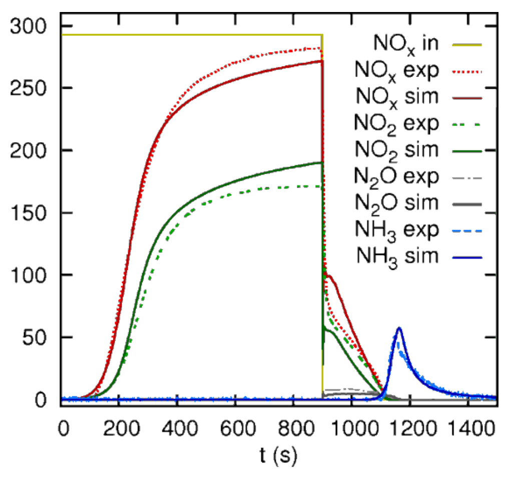


- NH_3 & N_2O yields peak at light-off T
  - Significant slip possible: NH_3 ~70%; N_2O ~20%
  - At light-off: reactions forming NH_3 (reductant + stored NO_x) & N_2O (NH_3 + stored NO_x) maximized
  - Above light-off: NH_3-consuming reactions without generating N_2O increase (NH_3 + CeO_2; decomposition)

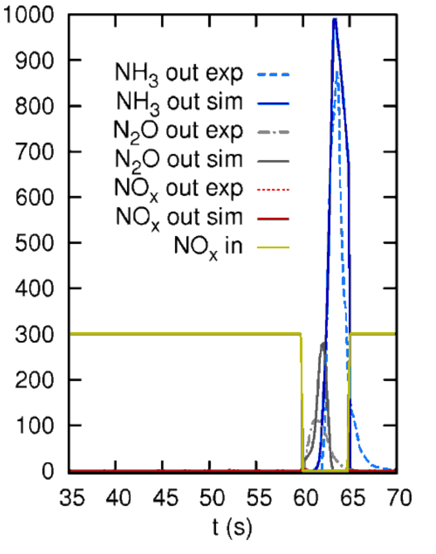
Experimental findings are enhancing models for CLEERS LNT

- Extended kinetics in global models to capture observed NH_3 and N_2O chemistry in collaboration with ICT Prague (Dr. Koci)
  - NH_3 + stored NO_x; NH_3 + stored oxygen; NH_3-N_2O correlations

Long cycling, 300 °C



Short cycling, 300 °C

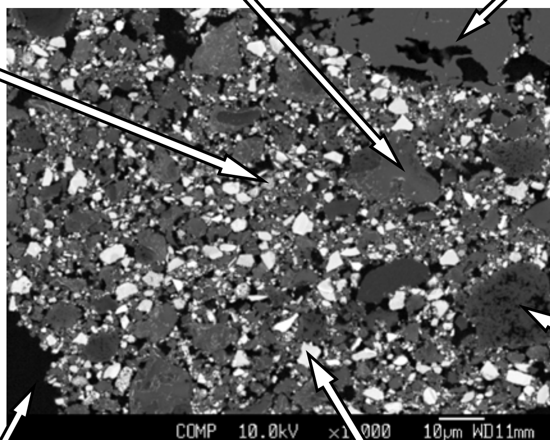


- Collaborated with SNL (Dr. Larson) on microkinetic model (see ACE035 talk)
  - Lean/rich cycling; sulfation/desulfation

New generation lean GDI LNT benchmarking against CLEERS reference initiated

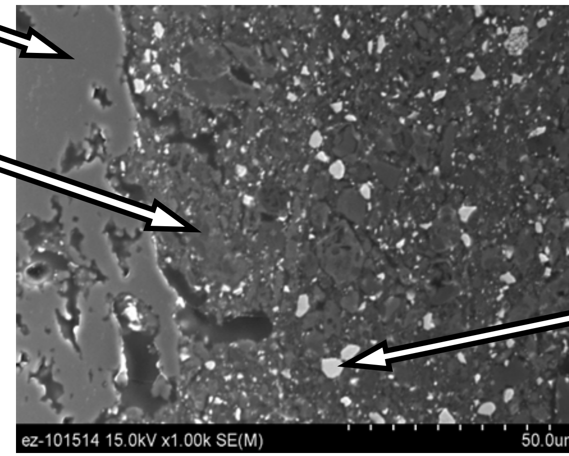
CLEERS reference

Lean GDI, 2004, provided by Umicore



New LNT

Lean GDI, 2009, from BMW 120i vehicle



	CLEERS reference	New LNT
Cell density (cpsi)	625	413
Ba loading (g/ft^3)	442	565
PGM loading (g/ft^3)	103	94
Pt/Pd/Rh ratio	8/3/1	7/3/1

- Responsive to FY10 review comments
- Initial characterization indicates similar basic components in both LNTs
  - Reactor evaluation planned
  - Catalyst used in an ORNL lean gasoline engine-based project (see ACE033 talk)

OAK RIDGE National Laboratory

Collaborations

- Partners
  - National laboratories: ORNL (HTML), PNNL, SNL
  - **Universities: Kentucky, Houston, ICT Prague (Dr. Kočí), Chalmers (Prof. Olsson)**
  - Industry: CLEERS Focus Group & DOE Advanced Engine Crosscut Team members including Cummins, Navistar, Ford, Umicore, BASF
- Technology Transfer
  - 18 publications & presentations (dissemination of DOE-funded research outcome via high visibility forums: SAE, int'l journals etc.)
  - SCR lab protocol publicly proposed
  - LNT & SCR models used for DOE Vehicle & System HEV/PHEV Simulations
  - Data, systems impact guidance for PNNL & SNL activities

Future Work

- CLEERS coordination to maximize research synergy
  - Planning Committee, Focus Groups, Workshop & website
  - Synchronizing ORNL-PNNL-SNL R&D
  - Complete and issue report on priority survey
  - Basic data & model exchange between CLEERS & other DOE projects
- SCR research to support modeling of catalyst performance after aging and fouling
  - Perform protocol experiments on hydrothermally aged samples and transfer data to PNNL partners
  - Use surface spectroscopy to investigate nature of Cu zeolite active sites and how they change with aging and fouling
- LNT research to reduce cost of lean exhaust aftertreatment
  - Evaluate the new LNT & compare to CLEERS reference catalyst
  - Refine global model on NH_3 & N_2O selectivities with ICT Prague & Chalmers
  - Enhance microkinetic model on fast cycling & sulfation with SNL

Summary

- Relevance
  – Assist DOE in coordinating & conducting R&D enabling development of energy & cost effective lean emissions control technologies
- Approach
  – Planning Committee, Focus Groups, website, Workshops, polling, Crosscut updates, data & model exchanges
  – Multi-scale lab R&D on commercial & model LNT & urea-SCR catalysts under relevant conditions (modeling & experiments)
- Technical Accomplishments
  – Monthly Focus meetings, website, 2010 & 2011 Workshops, Crosscut reports, systems implementation of CLEERS data & models
  – Fundamental understanding and modeling of practically relevant urea-SCR & LNT catalysts
- Collaborations
  – Non-proprietary collaborations among industry, national labs, universities, & foreign institutions through CLEERS organizational structure
  – Extensive publications/presentations
- Plans for Next Fiscal Year
  – Planning Committee, Focus Groups, Crosscut reports, website, workshops, enhanced database
  – Flow reactor and spectroscopic investigations of aging and fouling of Cu zeolite catalysts
  – Benchmark CLEERS ref to new-generation LNT with reactor, modeling, & characterization