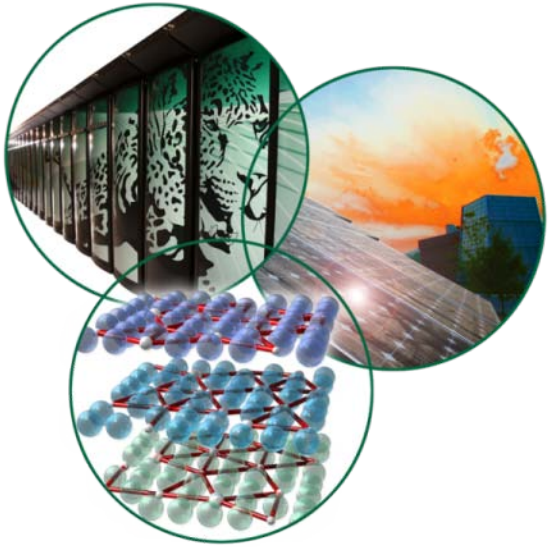
CLEERS Coordination & Joint Development of Benchmark Kinetics for LNT & SCR

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, Kalyana Chakravarthy, Todd Toops, Michael Lance, Stuart Daw

PI: Stuart Daw

Presenter: Jae-Soon Choi

Oak Ridge National Laboratory



Project ID: ace022

Vehicle Technologies Program Annual Merit Review
June 9, 2010, 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 FY09/FY10
  - CLEERS Coordination (8745): $200K/$200K
  - LNT & SCR Kinetics (8746): $450K/$500K
- Funding request for FY11
  - Similar to FY10

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

- Informal but close collaboration w/ CLEERS Focus Group members & DOE Diesel Crosscut Team
  - > 20 institutions
  - Nat'l labs: SNL, PNNL
  - Industry: GM, Ford, Cummins, DDC, Navistar, Delphi, Umicore …

Objectives

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 (LNT & SCR Kinetics)**
  - **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: types & interactions of surface species, HC poisoning
LNT: sulfur impact, NH_3 mechanism (growing interest with respect to NH_3 slip control or coupled LNT-SCR system)

Milestones

- **FY2009 milestones completed**
  - ✓ **8745: Organized 12th CLEERS public workshop**
  - ✓ **8746: Published LNT model and results for systems simulation**

- **FY2010 milestones on target for Sept. 2010 completion**
  - ✓ **8745: Organized 2010 CLEERS public workshop**
  - **8746: Publish joint results with PNNL on SCR catalyst kinetics**

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

Coordination

DOE Diesel Cross-Cut Team

Caterpillar, Cummins, Chrysler, Detroit Diesel, DOE-OVT, 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)
- Houshun Zhang (DDC)

Technology Focus Groups

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

Website (www.cleers.org)

- General information
- Meeting announcements
- Shared data

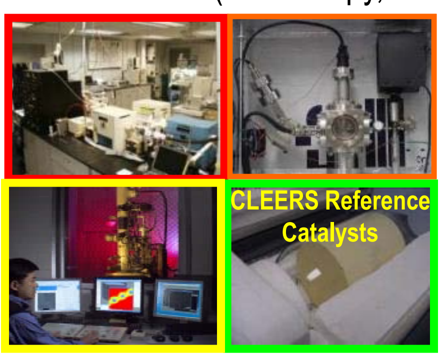
Workshops

- Public
- Annual in Detroit area
- Presentations on website

R&D

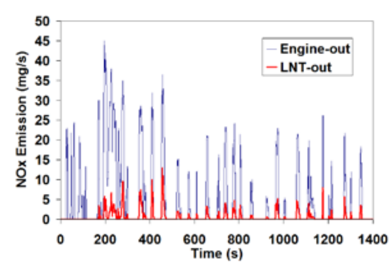
Experiments (LNT & SCR)

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



Modeling/Simulation (LNT)

- Microkinetic-based model
- Global model
- LNT lean/rich cycling
- Sulfation impact on performance



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

Collaboration w/ PNNL
Lee, Tonkyn, Devarakonda

Collaboration w/ SNL
Larson

Technical Accomplishments

- **CLEERS Coordination (8745)**
  - Organized 13th (2010) CLEERS Workshop
  - Coordinated monthly Focus Group teleconferences
  - Coordinated efforts to address 2008-2009 R&D priority survey and leverage ORNL, PNNL, SNL unique capabilities
  - Proposed draft protocol for transient SCR catalyst characterization
- **LNT & SCR Kinetics (8746)**
  - Continued DRIFTS HC poisoning analysis of CLEERS reference urea-SCR catalyst
  - Collaborated with PNNL on SCR modeling
  - Resolved S spatio-temporal details on CLEERS reference LNT catalyst with HR-EPMA, microscopy, DRIFTS, TPR, SpaciMS, and high-speed FTIR
  - Initiated detailed investigation of LNT NH_3 selectivity (reductant types, temperatures, sulfation; bench reactor, SpaciMS, high-speed FTIR, DRIFTS)
  - Began incorporating NH_3 results in global LNT models
  - Continued SNL collaboration micro-kinetic LNT modeling (lean/rich cycling, S)

Result Highlights: CLEERS Coordination (1/3)

- ORNL continued established coordination roles

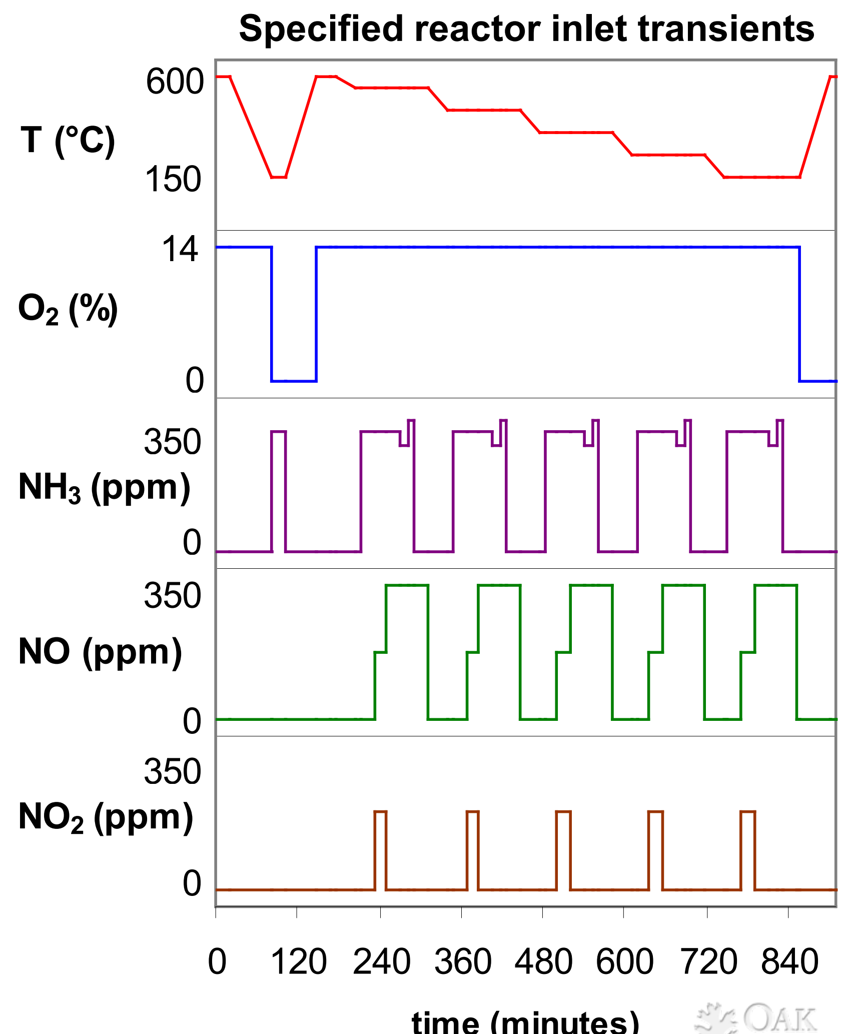
- CLEERS website
- Monthly teleconferences
  - Group telecon (20-30 domestic + int'l participants)
  - Presentations of very recent technical results
  - Host rotates among DPF, LNT, SCR Focus Groups
- Workshop #12, April 28-30, 2009, UM Dearborn
  - > 110 attendees (OEMs, suppliers, software companies, nat'l labs, universities)
  - OBD industry panel included in response to R&D gaps analysis
- Workshop #13, April 20-22, 2010, UM Dearborn
  - About 90 attendees (OEMs, suppliers, software companies, nat'l labs, universities
  - Industry panel on engine-aftertreatment systems and vehicle simulations
- Preliminary SCR transient catalyst lab protocol
  - Presented and discussed at public workshop
- CLEERS LNT model for system simulations
  - Demonstrated and published

12^{th} CLEERS Workshop

Result Highlights: CLEERS Coordination (2/3)

- In collaboration with PNNL, ORNL proposed a lab protocol for transient SCR catalyst characterization

- Monolith core reactor measurements with specified inlet transient sequence
- Provides key information needed for constructing accurate SCR device models at minimum time (~24 hrs) and expense
- Specifically reveals:
  - NH_3 storage and release
  - NH_3 and NO oxidation
  - NO SCR kinetics (and NH_3/NO impact)
  - NO + NO_2 SCR kinetics
- Presented at the CLEERS Workshop and in the CLEERS Focus Groups
- Undergoing experimental validation and utilization for systems simulations



Result Highlights: CLEERS Coordination (3/3)

- ORNL models are improving understanding of lean emissions control options on fuel economy

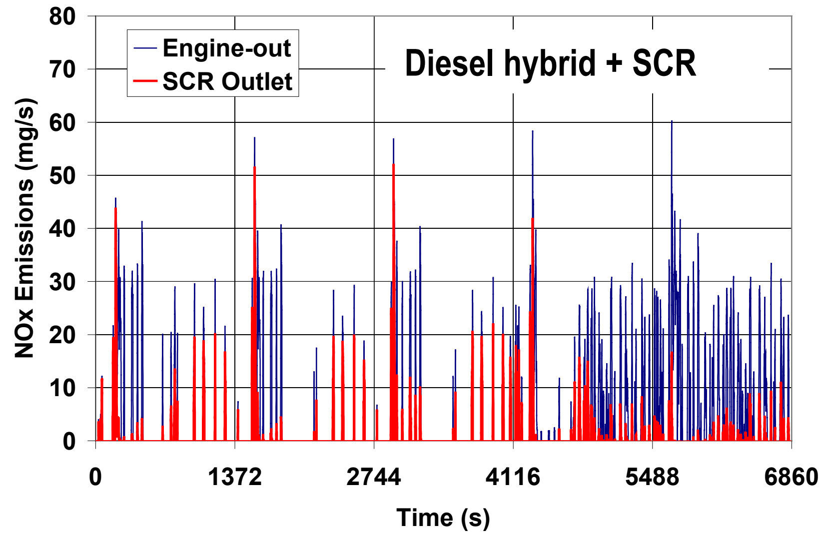
Example simulation of PHEV (see VSS017 talk)

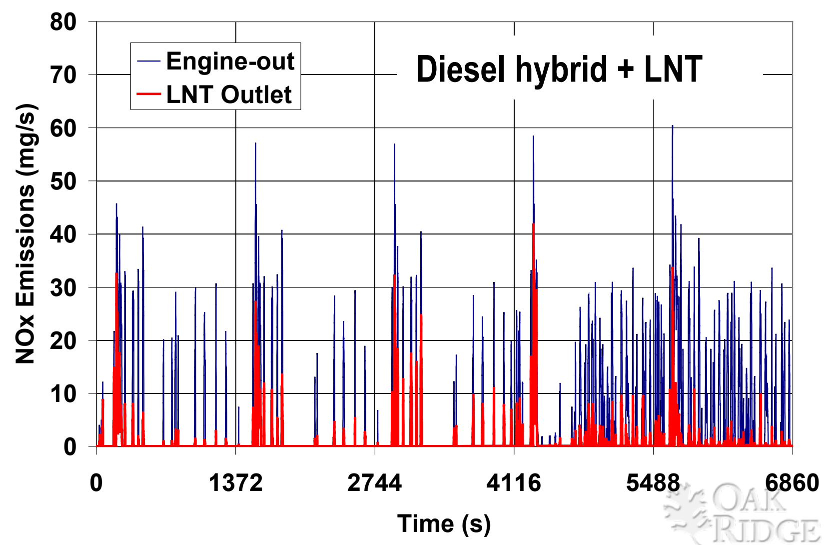
(PSAT modeling with simplified CLEERS SCR and LNT models)

- **Parameters:**
  - Diesel engine w & w/o NO_x control (LNT vs. SCR)
  - SCR with stoichiometric ratio NH_3 to NO_x
  - 1450 kg vehicle
  - 5 UDDS cycles from cold start
  - 100% initial charge in 5 kWhr battery
- **Results:**

Diesel + SCR		Diesel		Diesel + LNT	
Fuel Economy (mpg)	Tailpipe NO_x (g/mile)	Fuel Economy (mpg)	Tailpipe NO_x (g/mile)	Fuel Economy (mpg)	Tailpipe NO_x (g/mile)
136.3	0.16 (77% red)	136.4	0.69	133.8	0.15 (79% red)

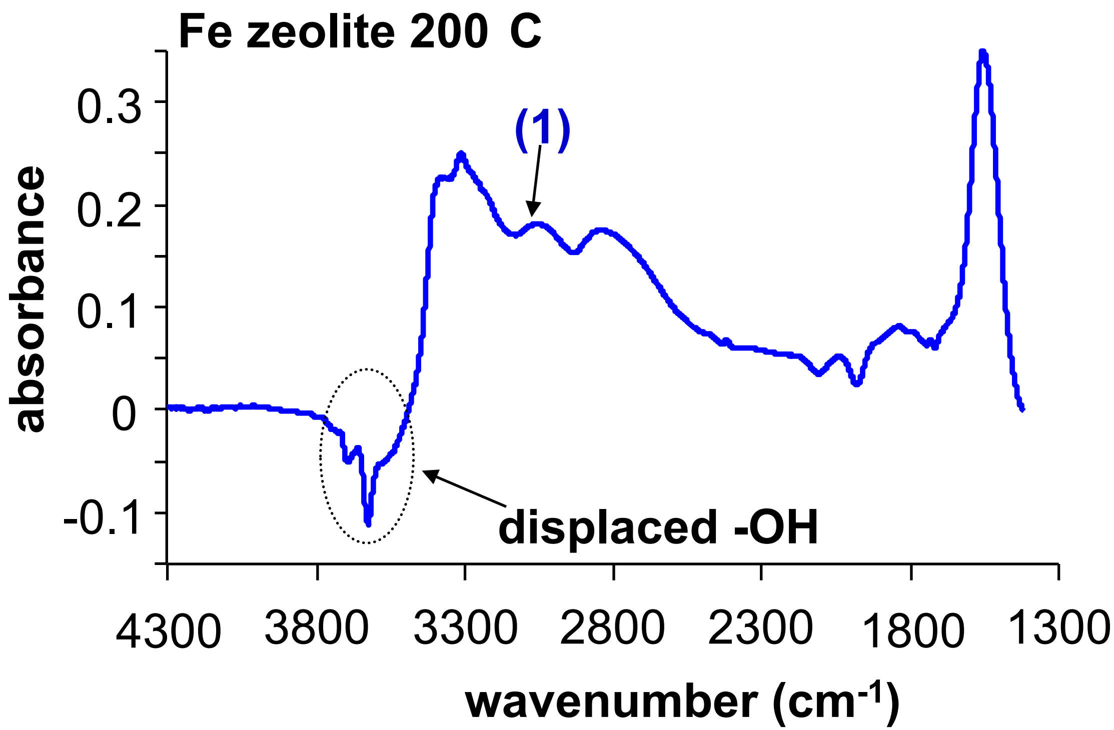
- 2% fuel penalty for LNT (higher for more NO_x removal)
- SCR almost eliminates direct fuel penalty
- But SCR has extra NH_3 emissions (0.068g/mile)

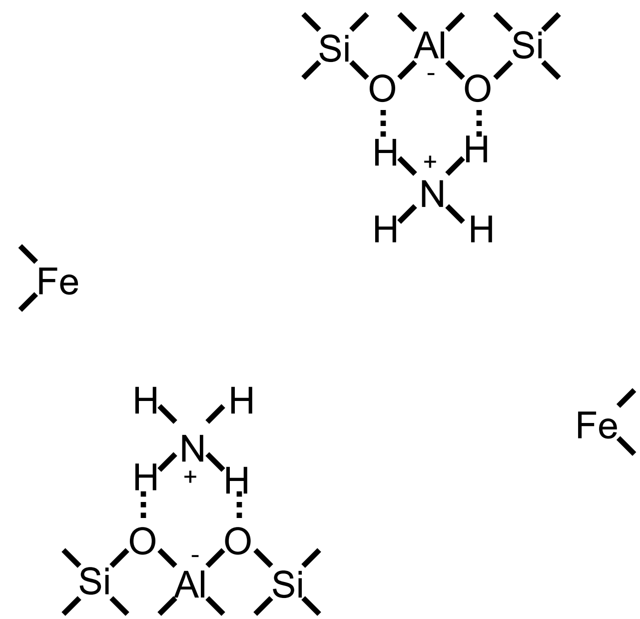




Result Highlights: SCR Research (1/2)

- Proposed mechanism for toluene poisoning of Fe zeolite SCR catalyst based on surface spectroscopy





(1) 350ppm NH_3: numerous spectral features due to adsorbed NH_3

note: all steps include 14% O_2, 4.5% H_2O, 5% CO_2

Insights shared with modeling teams at PNNL & ORNL

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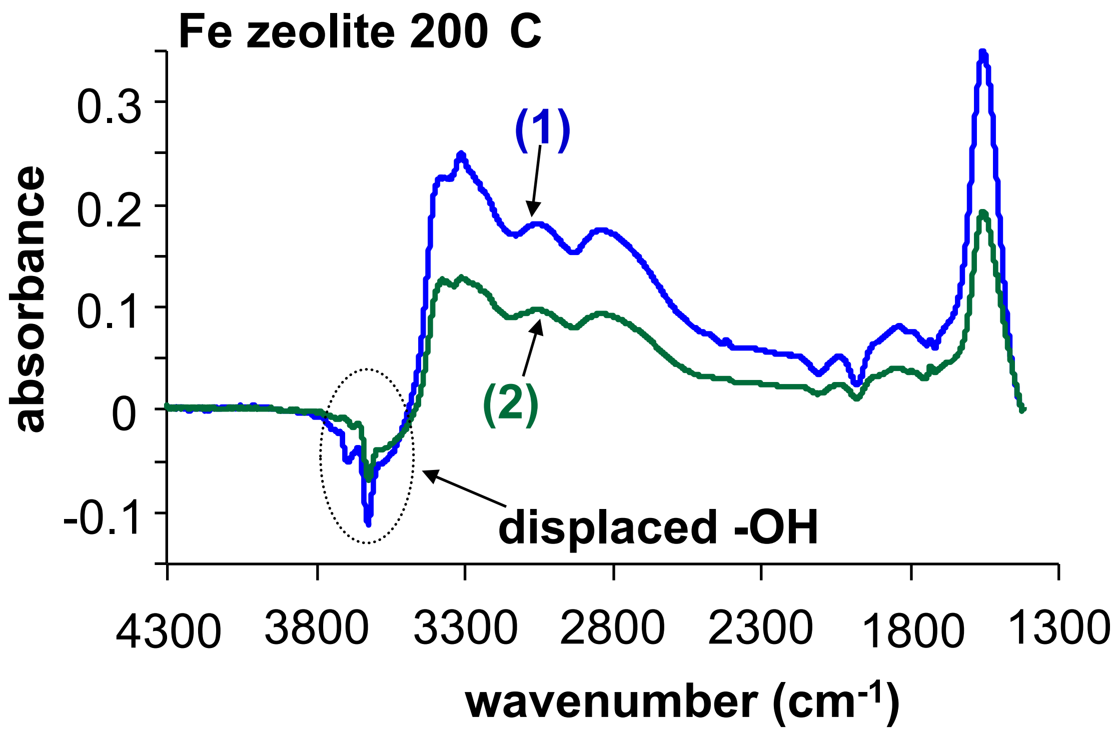

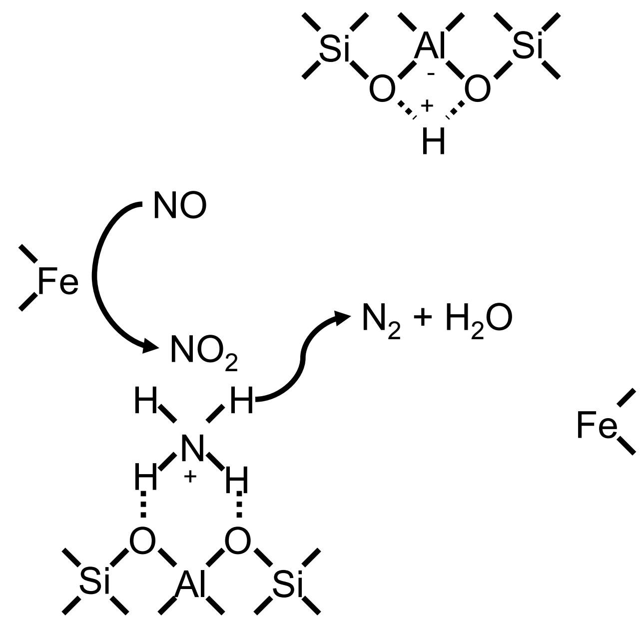

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note: all steps include 14% O_2, 4.5% H_2O, 5% CO_2

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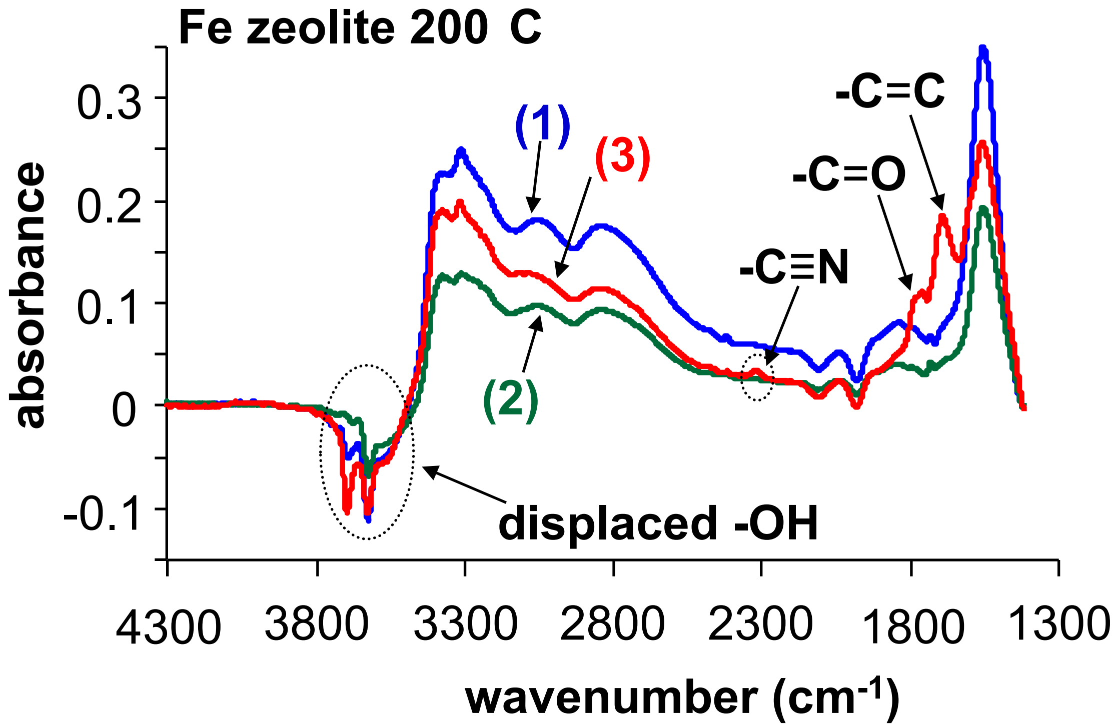
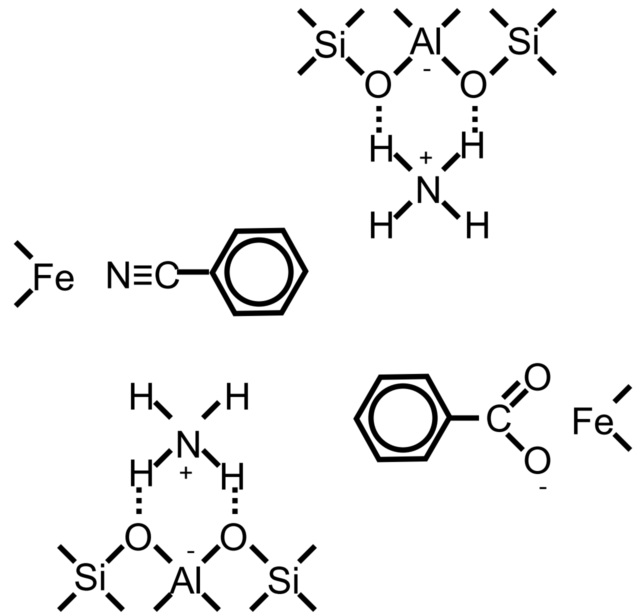




(1) 350ppm NH_3: numerous spectral features due to adsorbed NH_3

(2) + 350 ppm NO: surface NH_3 decreased due to consumption by SCR reaction

(3) + 50 ppm toluene: SCR reaction poisoned, surface NH_3 increases

note: all steps include 14% O_2, 4.5% H_2O, 5% CO_2

Insights shared with modeling teams at PNNL & ORNL

Result Highlights: SCR Research (2/2)

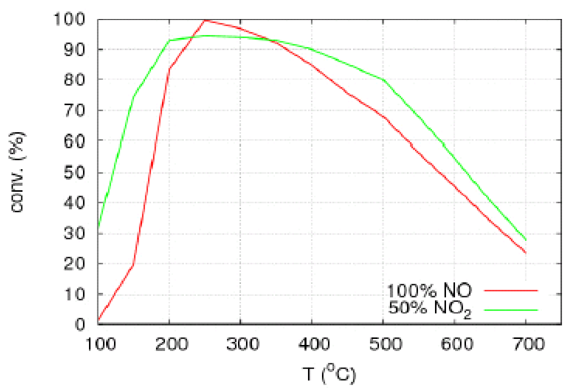
- ORNL is integrating multiple sources of data into SCR modeling

- Detailed model with PNNL (coding assistance & DRIFTS insights)
- Complementary global model for systems simulations
  - Based on published model catalyst data (Cu-ZSM5)
  - Will be updated with CLEERS SCR protocol data and DRIFTS results

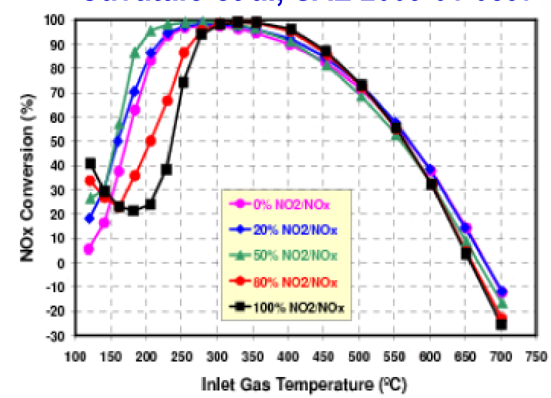
Global model features:

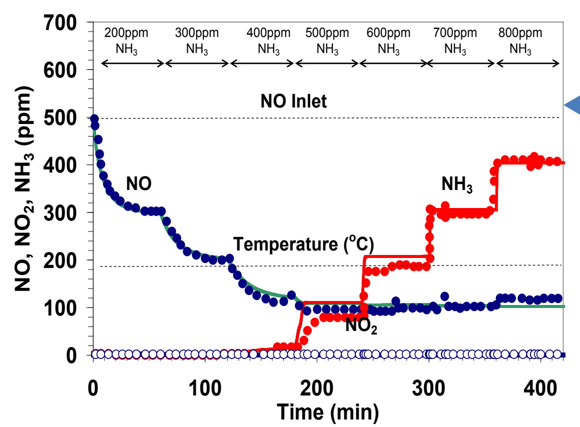
- NH_3 adsorption/desorption
- 3 SCR reactions
  NO, NO_2, "fast"
- NO, NH_3 oxidation reactions
- N_2O not tracked for simplicity
- Future plans
  - HC poisoning effects
  - O_2 effect on NO SCR
  - LNT-SCR systems

ORNL Model



Cavataio et al, SAE 2009-01-0897

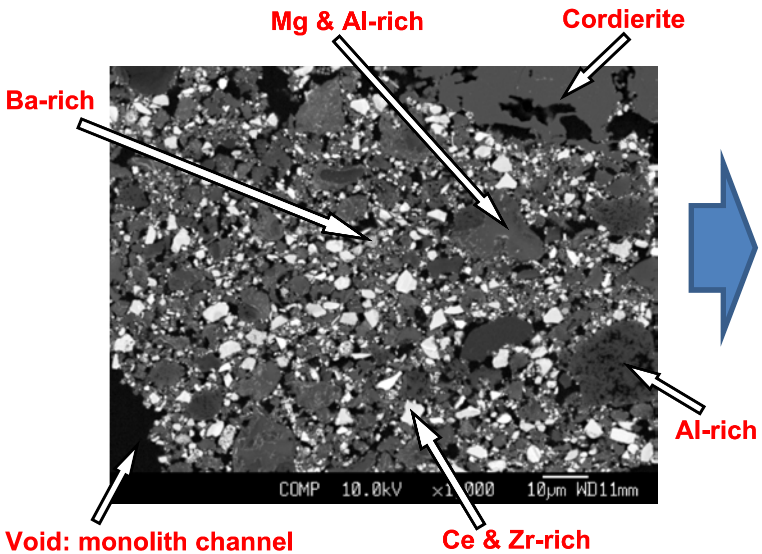




Points from experiments by Olsson et.al, Applied Catalysis B: Environmental 81(2008) 203-217. Lines from ORNL simulation.

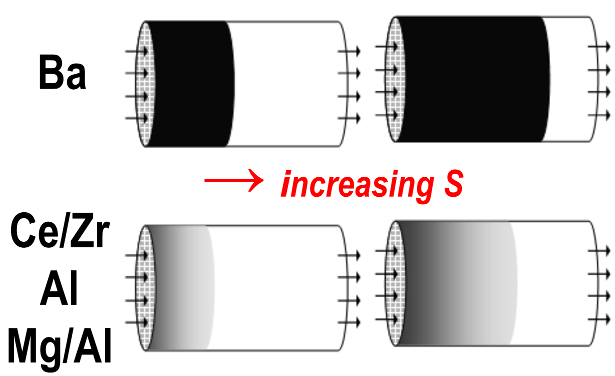
Result Highlights: LNT Research (1/5)
- In-depth characterization confirmed link between commercial LNT composition & sulfur chemistry

CLEERS LNT (lean GDI, Umicore) characterized with microscopy, HR-EPMA, TPR



Domain	Composition	S content (at.%)
Ba-rich	Ba (high), Ce/Zr, Pt, Pd	7.3
Ce/Zr-rich	Ba (low), Ce/Zr, Pt, Pd	2.1
Al-rich	Al, Rh, Pd	2.4
Mg/Al-rich	Mg/Al, Pt, Ce	1.2

corroborates previous conjectures



Ba sulfation is vigorous leading to plug-like poisoning of NO_x storage sites

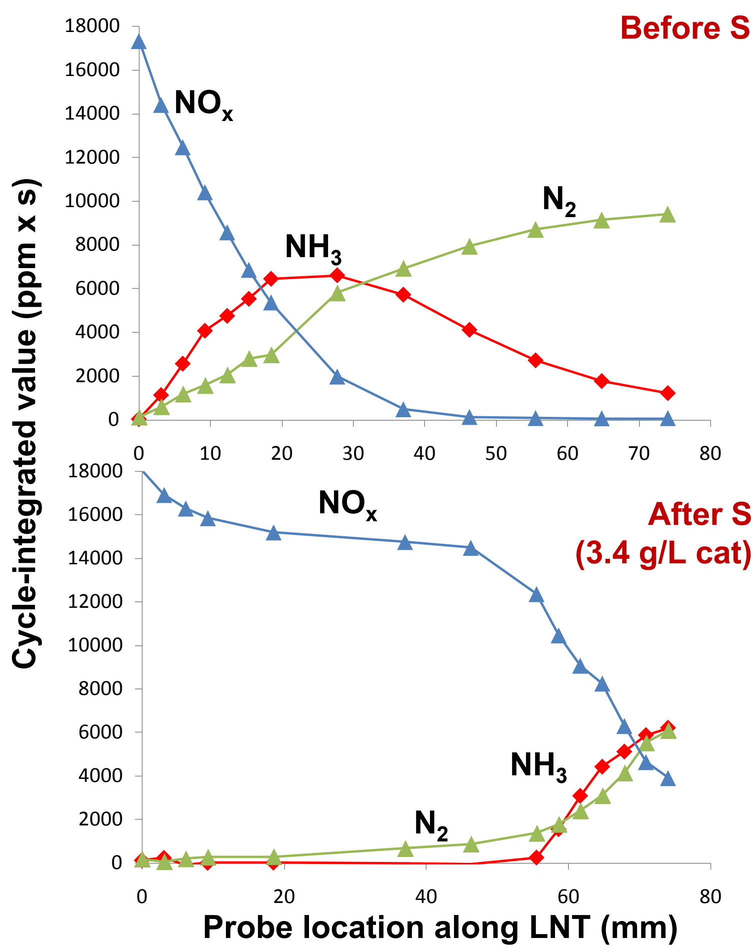
Sulfation of Ce/Zr, Al, Mg/Al is less efficient but significant ***"S-trap" delaying Ba sulfation***

Result Highlights: LNT Research (2/5)

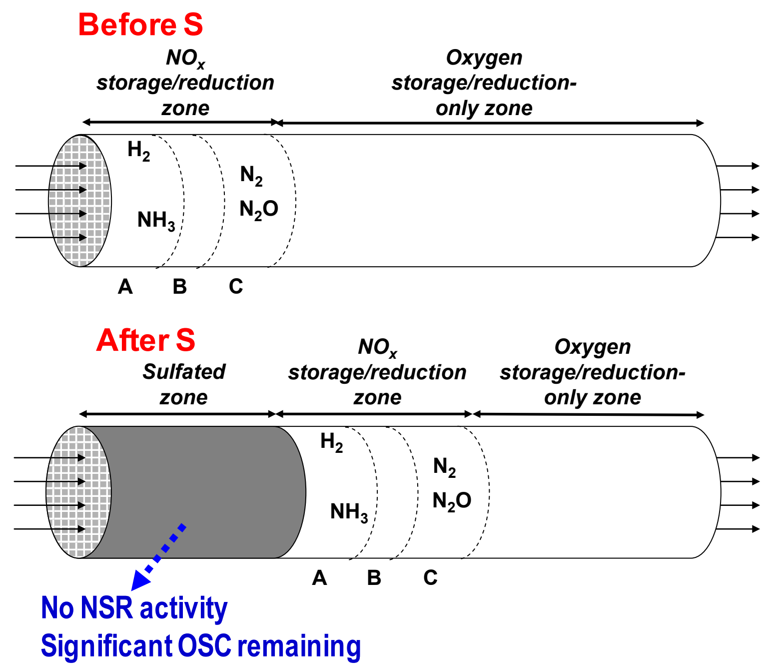
- Improved spatial & temporal resolution of gas analysis confirms sulfur - NH_3 correlation

Spatial resolved new data (SpaciMS)

before vs. after CLEERS LNT sulfation at 300 C (bench)



Previously proposed conceptual model



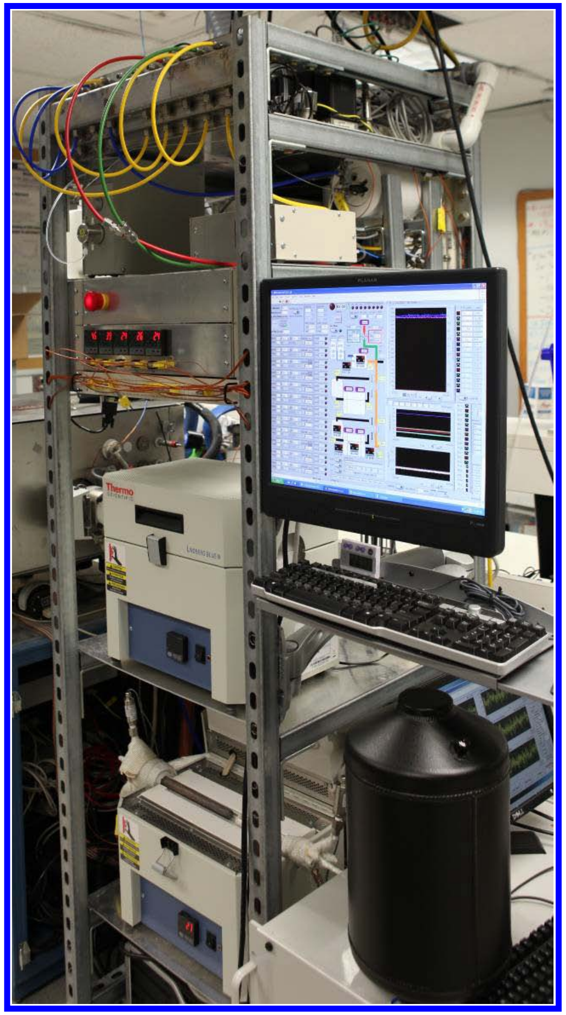
- Plug-like S poisoning of NO_x storage sites displaces active NO_x storage/reduction downstream
- As a result, length of OSC-only zone (downstream of active NSR zone) gets shorter
- More NH_3 (slipping from active NSR zone) manages to escape LNT without being oxidized by OSC

Result Highlights: LNT Research (3/5)

- Started in-depth study of NH_3 mechanisms

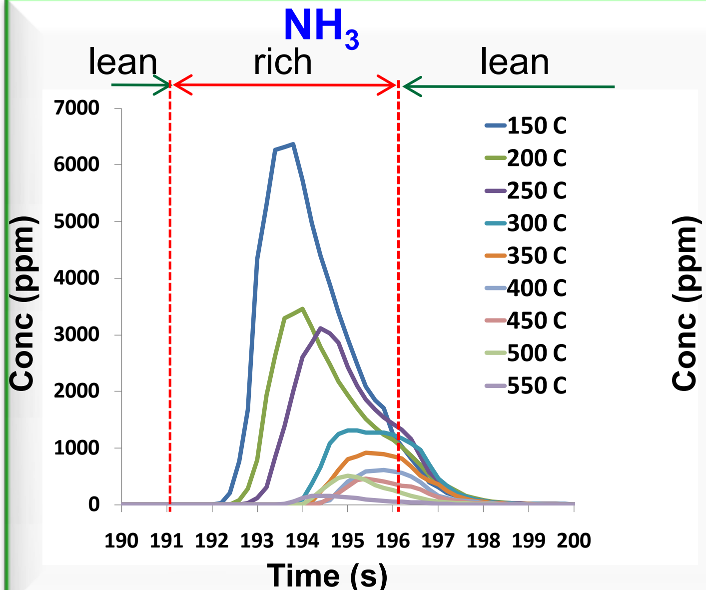
- NH_3 important for stand-alone LNT (slip control) & LNT-SCR
  - Recent ORNL chassis study of a European lean GDI (09 BMW) shows significant NH_3 slip can occur
- Current LNT models have limited NH_3 capability
  - Generally not tracking NH_3 profiles
  - Recent addition of 2-step mechanism: $NO_x + H_2 \rightarrow NH_3$; $NH_3 + NO_x \rightarrow N_2$
- S study (see previous 2 slides) highlights importance of spatiotemporal reactions & surface species
- This FY, we initiated systematic study of NH_3 on CLEERS LNT
  - Spatiotemporal resolution of reaction distributions
    - *Bench reactor, HS-FTIR (temporal), UEGO (temporal), SpaciMS (spatial)*
    - *Type of reductant (e.g., HC impact), temperature*
  - Transient NH_3 surface chemistry
    - *DRIFTS reactor*
    - *NH_3 interaction with catalyst surface (e.g., OSC)*
  - Complementary to U Houston DOE project
    - *Focused on coupled LNT-SCR synergy mechanisms*
    - *Catalyst formulation effects*

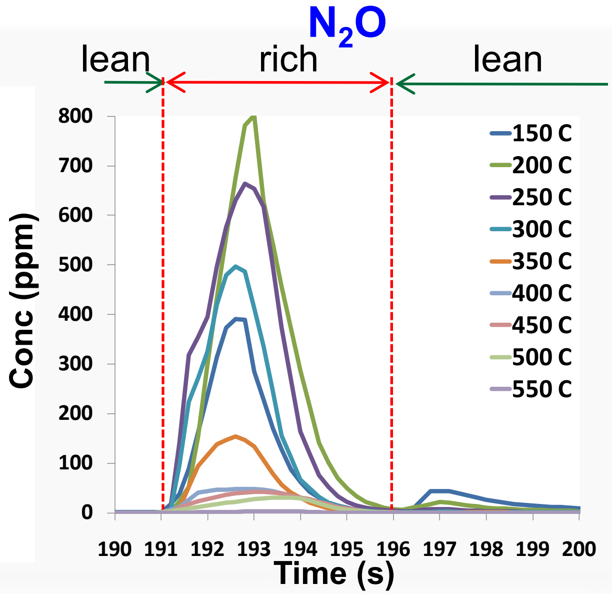
Automated bench reactor



Result Highlights: LNT Research (4/5)

- Initial results reveal some key NH_3 features to be captured by models

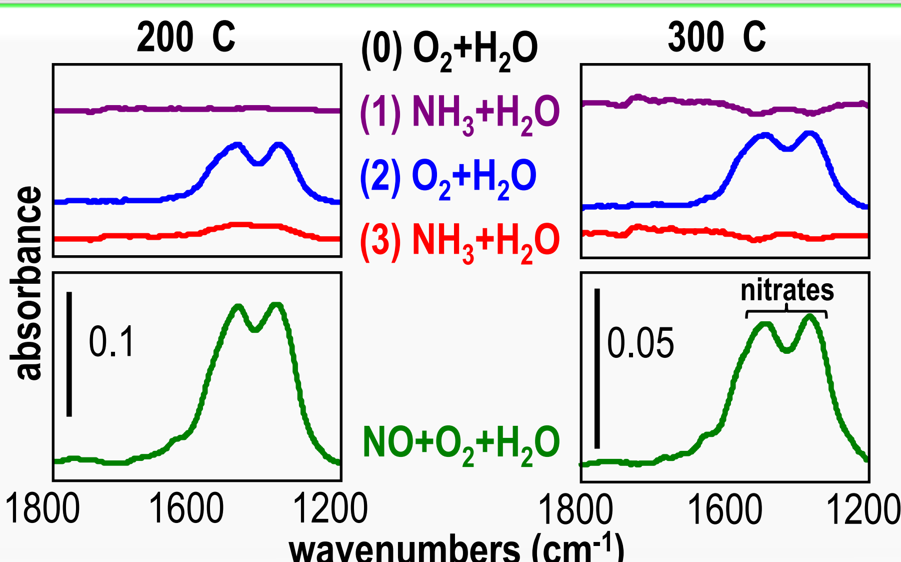




Bench reactor (CLEERS LNT)

60/5-s lean/rich cycling

- **Wide NH_3 peaks**
  significant NH_3 formation behind regen front
- **N_2O at rich → lean**
  indicate NH_3 storage & oxidation



DRIFTS ($Pt/Ba/Al_2O_3$)

- **NH_3 storage on surface**
- **NH_3 oxidation by**
  - OSC (during regeneration)
  - O_2 (inception of subsequent lean)
- **NH_3 storage as nitrates** *indicates*
  possible axial redistribution of NO_x via NH_3

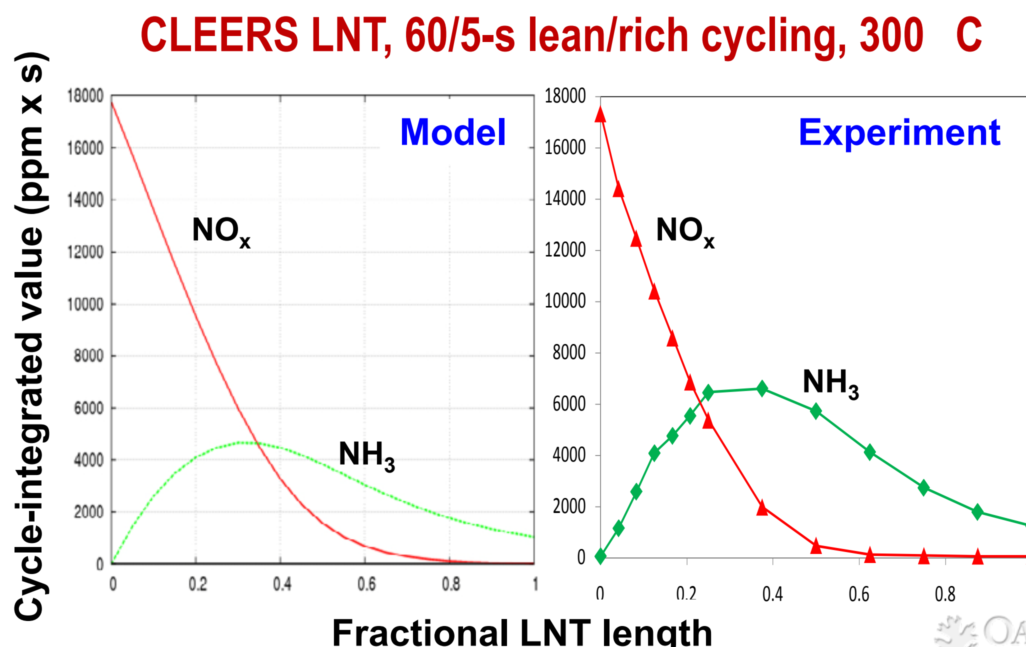
Result Highlights: LNT Research (5/5)

- LNT models are being used to better understand NH_3 & S chemistry and evaluate system impact

- Further SNL collaboration on microkinetic model (see ACE035 talk)
  - Implemented lean/rich cycling
  - Initial work on sulfation/desulfation
- Developed a global model to enable faster simulations than microkinetic model
  - Experimental findings used to improve NH_3 prediction

Global model features:

- Catalytic reactions on Pt sites
  - No storage
  - Global rate expressions
  - Inhibition terms where necessary
- NO_x storage on fast (near Pt) and bulk $BaCO_3$ sites
  - Carbonates, peroxides, nitrites, nitrates, bulk nitrates
  - Oxygen storage on CeO_2
- NO_x release rate adjusted using experimental data → better NH_3 match
- Currently isothermal



Collaborations

- Partners
  - National labs: ORNL-High Temperature Materials Lab, Pacific Northwest National Lab, Sandia National Labs.
  - Universities: Kentucky, Houston, ICT Prague (summer research by Dr. Kočí at ORNL), Chalmers (students from Prof. Olsson's group)
  - Industry: Cummins, Navistar, Ford, Umicore, BASF, other CLEERS Focus Group members and DOE Diesel Crosscut Team

- Technology Transfer
  - 18+ publications & presentations (dissemination of DOE-funded research outcome via high visibility forums: NAM, SAE, int'l journals etc.)
  - SCR lab protocol publicly proposed
  - LNT & SCR models used for DOE Vehicle & System HEV/PHEV Simulations (FY10 FreedomCAR Highlight)
  - Data, systems impact guidance for PNNL & SNL activities

Future Work

- **CLEERS Coordination (8745)**
  - Planning Committee, Focus Groups, Workshop & website
  - Synchronizing ORNL-PNNL-SNL R&D
  - Priority Survey in 2011 (every 2 years)
  - Basic data & model exchange between CLEERS & other VTP projects
- **LNT & SCR Kinetics (8746)**
  - LNT kinetics, durability (major focus on NH_3 chemistry)
    - Bench reactor studies (reductant type, HC impact)
    - Spatiotemporal analysis (SpaciMS, high-speed FTIR, DRIFTS)
    - Model NH_3 spatiotemporal profiles (with SNL)
    - Model LNT sulfation (with SNL)
    - CLEERS reference catalyst vs. latest European lean GDI (09 BMW)
  - Urea-SCR kinetics (HC poisoning)
    - CLEERS lab protocol implementation
    - DRIFTS surface analysis with reference catalysts (Fe vs. Cu)
    - PNNL collaboration

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, 12^{th} & 2010 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, and foreign institutions through CLEERS organizational structure
  - Collaboration with other VTP projects (e.g., DOE-system simulations, U. Houston)
  - Extensive publications/presentations
- **Plans for Next Fiscal Year**
  - Planning Committee, Focus Groups, Crosscut reports, website, Workshops, priority poll, VTP leveraging
  - LNT modeling of NH_3, N_2O & HC impact via spatiotemporal chemistry
  - NH_3-SCR modeling supported by DRIFTS and CLEERS lab protocol