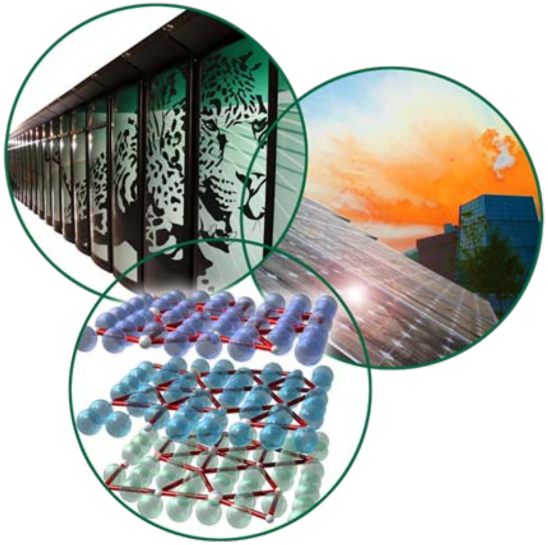
CLEERS Coordination & Development of Catalyst Process Kinetic Data

Agreements:
- Coordination of Cross-Cut Lean Exhaust Emission Reduction Simulation (8745)
  Vitaly Prikhodko, Charles Finney, Stuart Daw (PI)
- Joint Development of Benchmark Kinetics for LNT & SCR (8746)
  Jae-Soon Choi, Josh Pihl, Bill Partridge, Todd Toops, Michael Lance, Kalyana Chakravarthy, Stuart Daw (PI)
- Sulfur & Thermal Deactivation Effects on Transient LNT Chemistry (8744)
  Josh Pihl, Nathan Ottinger, Jae-Soon Choi, Todd Toops (PI)

Presenter: Jae-Soon Choi

Oak Ridge National Laboratory



Project ID: ace_20_choi

Vehicle Technologies Program Annual Merit Review
May 20, 2009, Arlington, VA

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
  - Sulfur and Thermal Effects (8744) FY00
- Project end date & percent complete:
  - All ongoing

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

Budget

- Project funding FY08/FY09
  - CLEERS Coordination (8745): $200/$200
  - LNT & SCR Kinetics (8746): $500/$450
  - Sulfur and Thermal Effects (8744): $100/$100
- Funding request for FY10
  - Similar to FY09

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/prioritize R&D needs within industry & coordinate DOE research efforts (CLEERS Coordination)**
- **Develop detailed technical data required to simulate energy efficient emission controls (LNT & SCR Kinetics, Sulfur & Thermal Effects)**
  - **Measure hydrocarbon poisoning & reaction intermediates on urea-SCR catalysts**
  - **Understand nature, spatial distribution, impact on performance, & desulfation characteristics of sulfur species on LNT catalysts**
  - **Explore the possibility of decreasing LNT desulfation temperature with dopants**
  - **Implement LNT lean/rich cycling model to elucidate reductant & NH_3 chemistry**

Milestones

- FY2008 milestones completed
  - ✓ 8745: Organized 11th CLEERS public workshop
  - ✓ 8746: Open literature publication on modeling sulfur impact on LNT kinetics
  - ✓ 8744: Published sulfation/desulfation experimental results on model catalysts
- FY2009 milestones on target for Sept. 2009 completion
  - 8745: Organize 12th CLEERS workshop
  - 8746: Publish LNT model benchmarking against experiments
  - 8744: Identify distinct sulfur coordination with specific components in Umicore LNT

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, International, U.S. Army TARDEC, U.S. EPA, Volvo

CLEERS Planning Committee

- Dick Blint (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

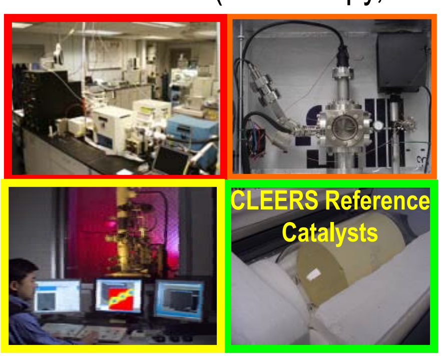
Workshops

- Public
- Annual in Detroit area
- Presentations on website

R&D

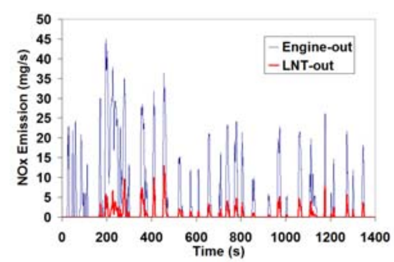
Experiments (LNT & SCR)

- 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
Drs. Herling, Tonkyn, Male

Collaboration w/ SNL
Dr. Larson

Technical Accomplishments

- **CLEERS Coordination (8745)**
  - Organized 11th & 12th **CLEERS Workshops** & facilitated monthly **telecons**
  - Completed 2nd **R&D priority survey** and follow-on **R&D gaps analysis**
  - Coordinated **multi-lab research efforts** to leverage each lab's unique capabilities (ORNL, PNNL, & SNL)

- **LNT & SCR Kinetics (8746); Sulfur & Thermal Effects (8744)**
  - Assessed **hydrocarbon impact on the CLEERS urea-SCR catalyst** with DRIFTS (8746; w/ PNNL)
  - Elucidated **sulfation & desulfation impact on the CLEERS LNT** (8746, 8744)
  - Quantified **dopant effects on desulfation** behavior of Pt/Ba/Al_2O_3 model LNT & characterized various LNT **components** (8744)
  - Investigated NH_3 mechanisms by implementing **microkinetic-based LNT models** (8746; w/ SNL)

Result Highlights 1: CLEERS Coordination (8745) (1/3)
- ORNL continued established coordination roles

- 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 #11 held May 13-15, 2008, UM Dearborn
  - 3 days of technical presentations (posted on website)
  - > 110 attendees (OEMs, suppliers, software companies, nat'l labs, universities)
- Workshop #12 April 28-30, 2009, UM Dearborn
  - OBD industry panel included in response to R&D gaps analysis
- Completed 2008 R&D priorities survey
  - Combined with 2007 survey results, report issued
- R&D gaps analysis completed
  - Reported to Crosscut Team, discussed at 12th Workshop
- Adapted CLEERS models for system simulations

CLEERS Workshop

Result Highlights 1: CLEERS Coordination (8745) (2/3)

- ORNL coordinated a 'gaps' analysis to determine if current emissions R&D meets industry needs

- Interfaced with CLEERS Planning Committee and Focus Groups
- Collated results from 2007 and 2008 surveys
- Included DOE projects and industry activities
- Summary of findings:
  - The overall DOE-VTP project portfolio aligns well with high priority needs in both diesel and gasoline industry categories
  - In the diesel category, OBD sensor and sensor utilization needs are not fully covered by existing DOE-VTP projects
    - Sensor needs are also not adequately covered by supplier or industry activities
    - The Crosscut Team should consider options for sensor project growth/ redirection

Result Highlights 1: CLEERS Coordination (8745) (3/3)

- ORNL models have improved understanding of lean emissions control impact on fuel economy

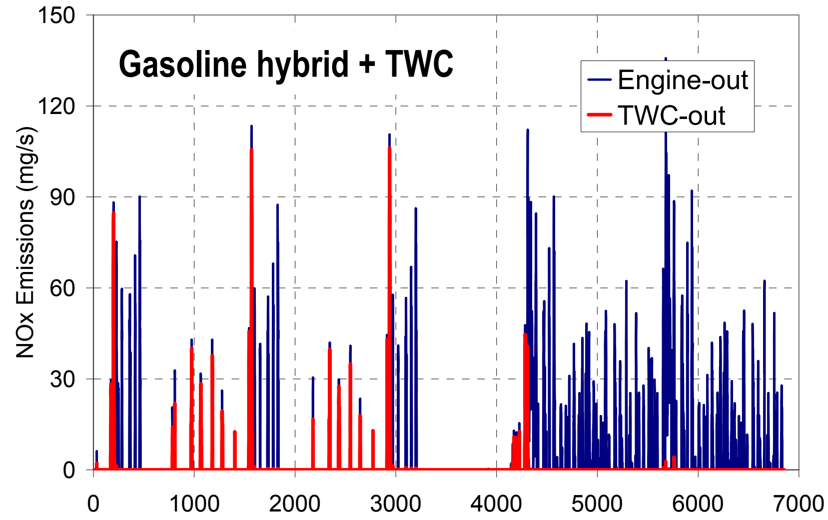
Example simulation of Prius PHEV

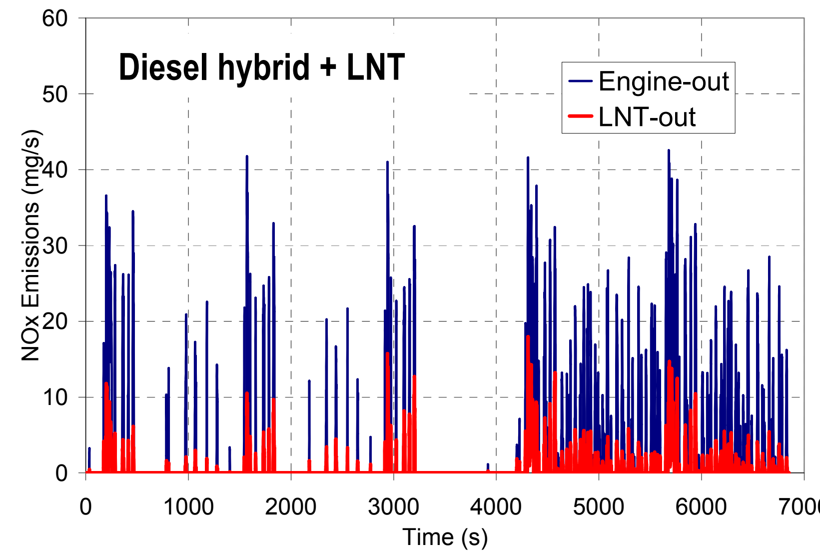
(PSAT modeling with simplified ORNL-CLEERS LNT model)

- Parameters:
  - Stoichiometric gasoline with TWC
  - Compared to diesel engine w & w/o LNT (no HECC, no DPF)
  - 5 UDDS cycles from cold start
  - 100% initial charge in 5 kWhr battery
- Results:

Gasoline + TWC		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)
113.7	0.11 (89% red)	136.5	0.50	132.4	0.10 (80% red)

  - 3% fuel penalty due to LNT
  - Diesel efficiency advantage reduced from 6% to 3% when LNT added (fuel density effect included)

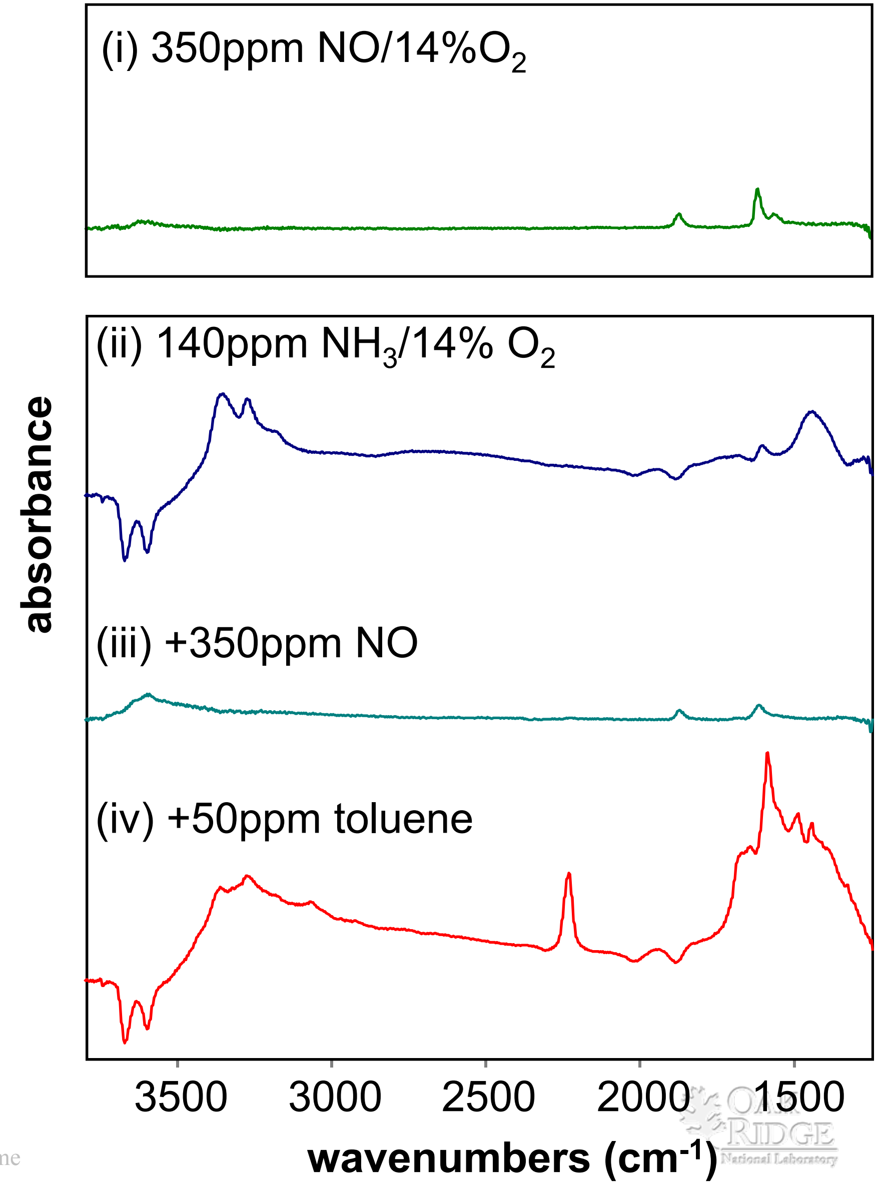




Result Highlights 2: Urea-SCR-HC Poisoning (8746) (1/2)

- Demonstrated DRIFTS is effective tool to probe HC poisoning of SCR functionality

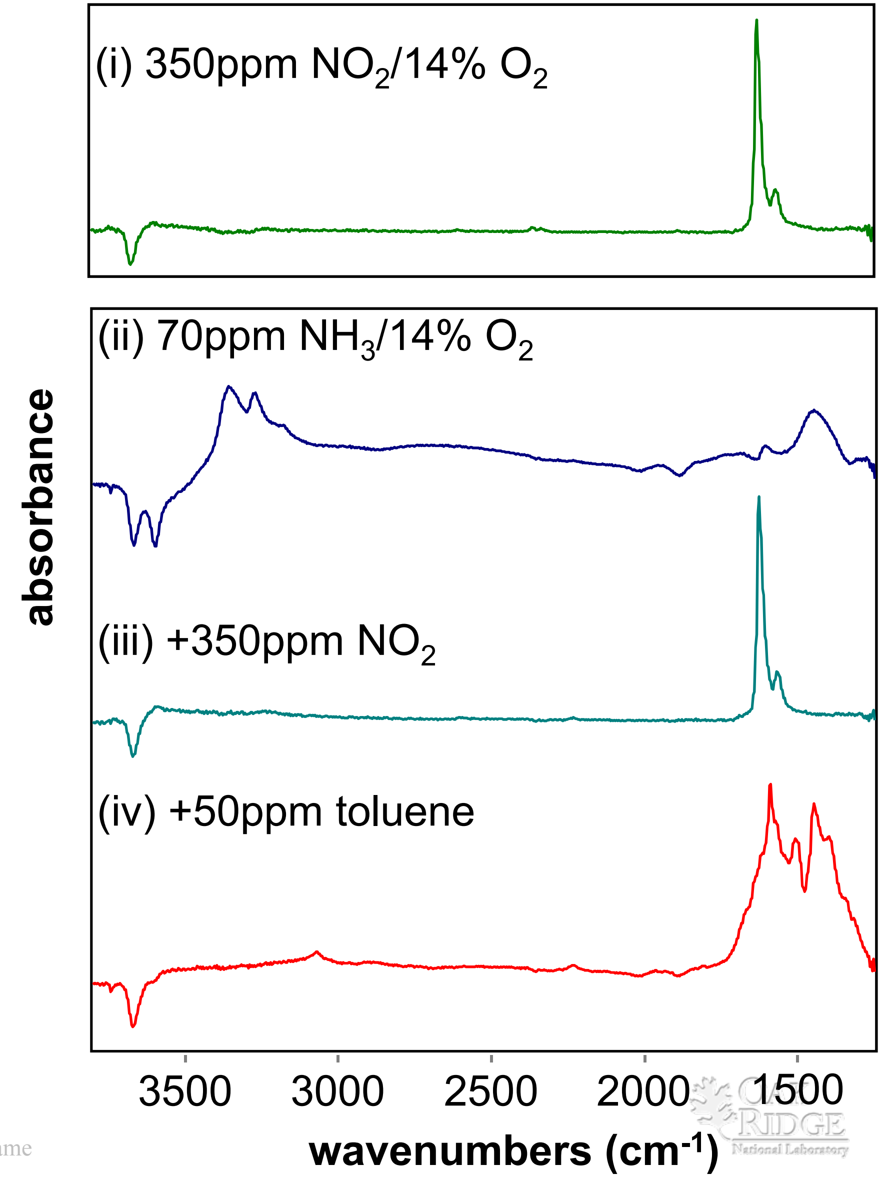
- Responsive to urea-SCR interest in CLEERS poll
  - Durability/poisoning is a high priority
  - We are ramping up SCR efforts this FY
- Changes in surface adsorbates reveal catalyst poisoning by toluene at 200 °C:
  - (ii) NH_3 + O_2 shows NH_3 adsorption
  - (iii) adding NO to flow starts SCR of NO; adsorbed NH_3 is consumed; spectrum looks like (i)
  - (iv) addition of toluene "shuts down" SCR reaction; adsorbed NH_3 reappears; toluene observed (1500 cm^{-1})
- After exposure to toluene, SCR reaction rate too slow to consume all surface NH_3
  cf. Cavataio et al. SAE 2007-01-1575
- Activity is not recovered with removal of toluene from feed gas



Result Highlights 2: Urea-SCR-HC Poisoning (8746) (2/2)

- Changing feed from NO to NO_2 mitigates impact of toluene at 200 °C

- Repeat experiment with NO_2 instead of NO in feed
  - (ii) NH_3 adsorption looks identical
  - (iii) NO_2 consumes all surface NH_3, resulting in a spectrum very similar to $NO_2 + O_2$ (i)
  - (iv) addition of toluene generates toluene adsorption features, but does not result in reappearance of surface NH_3
- Toluene does not degrade $NH_3 + NO_2$ reaction rate as much as in NO case
- Suggests toluene poisoning of NO oxidation function leads to inhibited NH_3 + NO reaction
- Will compare to PNNL flow reactor results & investigate at other temp's & HCs



Result Highlights 3: LNT-S/DeS Impact (8746, 8744) (1/4)

- Refined understanding of sulfur impact on real LNT

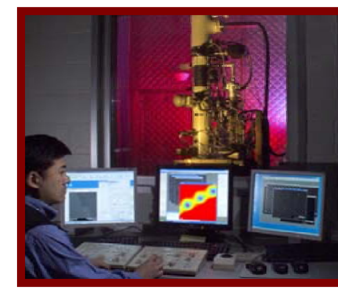
- **Responsive to LNT interest in CLEERS poll:** LNT durability/poisoning is a top priority
- **Characterize the CLEERS reference (Umicore) with a range of tools**
  - Technical barrier: quantitative assessment of sulfur impact is lacking for commercial catalysts

Bench reactor/SpaciMS
- Monolith cores
- Performance/sulfation-desulf.
- Spatial reaction distributions

Microreactor
- Powder
- TPR/chemisorption
- Total surface area

DRIFTS
- Powder/washcoated wafers
- Surface adsorbed species

Characterization
- Powder/washcoated wafers
- Elemental/XPS analyses
- Microscopy/EPMA



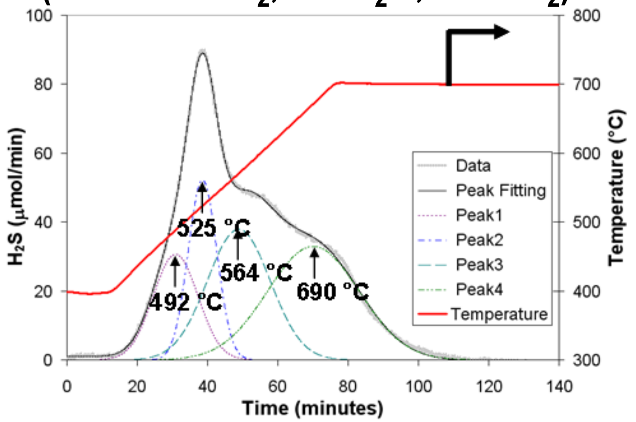
- **Goal is to understand correlations among chemical forms, spatial distribution & performance impact of sulfur on a practical LNT**
- **Status:**
  - Assessed impact of stepwise DeS on CLEERS LNT performance
  - Completed DeS of catalyst components & determination of nature & distribution of S species

Result Highlights 3: LNT-S/DeS Impact (8746, 8744) (2/4)

- Clarified the roles of different sulfur species by stepwise desulfation of CLEERS LNT

Typical "non-destructive" DeS profile of monolithic CLEERS LNT

(TPR in 1% H_2, 5% H_2O, 5% CO_2)



- Peak deconvolution suggests multiple components forming sulfates
- 4 intermediate T's chosen for partial desulfation & evaluation

Experimental sequence

- Before sulfation (after previous DeS)
- Sulfation (3.4 g S/L cat.): 400 °C
- 1st step of DeS: 400 to 492 °C
- 2nd step of DeS: 400 to 525 °C
- 3rd step of DeS: 400 to 564 °C
- 4th (final) step of DeS: 400 to 690 °C

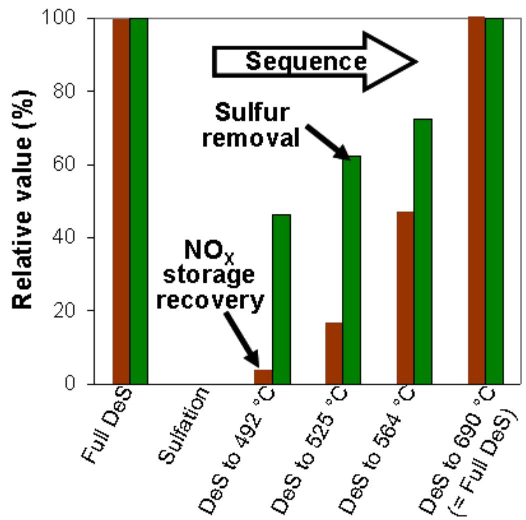
At each step, different LNT functions were evaluated:

- Total S removal
  from desulfation profiles
- Total NO_x storage recovery
  from long cycling at 400 °C
  (15-min lean/10-min rich)
- NO_x conversion & NH_3 selectivity
  from short cycling at 400 °C
  (60-s lean/5-s rich)

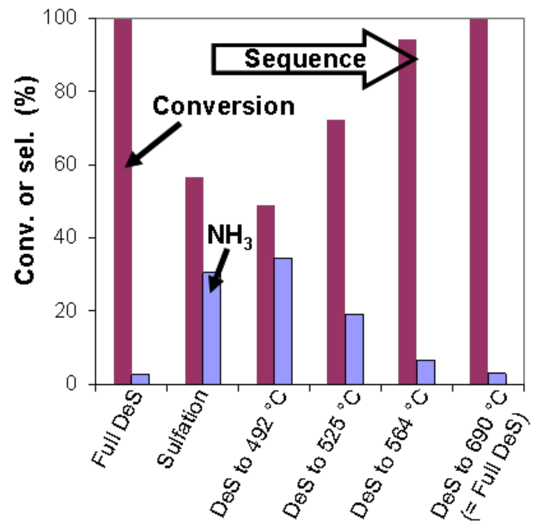
Result Highlights 3: LNT-S/DeS Impact (8746, 8744) (3/4)

- Different types of sulfates have distinct impact on LNT performance

Total S removal & total NO_x storage recovery



NO_x conversion & NH_3 selectivity (short cycling)



- Sulfation decreases total NO_x storage & NO_x conversion but increases NH_3 selectivity
- Stepwise desulfation reverses this trend but each step has distinct impact revealing roles of S:
  - 46% S recovered from 1st step: ~zero impact on both short & long cycling
    indicates association with components with insignificant NO_x storage capacity ("S-trap")
  - 26% S from 2nd+3rd steps: major impact on short cycling (NO_x conv. & NH_3 sel.)
    indicates association with NO_x storage components of practical relevance
  - 28% S from 4th step w/ major impact on long cycling (total NO_x capacity)
    indicates association with NO_x storage components of little importance to short cycling

Result Highlights 3: LNT-S/DeS Impact (8746, 8744) (4/4)

- Mater. analysis confirmed nature & distribution of S

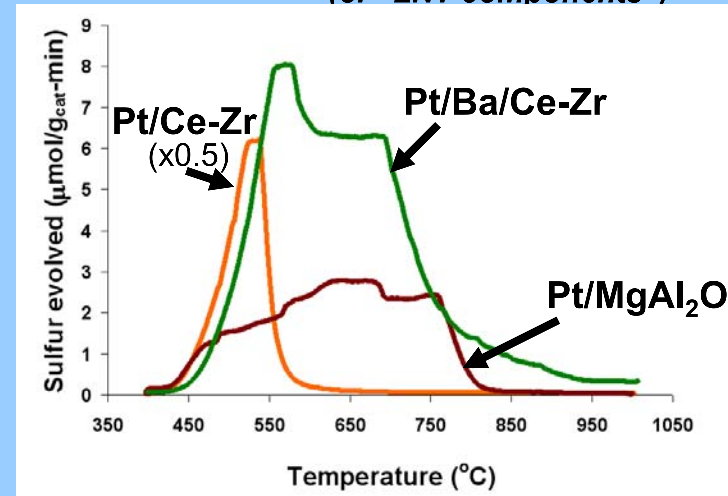
Characterization of CLEERS reference LNT

Elemental analysis, EPMA, SEM/TEM, XRD

Umicore GDI

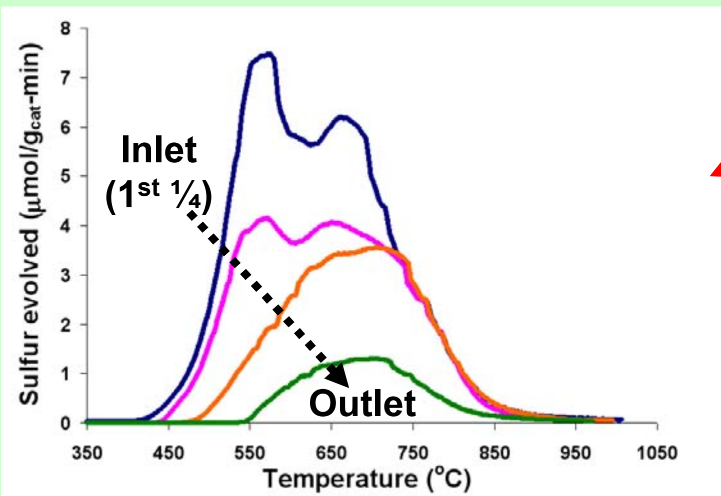
Major washcoat components
- Pt/Pd/Rh
- BaO
- CeO_2-ZrO_2
- $MgAl_2O_4$

Desulfation of bench-sulfated standards
(or "LNT components")



S affinity (i.e. sulfate stability):
Ce-Zr < $MgAl_2O_4$ < BaO

Desulfation of bench-sulfated CLEERS LNT sections



- Low T features contained in 1st half (Ce-Zr, Mg-Al)
- High T features throughout & axial progression more plug-like (Ba, minor Mg-Al)

- Results consistent w/ performance data from FY08
  - NO_x storage poisoning (Ba) is plug-like
  - Oxygen storage poisoning (Ce-Zr) is less efficient (i.e., no low T features in 4th ¼)
  - Ce-Zr, Mg-Al delay progression of Ba S ("S trap")
- Insights strengthen our conceptual model & useful for modeling & development work
  - Info. being transferred to SNL-ORNL modeling activity

Result Highlights 4: LNT-Dopant Impact on DeS (8744)

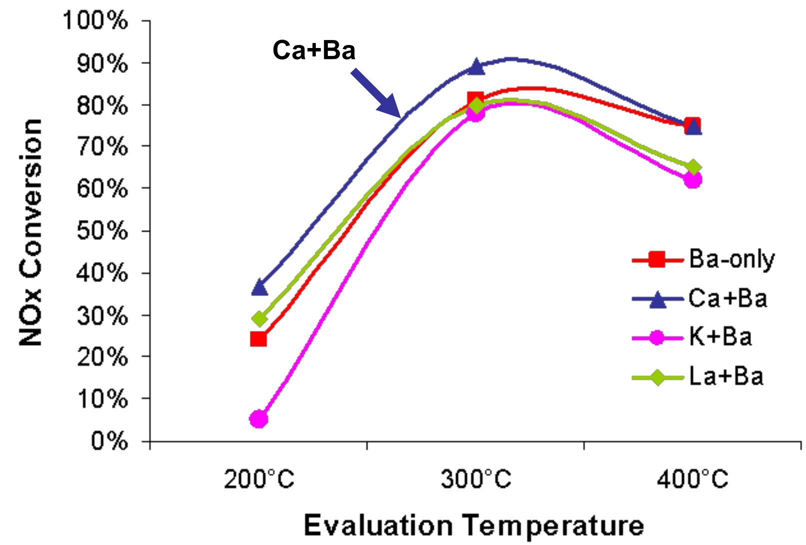
- Ca-doped LNT shows improved $DeNO_x$ & $DeSO_x$ performance

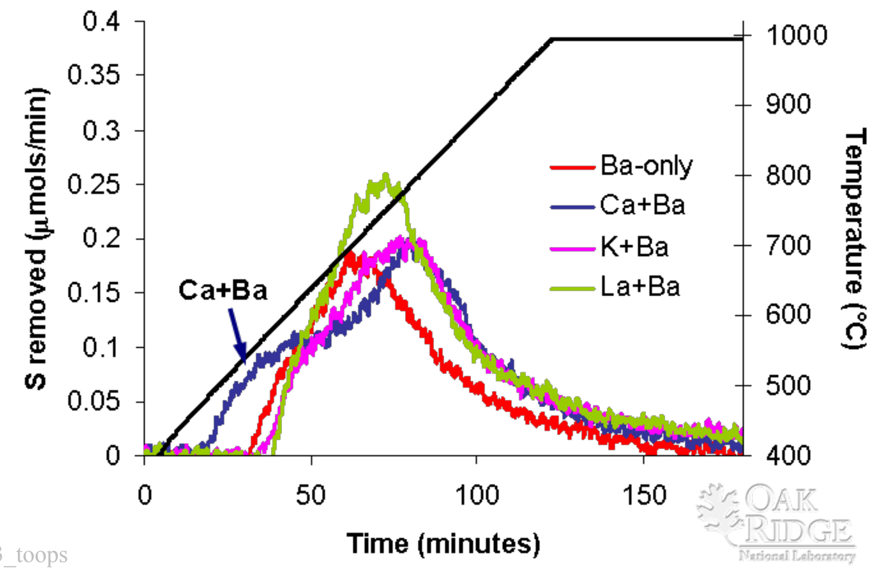
- Responsive to LNT interest in CLEERS poll
- Collaboration w/ BES-funded Center for Nanophase Material Science (CNMS) at ORNL: successful CNMS user center proposal
- Goal/status: completed proof-of-concept experiments (valence and lattice-spacing effects)

	Ba	Ca	K	La
Covalent Radius (Å)	1.98	1.74	2.03	1.69
Valence	+2	+2	+1	+3

  – Synthesized catalysts w/ substitute introduced into Ba-oxide lattice
    - Ca, K, or La at 5 mol% dispersed on $Pt/Ba/Al_2O_3$

  – Evaluated $DeNO_x$ & $DeSO_x$ performance
- Ca+Ba catalyst shows improved performance and desulfation behavior
  – 8-13% better NO_x conversion at 200 and 300°C
  – 50 °C lower onset in desulfation
- Next Step: confirmation & detailed materials characterization to probe promoting effects of Ca



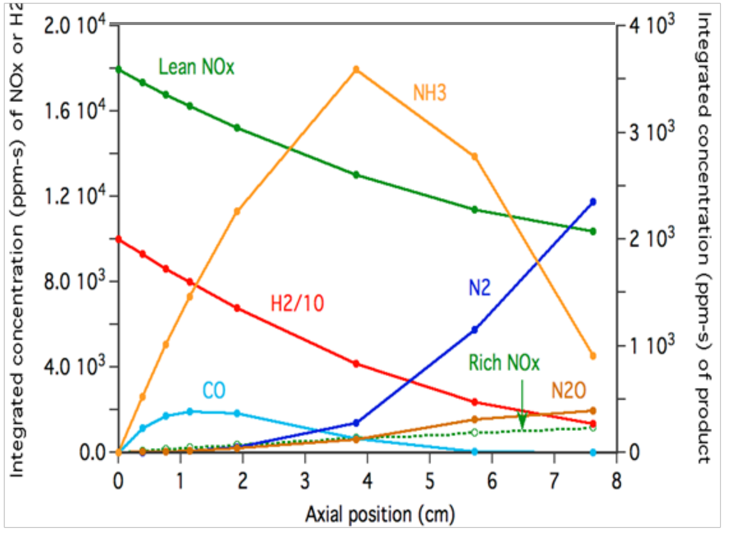


Result Highlights 5: LNT Modeling (8746)

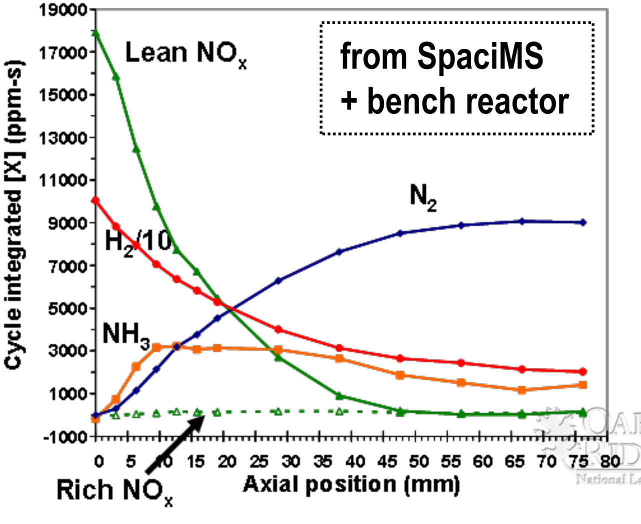
- We are implementing fast lean/rich cycling model to help clarify NH_3 chemistry on $Pt/Ba/Al_2O_3$

- Responsive to LNT interest in CLEERS poll
  - LNT kinetics/mechanisms: NH_3 formation
  - NH_3 slip control (coupled LNT-SCR)
- Collaboration with Dr. Larson (SNL)
- Goal: confirm NH_3 mechanisms with microkinetic-based CLEERS LNT model
  - i.e., if and how much intermediate NH_3 route is involved
  - Technical barrier: extent of NH_3 route contribution is difficult to quantify experimentally due to transient nature
  - Virtual experiments can provide high spatiotemporal resolution
- Status
  - Integrated storage & regen mechanisms to model, and began benchmarking model against experiments
  - Started simulations to resolve spatiotemporally NH_3

Simulation



Experiments



Future Work

- CLEERS Coordination (8745)
  - Continue Planning Committee, Focus Group, Workshop & website activities
  - Continue synchronizing R&D among ORNL-PNNL-SNL
  - Update Priority Survey (every 2 years)
  - Expand basic data & model exchange between CLEERS & other VTP projects
- R&D: Joint Development of Benchmark Kinetics (8746, 8744)
  - Confirm chemistry & kinetics of LNT sulfation/desulfation
    - Complete specialized analyses of CLEERS reference LNT segments, model components & dopants (XPS, EPMA, DRIFTS, TPR, bench reactors, SpaciMS)
    - Validate LNT model performance predictions against bench measurements
  - Implement combined LNT model in form that can be used for drive cycle simulations (e.g., PSAT) and shared with CLEERS community
    - Fast rich/lean cycling; sulfation effects; thermal aging effects
  - Detailed investigation of urea-SCR kinetics
    - Hydrocarbon poisoning; reaction intermediates
    - Compare to PNNL reactor results

Summary

- **Relevance to DOE objectives**
  - Coordinate & conduct DOE R&D to generate data, kinetics, correlations & models enabling development of energy & cost effective lean emissions control technologies
- **Approach**
  - Planning Committee, Focus Groups, website, Workshops, priority polling, Cross-Cut Team updates, data/model exchanges
  - Multi-scale laboratory research on commercial & model LNT & urea-SCR catalysts under practically relevant conditions (both modeling & experiments)
- **Technical Accomplishments**
  - Monthly Focus meetings, maintained website, 11^{th} & 12^{th} Workshops, 2008 poll, bi-monthly Crosscut reports, PSAT implementation of CLEERS data/models
  - Provided fundamental understanding of practically relevant urea-SCR (HC poisoning) & LNT ($DeSO_x$) catalysts enabling improved modeling, system design & optimization, and catalyst formulation
- **Technology Transfer**
  - Non-proprietary collaborations among industry, national labs, and universities through CLEERS organizational structure
  - Collaboration with other VTP projects (MCNARD, PSAT) & extensive publications/presentations
- **Plans for Next Fiscal Year**
  - Continued Planning meetings, Focus Group interactions, Cross-Cut reports, website, Workshops, priority poll, leveraging of data/models for VTP
  - Elucidate LNT desulfation mechanisms & HC impact on urea-SCR catalysts
  - Perform full cycle simulations with combined LNT mechanism