CLEERS Coordination & Development of Catalyst Process Kinetic Data

Presentation 1: Coordination of CLEERS Project (8745)

Stuart Daw

Presentation 2: ORNL Research on LNT Sulfation & Desulfation (8744, 8746)

Jae-Soon Choi

Oak Ridge National Laboratory

Vehicle Technologies Program Annual Merit Review
February 25, 2008, Bethesda, MD

DOE Managers: Ken Howden, Gurpreet Singh

This presentation does not contain any proprietary or confidential information.

OAK RIDGE National Laboratory

Coordination of Cross-Cut Lean Exhaust Emissions Reduction Simulation (CLEERS) Project

FY 2008 DOE Vehicle Technologies Program Annual Merit Review

Stuart Daw, Vitaly Prikhodko, Charles Finney

Tracy Bryant, Jan Draine

Oak Ridge National Laboratory

DOE Managers: Ken Howden, Gurpreet Singh

February 25-28, 2008

Session on CLEERS Coordination & Development of Catalyst Process Kinetic Data

ORNL Projects:

- **Coordination of Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Project-** ***Stuart Daw***
- **CLEERS LNT Kinetics and Multi-Lab Diesel Emissions Reduction Activities -** ***Jae-Soon Choi***
- **Pre-Competitive R&D on LNT Mechanisms-** ***Jae-Soon Choi***

PNNL Projects:

- **PNNL CLEERS Activities Overview-** ***Darrell Herling***
- **Diesel Soot Filter Characterization-** ***Darrell Herling***
- **Selective Catalytic Reduction Characterization and Kinetics-** ***Jonathan Male***
- **NOx Adsorber Fundamentals-** ***Chuck Peden***

SNL Project:

- **CLEERS Benchmark Kinetics for NOx Adsorbers and Catalyzed DPF-** ***Rich Larson***

Pacific Northwest National Laboratory ...delivering breakthrough science and technology

Sandia National Laboratories

Oak Ridge National Laboratory

What is CLEERS?

- **CLEERS: Cross-Cut Lean Exhaust Emissions Reduction Simulation**
- **Collaborative network of OEM's, emissions controls suppliers, national labs, and universities**
  - **Initiated and overseen by the DOE Diesel Cross-Cut Team**
  - **Focused on improving utilization of emissions controls simulation**
  - **Charged with identifying critical technology bottlenecks and potential solutions**
  - **High priority on sharing non-proprietary basic data/understanding among the community**
  - **Forum for defining common terminology/standards to facilitate communication (between researchers, between OEM's & suppliers...)**
  - **Mechanism for industry feedback to DOE**

CLEERS

Close collaboration among ORNL, PNNL, and SNL under CLEERS leverages their unique capabilities

- **Lab projects are synchronized to respond to specific CLEERS R&D priorities**
- **Stuart Daw (8745) explains overall structure and coordination of CLEERS and how R&D priorities are identified**
- **Two top priority R&D areas identified for labs are PM and NOx control**
  - **Top NOx control issues:**
    - **model capture/regeneration kinetics and S poisoning in Lean NOx Traps (LNTs)**
    - **model poisoning and storage in urea-based selective catalytic reduction (SCR)**
  - **Top PM control issue is to model filter cake accumulation and regeneration in Diesel Particulate Filters (DPFs)**
- **Jae-Soon Choi (8746, 8744) reviews CLEERS-funded studies of LNT sulfation and desulfation work at ORNL**
- **Darrell Herling, Jonathan Male, Chuck Peden review CLEERS-funded DPF, SCR, and LNT chemistry work at PNNL**
- **Rich Larson reviews CLEERS-funded studies of LNT kinetics at SNL**

How is CLEERS organized?

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 telecoms**
- **Limited membership**

Website(www.cleers.org)
- **General information**
- **Meeting announcements**
- **Shared data**

Workshops
- **Public**
- **Annual in Detroit area**
- **Presentations on website**

CLEERS

Purpose and Approach

- **General CLEERS Objectives:**
  - **Support DOE goal of reducing imported fuel consumption by minimizing penalties in fuel efficiency and cost for emissions controls in advanced combustion engines**
  - **Improve ability to simulate performance of advanced emissions controls**
- **Specific CLEERS Coordination Project Objective:**
  - **Coordinate emissions control simulation R&D to maximize benefits and efficiency**
- **Approach:**
  - **Co-lead CLEERS Planning Committee**
  - **Co-Lead LNT Focus Group**
  - **Provide general assistance to DPF and SCR Focus Groups and monthly telecoms**
  - **Maintain website (restricted and public domains)**
  - **Organize CLEERS public workshops**
  - **Coordinate CLEERS R&D priority polling**
  - **Provide regular updates to DOE Diesel Cross-Cut Team**
  - **Exchange data, models among OVT activities (e.g., use of CLEERS kinetic data for Systems Analysis)**

CLEERS addresses specific DOE-OVT challenges and barriers

OVT Multi-Year Program Plan (MYPP)

- **Market:**
  - **A. *Cost. "... The emission control devices required by engines* to meet emission targets add to the cost of the system...**
- **Technical:**
  - ***C. Emission control. "...NOX adsorbers appear to be the most viable NOX reduction devices for light-duty vehicles, but they are very sulfur-sensitive, resulting in an increasingly greater energy penalty over time to compensate for loss of activity... Particulate trap technology is costly, and certain regeneration technologies are energy-intensive. ..PM control technology will likely be pushed to its limits in favor of controlling NOX emissions, which currently is the more intractable of the two problems."***

FreedomCAR ACEC Tech Team 2006 Roadmap

  - ***"Development and optimization of catalyst-based aftertreatment systems are inhibited by the lack of understanding of catalyst fundamentals (e.g., surface chemistry, deactivation mechanisms...) and catalysts modeling capabilities."***

FY 2007 Merit Review Guidance and Responses

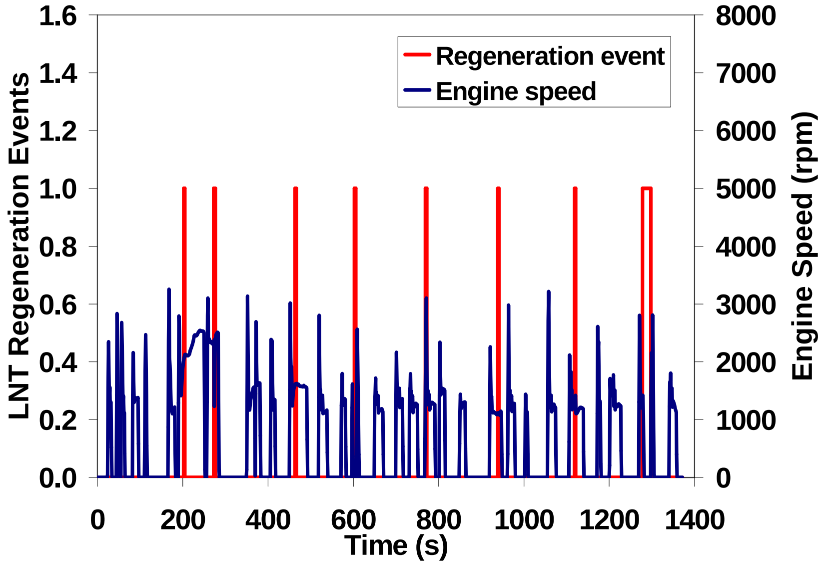
- **Last year's ORNL CLEERS coordination presentation combined with ORNL LNT kinetics discussion**
- **Comments very positive overall**
  - **"NOx reduction critical to reaching Tier 2 Bin 5..."**
  - **"good progress in catalyst understanding.."**
  - **"type of project National Labs should be involved in..."**
- **Guidance and responses**
  - **Too much detail presented in a short time**
    - **Restructured this year's presentation**
  - **Unclear how specific R&D topic areas are identified**
    - **More explanation about CLEERS R&D priority polling process**
  - **Relation between ORNL's dual CLEERS roles hard to follow**
    - **Separate presentations on CLEERS coordination (this presentation) and kinetics (presentation by Jae-Soon Choi)**

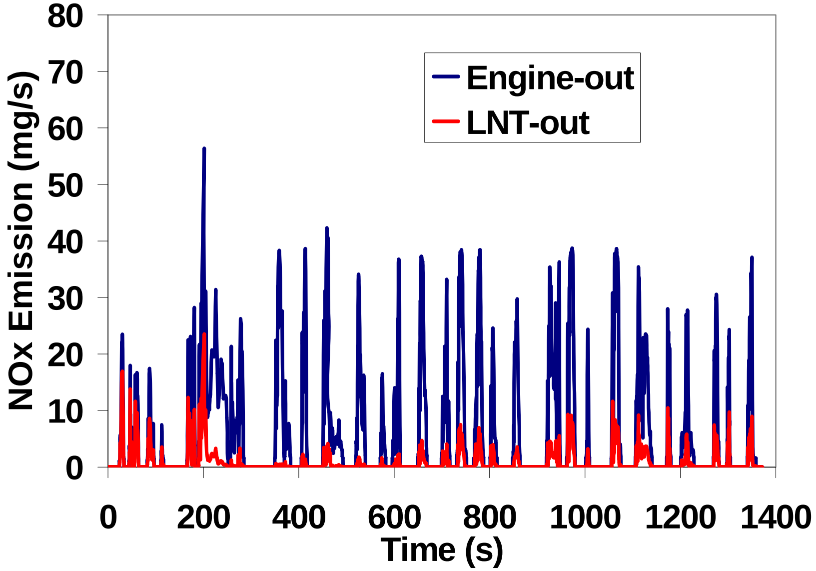
CLEERS Coordination Highlights

- **Continued new format for teleconferences**
  - **single combined monthly teleconference (typically 20-30 domestic and international participants)**
  - **host duties rotate among Focus Groups (DPF, LNT, SCR)**
- **Workshop #10 held May 1-3, UM Dearborn**
  - **3 days of presentations and discussion on DPF, LNT, SCR, device integration (posted on website)**
  - **> 110 attendees from OEMs, suppliers, software developers, national labs, universities**
- **Workshop #11 planned May 13-15, UM Dearborn**
  - **strong interest in informal workshop (restricted size)**
  - **already >50 registrations**
- **LNT model adapted for Powertrain Systems Analysis Toolkit (PSAT)**
- **Conducted 2007 R&D priorities survey**
  - **helped link, prioritize OVT emissions control projects**
  - **helped respond to shifts in industry priorities**
- **Restructured 2008 R&D priorities survey underway**

10th CLEERS Workshop

CLEERS LNT modeling results have been adapted in PSAT to simulate combined effects of engine type, hybrid configuration, and emissions control





Parameters

- Urban Dynamometer Driving Schedule (cold start)
- Mercedes 1.7-L diesel engine map
- Conventional diesel fuel
- Parallel hybrid Civic vehicle configuration
- Lean NOx Trap

Performance

- Fuel economy: 50.8mpg
- Engine-out NOx: 1.108g/ml
- LNT-out NOx: 0.178g/ml
- NOx reduction: 83.9%
- LNT fuel penalty: 2.31%

LNT model serves as template for other aftertreatment components

2007 CLEERS R&D Priorities Survey

- **Designed by CLEERS planning committee**
- **Conducted by independent third party (Mike Laughlin, New West Technologies) with anonymous reporting**
- **Requests sent to 22 organizations, 14 responded (18 total responses)**
- **Separate responses for diesel and gasoline applications**
- **Diesel priorities**
  - **DPF soot loading, regeneration, oxidation**
  - **DPF-system interactions**
  - **Urea-SCR catalyst poisoning, kinetics**
- **Gasoline priorities**
  - **LNT capture/regeneration kinetics**
  - **LNT sulfation/desulfation**
  - **LNT precious metal aging**
- **Results incorporated in PNNL, ORNL, and SNL operating plans**

2008 CLEERS R&D Priorities Survey

- **Revised design by CLEERS planning committee, conducted by Mike Laughlin, New West Technologies**
- **Revisions expand technical specialty areas, reduce ambiguity in priority ranking**
- **Maintain separate responses for diesel and gasoline applications**
- **Survey about to begin; report on results anticipated for 11th CLEERS Workshop**

CLEERS Coordination Future Plans

- **Continue basic coordination functions associated with the Planning Committee, Focus Groups, and Website**
- **Continue maximizing synchronization among ORNL-PNNL-SNL CLEERS R&D activities (e.g., new SCR characterization work)**
- **Complete and report on 2008 R&D priorities survey by March 31, 2008**
- **Carry out annual updates of R&D priorities survey beyond 2008**
- **Complete 11th CLEERS Workshop in May 2008**
- **Continue assistance to ORNL, PNNL, and SNL collaborators in targeting R&D efforts with most recent priority surveys**
- **Expand non-proprietary databases for DPF, LNT, and SCR on website**
- **Expand efforts to enhance basic data and model exchange between CLEERS and other OVT projects**

CLEERS Coordination Summary

- **Purpose**
  - **Coordinate emissions control simulation R&D to maximize benefits and efficiency**
- **Approach**
  - **Planning Committee, Focus Groups, website, workshops, priority polling, Cross-Cut Team updates, data/model exchanges**
- **Technical Accomplishments**
  - **Monthly Focus meetings, maintained website, 10th workshop, 11th workshop plan, 2007 poll, 2008 poll plan, bi-monthly Crosscut reports, PSAT implementation of CLEERS data/models**
- **Technology Transfer**
  - **Non-proprietary collaborations among industry, national labs, and universities through CLEERS organizational structure**
- **Future**
  - **Continued Planning meetings, Focus Group interactions, Cross-Cut reports, website**
  - **11th Workshop, 2008 priority poll, leveraging of data/models for OVT**

Upcoming presentations by ORNL, PNNL, and SNL cover technical results for LNT, SCR, and DPF work that responds to specific CLEERS priorities

- **Jae-Soon Choi (8746, 8744) on ORNL studies of LNT sulfation and desulfation**
- **Darrell Herling, Jonathan Male, and Chuck Peden on PNNL fundamental studies of DPF soot characterization and SCR and LNT chemistry**
- **Rich Larson on joint SNL-ORNL studies of LNT kinetics**
- **Presentations later today and tomorrow cover other CLEERS-related studies and industry CRADAs at ORNL and PNNL (Darrell Herling, Chuck Peden, Jim Parks, Bill Partridge, Todd Toops)**

Pacific Northwest National Laboratory
...delivering breakthrough science and technology

Sandia National Laboratories

Oak Ridge National Laboratory

ORNL Research on LNT Sulfation and Desulfation

Projects:

CLEERS LNT Kinetics and Multi-Lab Diesel Emissions Reduction Activities (8746)

Jae-Soon Choi, Bill Partridge, Josh Pihl, Michael Lance, Larry Walker, Charles Finney, Kalyana Chakravarthy, Vitaly Prikhodko, Stuart Daw (PI)

Pre-Competitive R&D on LNT Mechanisms (8744)

Josh Pihl, Jae-Soon Choi, Todd Toops (PI)

Presenter: Jae-Soon Choi

Fuels, Engines, and Emissions Research Center
Oak Ridge National Laboratory

Vehicle Technologies Program Annual Merit Review
February 25, 2008, Bethesda, MD

DOE Managers: Ken Howden, Gurpreet Singh

This presentation does not contain any proprietary or confidential information.

Purpose of Work

- **Develop and consolidate information about chemistry and kinetics for emissions control materials**
- **Develop analytical/numerical tools for device performance modeling, data correlation, basic understanding**
- **Use tools to identify sources of energy inefficiency, potential solutions to emissions control technology bottlenecks**

This fiscal year, ORNL R&D focuses on sulfation/desulfation (S/DeS) processes relevant to commercial Lean NO_x Traps (LNTs) applicable to both diesel & lean-burn gasoline

in accordance with FY 2007 VT Merit Review input & CLEERS R&D Priorities Survey

Activity Addresses Critical VT Barriers by Providing Insights Necessary to Develop/Model/Control Real LNT Systems

Sulfur causes increasing fuel penalty to maintain NO_x reduction: industry needs

- **Real LNT composition & functions are complex**
  - 3-way catalyst (Pt, Pd, Rh, CeO_2, ZrO_2, Al_2O_3) + NO_x storage component (Ba, K)
  - Function in cyclic mode between fuel lean & rich conditions:
    - *Normal lean phase: NO_x storage*
    - *Short rich excursion: NO_x release/reduction*

- **Little information available applicable to real system modeling**
  - Intrinsically transient, gradient-rich integral systems
  - Temporally & spatially varying chemistry
    - *NO_x Storage/Reduction (NSR); Oxygen Storage Capacity (OSC)*
    - *Reductant evolution/consumption; sulfation/desulfation*
  - Conventional approach (integral measurement; simple model LNT) alone insufficient to resolve intra-LNT details

Work to Provide a Framework Describing How Sulfation Develops & Impacts Real LNT Systems

- **Determine spatial nature of sulfation**
  - **Plug-like vs. axially distributed**
  - **Sulfation of Ba (NO_x storage) vs. Ce (O_2 storage)**

- **Evaluate impacts of sulfur on inside-the-catalyst distribution of LNT reactions**
  - **NO_x storage**
  - **Oxygen storage**
  - **Reductant consumption**

- **Develop a conceptual model on LNT operation**
  - **Able to describe global performance changes (e.g., NO_x conv. & NH_3 selectivity) with varying sulfation level**

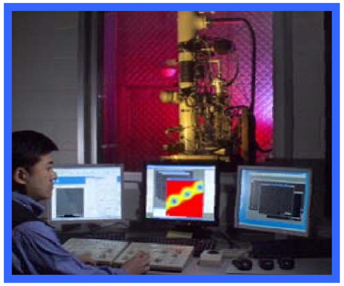
Approach: Characterize Commercially Relevant LNT System on a Range of Scales

Bench reactor w/ intra-cat speciation
- Monolith cores
- Performance/sulfation
- Spatial rxn. distributions

Microreactor
- Powders
- TPR
- Total surface area

DRIFTS
- Powders, washcoated wafers
- Surface adsorbed species

Characterization
- Powders, washcoated wafers
- Elemental/XPS analyses
- Microscopy/EPMA



Catalyst:
Umicore GDI LNT (CLEERS reference)

Composition:
Washcoated cordierite substrate (625 cpsi)
Pt/Pd/Rh, Ba, La, CeO_2, ZrO_2 , Al_2O_3, etc.

7/8” x 3” core taken from a 4.66” x 6” brick

Integration: conceptual model
- Performance evolution
- Distribution of rxns
- Nature of sulfation/sulfur species

New insights for
- Emission control modeling
- Development activities

Technical Accomplishments

- **Developed DRIFTS technique for direct monolith analysis**
  - Quantitative sample-to-sample comparison with measurements up to ~650 °C
- **Enhanced fundamental understanding of model and real LNT sulfur degradation mechanisms**
  - Sulfur impact on NO_x profiles
  - Reversible Pt sulfide formation at low temperature desulfation
- **Developed a conceptual model capable of describing the functioning of real lean NO_x traps (LNTs) at different stages of sulfur poisoning**
  - Sulfur impact on spatiotemporal distribution of reactions (Highlight I)
  - Changes in local physicochemical properties & nature of sulfur species (Highlight II)
  - Correlation between local chemistry and global LNT performance: a conceptual model (Highlight III)
- **Provided experimental data/insights to microkinetic LNT modeling effort at SNL (R. Larson)**

Highlight I

Performance Evaluation:

Sulfur Impact on Spatiotemporal Distribution of Reactions & Global LNT Performance

Bench Reactor Experimental Conditions

- **Procedure:**
  1. Degreening including 4 sulfation/desulfation cycles "***0 g/L S***"
  2. Performance evaluation
  3. 1st S dosing ***1.7 g/L S***
  4. Performance evaluation
  5. 2nd S dosing ***3.4 g/L S total***
  6. Performance evaluation

- **Performance evaluation (NSR & OSC) with fast cycling**
  - 60" lean/5" rich · SV=30000 h^{-1} · 200, 325, 400 ° C

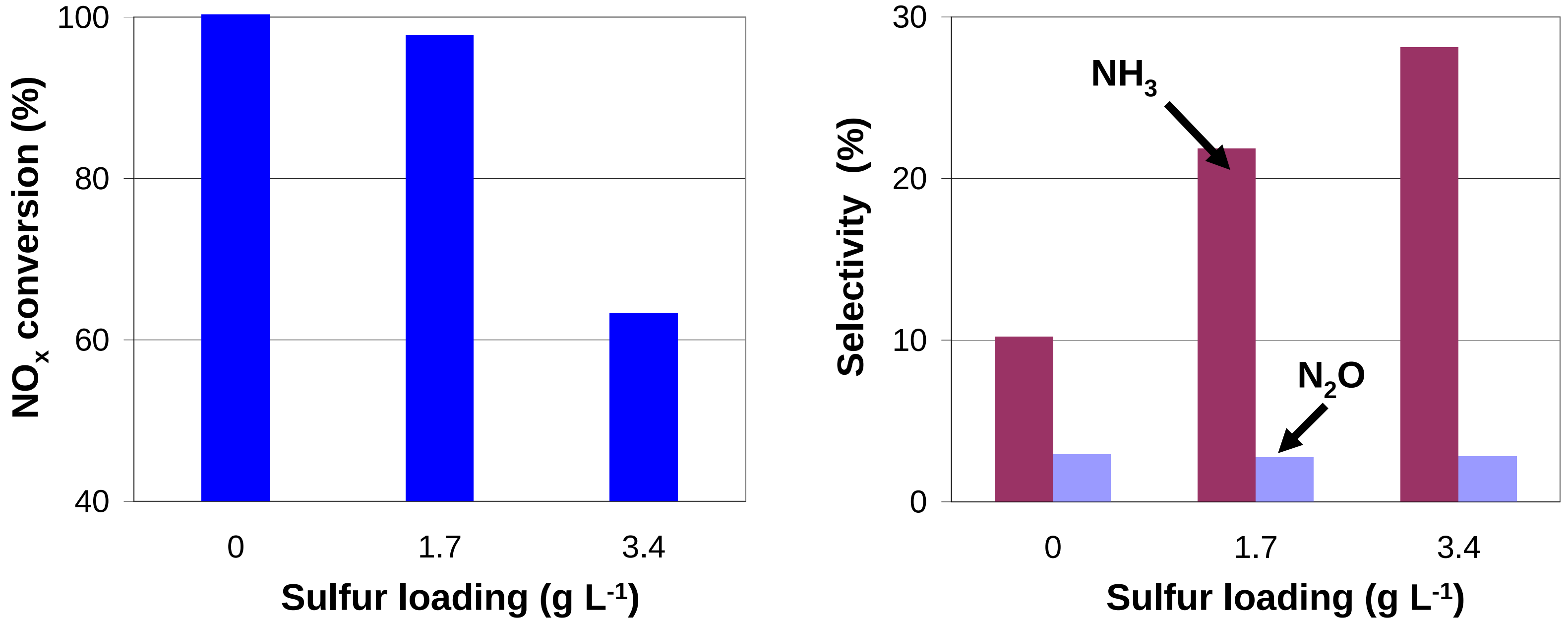
Environment	**Time**	**Gas Composition**					
		NO	**O_2**	**H_2**	**H_2O**	**CO_2**	**N_2**
Lean (storage)	**60 s**	300 (or 0) ppm*	10%	0%	5%	5%	Bal
Rich (regeneration)	**5 s**	0 ppm	0%	3.4%	5%	5%	Bal

***300 ppm NO for NSR & 0 ppm NO for OSC cycling.**

Results from Reactor Outlet Gas Analyses

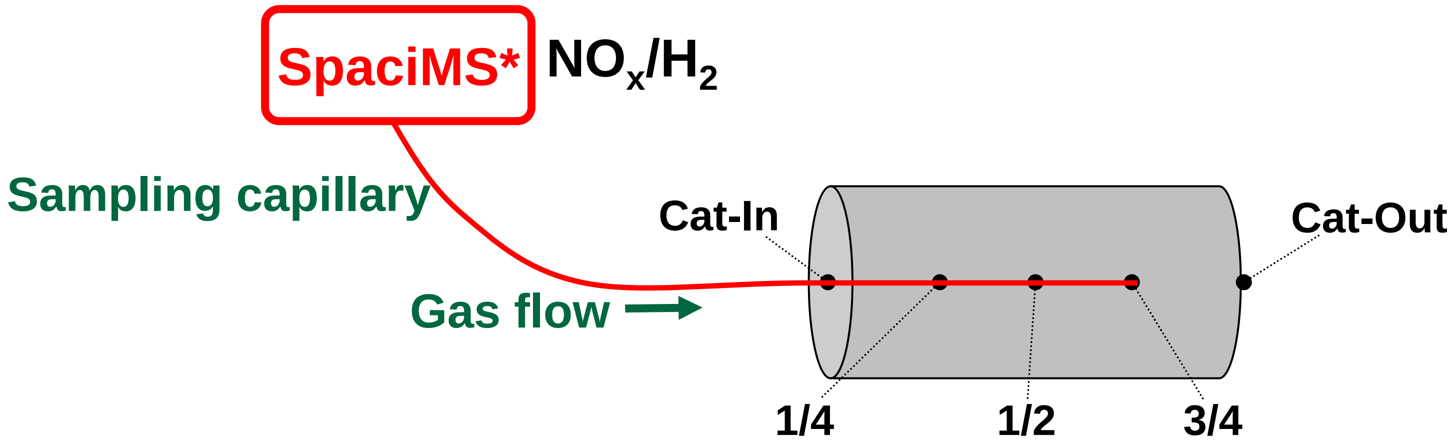
Chemiluminescent detector: NO/NO_x
FT-IR: N_2O/NH_3

Sulfation Decreases Global NO_x Conversion & Increases NH_3 Selectivity



- **Before sulfation, NO_x conv. was ~100%**
- **S decreased NO_x conv. but significant impact only at 3.4 g L^{-1}**
- **NH_3 increased significantly with each sulfur dosing**
- **N_2O was low & insensitive to S**

Results from Spatially Resolved Gas Analyses



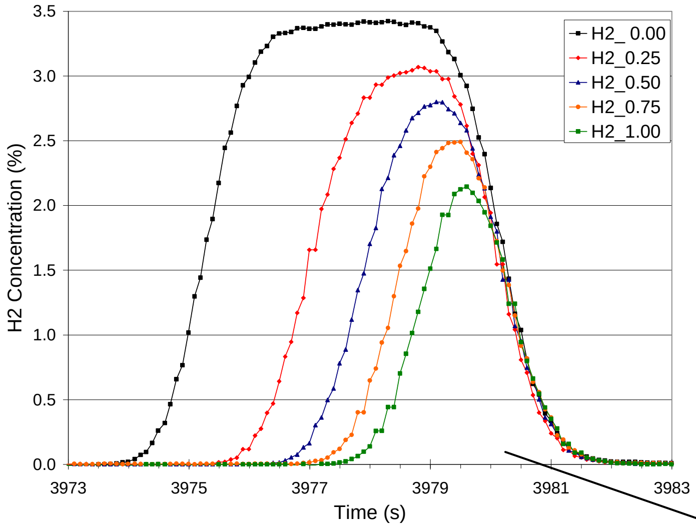
*Spatially Resolved Capillary Inlet Mass Spectrometer

SpaciMS H_2 Data Show NSR & OSC Distributions

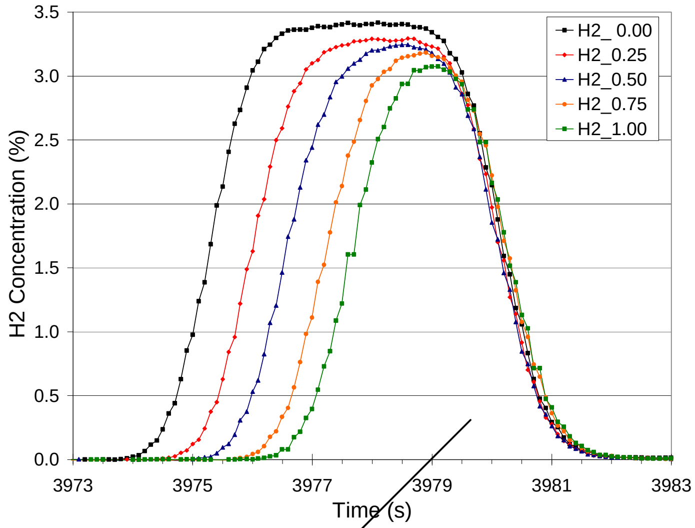
325 °C, 0 g S/L^{-1}

NSR: NO_x Storage/Reduction
OSC: Oxygen Storage Capacity

$NO+O_2$ in lean phase (NSR + OSC)

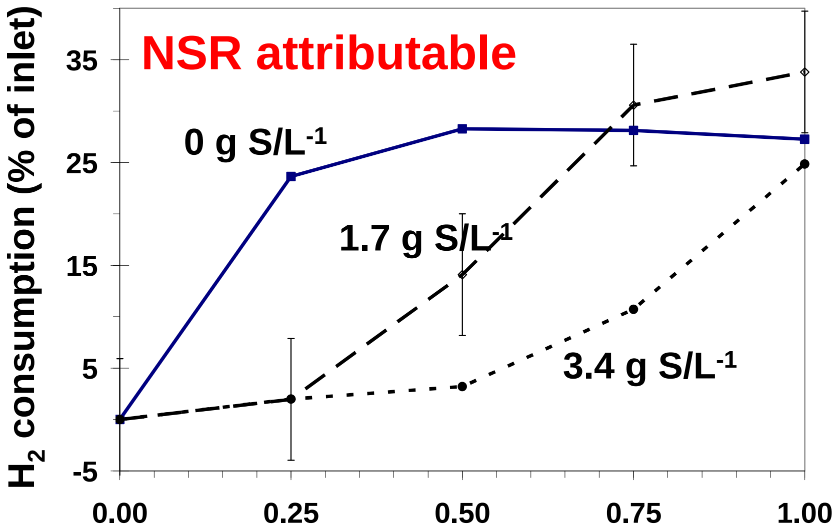


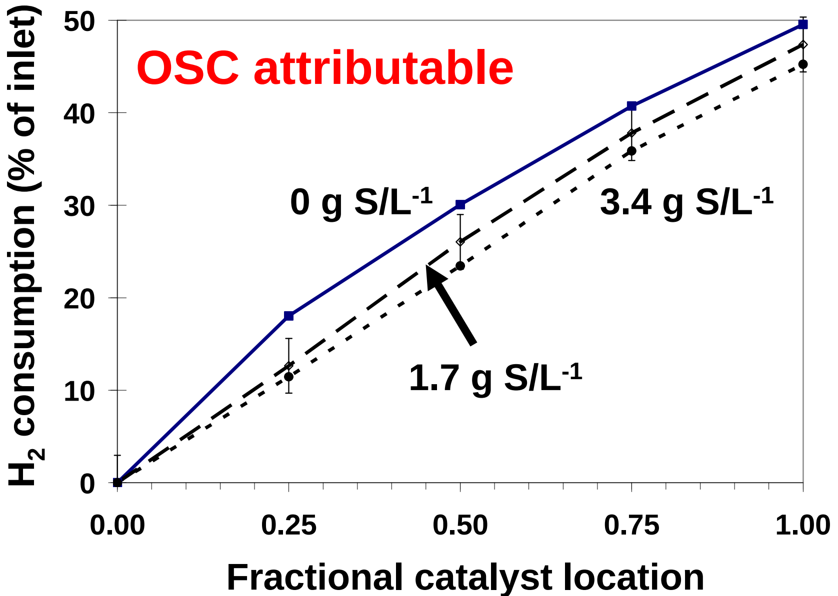
O_2 in lean phase (no NO) (OSC)



- **NSR-attributable H_2 consumption = Total H_2 – OSC H_2 consumption**
- **More H_2 consumption in LNT front with $NO+O_2$ than with O_2 only**

Localized Sulfation & its Distinctive Impact on NSR & OSC Evidenced





NSR distribution

Fresh-state:

- **NSR was localized in LNT front**

Sulfated-state:

- **Progressive poisoning from front**
  "Plug-like"

OSC distribution

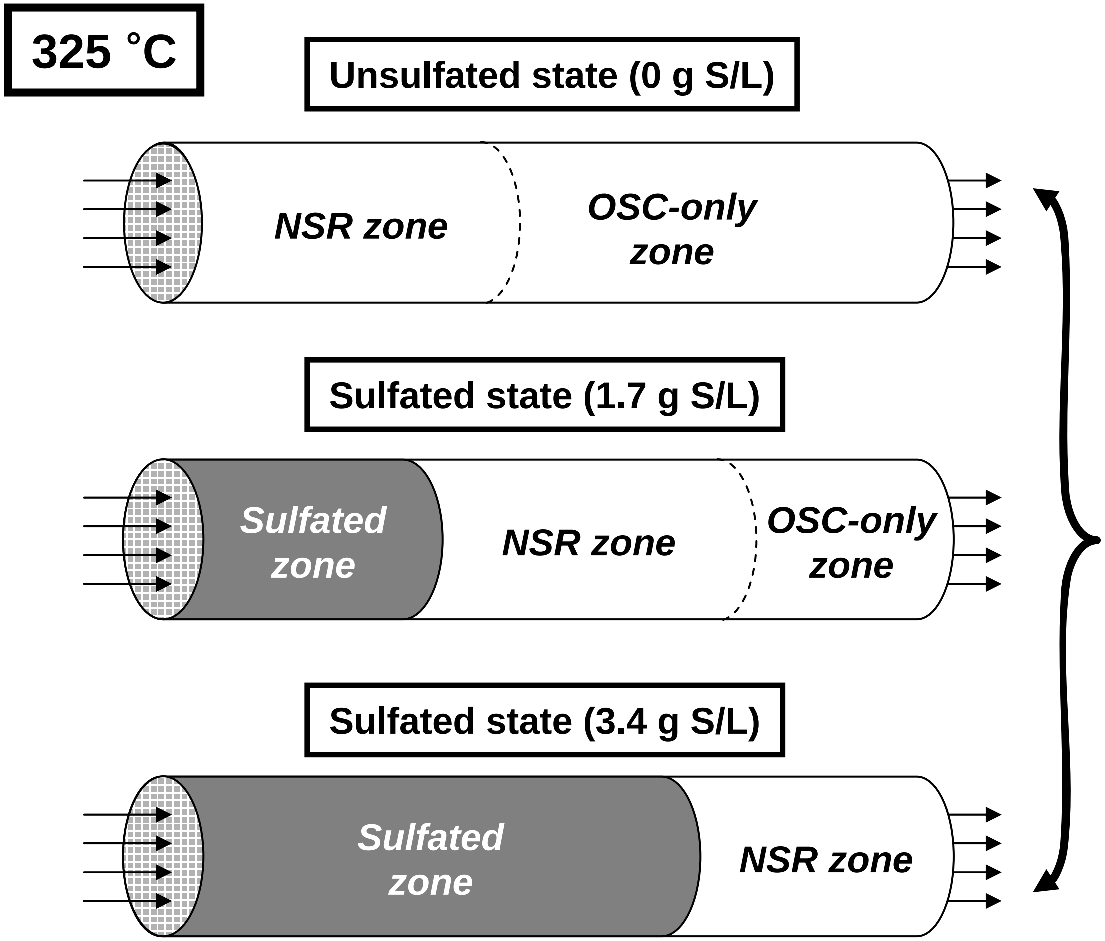
Fresh-state:

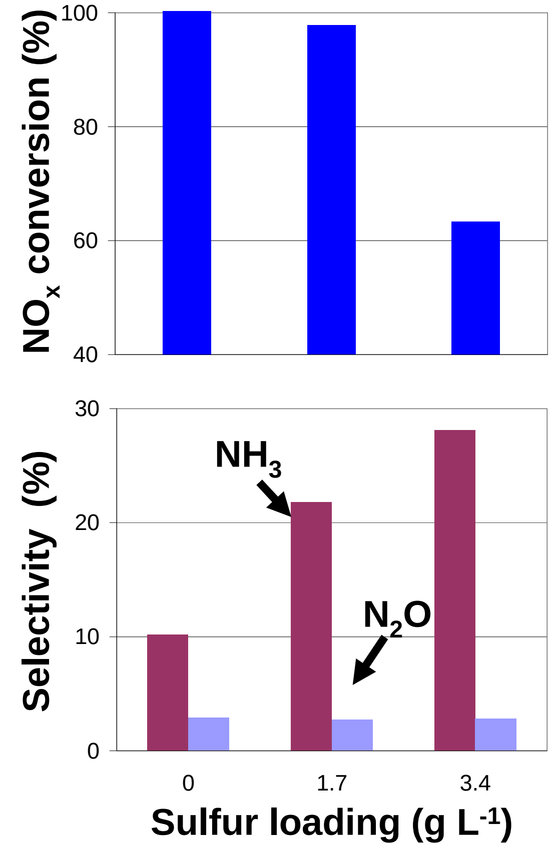
- **Abundant OSC uniformly distributed**

Sulfated-state:

- **Progressive degradation from front**
  much less plug-like

Interim Summary: Sulfur Degrades LNT in a Plug-Like Manner with Greater Impact on NO_x Storage Sites vs. OSC





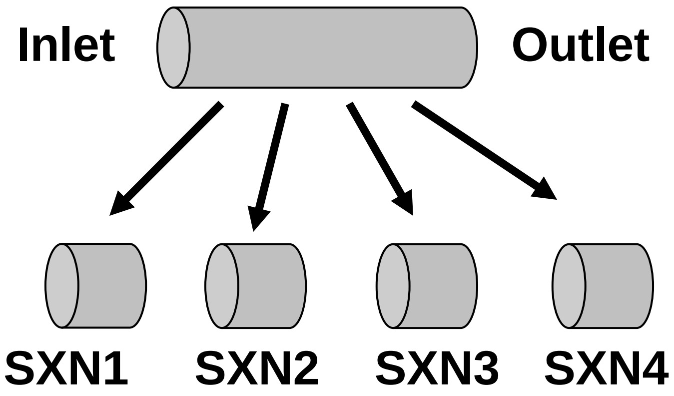
- **NSR zone: both NO_x & O_2 are stored & reduced**
- **OSC-only zone: O_2 is stored & reduced with little NO_x storage**
- **Sulfated zone: NO_x storage sites poisoned & OSC sites are partially degraded**

Highlight II

Postmortem Characterization:

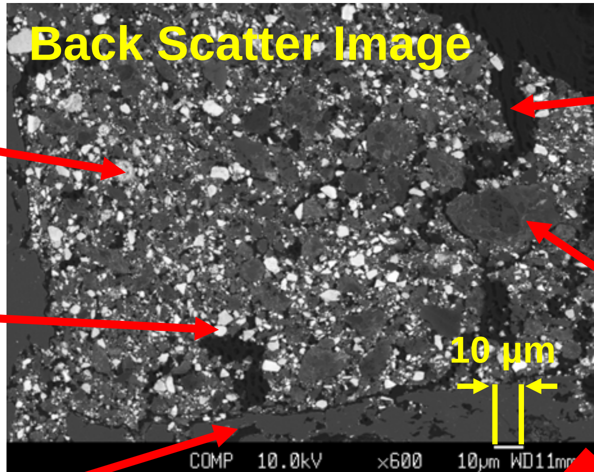
Identification of Surface Sulfur Species & their Spatial Distribution

3" Core with 3.4 g S/L loading



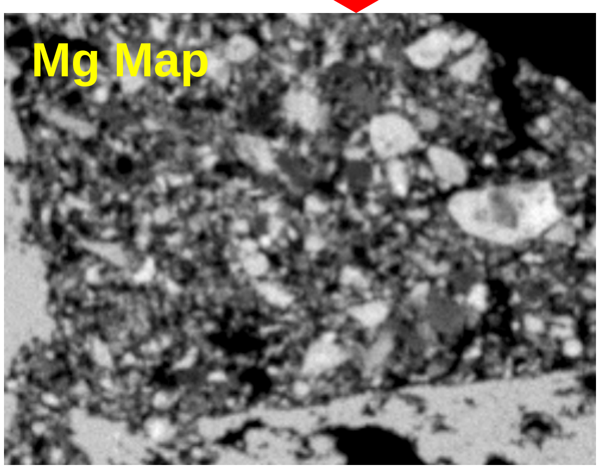
Microscopy/EPMA Reveals Complexity & Heterogeneity

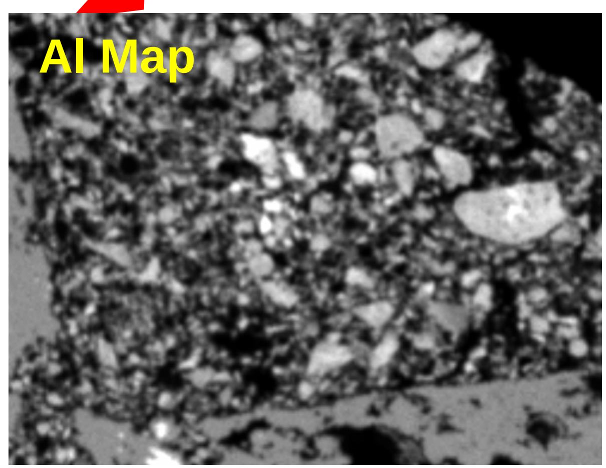
Electron Probe Micro Analysis (EPMA)



SXN1 – Cross Section

- **Overall uniform washcoat composition (e.g., not layered)**
- **Highly concentrated domains exist (grain size~ 1-10 μm)**
  - **Ba, Ce-Zr, Mg-Al**
- **Individual particle level assessment difficult**

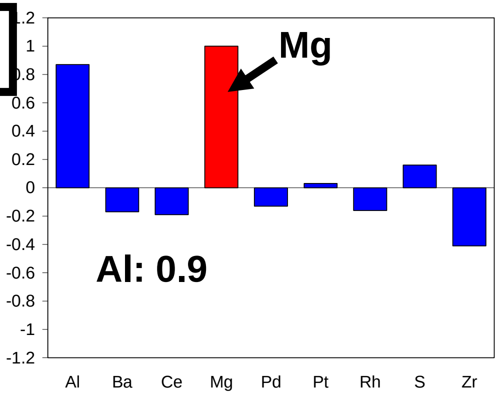


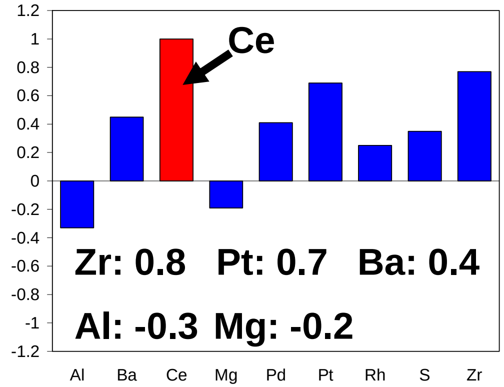


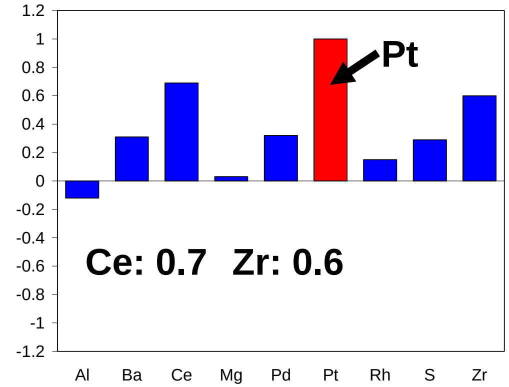
Statistical analyses necessary to obtain quantitative cross correlations

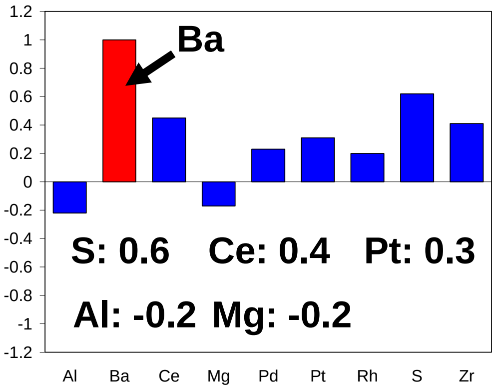
EPMA Cross-Correlation Analyses Indicate Two Distinct Domains & High Ba Sulfur Sensitivity

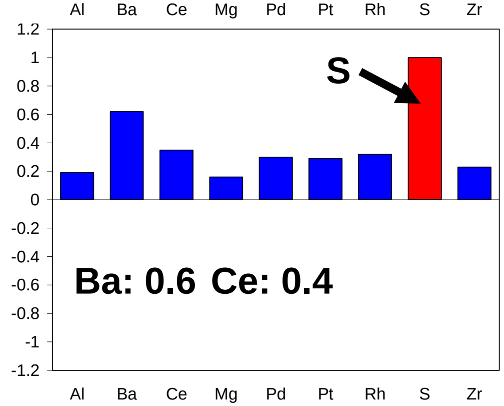
SXN1









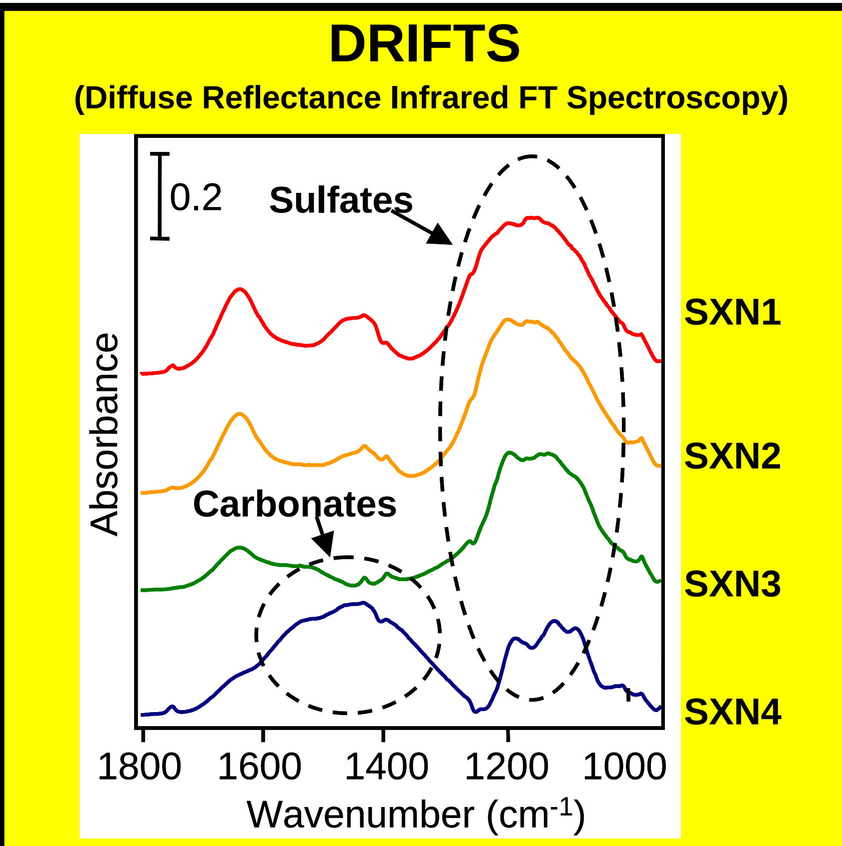


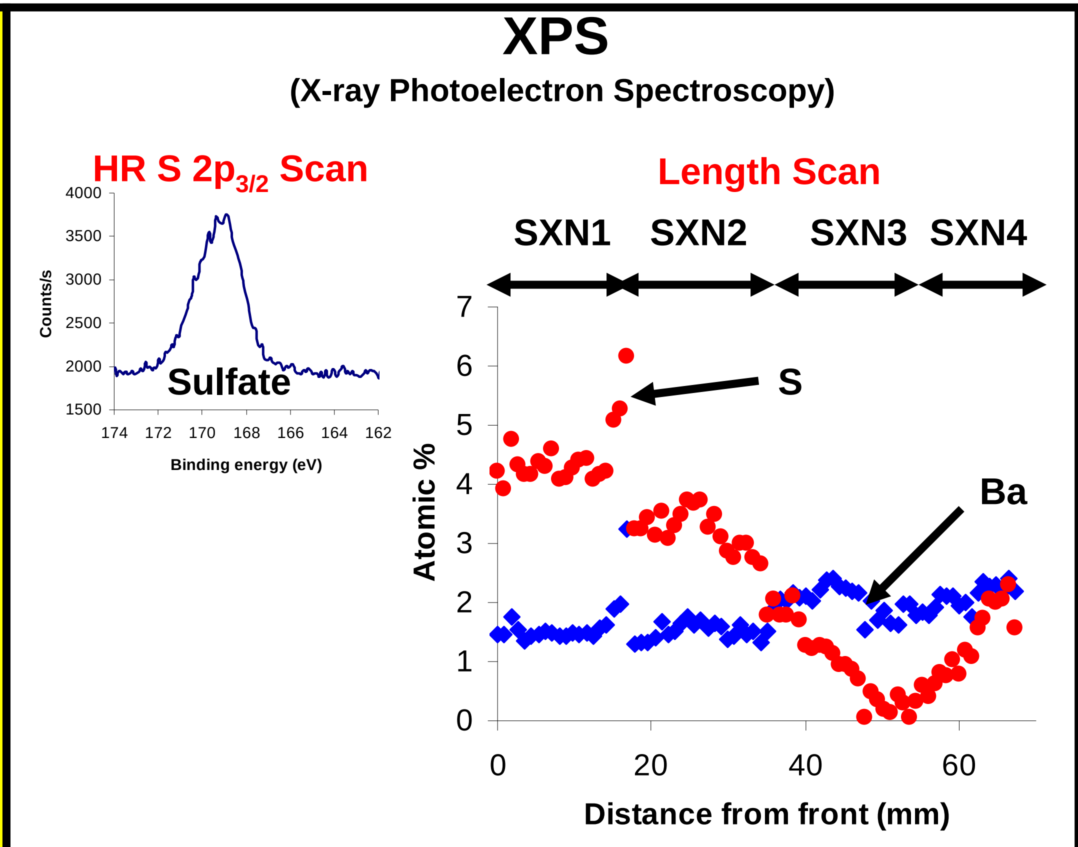
- **Red bar**: **element of interest (self)**
- **Blue bars**: **elements to compare with self**
- **Intensity (Y-axis):**
  +1=highest correlation (self)
  -1=lowest correlation

- **Mg, Al, Ce, Zr, present mainly as two distinct domains:**
  - $MgAl_2O_4$
  - CeO_2-ZrO_2 appearing to accommodate Ba & PGM
  - CeO_2-ZrO_2 is thus the major support component (XRD confirms)
- **Sulfur sensitivity: Ba > Ce-Zr, Mg-Al**
  - Resolution does not allow discrimination between Ce-Zr & Mg-Al

Work in progress (different length scale analyses)

Sulfates are Dominant Surface S Concentrated at Upstream LNT Region

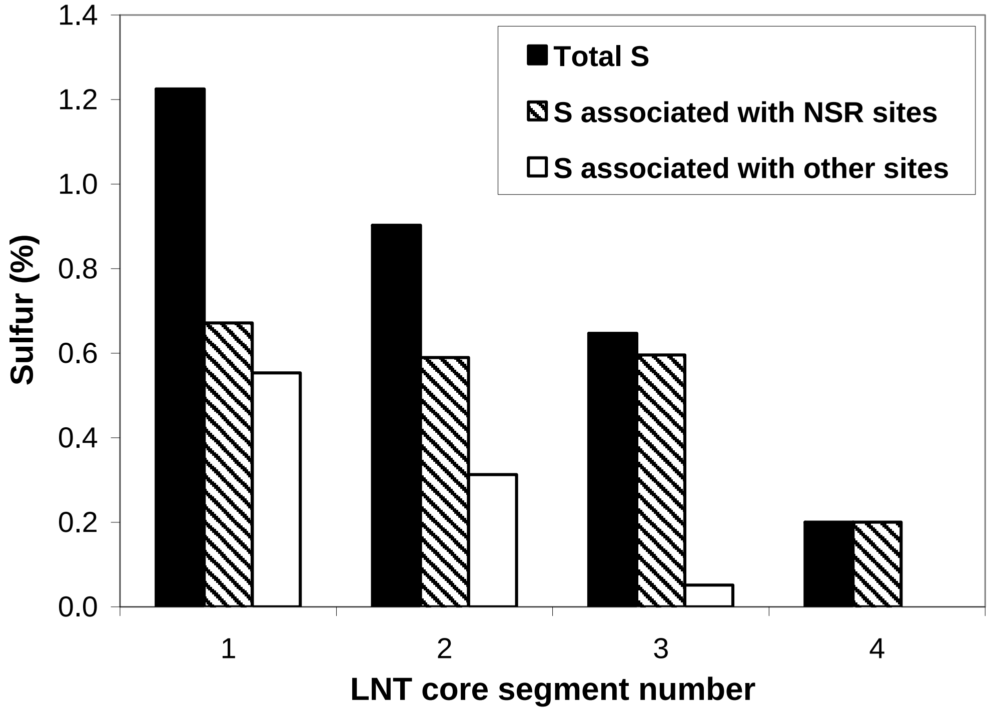




- **Sulfates greatest at front & carbonates were significant only near back face**
- **Axial S distribution (DRIFTS, XPS) consistent w/ elemental analysis: surface=bulk (except for SXN4: surface>bulk)**
- **Highly convolved peaks make precise attribution difficult (e.g. Ba vs. Ce)**
  Peaks identification using standards & depth scan (XPS) in progress

Elemental Analyses of Axial SXNs Consistent with Plug-Like NSR Sulfation/Inhibition Observed from Performance Evaluation

- **Total S in 1st, 2nd, 3rd SXNs > S necessary for full Ba sulfation**
- **Total S << S necessary for full Ce sulfation for all SXNs**
- **S associated w/ NSR was estimated assuming S went first to Ba until full sulf. w/ S:Ba=1:1**
- **Other sites: CeO_2-ZrO_2 etc.**



- **Plug-like NO_x storage/reduction sites sulfation**
- **More distributed OSC sites sulfation**
- **Surface-sensitive techniques necessary to refine these bulk analyses**

Temperature Programmed Reduction (TPR) Reveals Different Sulfur Species

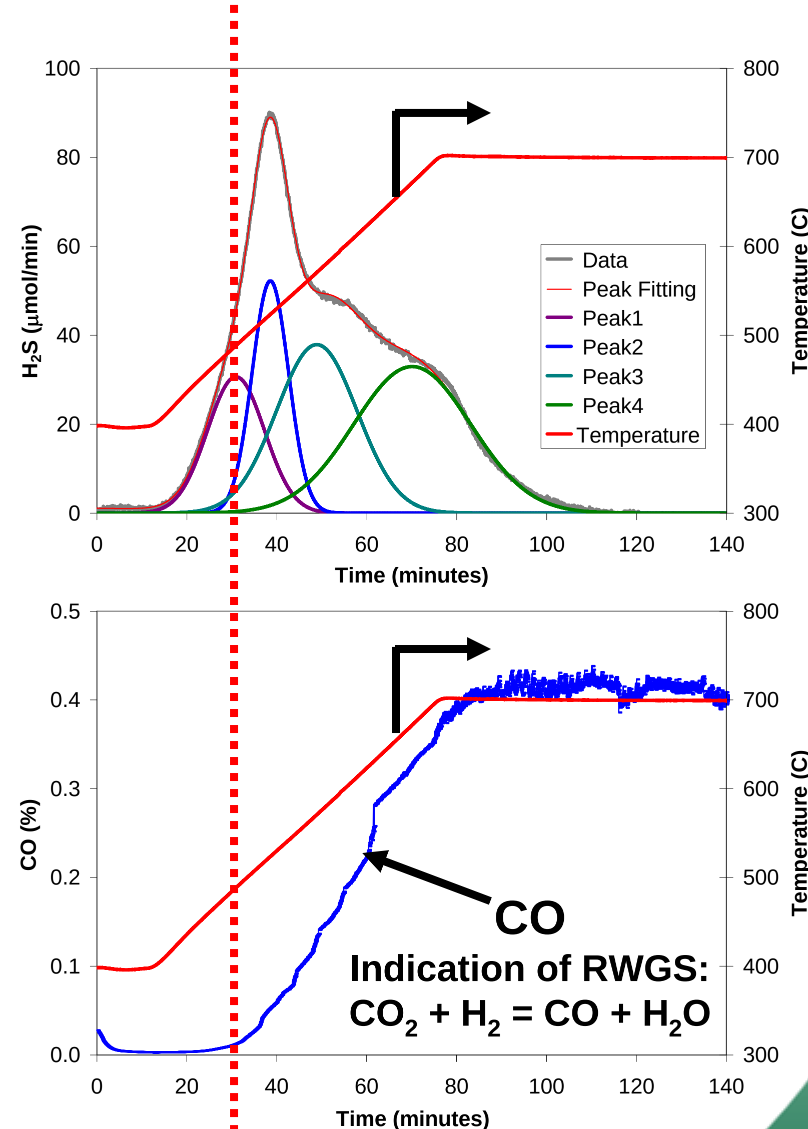
TPR of 3" Core

$1\%\ H_2$, $5\%\ H_2O$, $5\%\ CO_2$, N_2 bal

SV = 30000 h^{-1}

T ramping rate = 5 ° C/min

- **Four peaks deconvolved**
  - Low T: peaks 1 & 2
  - High T: peaks 3 & 4
- **Suppressed RWGS took off w/ elimination of peak 1**
  - Ce-Zr well known WGS promoter
  - Al_2O_3 contribution possible
- **Combined peaks 3 & 4 accounts for 65% of total S (surf. & bulk sulfates)**
  - cf., 69% Ba-attributed S from elemental analysis
- **Peak 2 due to Mg-Al?**
  - Work in progress for identification



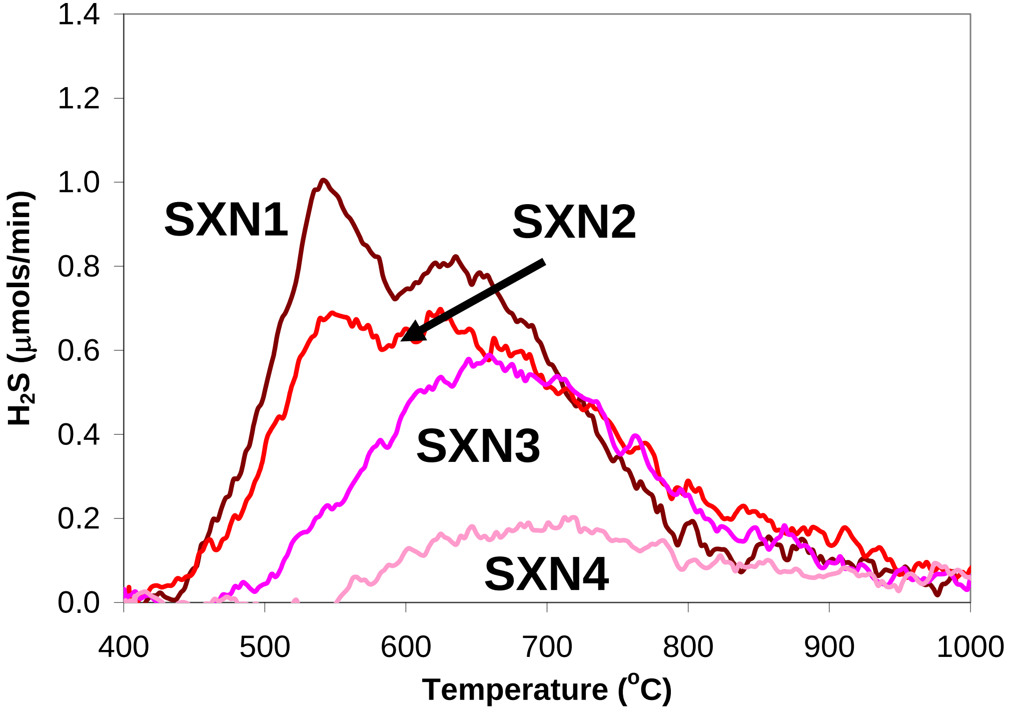
TPR of 4 Sliced SXNs Further Clarifies Nature & Axial Distribution of Sulfates Species

TPR of Four Sliced SXNs

Microreactor

In powder form

- **Only high T peaks for SXNs 3&4**
  cf. Only NSR degradation here
- **Low T peaks decrease from SXN1 (highest total S) to SXN4 (lowest total S)**
  cf. OSC degradation in SXNs 1&2
  cf. RWGS more active after Peak 1



Tentative conclusion:

Low T peaks: CeO_2-ZrO_2 & maybe $MgAl_2O_4$, Al_2O_3 sulfates in SXNs 1&2

High T peaks: Ba sulfates in SXNs 1-4

DeS activation energy determination & TPR of standards in progress

Interim Summary: Ba Sulfation is Much More Efficient (Plug-Like) than Ce Sulfation Leading to Harder-to-DeS Sulfates

Unsulfated state

- **Uniform washcoat distribution: not layered nor graded**
- **Local compositional heterogeneity with two distinct domains**
  - **"Active LNT": PGM, Ba, CeO_2-ZrO_2, Al_2O_3 (minor)**

    Ba is primary NO_x storage sites, CeO_2-ZrO_2 is support/OSC
  - **Mg-Al (spinel likely)**

    What's the role? Secondary NO_x storage possible (basicity)

Sulfated state

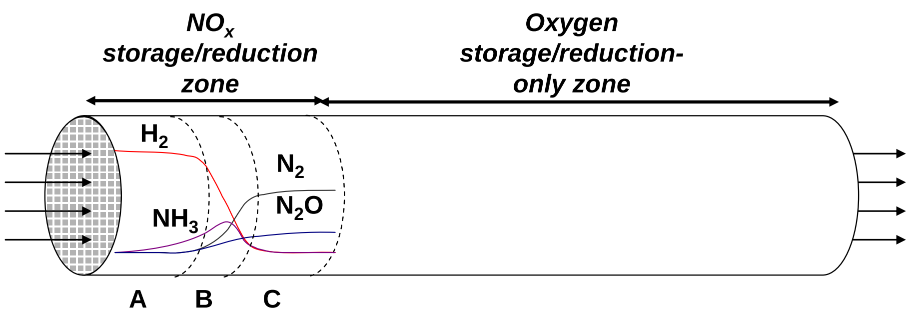
- **NO_x storage sites (Ba) sulfation very efficient ("plug-like")**
  - **Hard to DeS (high T necessary)**
- **OSC (Ce-Zr) sites inhibited but to a lesser extent**
  - **Easier to DeS (low T sufficient)**
- **Some Al_2O_3 sulfates possible**
- **More work necessary to assess Mg-Al sulfation ("S trap")**

Highlight III

Putting It All Together:

A Conceptual Model on the Functioning of a Commercial LNT at Varying Sulfation Levels

Conceptual LNT Model: Fresh State



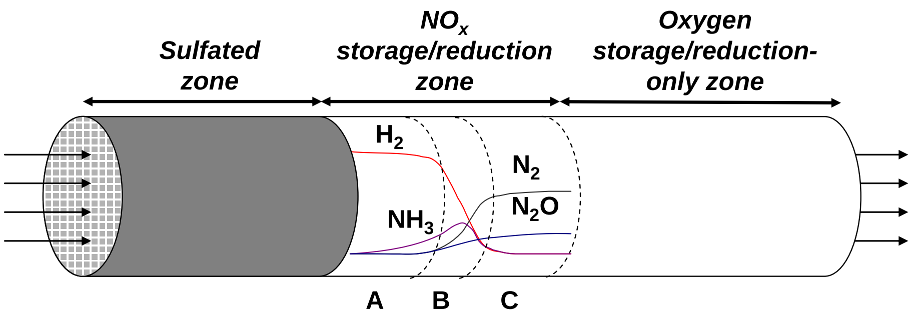
- **Complex realistic LNT formulation uniformly washcoated on the monolith**
  - **Two distinct domains**

  I. PGM, Ba, CeO_2-ZrO_2, Al_2O_3

  II. Mg-Al

- **NSR localized at catalyst front**
  - **Ba is the major NO_x storage sites**
- **OSC evenly distributed throughout**
  - **CeO_2-ZrO_2 (also serves as support for Ba and PGM phases)**
  - **Residual H_2 and NH_3 from NSR zone oxidized in OSR-only zone**
- **Role of Mg-Al phases not clear**
  - **Secondary NO_x storage?**

Conceptual LNT Model: Sulfated State



- **Sulfation creates a localized sulfated zone at the catalyst front**
- **Sulfation front progresses along LNT length**
  - **Ba sulfation: plug-like**
  - **Ce-Zr sulfation: distributed**
  - **Mg-Al sulfation: (between Ba and Ce-Zr?)**
  - **S affinity: Ba > Ce-Zr, Mg-Al (Ba harder to DeS)**
- **In the sulfated zone:**
  - **Ba sites (NSR) inactive**
  - **Ce-Zr sites (OSC) still active but degraded**
- **As sulfation progresses:**
  - **NSR zone moves downstream**
  - **High NO_x conv. maintained until high S load**
  - **OSC-only zone is reduced by advancing NSR**
  - **Reductant & NH_3 slip increases due to reduced OSC-only zone**

Technology Transfer

- **Results/insights continuously shared with the CLEERS community (> 50% industry) & other DOE programs**
  - **Work focused on Umicore LNT ("CLEERS reference")**
  - **Input to PSAT (Powertrain Systems Analysis Toolkit) LNT modeling (DOE Vehicle Systems Program)**
  - **Informal collaboration with Cummins/ORNL CRADA, PNNL etc.**

- **New findings broadly disseminated to the public**
  - **Frequent discussion with CLEERS members & OEMs**
  - **6 publications**
  - **6 conference presentations**

6 Publications & 6 Presentations Since Last Review

- **J.-S. Choi, W.P. Partridge, J.A. Pihl, and C.S. Daw, "Sulfur and temperature effects on the spatial distribution of reactions inside a lean NO_x trap and resulting changes in global performance", *Catalysis Today*, doi:10.1016/j.cattod.2008.01.008 (2008).**
- **T.J. Toops and J.A. Pihl, "Sulfation of model K-based lean NO_x trap while cycling between lean and rich conditions", *Catalysis Today*, doi:10.1016/j.cattod.2008.02.007 (2008).**
- **R.S. Larson, J.A. Pihl, V.K. Chakravarthy, T.J. Toops, and C.S. Daw, "Microkinetic modeling of lean NO_x trap chemistry under reducing conditions", *Catalysis Today*, doi:10.1016/j.cattod.2007.12.117 (2008).**
- **J.-S. Choi, W.P. Partridge, and C.S. Daw, "Sulfur impact on NO_x storage, oxygen storage and ammonia breakthrough during cyclic lean/rich operation of a commercial lean NO_x trap", *Applied Catalysis B: Environmental* 77, 145-156 (2007).**
- **C.S. Daw, "Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS): Joint Development of Benchmark Kinetics", *DOE Annual Progress Report for Advanced Combustion Engine Technologies* (2007).**
- **T.J. Toops, J.A. Pihl, "Fundamental sulfation/desulfation studies of lean NO_x Traps, DOE pre-competitive catalyst research", *DOE Annual Progress Report for Advanced Combustion Engine Technologies* (2007).**
- **J.-S. Choi, W.P. Partridge, J.A. Pihl, and C.S. Daw, "Sulfur effects on spatiotemporal distribution of reactions in a commercial lean NO_x trap", *AIChE National Meeting*, Salt Lake City, UT, November 4-9, 2007.**
- **T.J. Toops, J.A. Pihl, "Sulfation and desulfation studies of model lean NO_x traps", *AIChE National Meeting*, Salt Lake City, UT, November 4-9, 2007.**
- **J.-S. Choi, W.P. Partridge, and C.S. Daw, "Assessing a commercial lean NO_x trap performance via spatiotemporal species profile measurements", *North American Meeting (NAM) of the North American Catalysis Society*, Houston, TX, June 17-22, 2007.**
- **T.J. Toops, J.A. Pihl, "Sulfation and Desulfation Studies of Model Lean NO_x Traps", *North American Meeting (NAM) of the North American Catalysis Society*, Houston, TX, June 17-22, 2007.**
- **R.S. Larson, J.A. Pihl, V.K. Chakravarthy, and C.S. Daw, "Micro-kinetic modeling of lean NO_x trap regeneration chemistry" *North American Meeting (NAM) of the North American Catalysis Society*, Houston, TX, June 17-22, 2007.**
- **J.A. Pihl, J.-S. Choi, V. Prikhodko, W.P. Partridge, K. Chakravarthy, Z. Gao, C.S. Daw, T.J. Toops, "CLEERS coordination and development of catalyst process kinetic data", *DOE Advanced Combustion Engine Program Annual Merit Review*, Crystal City, VA, June 2007.**

Activities for FY 2008 and Beyond

- **Complete the planned physicochemical analyses of Umicore sample**
  - **XPS depth profiles for four sulfated SXNs**
  - **EPMA analyses for elemental cross-correlations**
- **Characterization of model compounds (CeO_2, $MgAl_2O_4$ etc.) to help understand Umicore sample S/DeS behavior**
  - **DRIFTS**
  - **TPR**
- **Desulfation mechanisms**
  - **Kinetic data for four sulfur species identified**
  - **Intermediate DeS & performance evaluation to further evaluate the roles of each species**
- **Numerical modeling**
  - **Refinement with physicochemical & performance data**
  - **Sulfur impact**
- **DRIFTS analysis of HC impacts on urea SCR catalysts**
  - **In collaboration with PNNL**

Summary

- **Relevance to DOE objectives**
  - **Generate kinetic mechanisms, correlations, and experimental data to support emissions control modeling & development activities**
  - **Fundamental understanding of S/DeS critical to energy efficient LNT**
- **Approach**
  - **Multi-scale research on a commercial LNT under practically relevant conditions to elucidate sulfation mechanisms**
- **Technical Accomplishments**
  - **Developed a comprehensive conceptual LNT sulfation model**
  - **Provided fundamental understanding of a practically relevant LNT: physicochmical properties; local and global performance changes**
- **Technology Transfer**
  - **CLEERS community, collaboration with other DOE programs, extensive publications**
- **Plans for Next Fiscal Year**
  - **Elucidate LNT desulfation mechanisms & urea-SCR HC impact**
  - **Perform full cycle simulations with combined LNT mechanism**

Stuart Daw
865-946-1341
dawcs@ornl.gov

Jae-Soon Choi
865-946-1368
choijs@ornl.gov