

Sulfation Impact on LNT Performance: Experimental Studies with Umicore CLEERS Reference Catalyst

Jae-Soon Choi, Bill Partridge, Josh Pihl, Todd Toops, Michael Lance
Charles Finney, Kalyana Chakravarthy, Stuart Daw

Oak Ridge National Laboratory



11th DOE CLEERS Workshop
May 13, 2008
Dearborn, MI

This Effort Aims to Provide Insights Necessary to Design/Model/Control Real LNT Systems

***Sulfur causes increasing fuel penalty to maintain NO_x reduction:
A major technical barrier for industry***

- **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 with 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

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

Results Part 1 of this talk: Performance Evaluation

- **Determine spatial nature of sulfation**
 - **Sulfation of Ba (NO_x storage) vs. Ce (O₂ storage)**
 - **Plug-like vs. axially distributed**

Results Part 2 of this talk: Postmortem Characterization

- **Develop a conceptual model on LNT operation**
 - **Able to describe global performance changes (e.g., NO_x conv. & NH₃ selectivity) with varying sulfation level**

Conclusions of this talk

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



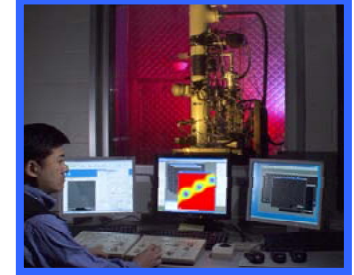
DRIFTS

- 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, CeO₂, ZrO₂, Al₂O₃, 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

Results Part 1

Performance Evaluation: Sulfur Impact on Global LNT Performance & Spatiotemporal Distribution of Reactions

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 ₂ O	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

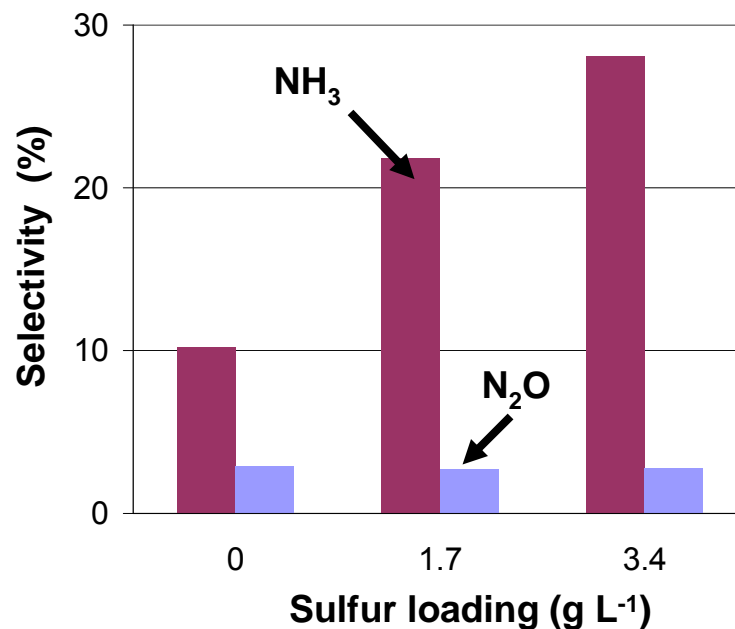
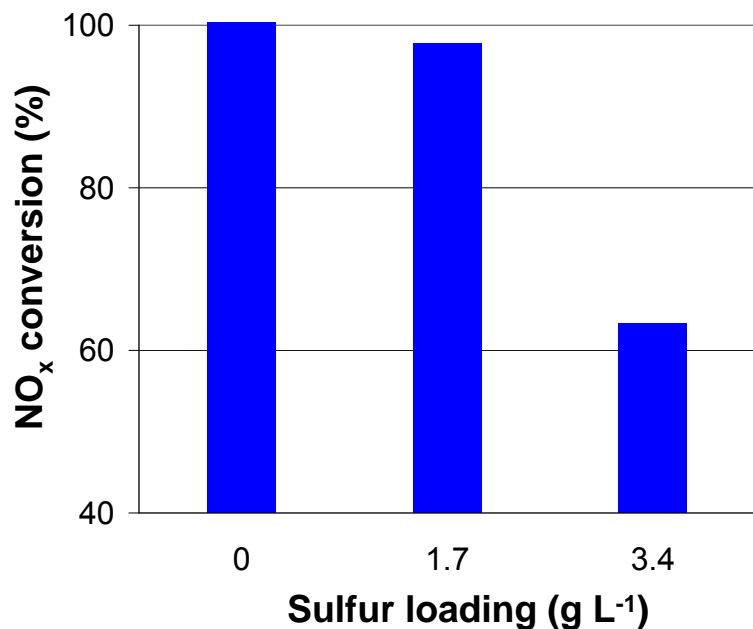
***300 ppm NO for NSR & 0 ppm NO for OSC cycling.**

Results from Reactor Outlet Gas Analyses

**Chemiluminescent detector: NO/NO_x
FT-IR: N₂O/NH₃**

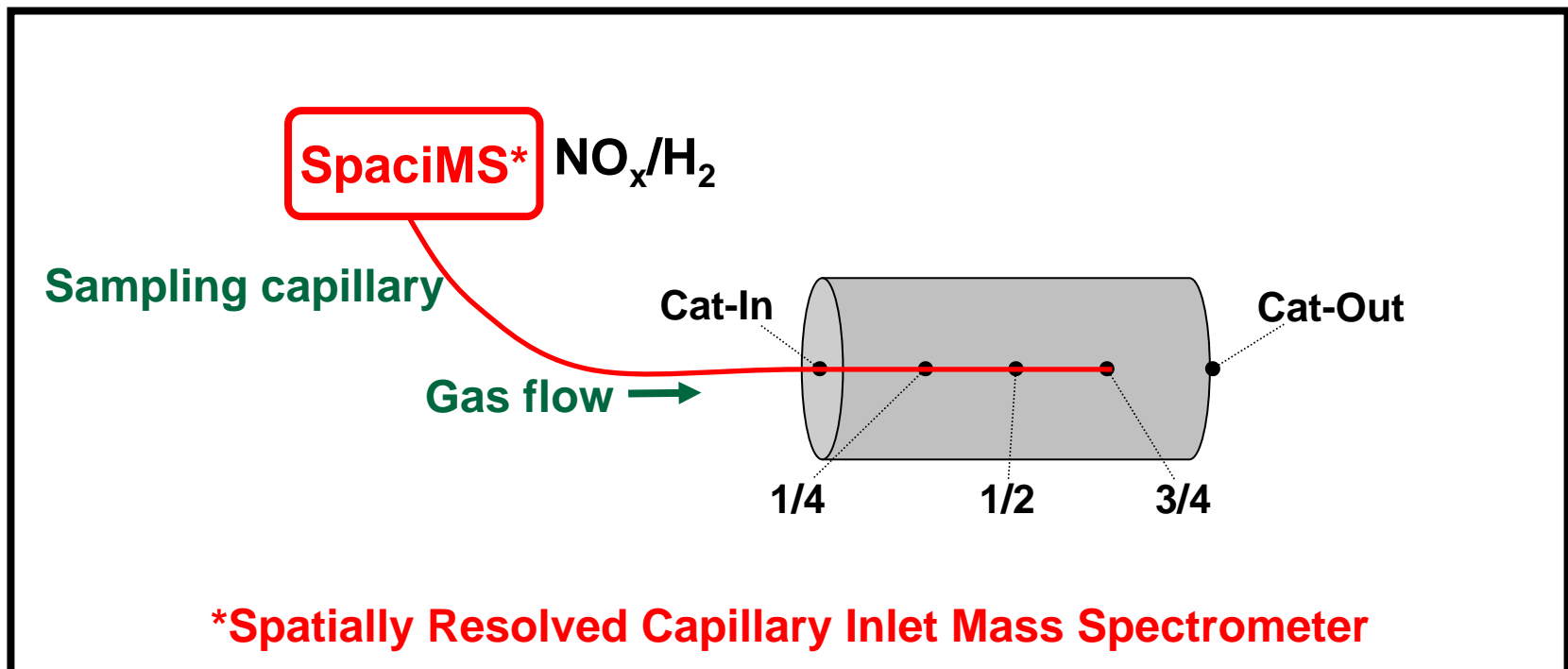
Sulfation Decreases Global NO_x Conversion & Increases NH_3 Selectivity

325 °C

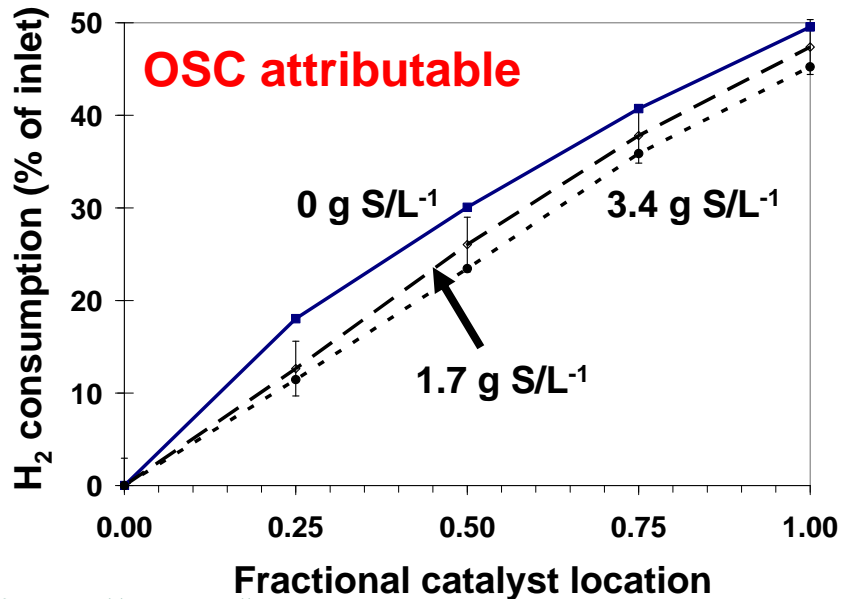
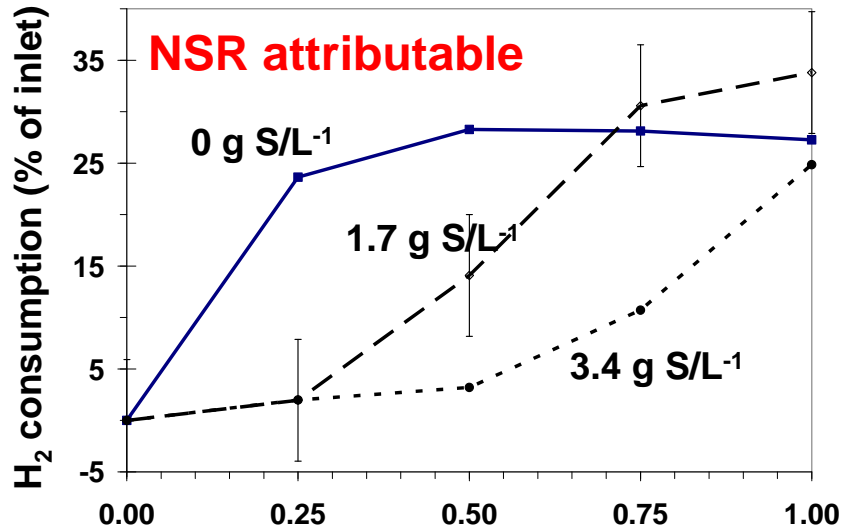


- Before sulfation, NO_x conv. was ~100%
- S decreased NO_x conv. but significant impact only at 3.4 g L⁻¹
- N_2O was low & insensitive to S (or decreased under different conditions)
- NH_3 increased significantly with each sulfur dosing

Results from Spatially Resolved Gas Analyses



Localized Sulfation & its Distinctive Impact on NSR & OSC Evidenced by Spatial RXNs Profile Changes



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

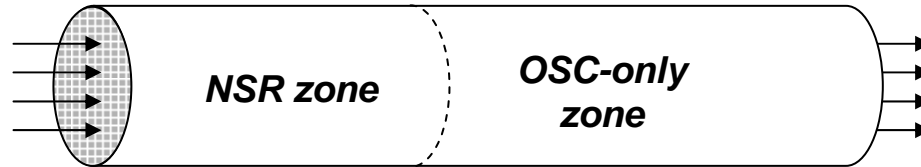
Sulfated-state:

- 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

325 °C

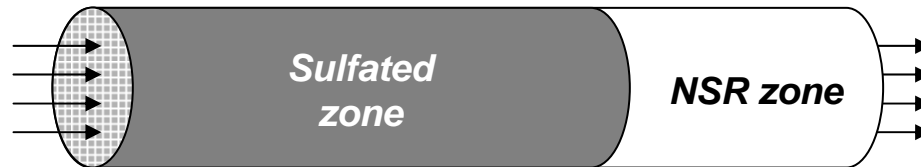
Unsulfated state (0 g S/L)



Sulfated state (1.7 g S/L)



Sulfated state (3.4 g S/L)

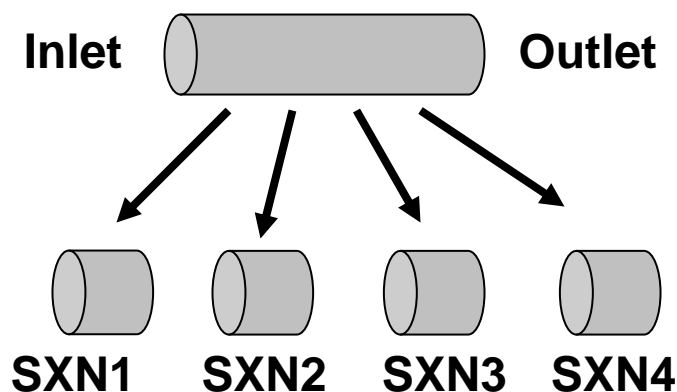


- NSR zone: both NO_x & O₂ are stored & reduced
- OSC-only zone: O₂ is stored & reduced with little NO_x storage
- Sulfated zone: NO_x storage sites poisoned & OSC sites are partially degraded

Results Part 2

Postmortem Characterization: Identification of Surface Sulfur Species & their Spatial Distribution (Techniques: EPMA, DRIFTS, XPS, TPR)

3" Core with 3.4 g S/L loading

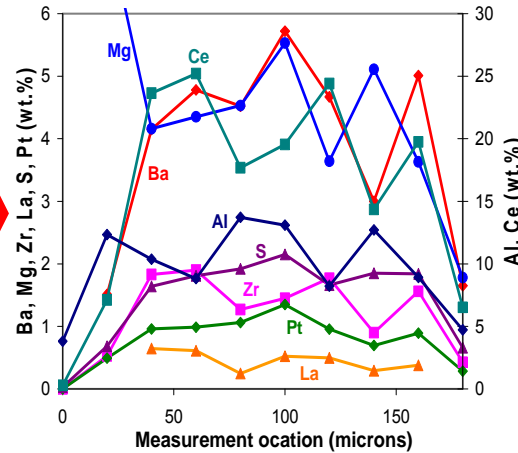
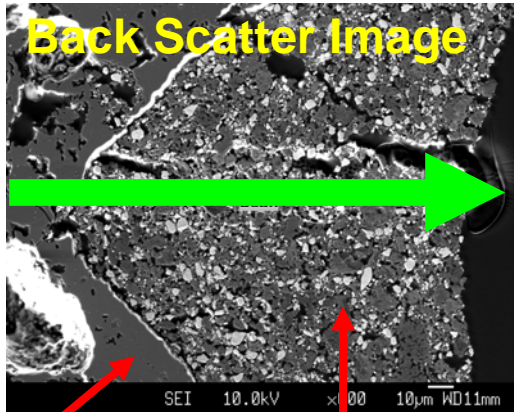


Microscopy/EPMA Reveals Complexity & Heterogeneity

EPMA (Electron Probe Micro Analysis) of SXN1 Cross Section

Compositional analyses:

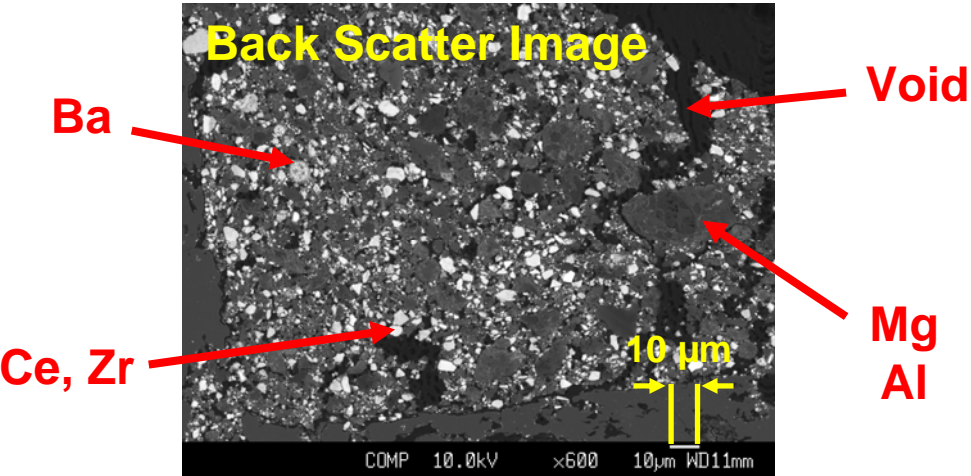
~25 micron spot, 10 measurements along the green arrow



AVG. washcoat composition (wt.%)

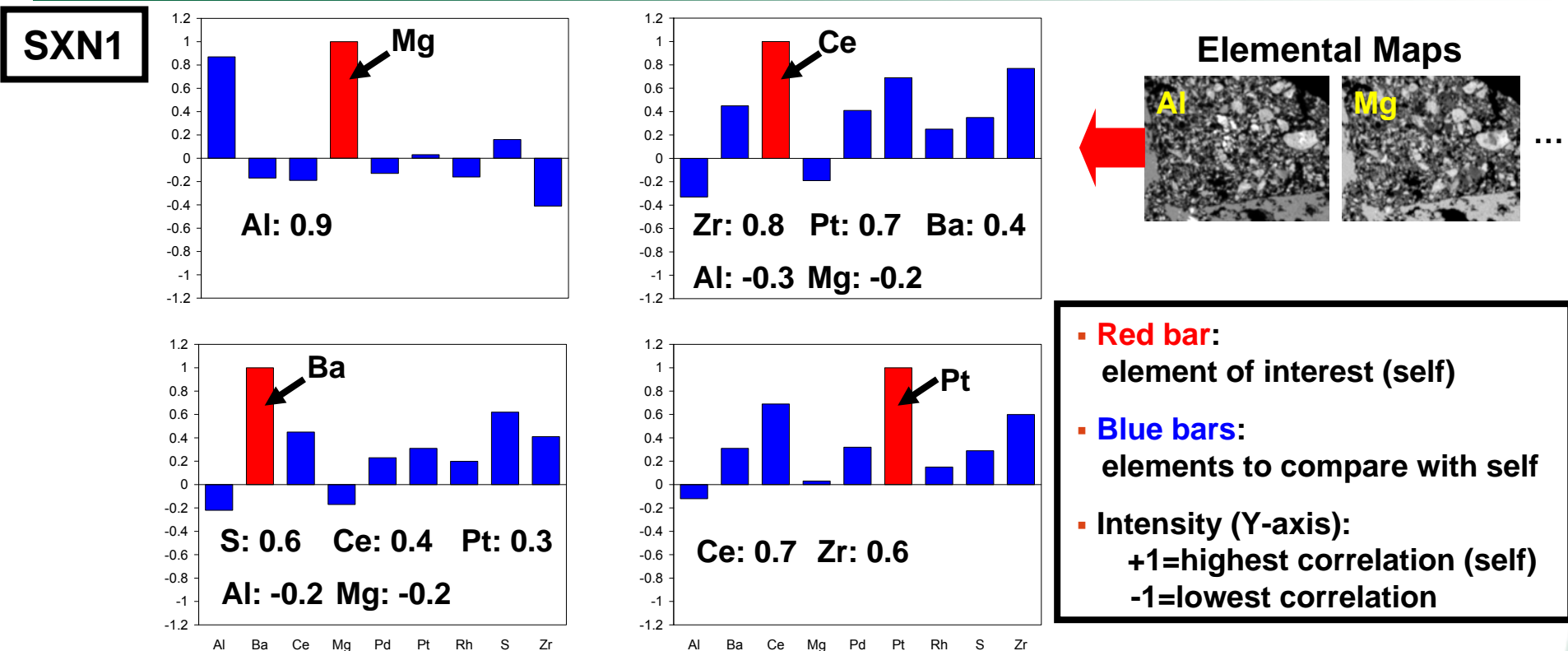
- 4.3% Ba
- 21.2% Ce, 1.6% Zr
- 4.9% Mg, 11.5% Al
- 1.1% Pt, 0.2% Pd
- Rh, La etc.

Cordierite Washcoat (WC)



- 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 Cross-Correlation Analyses of EPMA Elemental Maps Indicate Two Distinct Domains



- **Mg, Al, Ce, Zr, present mainly as two distinct domains:**

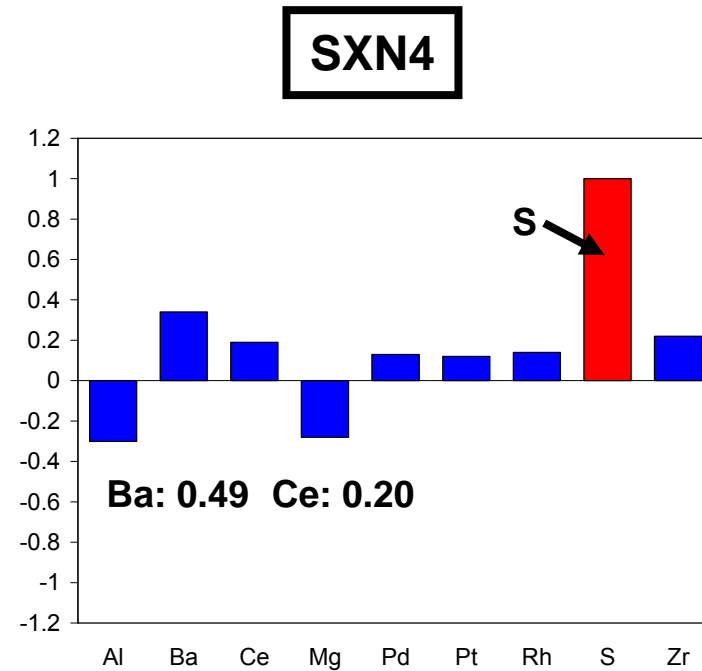
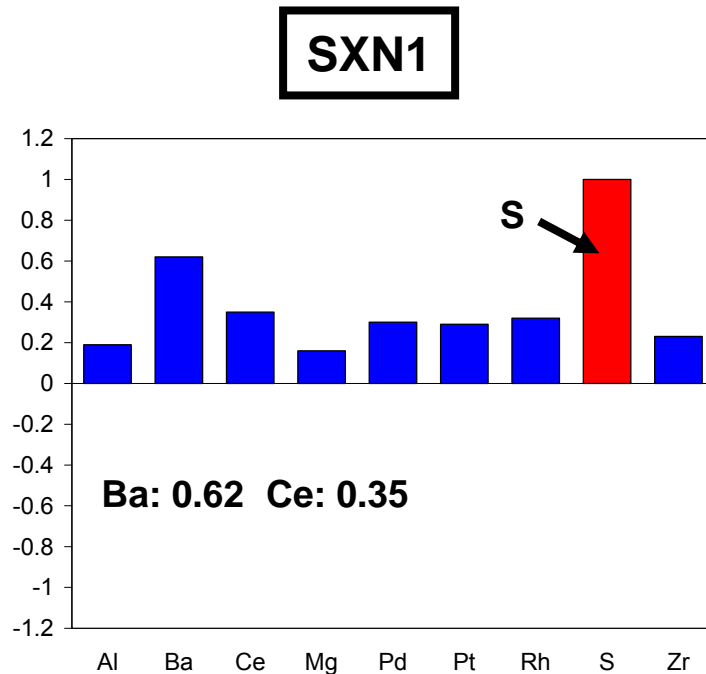
- **MgAl₂O₄**

- Consistent w/ WC compositional analyses (minor stand-alone Al)
 - ~90 g/L loading

- **CeO₂-ZrO₂**

- Appear to accommodate BaO (17 g/L) & PGM (3.5 g/L) acting as support (XRD confirms)
 - ~90 g/L loading with 9:1 atomic ratio based on WC compositional analyses

EPMA Cross-Correlation Analyses Indicate Highest Sulfur Sensitivity for Ba



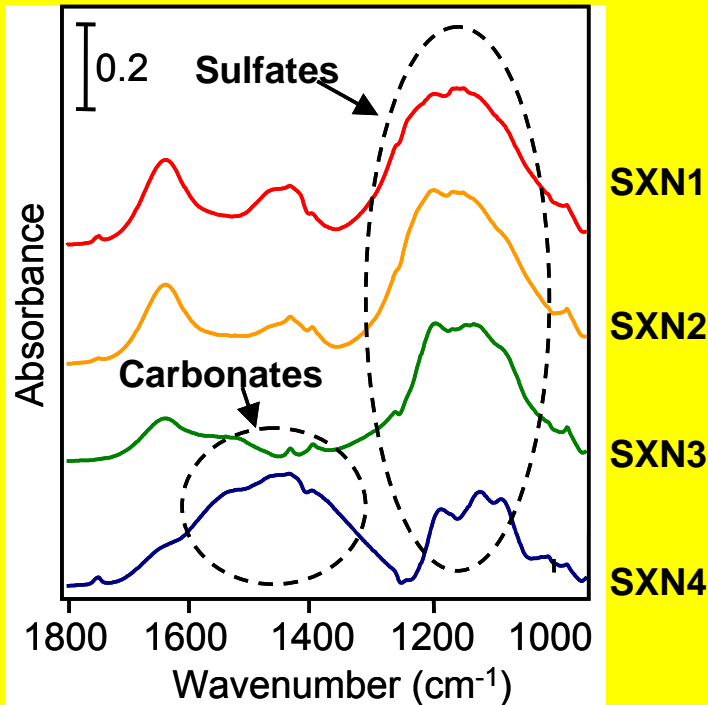
- **More S at catalyst upstream (SXN1) than downstream (SXN4)**
- **Sulfur sensitivity: Ba > Ce-Zr (> ?) Mg-Al**
 - Only Ba shows significant S correlation
 - Resolution does not allow discrimination between Ce-Zr & Mg-Al

Work in progress (e.g., different length scale analyses: Ba, Ce-Zr, Mg-Al, Al-rich areas etc.)

Sulfates are Dominant Surface S Concentrated at Upstream LNT Region

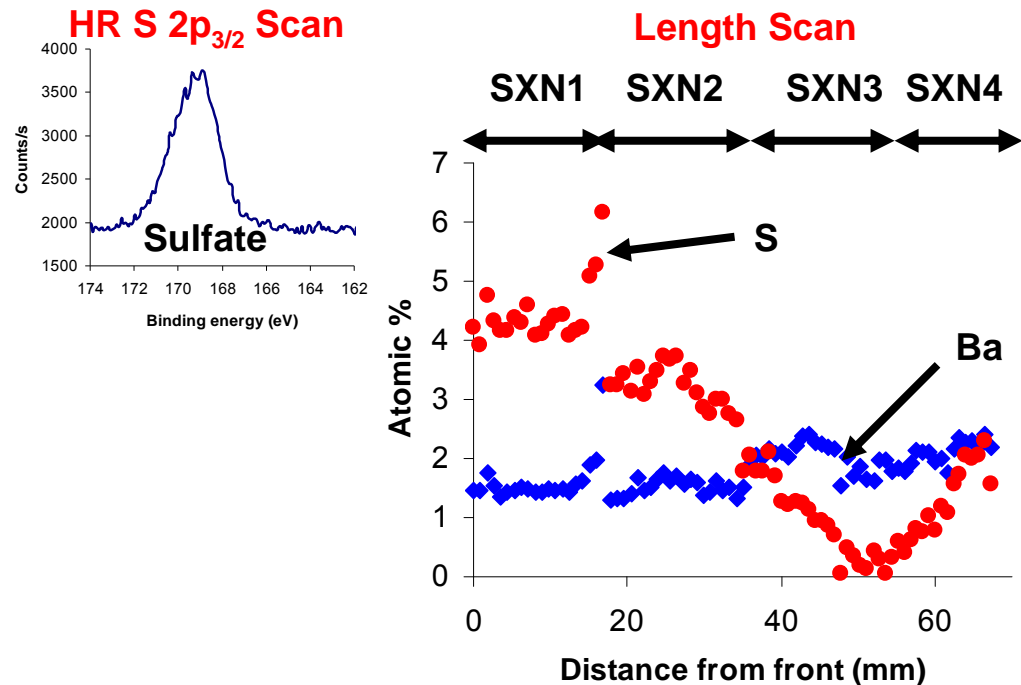
DRIFTS

(Diffuse Reflectance Infrared FT Spectroscopy)



XPS

(X-ray Photoelectron Spectroscopy)



- 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

Temperature Programmed Reduction (TPR) Reveals Different Sulfur Species

TPR of 3" Core



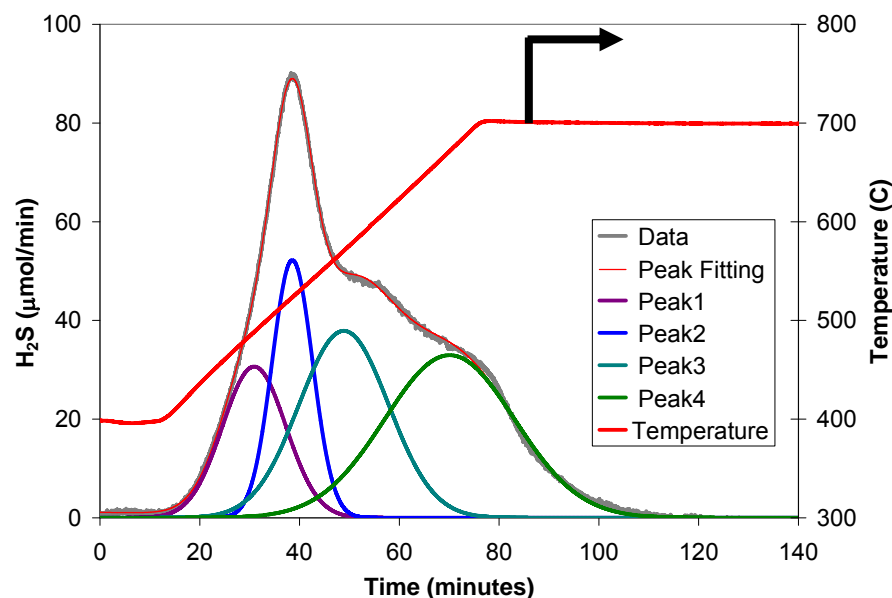
1% H₂, 5% H₂O, 5% CO₂, N₂ bal

SV = 30000 h⁻¹

T ramping rate = 5 °C/min

- **Four peaks deconvolved**
 - Low T (35% of total S):
Peak 1 at 492 °C; Peak 2 at 526 °C
 - High T (65% of total S):
Peak 3 at 571 °C; Peak 4 at 700 °C
- **From literature**
 - Low T peaks: Ce-Zr & Al₂O₃
 - High T peaks: Ba
- **Mg-Al contribution to low T peaks?**

Work in progress for identification



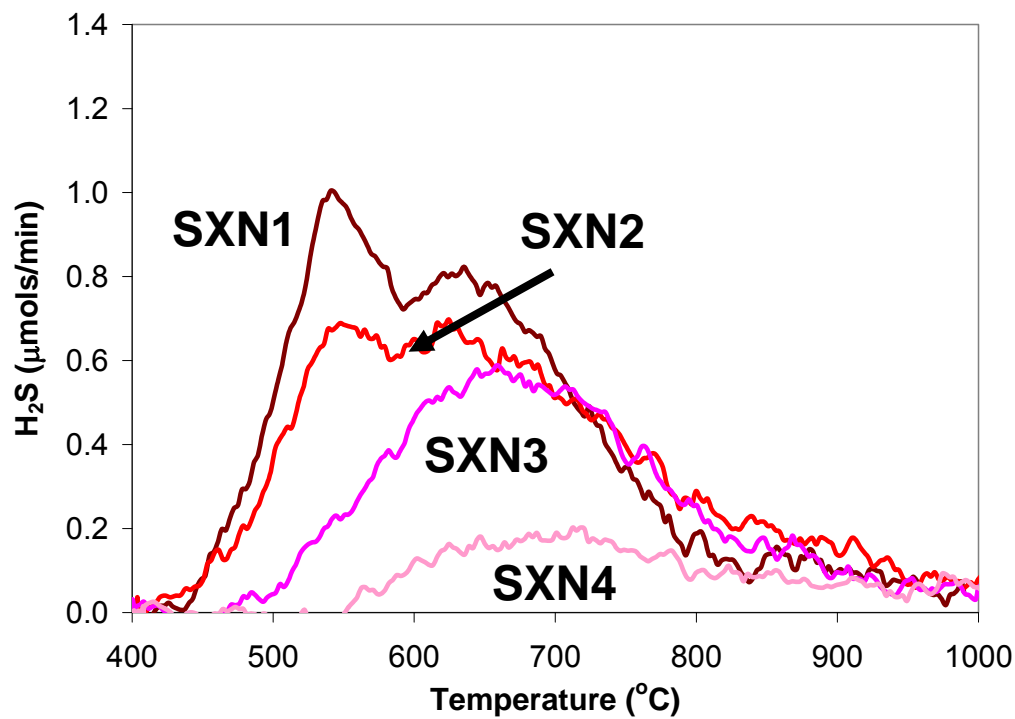
TPR of 4 Sliced SXNs Further Clarifies Nature & Axial Distribution of Sulfates Species

TPR of Four Sliced SXNs

Microreactor

In powder form

- Only high T peaks for SXNs 3&4
cf. Only NSR degradation (SpaciMS)
Ba S sensitivity (EPMA)
- Low T peaks decrease from SXN1
to SXN4
cf. OSC degradation only in SXNs 1&2



Tentative conclusion:

Low T peaks: $\text{CeO}_2\text{-ZrO}_2$, Al_2O_3 & maybe MgAl_2O_4 sulfates in SXNs 1&2
High T peaks: Ba sulfates in SXNs 1-4

Work in progress: peak deconvolution at each location, determination of DeS activation energy for each S species & TPR of standards

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, CeO₂-ZrO₂, Al₂O₃ (minor)
Ba is primary NO_x storage sites, CeO₂-ZrO₂ is support/OSC
 - Mg-Al (spinel likely)
What’s the role: 2nd NO_x storage? (basic but big particles & low PGM)

Sulfated state

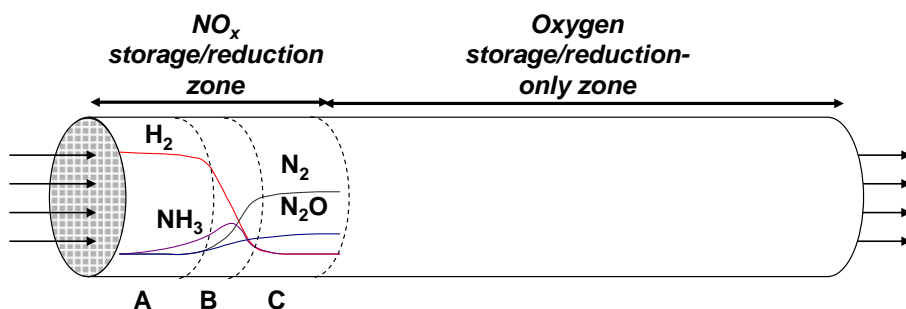
- NO_x storage sites (Ba) sulfation very efficient (“plug-like”)
 - Hard to DeS (high T necessary)
- OSC (Ce-Zr) sites inhibited but to a lesser extent
 - Easier to DeS (low T sufficient)
- Al₂O₃ sulfates
- More work needed to assess Mg-Al sulfation
 - Apparently low S sensitivity

Conclusions

Putting It All Together:

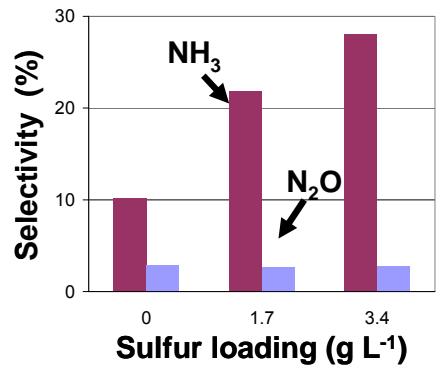
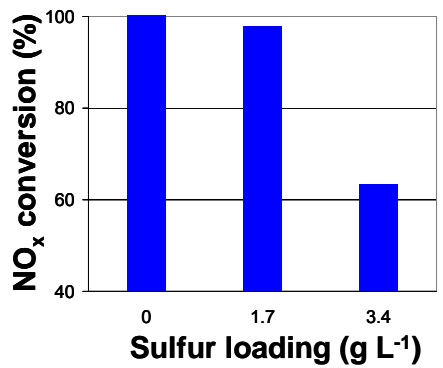
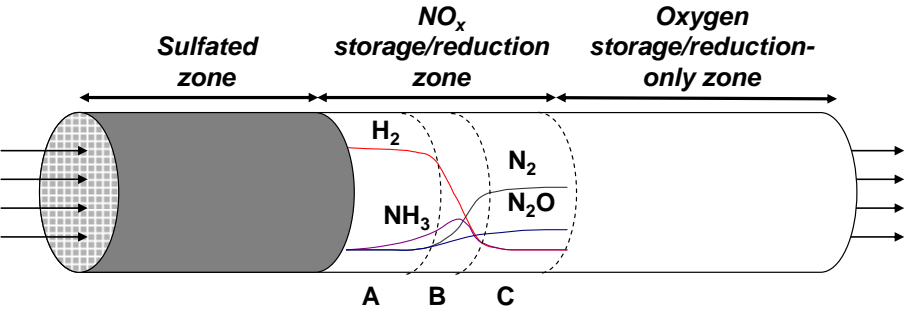
A Conceptual Model on the Functioning of a Commercial LNT at Varying Sulfation Levels

Conceptual LNT Model: Fresh State



- **Complex realistic LNT formulation uniformly washcoated on the monolith**
 - Two distinct domains
 - I. PGM, Ba, CeO₂-ZrO₂, Al₂O₃*
 - II. Mg-Al*
- **NSR localized at catalyst front**
 - Ba is the major NO_x storage sites
- **OSC evenly distributed throughout**
 - CeO₂-ZrO₂ (also serves as support for Ba and PGM phases)
 - Residual H₂ and NH₃ from NSR zone oxidized in OSR-only zone
- **Role of Mg-Al phases not clear**

Conceptual LNT Model: Sulfated State



Recently confirmed by direct NH₃ measurements inside the catalyst
cf. following talk by Bill Partridge

- 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: even less distributed?
 - 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
 - Ce-Zr+Al₂O₃+Mg-Al = ~35% S (“S trap”)
- 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 & NH₃ slip increases due to reduced OSC-only zone

Future Work

- **Complete the planned physicochemical analyses of Umicore sample**
 - EPMA & EDS analyses for elemental cross-correlations (Ba-S vs. Mg-Al-S)
 - XPS depth/length profiles of four sulfated SXNs
 - High-Resolution XPS to discriminate different sulfur species
- **Characterization of standard materials (CeO_2 , MgAl_2O_4 etc.) to help understand Umicore sample S/DeS behavior**
 - DRIFTS, TPR, EPMA, XPS
- **Desulfation mechanisms**
 - Kinetic data for the four sulfur species identified
 - Intermediate DeS & performance evaluation to further evaluate the roles of each sulfur species
- **Numerical modeling**
 - Microkinetic-based models in collaboration with R. Larson at SNL
 - Refinement with physicochemical & performance data
 - Sulfur impact

Acknowledgments

- **Research sponsored by DOE, Office of Vehicle Technologies**

- Program Managers: Ken Howden, Gurpreet Singh



- **Catalyst from Umicore**

- Owen Bailey



- **Useful discussion**

- Alex Yezerets, Neal Currier at Cummins
- Jim Parks at ORNL



- **Experimental assistance (ORNL)**

- Vitaly Prikhodko (bench reactor)
- Larry Walker, Harry Meyer (XPS, EPMA)



Thank You

Jae-Soon Choi

Oak Ridge National Laboratory
Energy & Transportation Science Division
Fuels, Engines & Emissions Research Center

865-946-1368

choijs@ornl.gov

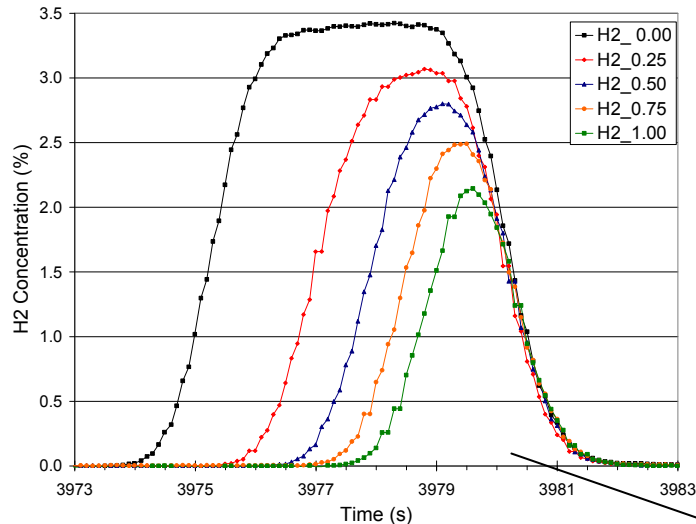
Additional Slides

SpaciMS H₂ Data Show NSR & OSC Distributions

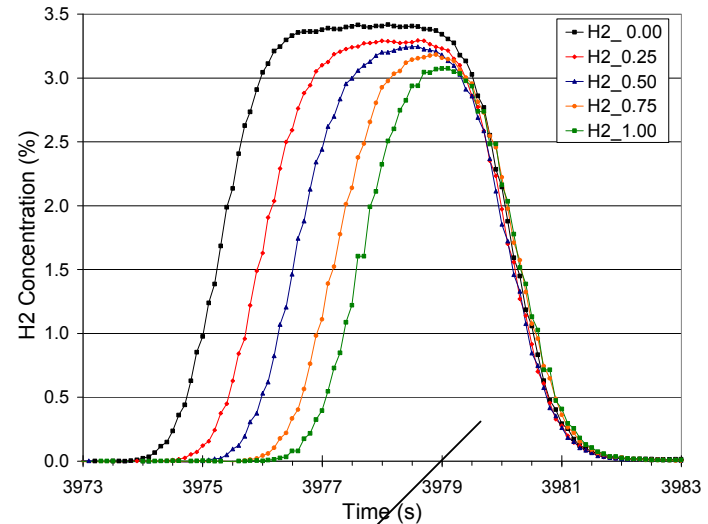
325 °C, 0 g S/L⁻¹

NSR: NO_x Storage/Reduction
OSC: Oxygen Storage Capacity

**NO+O₂ in lean phase
(NSR + OSC)**



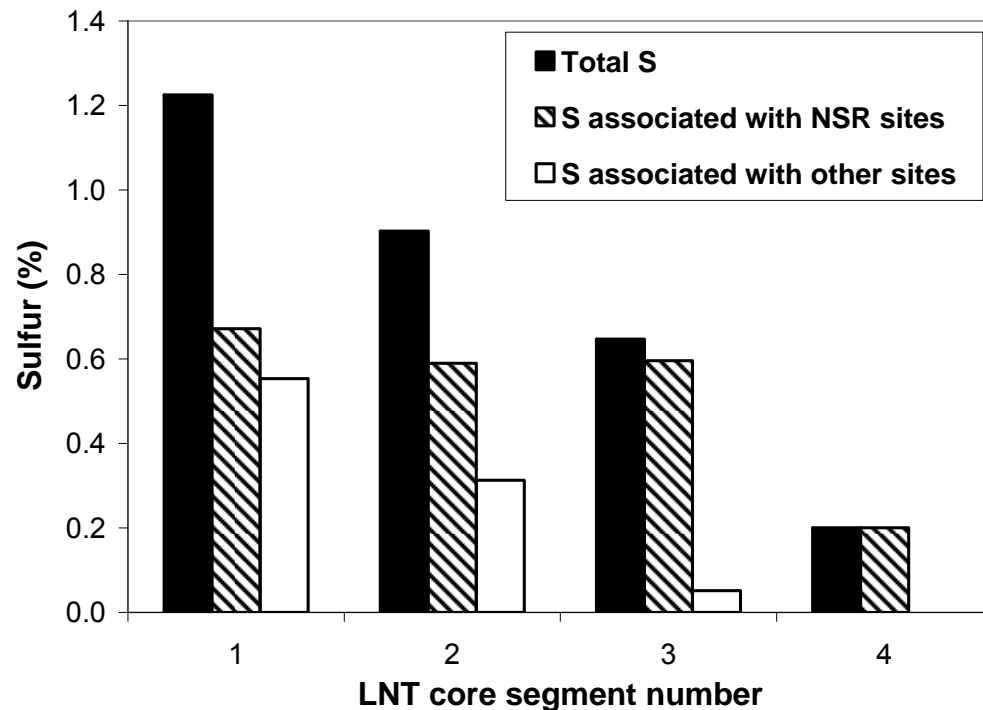
**O₂ in lean phase (no NO)
(OSC)**



- **NSR-attributable H₂ consumption = Total H₂ – OSC H₂ consumption**
- **More H₂ consumption in LNT front with NO+O₂ than with O₂ only**

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: CeO₂-ZrO₂ etc.**



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