Understanding the Distributed Intra-Catalyst Impact of Sulfation on Water Gas Shift in a Lean NO_x Trap Catalyst

Bill Partridge[1], Jae-Soon Choi[1], Josh Pihl[1], Todd Toops[1], Jim Parks[1], Nathan Ottinger[2], Alex Yezerets[2] , Neal Currier[2]

1: Oak Ridge National Laboratory

2: Cummins Inc

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U.S. DOE Program Management Team:
Ken Howden, Gurpreet Singh, Steve Goguen

U.S. DEPARTMENT OF ENERGY

Cummins

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Outline

- Background & Motivation
- Experimental Approach
- Sulfation Results
    - NSR: NO_x Storage & Reduction
    - OSC: Oxygen Storage Capacity
    - WGS: Water Gas Shift
- Global Conceptual Model
- Conclusions

Background

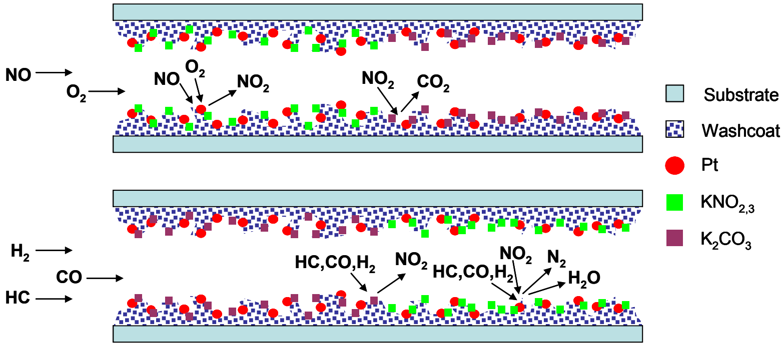
- **LNTs (e.g., Pt/Ba/Al_2O_3) operate in cyclic mode**
  - **LEAN-phase storage:**

    $2NO + 3/2O_2 + Pt + BaO$ ----> $Pt + Ba(NO_3)_2$

  - **RICH-phase reduction:**

    $5H_2 + Pt + Ba(NO_3)_2$ ----> $N_2 + 5H_2O + Pt + BaO$

  - **Internal spatial & temporal variations**

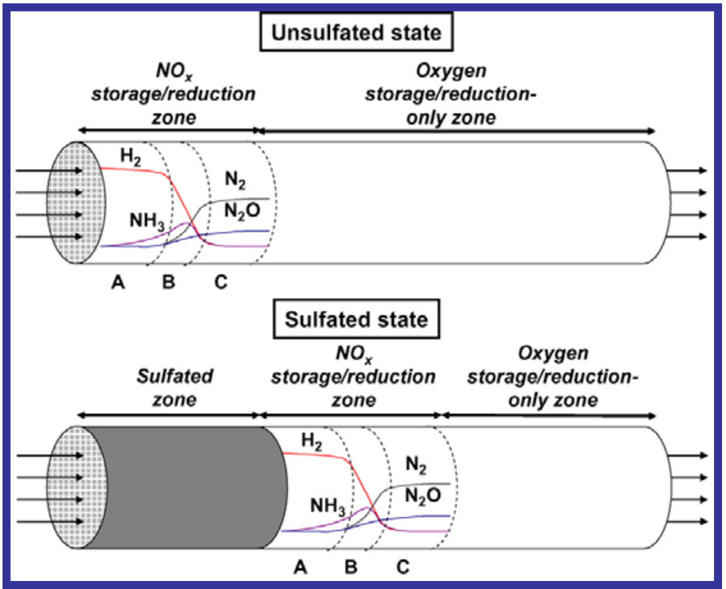


- **LNT catalysts are sensitive to sulfur poisoning**
  - **Sulfates more stable than nitrates:**

    $SO_2 + 1/2O_2 + Pt + BaO$ ----> $Pt + BaSO_4$

    $2NO + 3/2O_2 + Pt + BaSO_4 \cancel{\text{---->}} Ba(NO_3)_2 + Pt + SO_3$

  - **Sulfation changes reaction distributions**



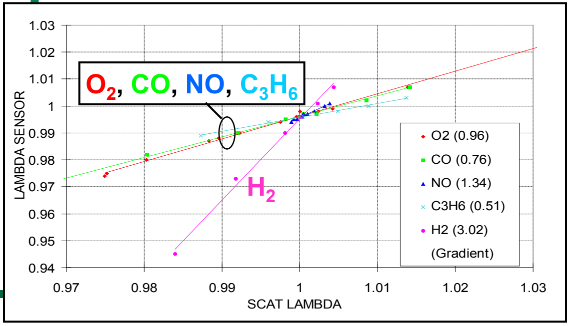
Choi, et al., Appl. Catal. B 77 (2007) 145.

- **High-temperature DeS can damage catalyst**
  - **Irreversible thermal aging: e.g., Pt sintering**
  - **Fuel penalty cost of process**

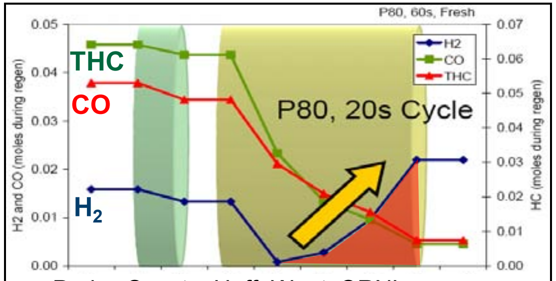
Motivation

- **Need to minimize high-T DeS events**
  - Basic control commands DeS too often and too long
- **WGS enables advanced control**
  - Cummins OBD Patent (US Patent App. 20080168824)
  - Active on-board assessment of catalyst state
  - Only DeS when & for as long as required
    - Better efficiency (lower fuel penalty)
    - Better durability (catalyst & engine last longer)

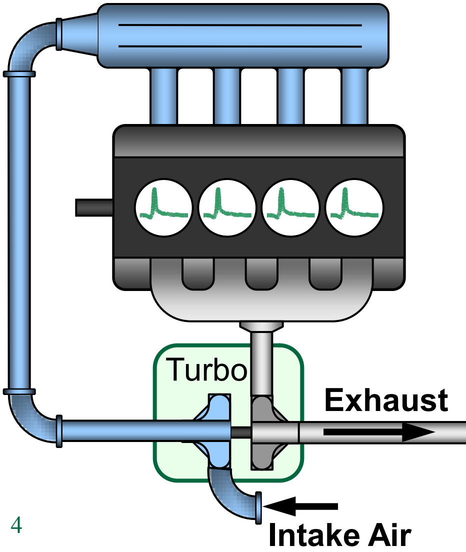
UEGO has unique H_2 cross sensitivity

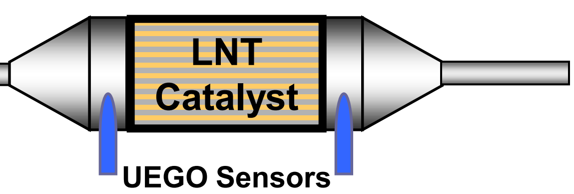


LNT WGS α Ageing

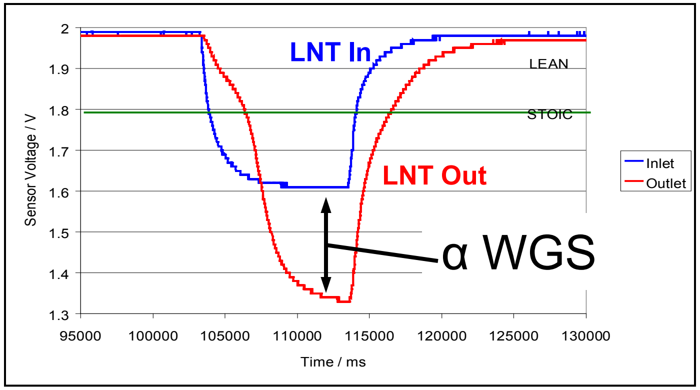


Parks, Swartz, Huff, West. ORNL.
DEER 2006, August 20-24, 2006, Detroit, MI





UEGO Signal α WGS



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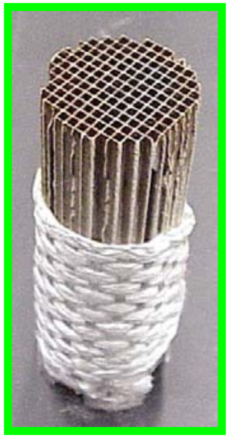
Approach: Controlled Bench Reactor Experiments with Spatially & Temporally Resolved Gas Analyses

Model LNT Catalyst

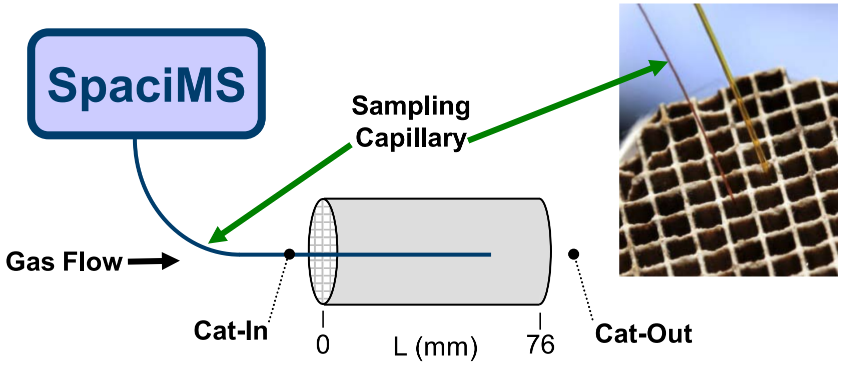
- Substrate: 300-cpsi cordierite
- Washcoat: Pt/Ba/Al_2O_3
- No Oxygen-Storage Capacity (OSC) such as Ce
- Evaluated as a 3/4” x 3” core



Procedure

- **Baseline: *0 g/L S***
- Performance evaluation
  Neutral; OSC; NSR
- **1st S dosing: *0.85 g/L S***
- Performance evaluation
  Neutral; OSC; NSR
- **2nd S dosing: *<1.7 g/L S***
- Performance evaluation
  Neutral; OSC; NSR
- Post mortem analysis
  DRIFTS
  Micro Reactor

In Situ Intra-Channel Speciation



Systematically Vary WGS Competition for CO Reductant

- **WGS converts CO to H_2 via:** **$CO + H_2O \rightarrow H_2 + CO_2$**
- **Lean-phase composition dictates CO reaction possibilities**
  - NSR: WGSR vs. OSC vs. LNT regeneration
  - OSC: WGSR vs. OSC
  - Neutral: WGSR only

	RICH (5s)		**LEAN (60s)**		
	CO	**H_2O**	**NO**	**O_2**	**H_2O**
NSR	**2%**	**5%**	**300ppm**	**10%**	**5%**
OSC	**2%**	**5%**	**0**	**10%**	**5%**
Neutral	**2%**	**5%**	**0**	**0**	**5%**

- **Fast Cycling** (60:5-s lean:rich cycling)
- **Temperature:** 325°C

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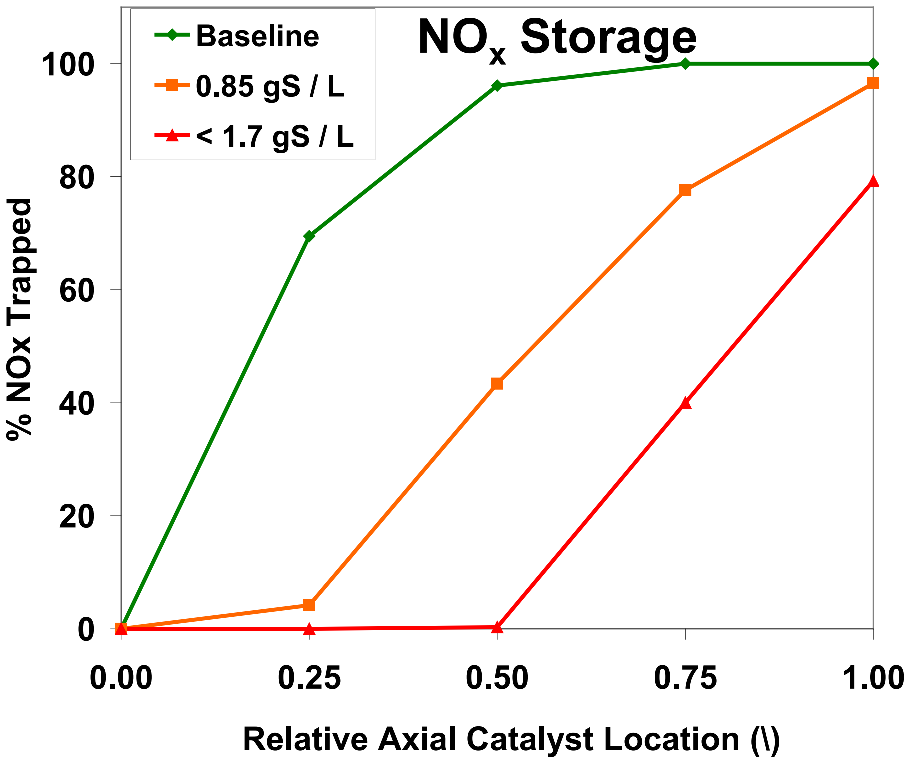
Sulfation Progressively Poisons NSR in Plug-Like Fashion

NSR Cycling



Baseline (0 gS / L$_{cat}$):

- NSR in front ½
- Back ½ unused

1st Sulfation (0.85 gS / L$_{cat}$):

- Front ¼ inactive
- NSR in back ¾

2nd Sulfation (<1.7 gS / L$_{cat}$):

- Front ½ inactive
- NSR in back 1/2

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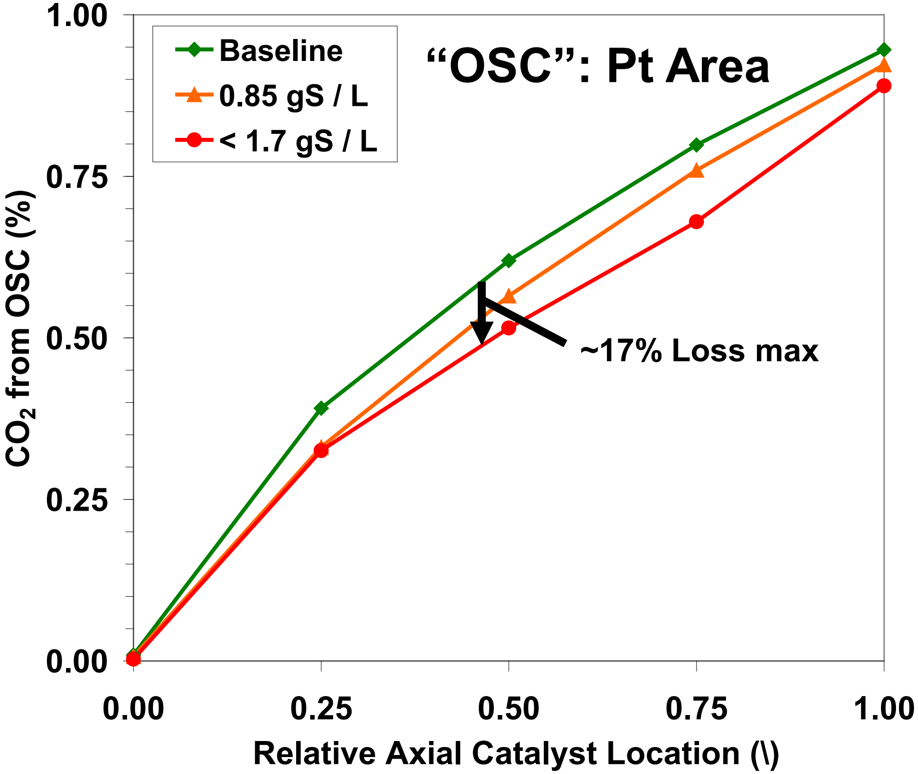
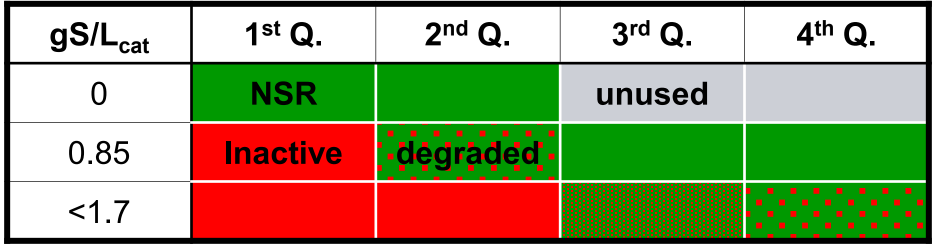
Sulfation Has Little Impact on "OSC"

OSC Cycling



Qualitative Pictorial Representation of NSR Activity



gS/L_{cat}	1st Q.	2nd Q.	3rd Q.	4th Q.
0	NSR	🟩	unused	
0.85	Inactive	degraded	🟩	🟩
<1.7	🟥	🟥	▨	▨

- **OSC due to Pt redox**
  - No Ce or support OSC
  - ~ active Pt area
- **OSC ~ uniform along catalyst**
  - i.e., uniform Pt distribution
- **Minor sulfation impact on OSC**
  - ~3-17% loss max
  - minor OSC on Ba?
- **OSC active in sulfated zone**
  - *Pt remains S free cf. poisoned NSR!*
  - Can change input to NSR zone

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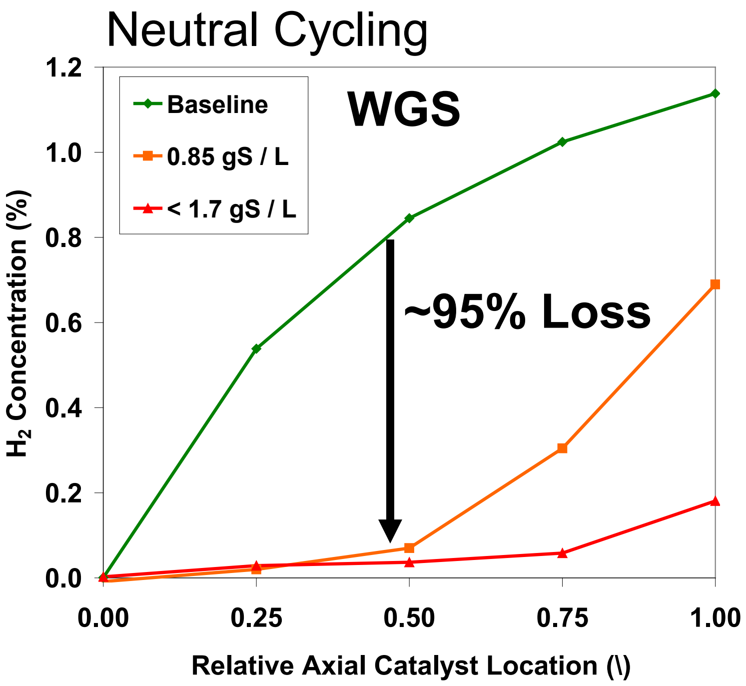
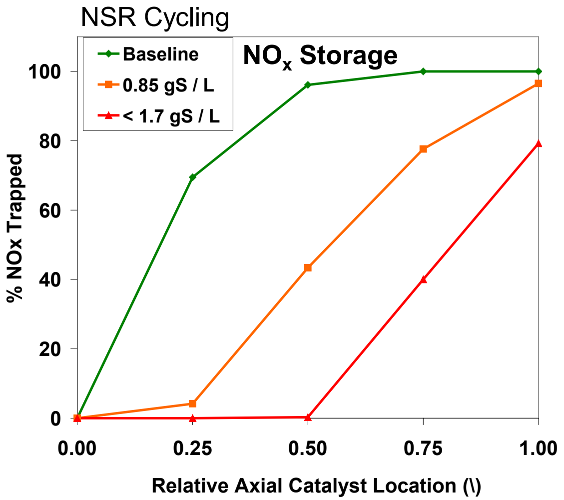
WGS Very Sensitive to Sulfur Degradation


Neutral Cycling


NSR Cycling

Baseline (0 gS / L_{cat}):

- WGS throughout

1st Sulfation (0.85 gS / L_{cat}):

- Front ½ : “Max” degradation
- ~90-95% loss from Baseline
- WGS in back ½

2nd Sulfation (<1.7 gS / L_{cat}):

- Front 3/4 : “Max” degradation
- WGS in back ¼

WGS S-front leads NSR S-front

- by ~ ¼ catalyst

WGS inactive upstream of NSR

WGS more sensitive to S than NSR

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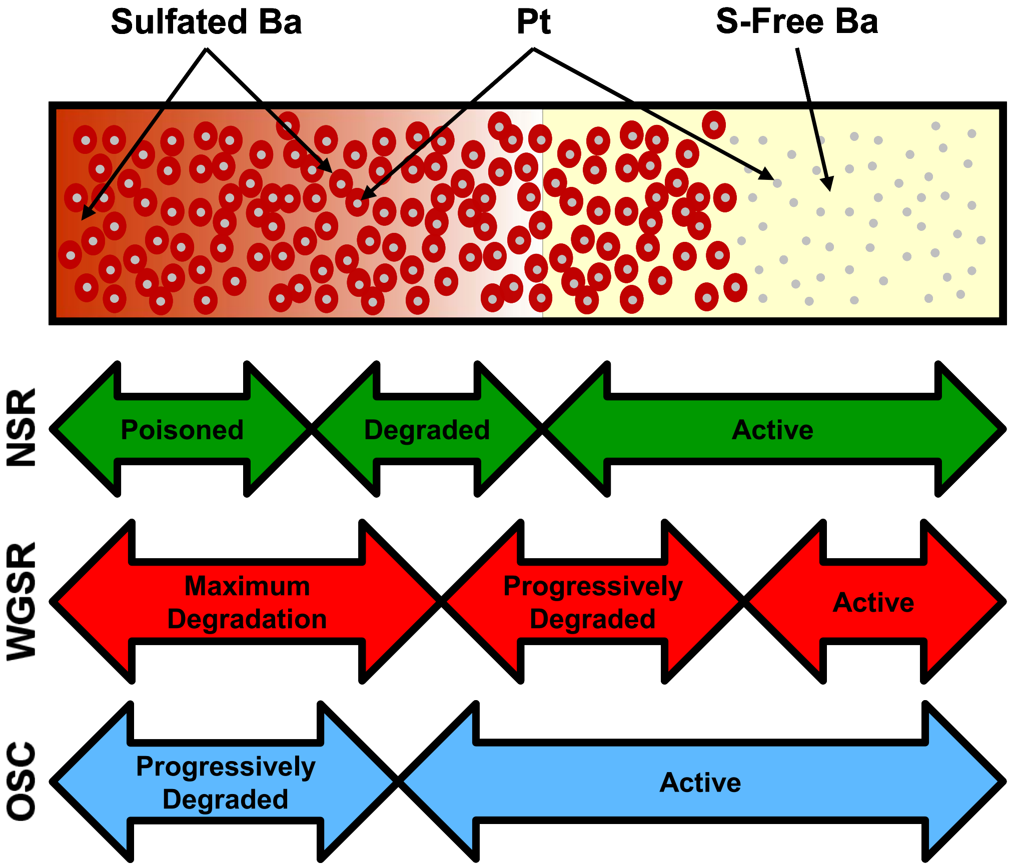
Global Model of Distributed S Impact on NSR, WGS & OSC

- **Fully active in S-free zone**

- **Initial Sulfation:**
  - WGS very sensitive to S - probably due to changes in Pt-support interface structure
  - NSR insensitive due to spillover, surface diffusion and $NO_{2,gas}$ accessing S-free Ba in field

- **Progressive Sulfation:**
  - Further incremental WGS degradation to max
  - Progressive NSR degradation as field Ba is sulfated
  - Ultimate NSR poisoning
  - Minor OSC degradation



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Conclusions

- **WGS occurs on Ba LNT catalysts** (not just Ce-containing catalysts)

- **Each LNT function has a different response to sulfation**
  - WGS: very sensitive to initial S
  - NSR: Progressively degraded and poisoned
  - OSC: Minor degradation

- **The S distribution is different w.r.t. each LNT function**

- **Conceptual model of distributed S impact on different LNT functions**

- **So what:**
  - Improved understanding of LNT sulfation
  - Enable better models and catalyst system design (device size/capacity)
  - Enable improved OBD & control (cf. Cummins Control Patent)
  - ***Better emissions control, efficiency & durability***

Acknowledgments

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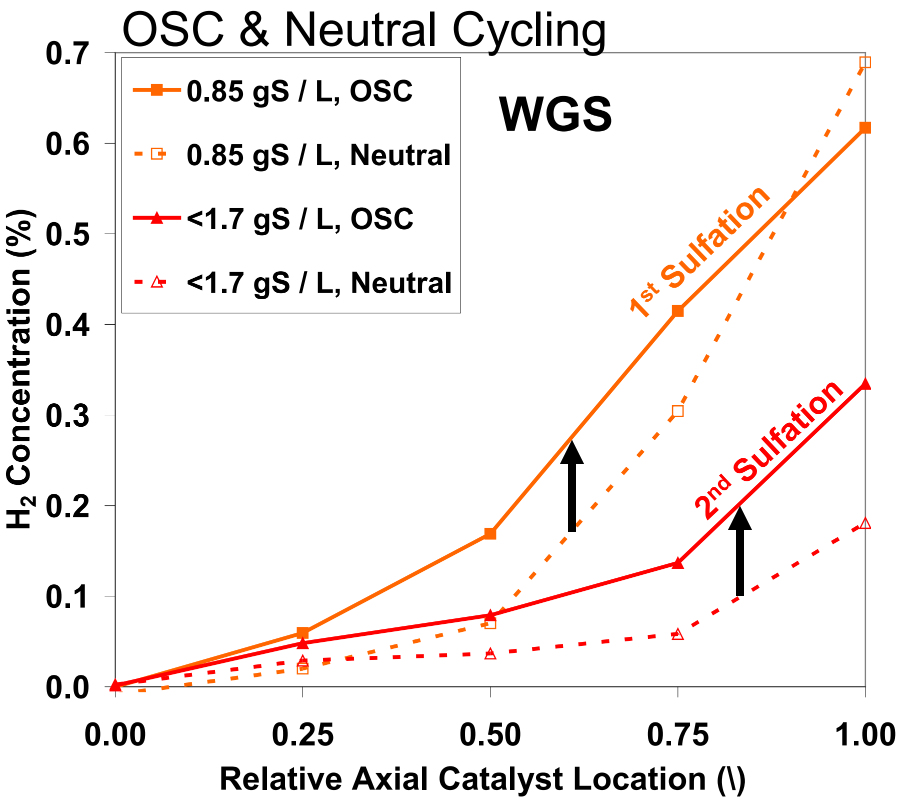
Ken Howden, Gurpreet Singh, Steve Goguen

Thank You

Bill Partridge
865-946-1234
partridgewp@ornl.gov

How does Sulfur Degrade WGS?

Oxygen Mitigates Sulfur Degradation of WGS



OSC enhances WGS in Sulfated states

- ~5-10% gain vs. Neutral
- Little recovery vs. ~95% loss w/ Sulfation

O_2 readily displaces S from Pt

- S_{gas} adsorbs on Pt during rich
  - Based on DRIFTS measurements
  - Fridell et al., Topics in Catal. V16/17, 133, 2001
- Pt is S free in OSC fast-cycling conditions
- O_2 improves WGS by desorbing S from Pt

S adsorption on Pt has minor impact on WGS degradation

Other non-Pt-S route accounts for primary WGS S-degradation

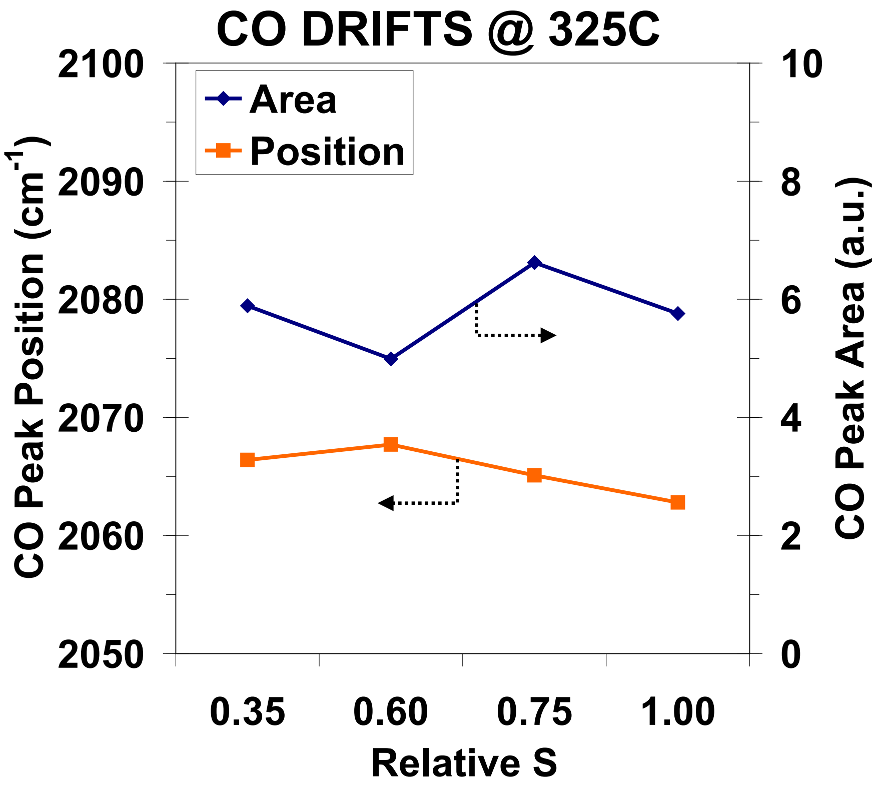
Does S Degrade WGS by Changing Pt Electronic Structure?

S doesn't change Pt-CO affinity

- cf. flat CO peak position
- Pt electronic density ~ constant

Pt sites are available

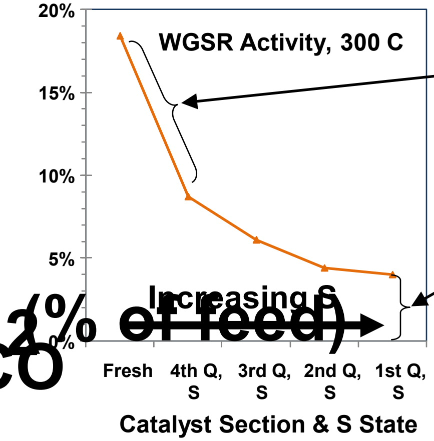
- cf. flat CO peak area
- consistent w/ other observations showing that Pt is available



Maybe initial S is detrimental to Pt-support\Ba interface

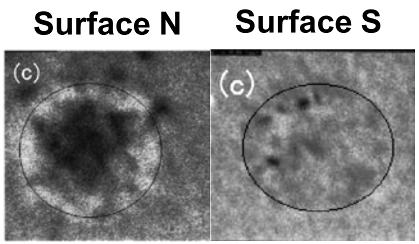
- Not yet verified for Pt\Ba\Al_2O_3 catalyst
- But,…Pt\Ce extensively studied for WGS & Reverse WGS
- &…common theme is *importance of metal-support interface* & activation on Pt

S May Concentrate or Minute S is Detrimental to Interface Structure Necessary for WGSR



Nonlinear S impact on WGS

- Small initial S dose has major impact on WGS (Fresh vs. 4th Q)
  - 4th Q has significant NOx capacity
- S has significant but *limited* impact
  - i.e., non-zero asymptote



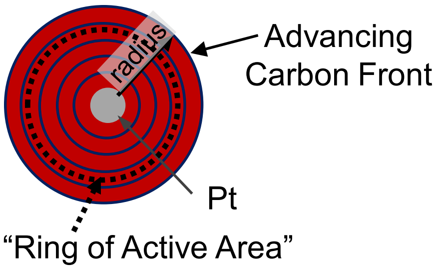
Sakamoto et al., J of Catal. 238, 361, 2006

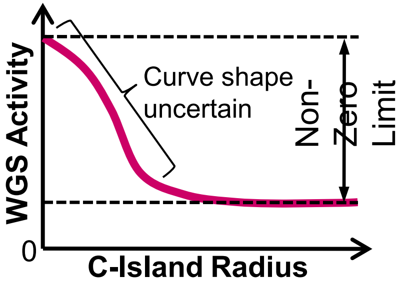
Different N & S deposition

- N goes through Pt
  - N concentrated around Pt
- S goes down everywhere
- Lean will oxidize S on Pt
  - Likely deposited close to Pt
  - *May concentrated S around Pt*

Goguet Model of WGS Carbon Poisoning

(Goguet et al., J. Phys. Chem. B 108, 20240, 2004)

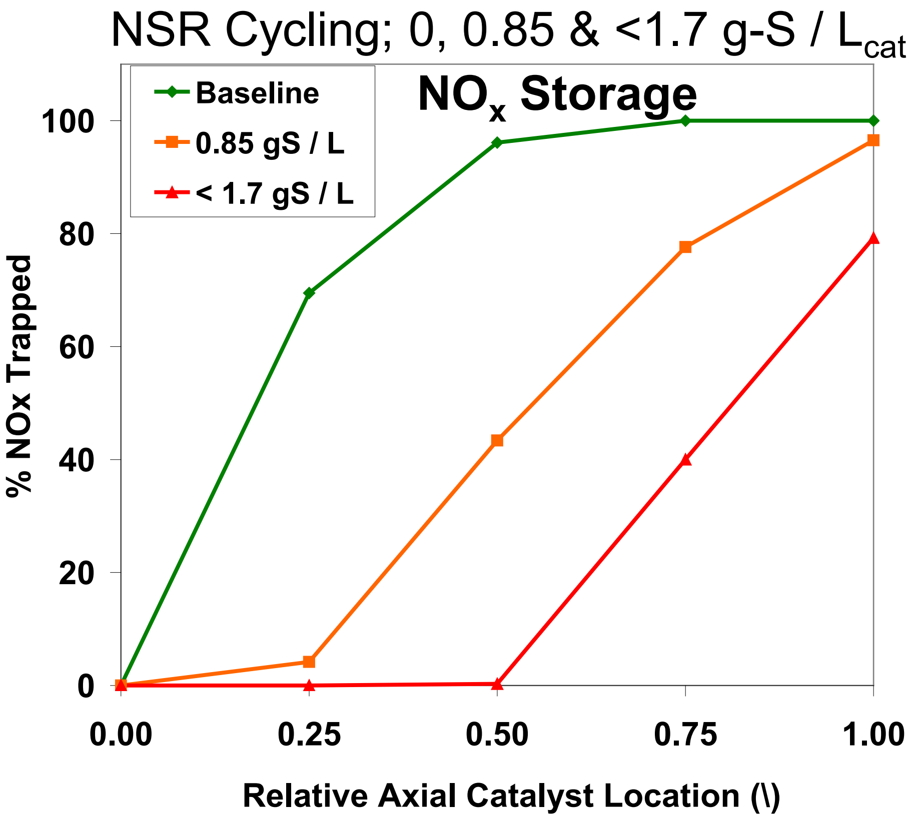




- C forms at Pt
- C island grows around Pt
- Proximal C impacts WGS
- No impact of distal C
- *Looks like S impact*

We don’t yet know……Further fundamental research needed

Sulfation Progressively Poisons NSR in Plug-Like Fashion



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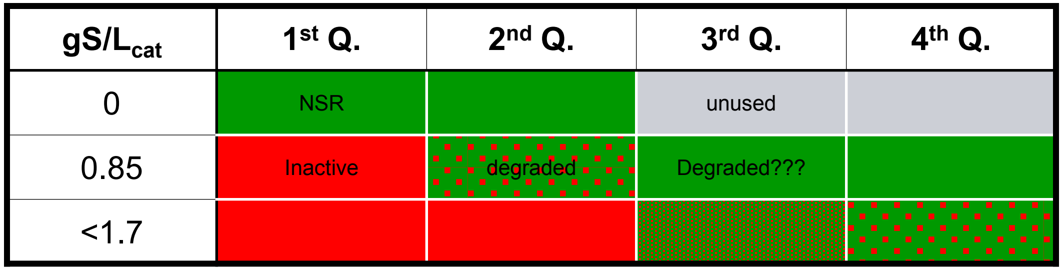

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0.85	🟥 Inactive	▨ degraded	🟩 Degraded???	🟩
<1.7	🟥	🟥	▨	▨

Baseline (0 gS / L$_{cat}$):

- NSR in front ½
- Back ½ unused

1st Sulfation (0.85 gS / L$_{cat}$):

- Front ¼ inactive
- NSR in back ¾
- Broadened NSR zone

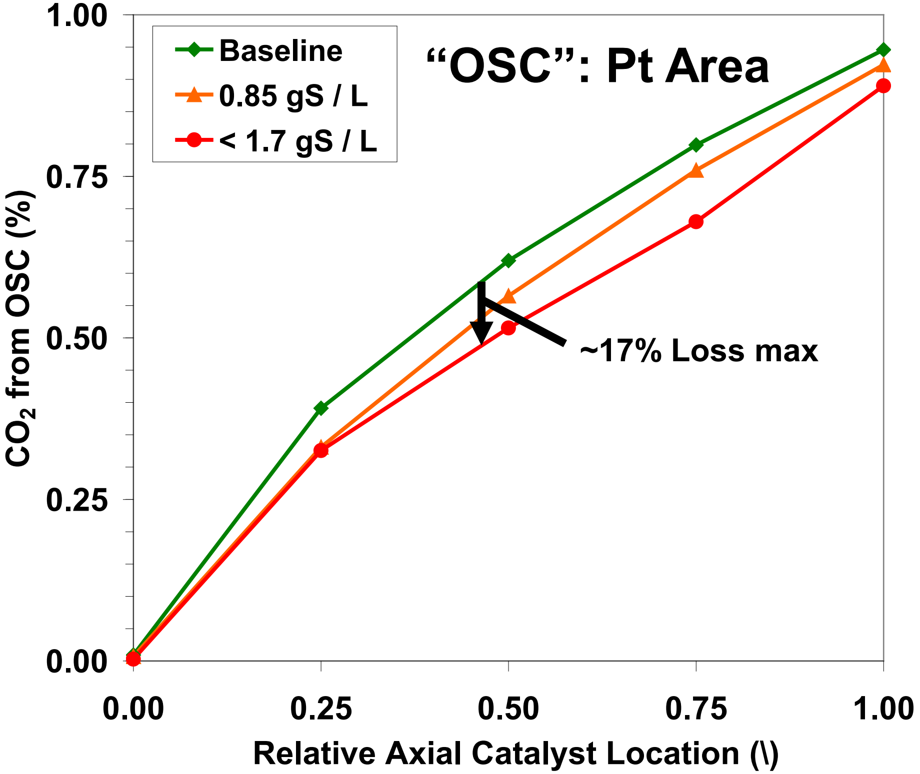
  (not perfectly “plug like”)

2nd Sulfation (>1.7 gS / L$_{cat}$):

- Front ½ inactive
- NSR in back 1/2

Sulfation Has Little Impact on “OSC”

OSC Cycling



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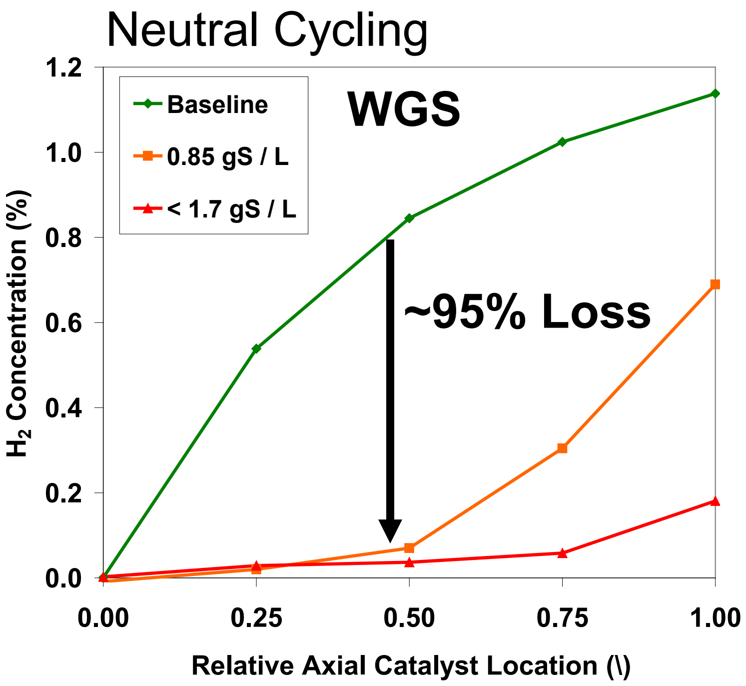

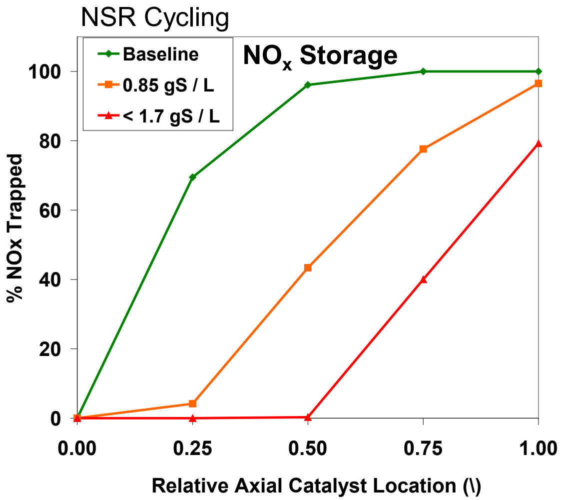

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WGS S-front leads NSR S-front

- By ~ ¼ catalyst
- WGS & NSR S degradation differs

WGS more sensitive to S than NSR