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

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Background

- Intra-catalyst measurements clarify LNT chemistry
 - Sulfation impact on spatiotemporal:
 - NO_x storage/regeneration, oxygen storage capacity, & and NH₃ Slip
 - NH₃ formation and utilization during regen
- Previous SpaciMS work on WGS in LNT
 - Choi, Partridge, Epling, Currier, Yonushonis, Catal. Today 114, 102, 2006
 - Based on Pt/K/Al₂O₃ EmeraChem LNT
 - Neutral, OSC, NSR cycling w/o sulfation
 - Assessed WGS contribution to LNT regeneration
- WGS relevant to Cummins OBD Patent (US Patent App. 20080168824)
- <u>GOAL</u>:
 - Clarify spatiotemporal sulfation impact on WGS
 - Expand conceptual model of LNT sulfation
 - Provide information relevant to catalyst and OBD development







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



Model LNT Catalyst

- Substrate: 300-cpsi cordierite
- Washcoat: Pt/Ba/Al₂O₃
- No Oxygen-Storage Capacity (OSC) such as Ce
- Evaluated as a 3/4" x 3" core

Bench Reactor



DRIFTS Reactor



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*Spatially Resolved Capillary Inlet Mass Spectrometer

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
 - Neutral: WGSR only
 - OSC: WGSR vs. OSC
 - NSR: WGSR vs. OSC vs. LNT regeneration

	RICH (5s)		LEAN (60s)		
	СО	H ₂ O	NO	O ₂	H ₂ O
Neutral	2%	5%	0	0	5%
OSC	2%	5%	0	10%	5%
NSR	2%	5%	300ppm	10%	5%

• **Fast Cycling** (60:5-s lean:rich cycling)







Experimental Procedure:

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



- SO₂ slip during 2nd S dosing ⁴
 - S expected in back of catalyst
 - <1.7 g/L sulfur stored</p>

- lower S capacity than Umicore GDI LNT
 - Umicore: BaO=17 g/L
 - Captured 40-ppm SO2 for 2hr
 - Ba-Model LNT: BaO=15 g/L





Ceria Is the Prominent WGS Promoter

Pt/Ceria extensively studied for WGS & Reverse WGS, e.g.:

- Goguet, Meunier, Tibiletti, Breen & Burch, J. Phys. Chem. B 108, 20240, 2004
- Luo & Gorte, Catal. Letters 85, 139, 2003
- Jacobs, Davis, Appl. Catal. A General 333, 192, 2007
- Many, many more; fundamental & applied; SO₂ poisoning...
- Common theme is importance of metal-support interface & activation on Pt
- Previous work w/ Pt/K/Al₂O₃ catalyst showed WGS activity

Barium appears to promote WGS

- ~3.5x gain from $Pt Ba Al_2O_3$ vs. $Pt Al_2O_3$
 - not implying Ba is comparable to Ce







NSR Response to Sulfation





Sulfation Progressively Poisons NSR in Plug-Like Fashion



Relative Axial Catalyst Location (\)

Qualitative Pictorial Representation of NSR Activity							
gS/L _{cat}	1 st Q.	2 nd Q.	3 rd Q.	4 th Q.			
0	NSR		unused				
0.85	Inactive	degraded	Degraded???				
<1.7							

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Baseline (0 gS / L_{cat}):

- NSR in front $\frac{1}{2}$
- Back ½ unused

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

- Front ¼ inactive
- NSR in back ³/₄
- Broadened NSR zone (not perfectly "plug like")

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

- Front ½ inactive
- NSR in back 1/2



OSC Response to Sulfation





Sulfation Has Little Impact on "OSC"



- OSC is due to Pt-site oxidation & reduction
 - No Ce or support OSC
 - Measures active Pt area
- OSC ~ uniformly distributed along catalyst
 - i.e., uniform Pt distribution
- OSC active in NSR-sulfated zone

Minor sulfation impact on OSC

- ~3-17% loss relative to Baseline
- ~ follows NSR poisoning
- Morphology changes around some Pt sites?
- Minor oxidation & reduction at Pt-Ba interface or Ba-Peroxide?



WGS Response to Sulfation





WGS Very Sensitive to Sulfur Degradation



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 (~ Baseline activity)

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 S degradation differs

WGS more sensitive to S than NSR



Oxygen Mitigates Sulfur Degradation of WGS





OSC reduces WGS at Baseline

OSC enhances WGS in Sulfated states

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

OSC gain @ max S degradation front

- Front ½ for 0.85 gS/L case
- Middle ½ for <1.7 gS/L case

OSC S mitigation is minor

Pt desulfation.....

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

Pt-support interface.....



Oxygen Readily Displaces S from Pt





Oxygen rapidly displaces S from Pt

Fast (<sec.) process

Mobile surface S slowly re-poisons Pt

OSC enhances WGS by freeing Pt of S

Pt-S is not major S degradation path

Carbon can also slowly degrade WGS

- This is separate from S degradation
- But OSC will rapidly remove C too

Carbon degrades via Pt-support interface

- Goguet et al., J. Phys. Chem. B 108, 20240, 2004
- C forms in a disk around the Pt
- Degrades "ring of active area" surrounding Pt
- Suggests similar mode for S degradation

WGS Very Sensitive to Sulfation of Pt-Support Interface

DRIFTS CO peak area and position doesn't trend w/ S level

- Pt sites are available (c.f. OSC)
- Pt electronic density & Pt-CO affinity not varying

S has nonlinear impact on WGS

- Small initial S dose has a major impact on WGS (Fresh vs. 4th Q)
- 4th Q has significant NO_x capacity

Growing S Disk Conceptual Model for WGS Degradation

- S disks or islands grow around Pt sites
- Impact support at interface & near Pt
- Inhibition of spillover between Pt and oxides
- Blocking of Pt-support interfacial sites
- CO or H₂O activation (Pt e⁻ density change)
- WGS more sensitive than NSR to S growth







Global Model of S Impact on NSR, WGS & OSC

- Fully active in S-free zone
- WGS sensitive to initial S
- O₂ keeps Pt S free in fast cycling
- S-islands grow around Pt sites
 - Progressive WGS degradation
 - NSR insensitive to initial S
 - × Due to surface N mobility?
 - × S-free Ba exists in field
 - Progressive NSR degradation
 - WGS degradation max
 - Field sulfation begins
- Field sulfation continues
 - NSR becomes poisoned
 - Fixed WGS degraded to max
 - Progressive minor OSC degradation
 - × Due to minor Ba-peroxide?







Conclusions

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

Sulfation impacts various LNT reactions

- NSR: Progressively degraded and poisoned
- OSC: Minor degradation
- WGS: Progressively degraded to non-zero max
- S impacts various LNT functions differently
- WGS is very sensitive to S
 - WGS S-degrdation front leads NSR by ~ $\frac{1}{4}$ catalyst
- Exhaust O₂ keeps Pt S free
 - WGS S-degradation not due to Pt-S
- Conceptual Growing-S-Island model impacts support at interface &near Pt
- So what:
 - Improved understanding global impact of sulfation on LNT functions
 - Enable better models and catalyst system design (device size/capacity)
 - Enable improved OBD & control (cf. Cummins Control Patent)
 - Better emissions control & efficiency





Sponsor:

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Thank You

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