Distributed Impact of Sulfation on LNT Catalyst Reactions

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Focus is on Spatial Nature of LNT Sulfation

Background and Motivation:

- **Sulfation details of strong interest to OEMs**
  - **Feedback from CLEERS Workshops and Focus Meetings**
  - **Recent CLEERS priority polling**
  - **ORNL CRADA interests**
- **Previous engine-based sulfation studies w/ high-S diesel show plug-like loss of NO_x capacity**
  - **Other works suggest both distinct and distributed S-front**

Goals:

- **Measure spatial nature of sulfation – plug or distributed**
- **Evaluate impact of sulfation on nitrogen selectivity**
- **Identify sulfur species involved in desulfation**

Experimental Approach

- **Catalyst: Umicore GDI LNT (CLEERS Reference)**
  - 7/8” x 3” x 625cpsi core, CLEERS degreened
  - Further degreened before starting S/DeS study
    (NSR short cycling at 550 C for 5 h)
- **Measurements & Analytical Techniques Applied:**

Technique	Location	Species	Probe Size
Chemi.	Cat. Out	NO, NO_x	n/a
FTIR	Cat. Out	NH_3, N_2O, NO_2	n/a
SpaciMS	Intra-cat.	H_2, NO_x, H_2S, SO_2, COS	150-μm O.D.
Thermocouple	Intra-cat.	T	250-μm O.D.

- **Procedure:**
  1. Performance evaluation (short NSR & OSC)
  2. 1st S dosing, continuous S dosing w/ short NSR cycling
  3. Continue short NSR w/o S dosing for 30 min (SO_2 purging)
  4. Performance evaluation (short NSR & OSC)
  5. 2nd S dosing, repeat 2 thru 4
  6. Desulfation by TPR (325 to 700 C at 5 C/min)
  7. Repeat 1 thru 6

Conditions for LNT Bench Performance Evaluation

T=325 °C, SV=30000 h^{-1} (total flow=13354 sccm)

NSR
Short Cycling

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

OSC
Short Cycling

Lean (storage)	**60 s**	0 ppm	10%	0%	5%	5%	Bal
Rich (regeneration)	**5 s**	0 ppm	0%	3.4%	5%	5%	Bal

TPR
DeSulfation

Rich T: 325-700C	**n.a.**	0 ppm	0%	0.1%	5%	5%	Bal

4 Consecutive S/De-S Cycles Performed

#	[SO2] (ppm)	Exposure Time (h)	Total S Loading (g/L)	Note
1	20	2+4	5.1	H2/CO for short NSR; long NSR performed
2	40	1+1	3.4	
3	40	1+1	3.4	OSC performed; longer soak time for deS
4	20	2+2	3.4	OSc performed

Results similar for all studies

Here we focus on the 4th S/De-S cycle

Sulfation Results to be Discussed

- Nitrogen Selectivity
- NO_x Storage and Reduction, NSR
  - Spatiotemporal NO_x profiles
  - Spatiotemporal H_2 profiles
- Oxygen Storage Capacity, OSC
  - Spatiotemporal H_2-consumption\OSC profiles
- Reaction exotherms
  - Spatiotemporal Temperature profiles
- TPR DeSulfation
- Conceptual model of NSR Sulfur Effects

Outline of Sulfation Results

- **Nitrogen Selectivity**
- NO_x Storage and Reduction, NSR
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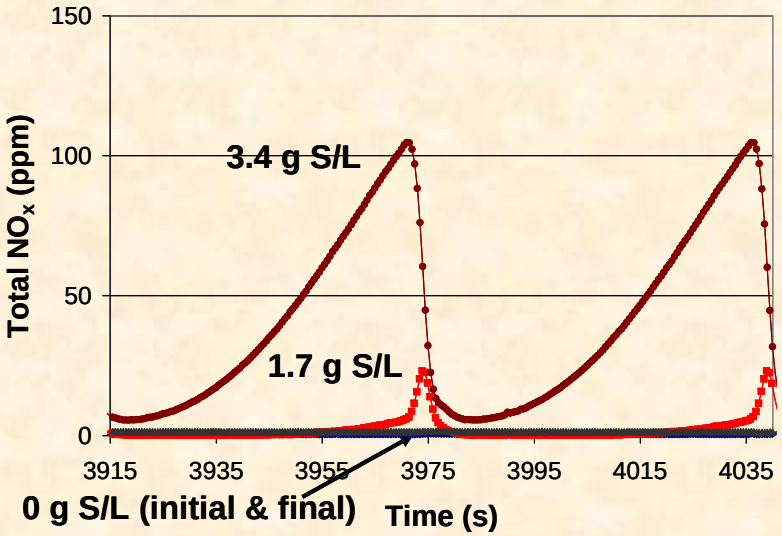
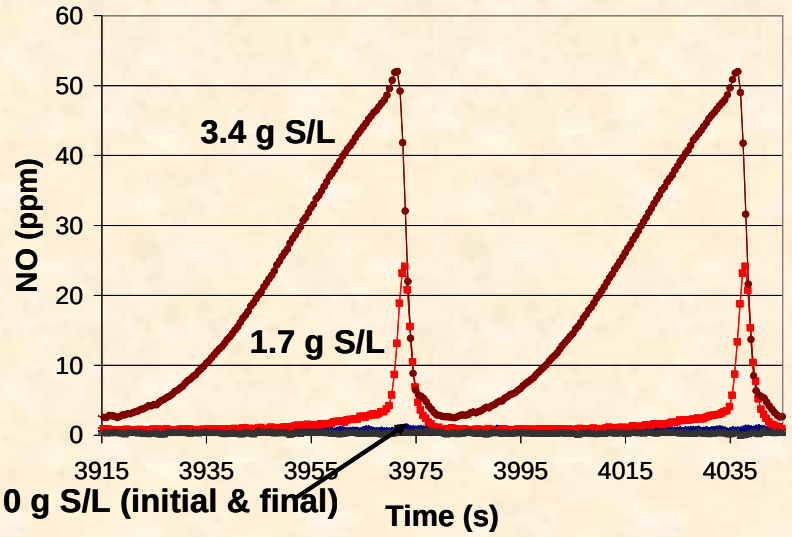
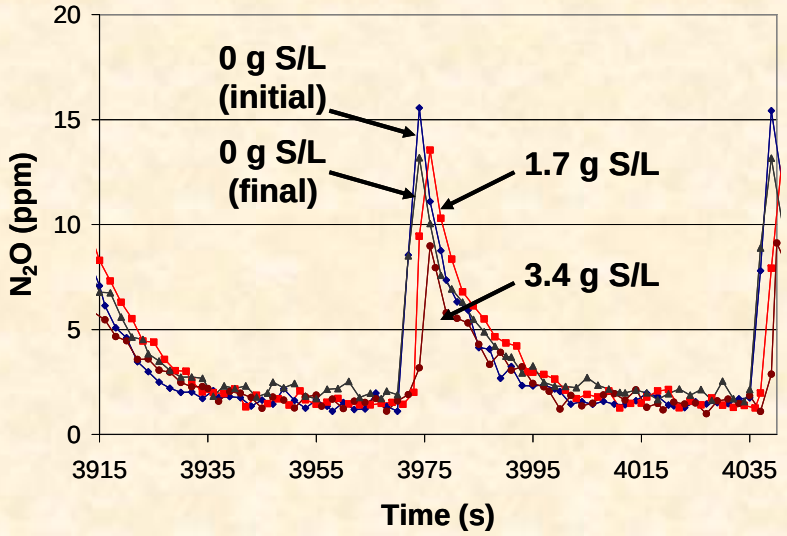
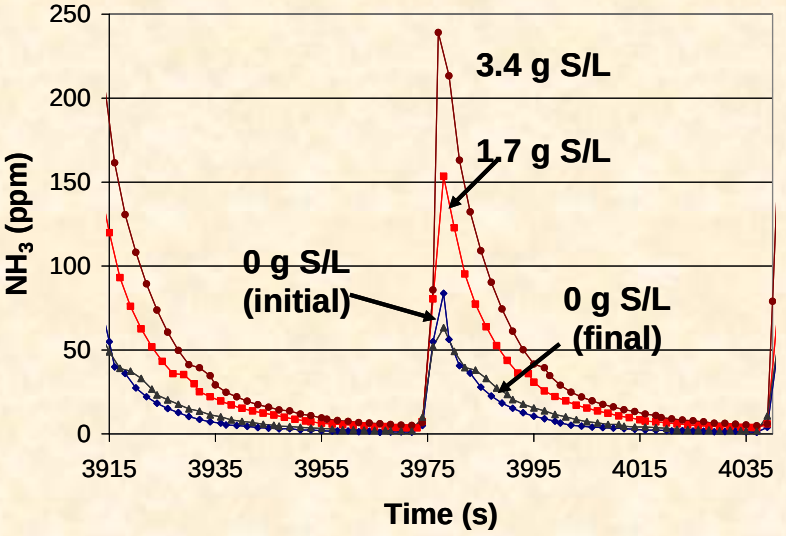
Sulfation clearly impacts integral LNT performance

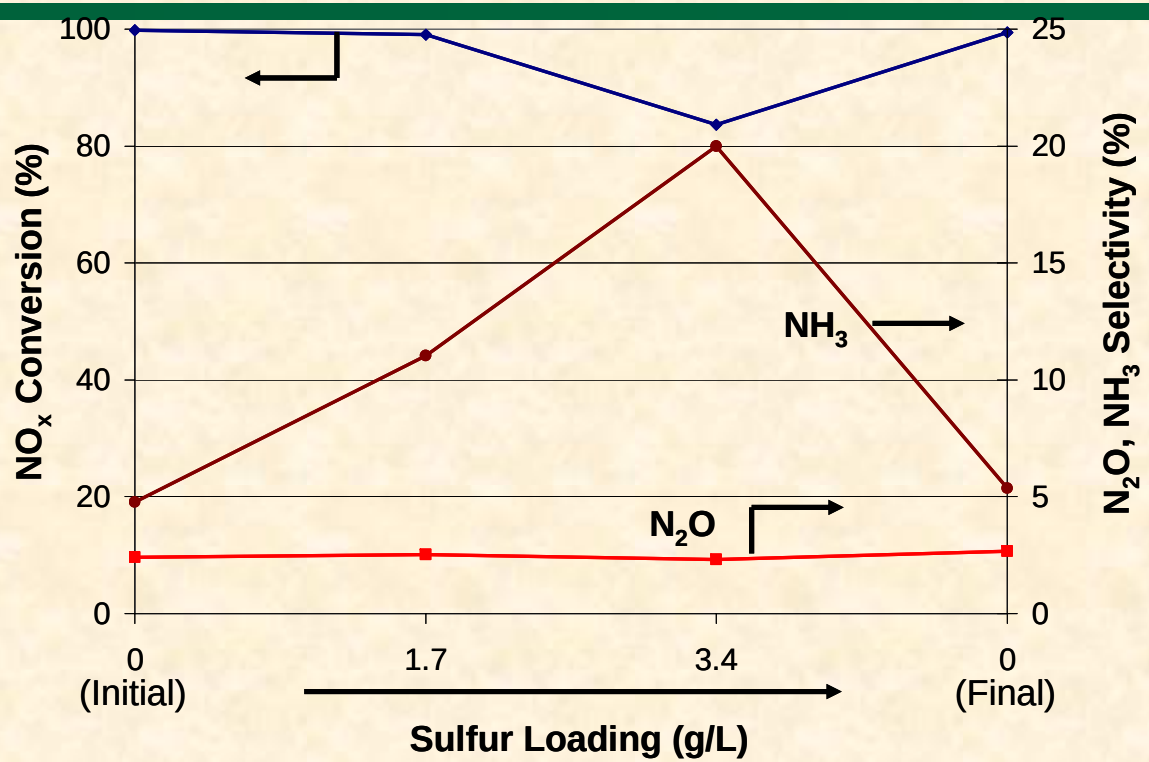








Sulfation strongly influenced NH_3 formation and NO_x slip

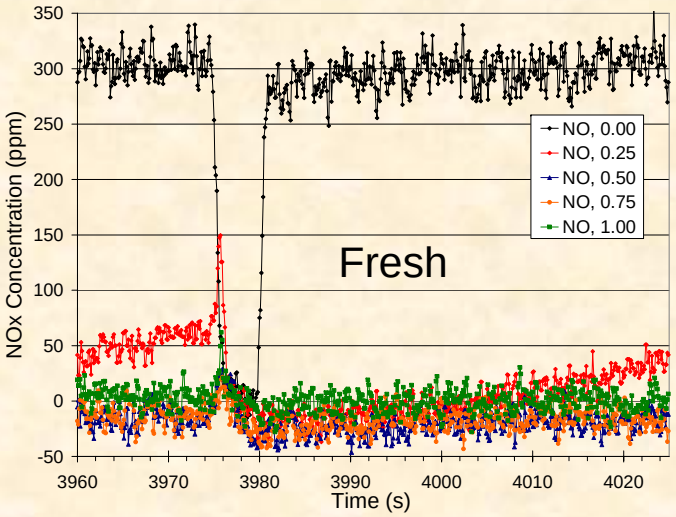


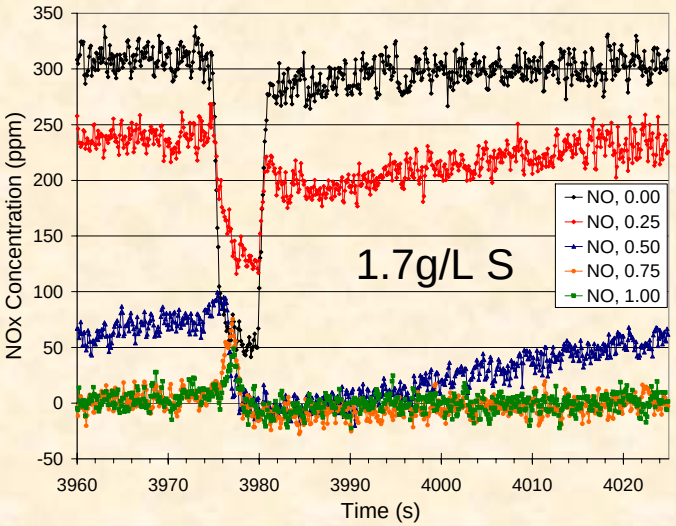
- NO_x conversion decreased with increasing sulfur loading
- NH_3 increased with each S dosing (largest effect)
- N_2O unaffected by sulfation
- Sulfur effects were stable w/o desulfation
- TPR DeSulfation recovered original performance

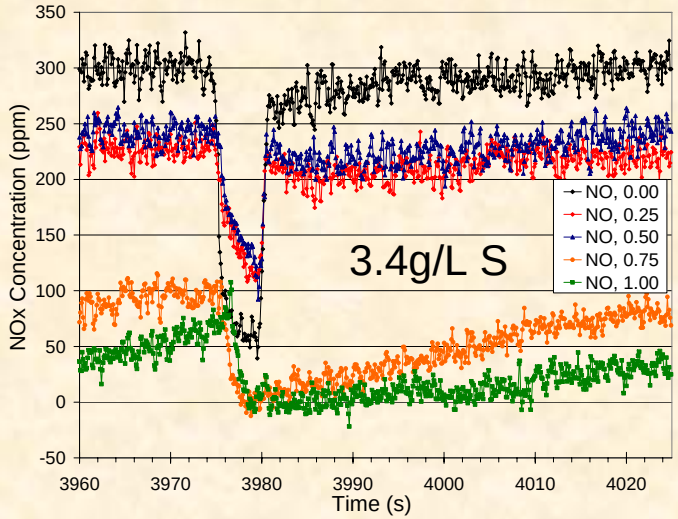
Outline of Sulfation Results

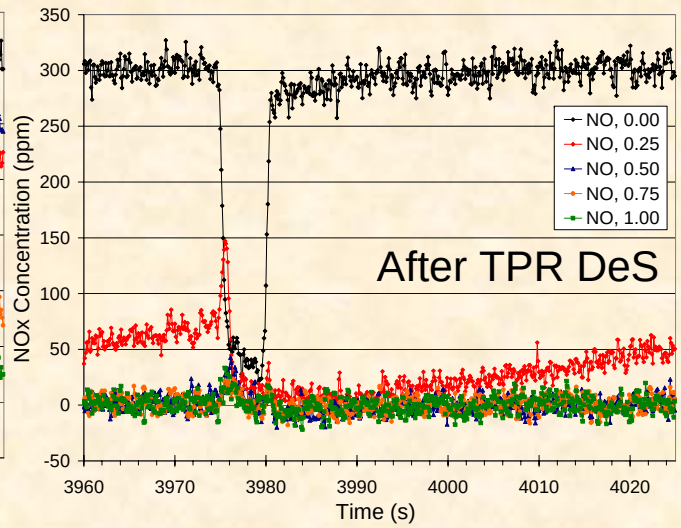
- Nitrogen Selectivity
- **NO_x Storage and Reduction, NSR**
  - **Spatiotemporal NO_x profiles**
  - **Spatiotemporal H_2 profiles**
- Oxygen Storage Capacity, OSC
  - Spatiotemporal H_2-consumption\OSC profiles
- Reaction exotherms
  - Spatiotemporal Temperature profiles
- TPR DeSulfation
- Conceptual model of NSR Sulfur Effects

Sulfation produced distinct stepped effect on NO_x-loading profiles









Fresh-state:
- **NSR localized**

1st Sulfation:
- **Poisoned 1st quarter**
- **NSR localized in 2nd 1/4**

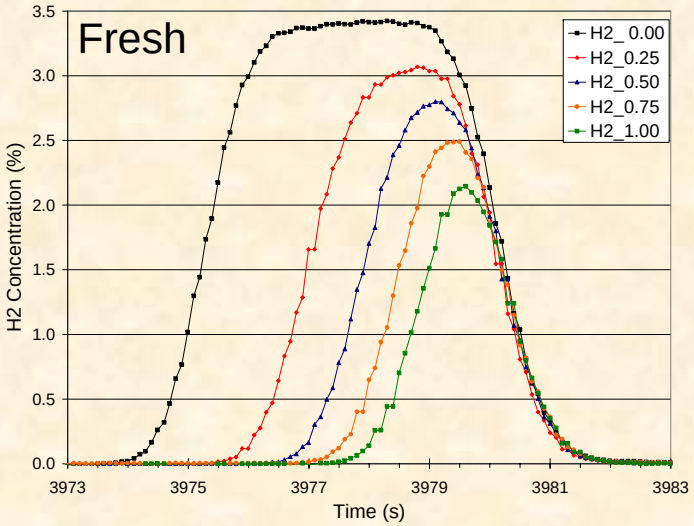
2nd Sulfation:
- **Poisoned 2nd quarter**

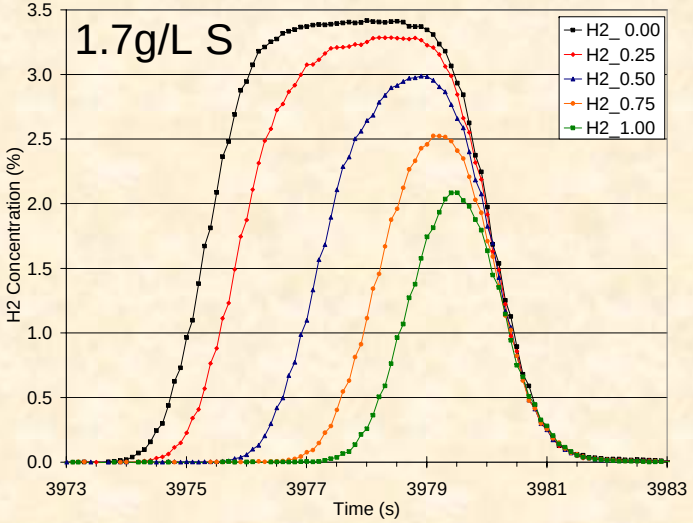
TPR DeS:

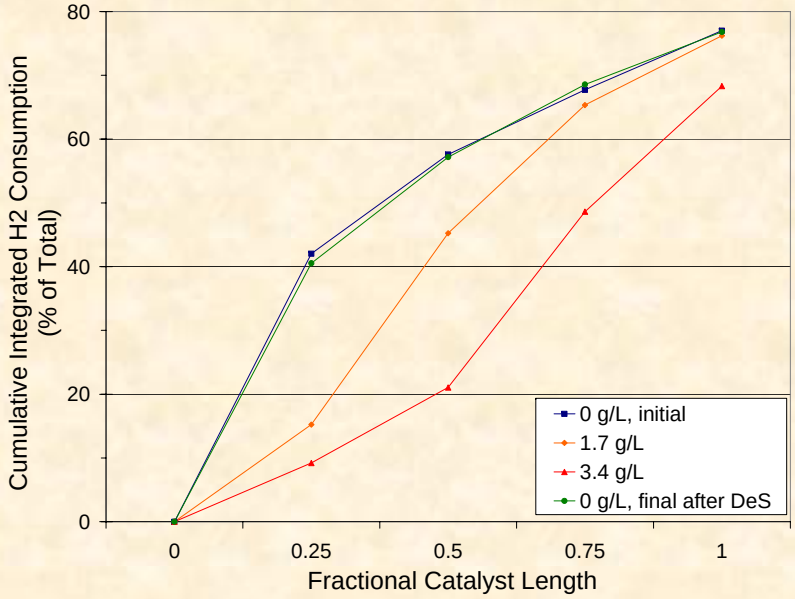
Recovered fresh performance

Non-inlet NO_x slip @ saturation:
- **Differing NO\NO_2 response at 30amu**
- **~240ppm NO_2 + 60ppm NO**
- **~ equilibrium**

NSR H_2 utilization showed similar distinct stepped response to sulfation







Fresh-state:

- NO_x-attributable H_2-Util. localized in front
- H_2-Util. in back ¾ due to OSC

Sulfated-state:

- Localized NO_x-attributable H_2-Util. moved downstream
- OCS remained active in sulfated region
- Post-NSR OSC region shortened by sulfation

TPR DeSulfation:

- Fresh performance recovered

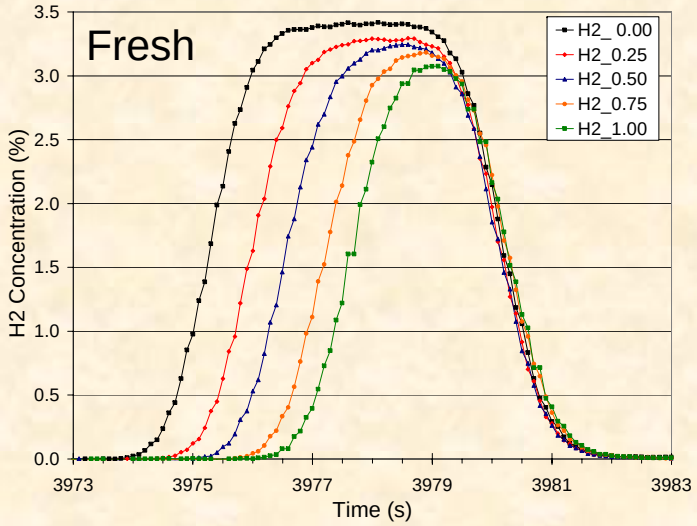
NSR sulfur response was plug-like and progressive with increasing sulfur dosing

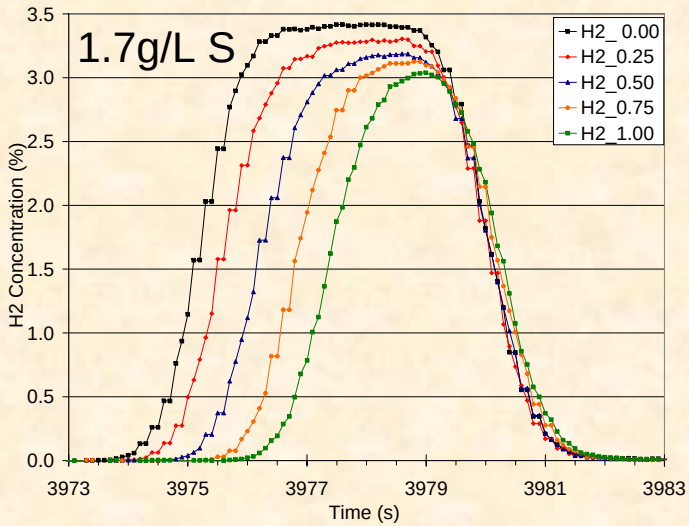
- NSR was localized in fresh and sulfated states
- NSR completely poisoned in sulfated zone
- Localized NSR zone moved progressively down the catalyst axis with increasing sulfur dosing
- Post-NSR OSC-only zone shortened by sulfation
- NO oxidation could equilibrate in S-poisoned zone and affect downstream NSR

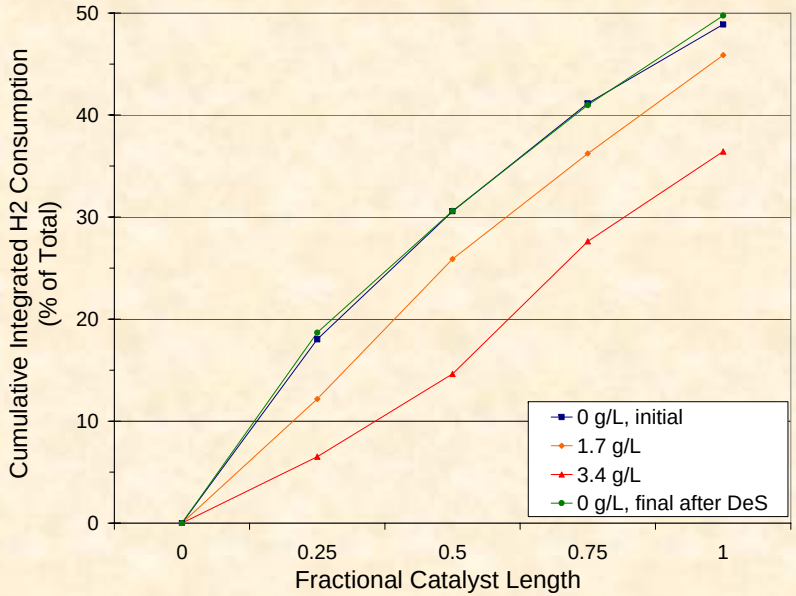
Outline of Sulfation Results

- Nitrogen Selectivity
- NO_x Storage and Reduction, NSR
  - Spatiotemporal NO_x profiles
  - Spatiotemporal H_2 profiles
- **Oxygen Storage Capacity, OSC**
  - **Spatiotemporal H_2-consumption\OSC profiles**
- Reaction exotherms
  - Spatiotemporal Temperature profiles
- TPR DeSulfation
- Conceptual model of NSR Sulfur Effects

OSC sulfur response was plug-like and progressive with increasing sulfur dosing







OSC is uniformly distributed in the fresh-state and unsulfated zones

1st sulfur dosing:

- **Impacts 1st ¼ only**
- **Did not completely poison 1st ¼ OSC**

2nd sulfur dosing:

- **Continued 1st ¼ OSC degradation**
- **Proceeded to 2nd ¼ OSC**

Downstream OSC ~ constant

TPR DeS recovered Fresh performance

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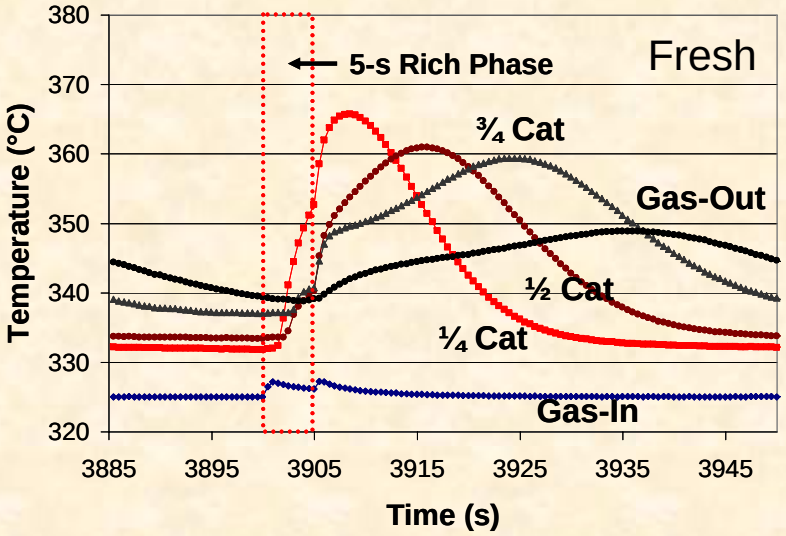
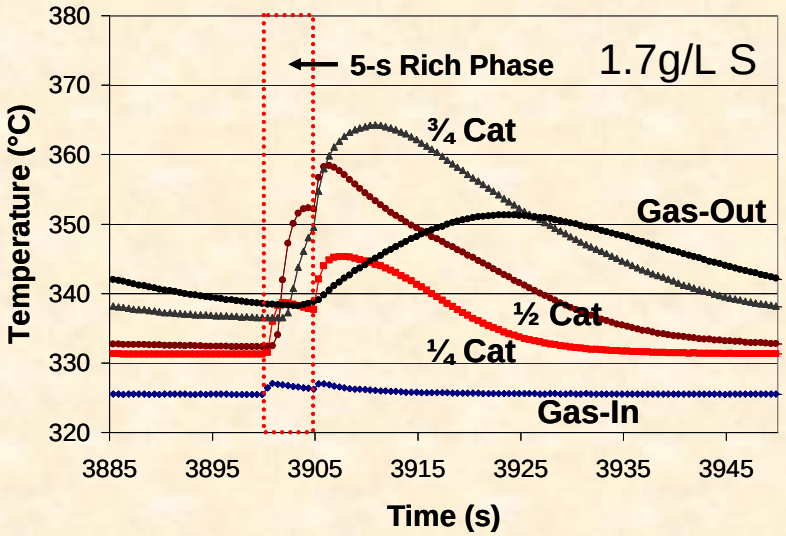
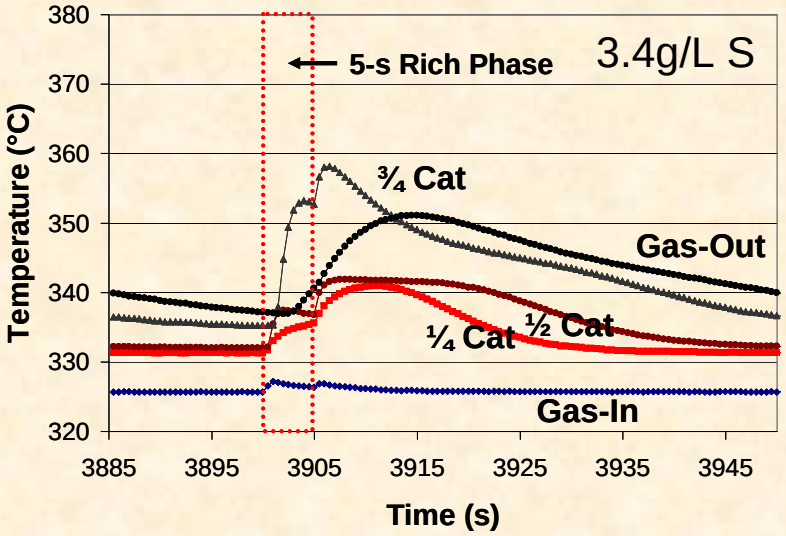
  - Spatiotemporal H_2-consumption\OSC profiles
- **Reaction exotherms**
  - **Spatiotemporal Temperature profiles**
- TPR DeSulfation
- Conceptual model of NSR Sulfur Effects

Reaction exotherms confirmed localized nature of NSR, and plug-like NSR response to sulfation







NSR-attributable exotherm was localized & S-effect was localized and progressive

- **1st ¼ : Fresh state**
- **2nd ¼ : 1.7g/L Sulfur state**
- **3rd ¼ : 3.4g/L Sulfur state**

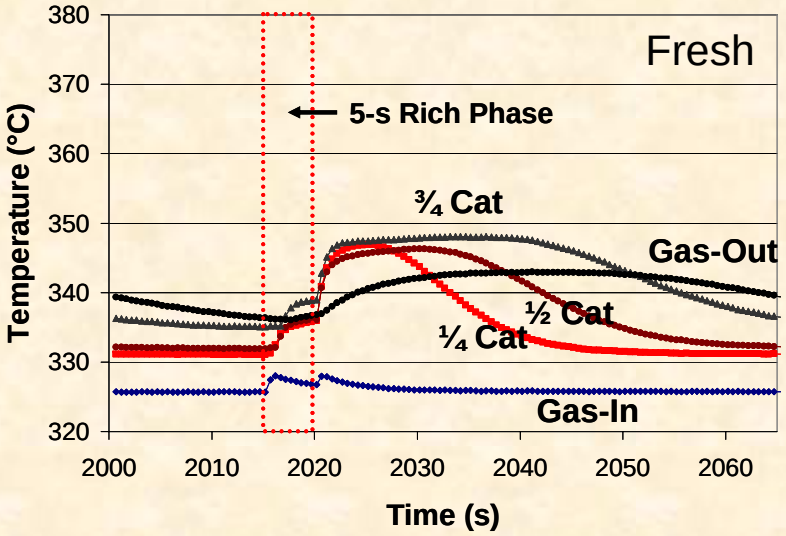
Total NSR exotherm moved but was ca. constant as sulfation progressed

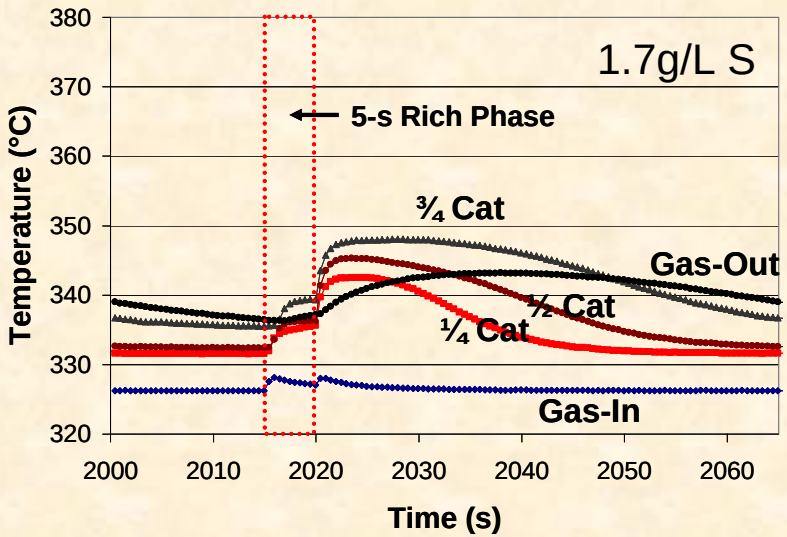
TPR DeS recovered Fresh-state performance

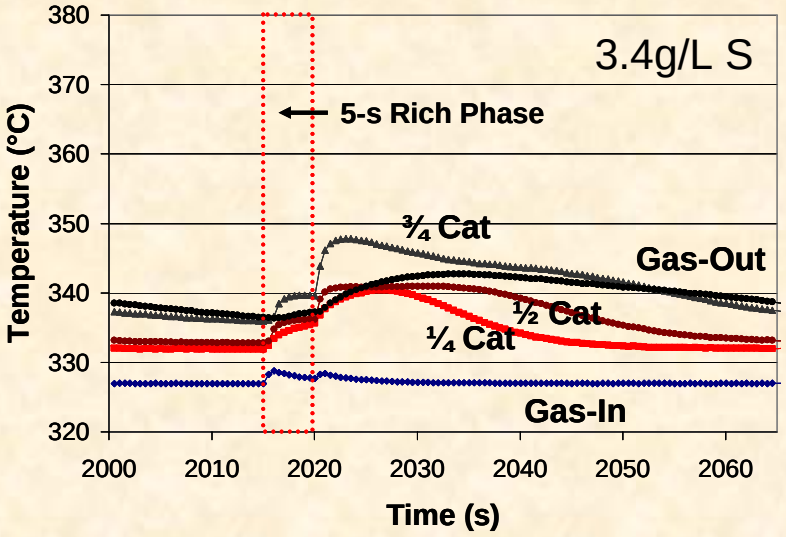
Confirmed SpaciMS-based observations

NSR and OSC S-zone exotherms similar

Reaction exotherms confirmed distributed nature of OSC, and OSC response to sulfation







- **Rich-phase exotherm : H_2+stored O_2**
- **Rich-Lean transition exotherm : reoxidation of Ce_2O_3 to $2CeO_2$**
- **OSC-attributable exotherms :**
  - **evenly distributed in fresh state**
  - **progressively poisoned by sulfur exposure**
- **Sulfated-zone NSR exotherm due to OSC**
  - **Note similarity in sulfated zones**

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- **TPR DeSulfation**
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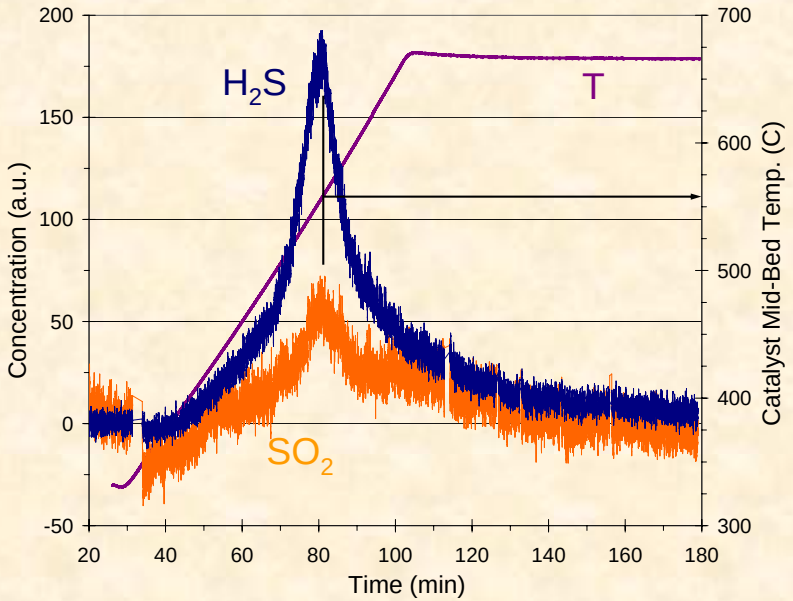
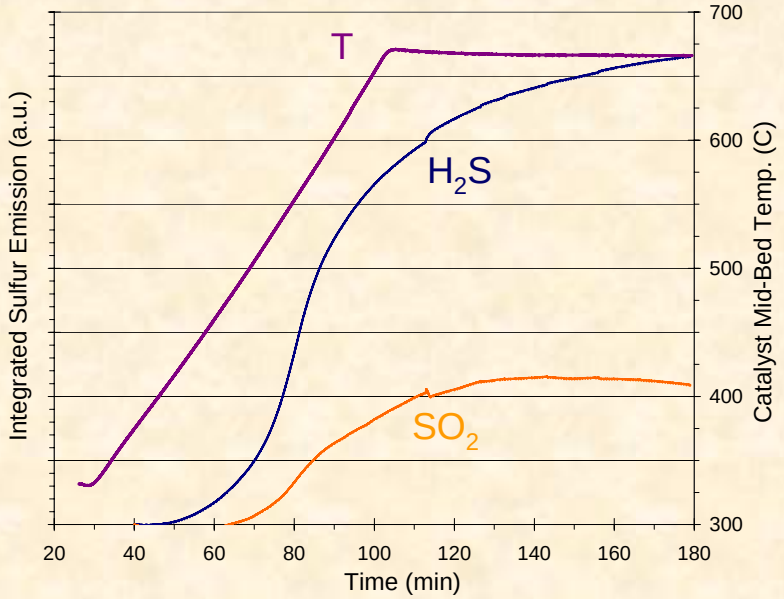
H_2S was major product of TPR DeSulfation





H_2S was major product of TPR DeSulfation

- **SO_2 more significant after 1st DeS**
- **COS negligible**

H_2S & SO_2 emission ~symmetric around peak at 560C

Major sulfur was released between 500 and 600C

H_2S & SO_2 emission slow after peak

- **~80min high-Temp soak required to reach baseline**

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- TPR DeSulfation
- **Conceptual model of NSR Sulfur Effects**

Observation Summary

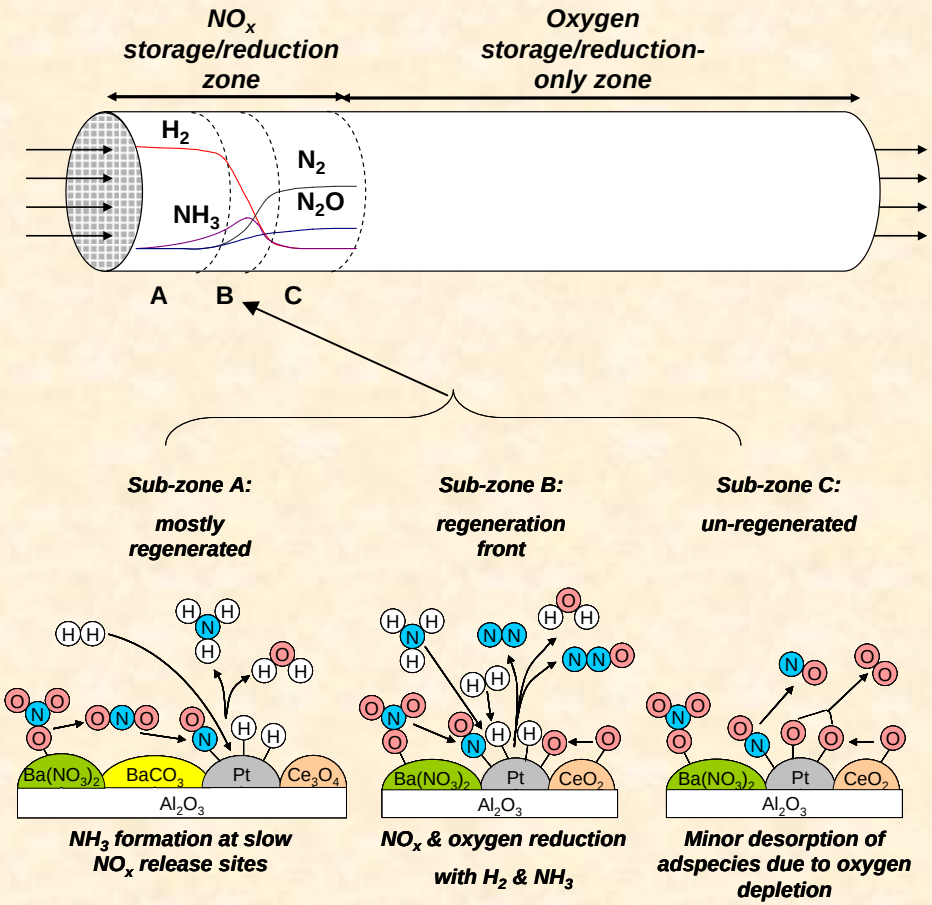
NSR was localized and OSC was distributed

Sulfation:

- Impacted NSR and OSC in a progressive plug-like manner
- Poisoned NSR but only degraded OSC
- Results in varying and different NSR and OSC zones
  - Displaced NSR zone downstream
  - Created upstream OSC-only zone
  - Shortened downstream OSC-only zone
- Could change NO_x partitioning at NSR zone
- Could change peak lean-phase T
- Affected NO_x conversion
- Affected NH_3 selectivity (major LNT-out effect)

TPR DeSulfation recovered fresh-state performance

Conceptual LNT model: fresh state



NH_3 formation at slow NO_x release sites

NO_x & oxygen reduction with H_2 & NH_3

Minor desorption of adspecies due to oxygen depletion

Fresh State:

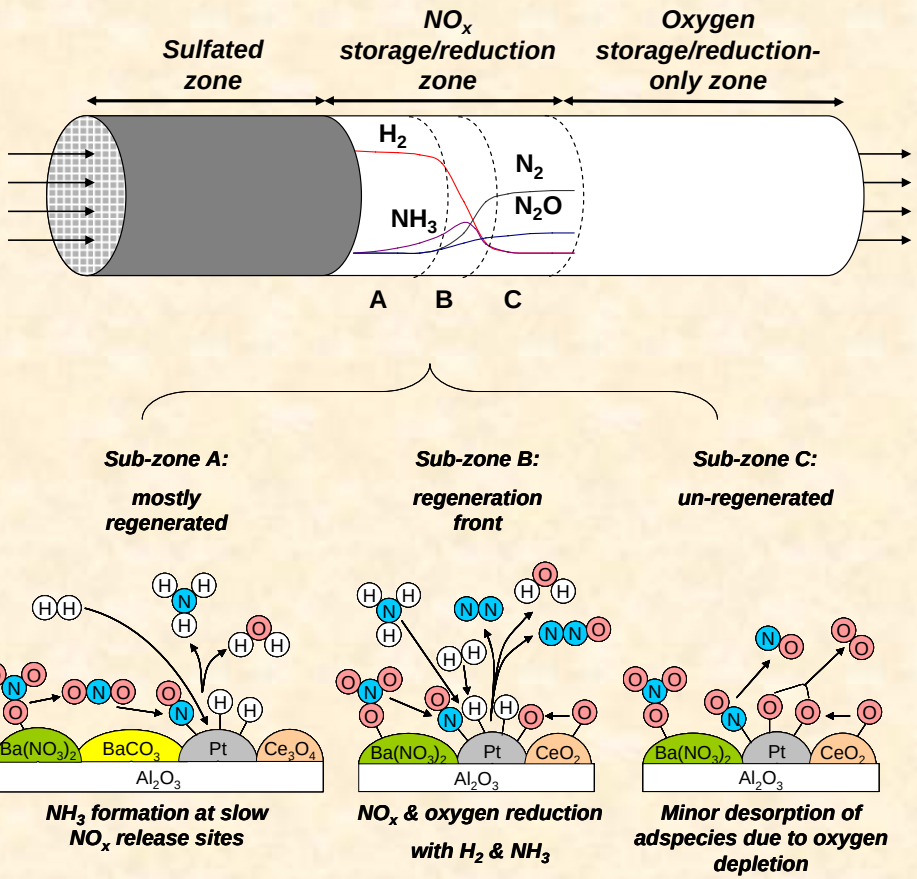
- NSR localized at catalyst front
- OSC evenly distributed throughout
- Residual H_2 and NH_3 from NSR zone oxidized in OSR-only zone

Three NSR Sub-Zone Regions:

(ref: Pihl, SAE 2006-01-3441)

1. Mostly Regenerated
   - H_2+Slow NO_x sites→NH_3
2. Regeneration Front
   - NO_x and O_2 reduction via H_2 and NH_3 (upstream product)
3. Un-Regenerated
   - Minor desorption

Conceptual LNT model: sulfated state



Sulfation:

- Creates a localized sulfation zone at the catalyst front
- Sulfation front is distinct and progresses like a plug
- In the sulfated zone:
  - NSR is inactive
  - OSC is active but degraded
- OSC in sulfated zone:
  - Equilibrates NO/NO_2
  - reduces reductant to NSR zone

As Sulfation progresses:

- NSR zone moves downstream
- OSC-only zone is reduced by advancing NSR zone
- NH_3 slip increases due to reduced OSC-only zone

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