Intra-catalyst Reductant Chemistry in Lean NOx Traps: A Study on Sulfur Effects

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Study Focus Area: Sulfur Effects on Reductant Utilization by Lean NOx Trap Catalysts

- Lean NOx Trap (LNT) catalysts are effective at reducing NOx from diesel engines but need...
  - Periodic “regeneration” (rich exhaust) with suitable reductants
  - Durability against negative sulfur effects
    - Sulfur degrades performance over time by poisoning NOx sites
    - deSulfation (high temperature clean up) recovers lost site activity

- ORNL has studied regeneration chemistry on a light-duty diesel engine platform with in-cylinder combustion techniques
  - Intra-catalyst sampling has been applied to characterize reductant utilization [SAE 2006-01-1416, SAE 2005-01-3876, SAE 2004-01-3023]

- Study presented here focuses on the effects of sulfur on intra-catalyst chemistry during in-cylinder regeneration
Two LNT Regeneration Strategies Chosen Based on Difference in Chemistry

- **Delayed and Extended Main (DEM):**
  - Throttle for reduced air flow
  - Extra fuel injected near main injection timing to achieve rich conditions

- **Post 80 Injection (P80):**
  - Throttle for reduced air flow
  - Extra fuel injected after main injection later in cycle to achieve rich conditions

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Two engine control strategies for achieving intermittent rich combustion for regeneration of LNT

“Delayed and Extended Main” (DEM)  
“Post 80 Injection” (P80)
Two engine control strategies for achieving intermittent rich combustion for regeneration of LNT

- **Delayed and Extended Main (DEM):**
  - High H₂ and CO
  - Low HC
  - High PM

- **Post 80 Injection (P80):**
  - Moderate CO and H₂
  - High HC
  - Low PM

![Graphs showing species concentration and airflow](image)
Experimental setup allows full exhaust species characterization throughout the catalyst system

- DOC upstream of LNT catalyst
- UEGO2 sensor is feedback point for A/F control
- Exhaust samples obtained at ¼, ½, and ¾ intra catalyst locations in LNT
- Analysis for: H₂, CO, HC, NOx, CO₂, O₂
Exhaust Speciation: DEM Strategy, 60s Cycle (DEM, 60s)

DEM, 60s

• NOx Reduction Efficiency (NRE) = 96.9%
• Mean LNT Temp = 329°C
• Minimum A/F = 13.5

• 60 second Cycle:
  • 57 seconds Lean
  • 3 seconds Rich
Strategy and Cycle Time Combinations in Study

DEM, 60s

NRE=96.9%
LNT Temp=329°C
PM(relative)=0.46

DEM, 20s

NRE=99.8%
LNT Temp=392°C
PM(relative)=1.0

P80, 60s

NRE=78.3%
LNT Temp=333°C
PM(relative)=0.10

P80, 20s

NRE=99.3%
LNT Temp=434°C
PM(relative)=0.09
Catalyst chemistry characterized under sulfated and desulfated conditions

**Sulfation procedure**
- Degreened in air
- BP15 fuel
- 1% bottled SO$_2$ at 3.4slpm
- Three loading states (fuel S + bottled S)
  - 3.06g S $\approx$ 2888 miles
  - 5.63g S $\approx$ 5319 miles
  - 9.63g S $\approx$ 9087 miles
- Full characterization done at each loading state

**Desulfation procedure**
- Engine based desulfation
  - Target 700°C / 14AFR
  - Fixed boost to 0kPa
  - Use RPM to control airflow
  - Control catalyst inlet AFR using in-pipe injection
- 20 minute desulfation event

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**Fuel loading**
- Fuel Flowrate 0.6 g/s
- Fuel Economy (assumed) 45 mi/gal
- BP 15 Sulfur Content 0.0015%
- Fuel Density 0.143 gal/lb
- Miles per gram S 944 mi/g
- grams S /min 0.00054 g/min

**Bottle loading**
- Molecular Weight of S 32.06 g/mol S
- 1% SO2 flowrate 3.4 slpm
- SO2 concentration 1.00%
- S flowrate 0.0486 g/min

<table>
<thead>
<tr>
<th>1% SO2 Injected (min)</th>
<th>state 1</th>
<th>state 2</th>
<th>state 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injected S (g)</td>
<td>1.35</td>
<td>2.18</td>
<td>2.92</td>
</tr>
<tr>
<td>Cumulative Engine S (hrs)</td>
<td>52.8</td>
<td>64.9</td>
<td>98.0</td>
</tr>
<tr>
<td>Cumulative Engine S (g)</td>
<td>1.71</td>
<td>2.10</td>
<td>3.18</td>
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<tr>
<td>Running Total S (g)</td>
<td>3.06</td>
<td>5.63</td>
<td>9.63</td>
</tr>
<tr>
<td>Equivalent miles</td>
<td>2888</td>
<td>5319</td>
<td>9087</td>
</tr>
</tbody>
</table>
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P80 strategies (Higher in HCs, Lower H₂/CO) appear to degrade more with S/deS; Why???
Small downstream shift in reductant utilization with S exposure

P80, 60s
Small downstream shift in reductant utilization with S exposure

H2 and CO (moles during regen)

HC (moles during regen)

P80, 60s
Small downstream shift in reductant utilization with S exposure
Small downstream shift in reductant utilization with S exposure
Small downstream shift in reductant utilization with S exposure
Significant changes observed in N$_2$ selectivity with S/deS

![Graph showing changes in NOx and NH3 concentrations](image)

**P80, 60s**

*Note: NH$_3$ and NOx not in same units. EO NOx ~ 500ppm*
Significant changes observed in N₂ selectivity with S/deS

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Significant changes observed in $N_2$ selectivity with S/deS

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P80, 60s

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NH₃ formation increases after deSulfation

- NH₃ formation after deSulfation was higher for all cases

Potential causes:
- Sintering of Sorbate
  - suspect thermal sintering of sorbate may be the cause of higher NH₃
  - Castoldi et al. Report NH₃ formation corresponds with higher sorbate loading (bulk crystallites)
- Change in Reductant:NOx ratio
  - CLEERS, Pihl, and other work on N₂ selectivity show NH₃ increases with increasing Reductant:NOx ratio
    - Pihl, et.al. SAE 2006-01-3441
**H₂ Produced In Catalyst During 20s Cycles**

- In 20s cycles, H₂ observed being created in catalyst most likely from reforming reactions (water-gas shift, etc.)

- Same process may occur in 60s data, but H₂ may be consumed immediately for NOx reduction
Catalytic H₂ production: Effect of S/deS

- Increase in catalytic-produced H₂ greater for P80 strategy
- H₂ production degrades with S/deS aging
- LNT performance may degrade more rapidly for strategies that depend on catalyst utilizing HCs from engine
Summary

- In general, reductant utilization in LNT moved downstream only slightly with S/deS
  - Process is consistent; optimism for modeling

- NH$_3$ formation increased after deSulfation process
  - Regeneration control strategies must adjust accordingly with age

- Strategies with high HC and low H$_2$/CO (P80) may depend on catalytic H$_2$/CO production for regeneration
  - S/deS degradation of catalytic H$_2$/CO production may have greater degradation impact on the effectiveness of P80-like strategies

- Preparing Paper for SAE Fall Powertrain and Fluids Conference