Investigation of Aging Mechanisms in Lean NOx Traps

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February 26, 2008

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Purpose of Work

- Understand main chemical and physical processes occurring during LNT aging

- Correlate washcoat composition with catalyst durability ⇒ Effect of Pt, Rh, Ba, CeO$_2$, CeO$_2$-ZrO$_2$

- Establish effect of LNT catalyst aging on NOx performance and desulfation behavior

- Provide insights that will assist the design of more durable catalysts and/or allow for optimized catalyst operation as it ages
Barriers

• **Aftertreatment needed to meet NOx emission goals**
  - Engine conditions that have the highest overall efficiency typically give rise to NOx levels exceeding the 2010 regulations

• **Limited durability of LNT catalysts impediment to widespread use**

• **Deeper understanding of “commercial” catalyst materials required:**
  - role of individual components
  - effect on aging characteristics

• **Providing insights that optimize catalyst operation over the lifetime of the vehicle**
  – Improve catalyst efficiency and therefore minimize fuel penalty
Approach

• Employ well characterized model catalysts which are representative of 2nd generation LNT formulations
  ⇒ use of ceria; also of relevance for lean-burn gasoline LNTs

• Examine effect of washcoat components/loadings on catalyst durability:
  ⇒ systematic variation of component concentrations: Pt, Rh, Ba, CeO$_2$(ZrO$_2$)

• Employ realistic aging protocol, with simultaneous measurement of catalyst NOx storage/reduction performance

• Perform detailed physico-chemical characterization of aged catalysts

  ➢ U. of Kentucky, ORNL, Ford and Umicore as partners
Performance Measures

• Prepare model LNTs with sequential variation of component loadings: Pt, Rh, Ba, CeO$_2$(-ZrO$_2$)

• Evaluate de-greened catalysts to determine key component effects:
  - NOx performance (conversion, selectivity)
  - intra-catalyst chemistry
  - desulfation behavior

• Age catalysts in realistic and reproducible manner for subsequent studies (bench reactor + physico-chemical analysis)
Accomplishments

- Prepared model monolith and powder catalysts with well defined compositions
- Demonstrated that ceria improves low temperature NOx conversion and improves selectivity to $N_2$
- Demonstrated that ceria significantly improves storage capacity and regeneration of LNTs, especially at low temperature
- Demonstrated that balanced ceria loading is required to maximize *in situ* $H_2$ generation via WGS reaction
- Demonstrated that ceria improves catalyst desulfation
- Implemented LNT aging cycle on UK bench reactor
# Model Monolith Catalyst Compositions Prepared

<table>
<thead>
<tr>
<th>Component</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Series 1</strong></td>
</tr>
<tr>
<td>Pt, g/L (g/cuft)</td>
<td>3.53 (100)</td>
</tr>
<tr>
<td>Rh, g/L (g/cuft)</td>
<td>0.71 (20)</td>
</tr>
<tr>
<td>BaO, g/L</td>
<td>15, 30, 45</td>
</tr>
<tr>
<td>CeO₂, g/L</td>
<td>0, 50, 100</td>
</tr>
<tr>
<td>CeO₂-ZrO₂, g/L</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃, g/L</td>
<td>Balance</td>
</tr>
</tbody>
</table>

- Target washcoat loading = 260 g/L
- Actual average loading = 262 g/L, stand. dev. = 16.6 g/L (6.3%)
- Monoliths coated at DCL Int. Inc.
Ceria Addition Improves N₂ Selectivity and Low Temperature Performance

- Ceria improves NOx conversion for T < 350°C
  - most significant at 150°C
- Ceria-addition improves N₂ selectivity
  - increases w/ OSC
Ceria Improves Effective NOx Storage Capacity at 150 °C

- NOx storage capacity improves with increasing ceria loading
  - NO₂ in effluent shows NO to NO₂ oxidation not limiting for 30-0 and 30-50
- Rich phase NOx release also increases with ceria loading
  - More NOx released with ceria-based LNTs ⇒ reduction kinetics are too slow

Key: 30-0 = 30 g BaO/L\text{cat.} + 0 g CeO₂/L\text{cat.}, etc.
Studies with Model Powder Catalysts Provide Basis for Explaining Monolithic Catalyst Results

- In situ DRIFTS studies performed on two model powder catalysts:
  - **PBA**: 1 wt% Pt/BaO/Al₂O₃ (equivalent to monolith catalyst 30-0)
  - **PBAC**: PBA (74 wt%) + 1 wt% Pt/CeO₂ (26 wt%), physical mixture (equivalent to monolith catalyst 30-50)

In situ DRIFTS spectra during lean-rich cycling:

- In situ DRIFTS:
  - only a fraction of stored NOx is purged during L/R cycling
  - PBAC shows superior rich phase regeneration

- Microreactor results consistent
  - PBAC shows superior dynamic NOx storage capacity while cycling between lean and rich

Conditions: lean phase (6 min): 300 ppm NO and 8% O₂; rich phase (0.5 min): 5625 ppm CO, 3375 ppm H₂, with 5% H₂O and 5% CO₂ added in both phases.
Intra-Catalyst Chemistry: \( \text{H}_2 \) Concentration Profile from SpaciMS \((T = 350 \, ^\circ\text{C})\)

- **During OSC test**
- **During testing w/ NOx (rich phase)**

- High water-gas shift activity of 30-100 results in greatly increased \( \text{H}_2 \) production compared to 30-0. However, \( \text{H}_2 \) was largely consumed at the end of the bed for 30-100
Balanced Ceria/OSC Loading Required for Optimum Water-Gas Shift Activity

**30-0**

**30-100**

**30-100Z:**
100 g CeZrO$_2$/L$_{cat.}$

Outlet CO concn. during rich purge: low CO $\Rightarrow$ consumption by WGS reaction and by stored oxygen

$T = 350 \, ^\circ\text{C}$
Desulfation Studies: Effect of Catalyst Composition on Efficiency of Sulfur Removal

Conditions:
Sulfation: 350 °C, 100 ppm SO₂, 10% O₂, 5% CO₂, 5% H₂O, bal. N₂; ca. 2 g S/L cat.;
Desulfation: 1% H₂, 10 min, bal. N₂

Key:
- Pt-100 = same as 30-50 but with half the Rh loading (10 vs. 20 g Rh/cuft)
- Pt-50 = same as Pt-100 but with half the Pt loading (50 vs. 100 g Pt/cuft)

- Beneficial effect of ceria confirmed
- Reduction of precious metal content has adverse effect
Catalyst Aging

• Goal is to subject model monolith catalysts to realistic accelerated aging for subsequent reactor studies and physico-chemical characterization

• Catalyst aging on automated bench reactor

• Initial aging to 50 cycles: ca. 50-75 k miles road equivalent based on fuel sulfur content

• Catalyst performance check every ~10 cycles
LNT Aging Protocol

**MODE #1**  
Sulfur Exposure  
30 minutes  
Exposed to 0.50 – 1.0g S/L  
L(s)/R(s) = 60/5  

**MODE #2**  
DeSOx  
10 minutes  
L(s)/R(s) = 5/15  
Rich lambda=0.90  

**MODE #3**  
DPF Regeneration  
30 minutes  
Lean only condition  

* Optimized DeSOx temperature that balances chemical and thermal deactivation  

- Based on Ford protocol  
- Optimized desulfation temperature balances desulfation with thermal deactivation (→ 700 °C)  

Aging profile for catalyst 30-100  
(T = 300 °C)
Technology Transfer

- Technology transfer via Ford Motor Co. (project partner)

- Model monolith catalysts prepared in this project currently being utilized in Ford R&D (Bob McCabe):
  - fundamental studies pertaining to catalyst sulfation and desulfation
  - effect of catalyst composition on selectivity to different N-species

- Joint U. of Kentucky/Ford project planned as follow up to current DOE-sponsored project (Ford University Research Program)

- Results of the project presented at conferences and in the literature:
  - 3 publications, 7 presentations to date
Publications:


Presentations:

Plans for Next Fiscal Year

- Complete accelerated aging of monolith catalysts according to Ford protocol

- Characterize NOx storage and reduction properties of aged model monolith catalysts:
  → ORNL bench reactor, with use of spaci-MS

- Performed detailed physico-chemical characterization of aged catalysts:
  → SEM, TEM, N₂ physisorption, H₂ chemisorption, XRD

- Derivation of LNT deactivation model:
  → spatial resolution possible?
Summary

- Model LNT catalysts have been prepared & characterized with systematic variation of Pt, Rh, Ba and CeO$_2$(-ZrO$_2$) loadings
- Correlations have been identified between catalyst performance and CeO$_2$, Ba and Pt loading
- SpaciMS studies have revealed a strong dependency of intra-catalyst H$_2$ concentration profiles on the ceria/oxygen storage content in model LNT catalysts
  ⇒ need for balanced OSC
- The model catalysts are currently being aged (accelerated LNT aging cycle)
- In the next phase, the aged catalysts will be characterized (NOx storage and reduction, physico-chemical analysis)