Lean NOx Reduction With Dual Layer LNT/SCR Catalysts

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Acknowledgements:
DOE-EERE – Office of Vehicle Technologies, BASF, Ford, U. Kentucky, ORNL
NSR/SCR Technology

- Promising non-urea deNOx technology for light- & medium-duty diesel & lean burn gasoline
- Synergistic benefits demonstrated: Increased NOx conversion by adding SCR unit downstream
- Understanding of the coupling between LNT & SCR series-brick configuration is emerging
Goal: Reduce PGM & minimize fuel penalty in meeting NOx emission targets
Fundamental Issues for Dual Layer

- LNT – SCR proximity: Dual layer vs. physical mixture
- LNT composition, structure & loading
- SCR composition & loading
- Thermal durability
- Dual layer vs. sequential monolith configuration
- etc.
Fundamental Issues for Dual Layer

- LNT – SCR proximity: Dual layer vs. physical mixture
- LNT composition, structure & loading
- SCR composition & loading
- Thermal durability
- Dual layer vs. sequential monolith configuration
- etc.

Our aim is to resolve some of these issues...
NSR/SCR: A Different Role for the LNT

LNT Ideal Target: 50% NOx conversion & 100% NH₃ selectivity:

LNT: \[ \text{NO} + 4 \text{H}_2 + 0.75 \text{O}_2 \rightarrow \text{NH}_3 + 2.5 \text{H}_2\text{O} \]
SCR: \[ \text{NO} + \text{NH}_3 + 0.25 \text{O}_2 \rightarrow \text{N}_2 + 1.5 \text{H}_2\text{O} \]
Overall: \[ 2 \text{NO} + 4 \text{H}_2 + \text{O}_2 \rightarrow \text{N}_2 + 4 \text{H}_2\text{O} \]

LNT does not have to be highly effective NSR catalyst in the combined NSR/SCR application
LNT/SCR Catalyst Synthesis

- **LNT layer** monolith (from BASF)

<table>
<thead>
<tr>
<th></th>
<th>LNT1</th>
<th>LNT2</th>
<th>LNT3</th>
</tr>
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<tbody>
<tr>
<td>PGM (g/ft³)* (Pt:Rh = 7)</td>
<td>90</td>
<td>90</td>
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</tr>
<tr>
<td>Ba (wt%)</td>
<td>14</td>
<td>14</td>
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<tr>
<td>Ce (wt%)</td>
<td>0</td>
<td>17</td>
<td>34</td>
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</table>

*~4.6 g/in³ washcoat loading; 1.1wt.% PGM in γ-Al₂O₃

- **SCR top-layer** contains Fe/ZSM5 or Cu/ZSM5
  ~0.9 g/in³ washcoat loading (unless otherwise stated)
Dual-Layer Catalyst Structure

(a) NO → Flowing Gas → N₂

[Cu- or Fe- ZSM-5]

δ_{SCR}=40-50μm

Pt/Rh/BaO/CeO₂/Al₂O₃

δ_{LNT}=60-80μm

Monolith Substrate

(b)

LNT before washcoating

LNT after washcoating

TcSUH SEI 15.0kV 100μm WD10mm
Comparison of LNT & LNT/SCR Lean-Rich Cycle

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
Temperature: 300°C
Comparison of LNT & LNT/SCR Lean-Rich Cycle

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
Temperature: 300°C

Prominent dual N₂ peaks during rich & lean
Rcn. of stored NH₃ with O₂ & NOx during lean phase
No NH₃ for CuZ+LNT

Sustained N₂ production for entire lean period; due to slow NH₃ release from Cu-Z & reduction
Summary of Results w/o CO₂ & H₂O*

- Dual layer concept works
- LNT/SCR has slightly lower NO conversion than LNT only
- Low temperatures (< 225 °C): Undesired oxidation of NH₃ on Pt (to N₂O) occurs due to trapped NH₃ migrating to LNT layer
- Higher temperatures (> 250 °C): Undesired oxidation of NH₃ on Pt (to NO) occurs
- LNT/SCR dual layer out-performs LNT+SCR single layer
- Aged LNT/SCR can lead to improved performance

LNT/SCR: $H_2$
Reductant in Presence of $CO_2$ & $H_2O$

Conditions:
Lean: 500 ppm NO, 5% $O_2$; 60s
Rich: 2.5% $H_2$; 5s
(Both: 2.5% $H_2O$, 2% $CO_2$)
LNT/SCR: H₂ Reductant in Presence of CO₂ & H₂O

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
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LNT/SCR: H₂ Reductant in Presence of CO₂ & H₂O

**Conditions:**
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
(Both: 2.5% H₂O, 2% CO₂)

LNT/SCR: Enhanced NOx conversion & N₂ selectivity over wide temperature range
LNT/SCR Performance in Presence of CO₂ & H₂O

LNT: Serves as NO₂ generator during lean phase & NH₃ generator during rich phase

LNT/SCR: SCR stores NH₃ during rich and reacts with NO/NO₂ during lean

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\]

Fast SCR
Ceria Addition

Ceria effects:

- Improved low T performance
- Mitigation of CO poisoning at low T
- Promotes WGS reaction (CO + H₂O ⇌ CO₂ + H₂)
- Stabilization of Pt
- Increased NH₃ oxidation at high T

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Ceria Loading Effect

(a) 2.5% H₂

(b) 1.5% H₂ & 1.0% CO

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
or 2.5% H₂, 1.0% CO
(with 2.5% H₂O, 2% CO₂)
Ceria Loading Effect

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
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(a) 2.5% H₂

(b) 1.5% H₂ & 1.0% CO

Feed Temperature (°C)

NOₓ Conversion (%)
Ceria Loading Effect

(a) 2.5% H₂

(b) 1.5% H₂ & 1.0% CO

CeO₂ beneficial
CeO₂ detrimental

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
or 2.5% H₂, 1.0% CO
(with 2.5% H₂O, 2% CO₂)
LNT/SCR Dual-Layer: \( \text{CeO}_2 \) Axial Zoning

\[(\text{Pt/Rh/BaO+Cu/ZSM5}) \quad \text{CuZ-LNT1} \quad \text{CuZ-LNT3} \quad (\text{Pt/Rh/BaO/CeO}_2+\text{Cu/ZSM5}) \]

LNT/SCR: Ceria Zoning

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
or 2.5% H₂, 1.0% CO
(with 2.5% H₂O, 2% CO₂)

(a) 2.5% H₂

(b) 1.5% H₂ & 1.0% CO

NOₓ Conversion (%) vs. Feed Temperature (°C)
“Dual-Layer/Dual-Zone” Catalyst

- Ceria zoning: achieves low temperature activity enhancement & minimized high temperature oxid. of NH₃
- Aged LNT upstream + Higher SCR loading beneficial
  - Lower PGM dispersion benefits NH₃ selectivity
  - Higher loading of SCR sustains high NOx conversion
- Further improvements with cycle timing
Dual Layer vs. Sequential: Comparison

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
With H₂O and CO₂

NOₓ Conversion (%)

Temperature (°C)

CuZ-LNT3 1.0 cm (Cu/ZSM-5, 2.0 g/in³)
Dual Layer vs. Sequential: Comparison

**Conditions:**
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
With H₂O and CO₂

**CuZ-LNT1 1.0 cm + CuZ-LNT3 1.0 cm**
(Cu/ZSM-5, 0.9 g/in³)

**Graph Details:**
- **NOₓ Conversion (%)** vs. **Temperature (°C)**
- **DL-13**
- **2x PGM**
- **1x SCR**
- **0.5x GHSV**

**Legend:**
- Substrate
- LNT1
- LNT3
- Cu/ZSM-5
Dual Layer vs. Sequential: Comparison

**Conditions:**
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
With H₂O and CO₂

- **DL-13**
  - LNT1 0.5 cm +
  - SCR 0.5 cm +
  - LNT3 0.5 cm +
  - SCR 0.5 cm
  - (Cu/ZSM-5, 2.0 g/in³)

- **S-1C3C**
  - 0.5x PGM
  - 1x SCR
  - 1x GHSV
Dual Layer vs. Sequential: Comparison

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
With H₂O and CO₂

NOₓ Conversion (%)

Temperature (°C)

DL-13

S-1C3C

DL-1

0.5x PGM
1x SCR

1x PGM
1x SCR
Dual Layer vs. Sequential: Factors

- LNT vs. SCR proximity:
  More NH₃ oxidation on dual layer catalysts due to closer proximity of NH₃ storage and Pt sites

- Diffusion limitations:
  Dual layer catalyst has more extensive diffusion limitations; SCR top layer inhibits transport to LNT bottom layer
Conclusions

- Dual-layer LNT/SCR works
  - Increased N$_2$ yield, decreased NH$_3$ yield
  - NOx conversion: depends on conditions & catalysts
  - Close proximity of LNT and SCR functions important but segregated layers needed

- Ceria addition to LNT helps on many fronts
  - Low temperature conversion
  - Lessens effects of CO inhibition
  - Mitigates effects of thermal degradation

- Axial profiling & customized cycle timing hold promise
- Further opportunities for optimization
THANKS!
Introduction
### Storage & Reaction on Multi-Functional Catalysts in Exhaust Aftertreatment

<table>
<thead>
<tr>
<th>Method</th>
<th>Application</th>
<th>Reaction</th>
<th>Catalyst</th>
<th>Stored Species</th>
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<tbody>
<tr>
<td>TWC</td>
<td>Spark-ignited gasoline</td>
<td>$\text{H}_2/\text{CO}/\text{HC} + \text{O}_2$</td>
<td>Pt/Pd/Rh/CeO$_2$/Al$_2$O$_3$</td>
<td>O$_2$</td>
</tr>
<tr>
<td>DOC</td>
<td>Diesel</td>
<td>$\text{CO}/\text{HC} + \text{O}_2$</td>
<td>Pt/Pd/zeolite-$\beta$/Al$_2$O$_3$</td>
<td>High MW HC</td>
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<tr>
<td>DPF</td>
<td>Diesel</td>
<td>$\text{C} + \text{O}_2/\text{NO}_2$</td>
<td>Pt/cordierite</td>
<td>PM</td>
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<td>NSR + SCR</td>
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<td>$\text{NH}_3 + \text{O}_2$</td>
<td>Cu/zeolite + Pt/Al$_2$O$_3$</td>
<td>$\text{NH}_3$</td>
</tr>
</tbody>
</table>
Collaborative Project Team

- **University of Houston**
  - *Mike Harold (PI), Vemuri Balakotaiah, Dan Luss*
  - Bench-flow, TAP reactors; LNT - NH₃ generation; LNT/SCR multi-layer catalyst synthesis & reactor studies; NH₃ SCR kinetics on Fe and Cu zeolite catalysts

- **University of Kentucky - Center for Applied Energy Research**
  - *Mark Crocker (CoPI)*
  - Bench-flow reactors, SpaciMS: LNT, HC SCR, LNT/SCR segmented reactor studies

- **Oak Ridge National Laboratory**
  - *Jae-Soon Choi*
  - Bench-flow reactor, SpaciMS: LNT, SCR spatio-temporal studies

- **BASF Catalysts LLC (formerly Engelhard Inc.)**
  - *C.Z. Wan*
  - Model catalyst synthesis & characterization; Commercial SCR catalyst

- **Ford Motor Company**
  - *Bob McCabe, Mark Dearth, Joe Theis*
  - Bench-flow reactors, SpaciMS: LNT studies – desulfation, aging
  - Vehicle testing of LNT/SCR system
Different LNT-SCR Architectures

LNT-SCR series configuration

- Daimler
- Ford

LNT-SCR layered configuration

- Honda

Several architectures under investigation in DOE project
NSR/SCR Technology

- LNT/SCR is promising non-urea deNOx technology for light- & medium-duty diesel & lean burn gasoline
- Synergistic benefits of LNT/SCR have been demonstrated: Previous studies show increased NOx conversion by adding SCR unit downstream of LNT
- Understanding of the coupling between LNT & SCR series-brick configuration is emerging
NSR/SCR: A Different Role for the LNT

NSR Target: 100% NOx conversion with 100% N₂ selectivity

\[
\begin{align*}
2 \text{ NO} & \rightarrow \text{NSR} \\
& \rightarrow 1.0 \text{ N}_2
\end{align*}
\]

LNT: \( 2 \text{ NO} + 4 \text{ H}_2 + \text{ O}_2 \rightarrow \text{ N}_2 + 4 \text{ H}_2\text{O} \)
Objectives

• Gain understanding of impact of LNT-SCR multilayer architecture

• Determine impact of multilayer catalyst design variables and operating strategies

• Provide data to develop LNT-SCR models for design and optimization
Fundamental Issues/Questions

- What should be proximity between LNT and SCR functions?
- Does SCR layer always increase the overall NOx conversion or could it reduce it (e.g. serve as diffusion barrier)?
- What are the optimal thicknesses and compositions of the LNT and SCR layers? Pt dispersion? Ceria? Fe- or Cu-zeolite?
- What about thermal durability? What about migration of Pt from LNT layer to SCR layer?
- How does the dual layer compare to sequential monolith configuration?

Our goal is to answer some of these questions...
Summary of Results w/o CO₂ & H₂O*

- Without H₂O & CO₂ in feed, LNT/SCR has slightly lower NO conversion than LNT only.
- At low temperatures (< 225 °C) most reaction occurs in LNT layer with generated NH₃ effectively trapped by Cu-zeolite; trapped NH₃ desorbs to Pt layer & is oxidized to N₂O.
- At higher temperatures (> 250 °C) undesired oxidation of NH₃ on Pt (to N₂O & NO) occurs.

Results w/o CO2 & H2O
Typical Lean-Rich Cycle for PGM/BaO (LNT1)

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
Temperature: 250°C
**LNT vs. LNT/SCR: Integral Results**

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
No CO₂ or H₂O in feed

**LNT1 + CuZ:**
- Slight decrease in NOx conversion
- Consumption of NH₃
- Some increase in N₂O
- Better catalyst than LNT1 + FeZ
Dual Layer LNT/SCR Catalysts

- Dual layer LNT/SCR catalyst comprises:
  - **Bottom layer:** Pt/Rh/BaO/alumina
    - 0.7wt.%/0.07wt.%/20wt.%
    - LNT only
  - **Top layer:** Fe-ZSM-5/alumina
    - 3-3.5 wt.% (10% washcoat loading)
    - LNT/SCR (Fe-ZSM-5)
Dual Layer LNT/SCR Catalysts

- Dual layer LNT/SCR catalyst comprises:
  - Bottom layer: Pt/Rh/BaO/alumina
  - Top layer: Fe-ZSM-5/alumina

  - Bottom layer: 0.7wt.%/0.07wt.%/20wt.%
  - Top layer: 3-3.5 wt.% (10% washcoat loading)

LNT only

LNT/SCR (Fe-ZSM-5)

- Dual-layer catalyst: reduced NH₃, increased N₂O, but a small reduction in NOx conversion!
Comparison: LNT vs. LNT/SCR (Fe- or Cu-ZSM5)

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
No CO₂ or H₂O in feed

Cu/ZSM5 out-performs Fe/ZSM5 under identical conditions
Comparison of Fe/ZSM5 and Cu/ZSM5

Fe/ZSM-5 has lower standard SCR activity & NH₃ storage capacity

Conditions:
500 ppm NO, 5% O₂
500 ppm NH₃

Conditions:
500 ppm NH₃
20 minute storage

(a) Standard SCR with NO conversion
(b) NH₃ Storage
Low Temperature LNT/SCR Behavior

![Graph showing NO conversion (%)](image)

- **CuZ+LNT**
- **LNT**

**Y-axis:** NO Conversion (%)

**X-axis:** Feed Temperature (ºC)

- From 100 to 400 ºC, NO conversion increases significantly.
- CuZ+LNT generally shows higher NO conversion compared to LNT.

**Key Points**
- At lower temperatures, CuZ+LNT has a higher NO conversion efficiency.
- As temperature increases, the difference in NO conversion between CuZ+LNT and LNT diminishes.

**Conclusion**
- The behavior of CuZ+LNT and LNT is crucial for understanding temperature effects on NO conversion in LNT/SCR systems.
Low Temperature LNT/SCR Behavior

Steady State Standard SCR on CuZ

$4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightleftharpoons 4\text{N}_2 + 6\text{H}_2\text{O}$

$\text{NO} = \text{NH}_3 = 500 \text{ ppm}$
$5\% \text{ O}_2$

$\text{SCR} = 0.9 \text{ g/in}^3$

Low activity of CuZ .... NOx reduction in LNT layer mostly but involves NH$_3$ trapped in Cu/ZSM5

$T < 250 \, ^\circ\text{C}$
N\textsubscript{2}O Formation at Low Temperature

![Diagram showing NO Conversion vs. Feed Temperature and N\textsubscript{2}O Concentration vs. Time.](image)

**Pathway:**
- \(NH\textsubscript{3}\) trapped on zeolite
- \(NH\textsubscript{3}\) migration to LNT
- \(NH\textsubscript{3}\) + \(O\textsubscript{2}\) & NO on LNT
- \(N\textsubscript{2}O\) & \(N\textsubscript{2}\)
NH$_3$ Oxidation to NOx at High Temp.

![Graph showing NO conversion (%)](Image)

Feed Temperature (ºC)

NO Conversion (%)

- CuZ+LNT
- LNT
NH₃ Oxidation to NOx at High Temp.

NH₃ oxidation in LNT layer involving NH₃ trapped by CuZ.

\[ 4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 4\text{NO} + 6\text{H}_2\text{O} \]

\[ 4\text{NH}_3 + 4\text{O}_2 \rightleftharpoons 2\text{N}_2\text{O} + 6\text{H}_2\text{O} \]
Mixed Washcoat Results
**Mixed Washcoat Performance**

**Conditions:**
Lean: 500 ppm NO, 5% O₂; 60s  
Rich: 2.5% H₂; 5s  
Temperature: 250°C

**Washcoat:**  
Physical mixture of LNT1 & CuZ  
2.1 g/in³ LNT1, 0.9 g/in³ CuZ
Mixed Washcoat Performance

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
Temperature: 250°C

Washcoat:
Physical mixture of LNT1 & CuZ
2.1 g/in³ LNT1, 0.9 g/in³ CuZ

LNT & Cu/ZSM5 mixture:
- significant N₂O at low T
- significant NO₂ generation & breakthrough
- most N₂ made during lean

LNT/SCR: H₂ Reductant in Presence of CO₂ & H₂O

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
(Both: 2.5% H₂O, 2% CO₂)

LNT/SCR: Favorable NO₂/NOx ratio for SCR
CO + H2 Results
## Experiments

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<th>Reductant</th>
<th>CO$_2$ + H$_2$O?</th>
<th>Dual Layer Catalyst</th>
</tr>
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<tbody>
<tr>
<td>H$_2$</td>
<td>No</td>
<td>LNT1/Cu-ZSM5, Fe-ZSM5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>No</td>
<td>LNT1/Cu-ZSM5 (mixed layer)</td>
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<tr>
<td>H$_2$</td>
<td>Yes</td>
<td>LNT1/Cu-ZSM5</td>
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<td>Yes</td>
<td>LNT1+LNT3/Cu-ZSM5</td>
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LNT/SCR with CO + H₂ Reductant

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
or 2.5% H₂, 1.0% CO
(with 2.5% H₂O, 2% CO₂)

LNT: Overall lower NOx conversion with CO in feed

LNT/SCR: Increase in NOx conversion & N₂ selectivity
Ceria Loading Effect

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
LNT: Impact of CeO₂ Addition

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
or 2.5% H₂, 1.0% CO
(with 2.5% H₂O, 2% CO₂)

rWGS: \[ H₂ + CO₂ \rightleftharpoons H₂O + CO \]

...... CO adsorbs on Pt crystallites

WGS: \[ H₂O + CO \rightleftharpoons H₂ + CO₂ \]

...... Cleans off Pt crystallites
LNT: Impact of CeO$_2$ Addition

Conditions:
Lean: 500 ppm NO, 5% O$_2$; 60s
Rich: 2.5% H$_2$; 5s
or 2.5% H$_2$, 1.0% CO
(with 2.5% H$_2$O, 2% CO$_2$)

Lower temperature performance not good in presence of CO – requires addl. measures

Addition of CeO$_2$ to LNT beneficial:
* Provides additional NOx storage sites
* Mitigates CO inhibition
* Promotes WGS chemistry

WGS: H$_2$O + CO $\leftrightarrow$ H$_2$ + CO$_2$

....... Cleans off Pt crystallites
CeO₂ Promotion of WGS Reaction

Pt/Rh/BaO/CeO₂ catalyst exhibits enhanced water gas shift activity
Comparison of LNT2 & LNT3: Ceria Loading Effect

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s

(a) LNT2
(b) CuZ-LNT2
(c) LNT3
(d) CuZ-LNT3
Effect of Ceria on LNT/SCR

Ceria increases cycle-averaged NO conversion at low temperature

Conditions:
Lean: 500 ppm NO, 5% O$_2$; 60s
Rich: 2.5% H$_2$; 5s
Effect of Ceria on LNT/SCR

Roles of ceria in LNT/SCR:
- Increases NOx storage & NO conversion at low temperature
- Promotes WGS reaction

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
LNT/SCR: Ceria Zoning

(a) 2.5% H₂

(b) 2.0% H₂ & 0.5% CO

(c) 1.5% H₂ & 1.0% CO

Sample | Upstream Ceria Level (wt.%) | Downstream Ceria Level (wt.%) |
-------|-----------------------------|------------------------------|
CuZ-LNT2 | 17 | 17 |
UL-DH | 0 | 34 |
UH-DL | 34 | 0 |

UL-DH > UH-DL > CuZ-LNT2

Nonuniform ceria works better
Zoning of ceria:
Achieves beneficial trade-off
- Approaches LNT3 performance at low temperature
- Approaches LNT1 performance at high temperature

UL-DH-3:
- First half: CuZ-LNT1; aged
- Second half: CuZ-LNT3; 2.0 g/in³

Ceria Loading Effect

Zoning of ceria:
Achieves beneficial trade-off
- Approaches LNT3 performance at low temperature
- Approaches LNT1 performance at high temperature

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
Aging Effects
Aging Effects: Stabilization by Ceria

Aging: 600 °C for 100 hours in air

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
(with 2.5% H₂O, 2% CO₂)

Aging reduces lowers NOx conversion for all temp.’s

Ceria-free LNT/SCR shows large NH₃ release

Ceria-based LNT/SCR shows less thermal degradation

SEM microprobe shows less Pt migration from LNT to SCR
Ceria: Mitigation of Pt Migration

Pt/Pt_{max}

LNT/SCR interface

(a) CuZ + LNT1

(b) CuZ+LNT2

(c) CuZ+LNT3

Dimensionless concentration (%) vs. Dimensionless Distance
LNT/SCR: Effect of Aging & Loading

**Improvement achieved with different reductant compositions**

**UL-DH-3 superior to UL-DH-2:** Higher loading of CuZ layer

<table>
<thead>
<tr>
<th>Sample</th>
<th>LNT1 Activity</th>
<th>LNT3 Activity</th>
<th>SCR Loading (g/in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UL-DH-1</td>
<td>Fresh</td>
<td>Fresh</td>
<td>0.9</td>
</tr>
<tr>
<td>UL-DH-2</td>
<td>Aged</td>
<td>Fresh</td>
<td>0.9</td>
</tr>
<tr>
<td>UL-DH-3</td>
<td>Aged</td>
<td>Fresh</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Ceria Loading & Aging Effects

Increased ceria results in higher NO conversion and generally higher N₂ selectivity

Ceria slows degradation by stabilizing Pt and Pt migration

Conditions:
Lean: 500 ppm NO, 5% O₂; 60s
Rich: 2.5% H₂; 5s
Aging: 600 °C for 100 hours
## Results Matrix

<table>
<thead>
<tr>
<th>Reductant</th>
<th>CO$_2$ + H$_2$O?</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>Yes</td>
<td>LNT1/Cu-Z</td>
</tr>
<tr>
<td>H$_2$</td>
<td>No</td>
<td>LNT1/Cu-Z (mixed layer)</td>
</tr>
<tr>
<td>H$_2$ + CO</td>
<td>Yes</td>
<td>LNT1, LNT3</td>
</tr>
<tr>
<td>H$_2$ + CO</td>
<td>No</td>
<td>LNT1/Cu-Z $\rightarrow$ LNT3/Cu-Z</td>
</tr>
<tr>
<td>H$_2$ + CO</td>
<td>Yes</td>
<td>LNT1+LNT3/Cu-Z zoned ceria</td>
</tr>
</tbody>
</table>

**Final step:** optimize cycling parameters:
*Total cycle time, reductant feed intensity*
Optimization of Cycle Timing: Intensity of Reductant Pulse

Comparisons of (a) NO\textsubscript{x} conversion and (b) H\textsubscript{2} conversion under different lean-rich cycles using a 2.0 g/in\textsuperscript{2} CuZ-Front Aged LNT1 back LNT3 dual-layer catalyst.

Catalyst: UL-DH-3
Lean: 500 ppm NO, 5\% O\textsubscript{2},
(with 2.5\% H\textsubscript{2}O, 2\% CO\textsubscript{2})

Rich Feed:
\begin{align*}
\text{C}_{\text{H}_{2}}\%) \\
60-20: & \quad 0.63 \\
60-10: & \quad 1.25 \\
60-5: & \quad 2.50 \\
60-3: & \quad 4.17 \\
2.5\% H_{2}O, 2\% CO_{2}
\end{align*}

Optimal rich pulse time for fixed amt. reductant & storage time:
60 s lean, 10 s rich (1.25\% H\textsubscript{2})

Optimization of Cycle Timing: Total Cycle Time

Catalyst: UL-DH-3
Lean: 500 ppm NO, 5% O₂, Rich: 2.5% H₂ (with 2.5% H₂O, 2% CO₂)

Varied lean/rich timing:
Lean Rich
60 s 10 s
30 s 5 s
6 s 1 s

Optimal total cycle time with fixed reductant duty cycle:
30 s lean, 5 s rich