Synergy of LNT and SCR Catalysts in Coupled LNT-SCR Systems

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CLEERS Workshop, April 12, 2013

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Synergy of LNT and SCR Catalysts in Coupled LNT-SCR Systems

Overview:

- Coupled LNT-SCR systems: concept and development
- Role of HCs in NOx reduction over coupled LNT-SCR (Cu-CHA) system
- NOx reduction using HCs and NH\textsubscript{3} over Cu-CHA
- Mitigation of N\textsubscript{2}O and H\textsubscript{2}S emissions over Cu-CHA in LNT-SCR configuration
- Plasma-assisted LNT catalyst regeneration
- Summary
LNT-SCR Concept: Utilization of *In Situ* NH$_3$

- “Classical” explanation:
  - LNT produces NH$_3$ during rich purges (similar to TWC under rich engine conditions)
  - NH$_3$ stores on downstream SCR catalyst
  - Stored NH$_3$ reacts with “breakthrough” NOx during lean operation
  - Similar to urea-SCR except that NH$_3$ is generated “in-situ” or “passively” by the LNT

LNT-SCR Concept: History

• First U.S. patent to DaimlerChrysler in 2001 (US 6,176,079)

• Other U.S. patents to SwRI, Ford, Eaton, DaimlerChrysler, GM, BASF, Umicore, Johnson-Matthey

• First open literature publications:
  2006, Eaton Corp., use of LNT-SCR system for HDD applications
  2006-2007, Ford, use of LNT-SCR for LDD applications

• First application: Daimler, BlueTEC Mercedes E320 (introduced in October 2006 in U.S.)

• 2nd generation LNT-SCR system reported by Ford in 2009
  (Fe-zeolite SCR catalyst replaced by Cu-CHA)

• LNT-SCR system models published:
  2009-2010: Daimler group
  2010: Kočí et al.
  2012: Balakotaiah et al.
LNT-SCR Concept: Applications

BlueTEC Mercedes E320 (MY 2007 in U.S.) and E300 (MY2008 in Europe)
V6 CDI engine

- Aimed at Tier II Bin 8, corresponding to ca. 50% NOx conversion requirement
- DOC-LNT-CDPF-SCR exhaust catalyst configuration
- Function of SCR catalyst appears to have been mainly for avoidance of NH₃ slip
- Used in MY2007-2009
- Superceded by BlueTEC II urea-SCR system (Tier II, Bin 5)

2nd Generation LNT + SCR

• Key points:
  – enabled by advances to both LNT catalyst technology and SCR catalyst technology
  – NH$_3$ *in situ* mechanism does not fully explain LNT+SCR vehicle data: HC-SCR in Cu-CHA catalyst also contributes to NOx reduction
  – Cu-CHA also plays active role in mitigation of N$_2$O and H$_2$S emissions
  – excellent NOx reduction activity of Cu-CHA catalyst (and stability w.r.t. aging) enables decrease in LNT PGM loadings

Vehicle Testing: Steady-Speed (Ford data: R. McCabe and M. Dearth)

NOx & NH₃ concentration during a steady state
(55mph, catalyst temperature at 380°C (lean) and 430°C (rich))

NH₃ produced cannot explain extra NOx conversion by SCR catalyst
Reactor Studies

**LNT-SCR studies:**

- **BASF catalysts:**
  - Low PGM-loaded LNT + Cu-chabazite SCR catalyst
- **3” x 0.9” cores, de-greened at 500 °C for 5 h under L/R cycling**
- **Separate catalysts/reactors with gas sampling at three positions**
- **60 s lean/5 s rich cycles**
- **Gas analysis using FTIR gas analyzer**
NOx and NH₃ Conversion in LNT-SCR System: Effect of Added Propene (Rich Phase)

60 s lean – 5 s rich cycles:
Rich condition #1: 1% CO, 0.3% H₂, 3333 ppm C₃H₆
Rich condition #2: 1% CO, 0.3% H₂

Benefit of SCR catalyst most apparent when hydrocarbon (propene) is present
→ SCR catalyst is able to utilize propene - or a derivative thereof - as a reductant

Nitrogen Balance Across SCR Catalyst
Reductant = 1% CO + 0.3% H₂ + 3333 ppm C₃H₆

<table>
<thead>
<tr>
<th>LNT Inlet Temperature (°C)</th>
<th>NH₃ converted over SCR catalyst (ppm)</th>
<th>NOx converted over SCR catalyst (ppm)</th>
<th>NH₃ converted – NOx converted (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>149</td>
<td>0.1</td>
<td>9.3</td>
<td>-9.1</td>
</tr>
<tr>
<td>166</td>
<td>0.3</td>
<td>6.7</td>
<td>-6.3</td>
</tr>
<tr>
<td>183</td>
<td>0.9</td>
<td>23.9</td>
<td>-23.0</td>
</tr>
<tr>
<td>196</td>
<td>1.9</td>
<td>21.5</td>
<td>-19.6</td>
</tr>
<tr>
<td>232</td>
<td>8.7</td>
<td>52.6</td>
<td>-43.9</td>
</tr>
<tr>
<td>275</td>
<td>11.9</td>
<td>42.4</td>
<td>-30.5</td>
</tr>
<tr>
<td>316</td>
<td>14.6</td>
<td>26.8</td>
<td>-12.2</td>
</tr>
<tr>
<td>375</td>
<td>15.9</td>
<td>27.7</td>
<td>-11.8</td>
</tr>
<tr>
<td>421</td>
<td>11.4</td>
<td>34.7</td>
<td>-23.3</td>
</tr>
</tbody>
</table>
Speciation Study of LNT Exhaust Gas

- FT-IR applied to study formation of potential NOx reductants over LNT (other than NH₃); only HCN is consistently observed in gas phase, but in low concentrations.
- GC-MS also failed to detect significant gas phase organo-N species.
- Hence, formation of organo-nitrogen species over LNT does not appear to be important for SCR.

- Slipped hydrocarbon is responsible for NOx reduction in SCR catalyst.

Measured HCN downstream of LNT during lean/rich cycling (for 3 different reductant mixtures).
Lean/Rich Cycling over SCR Catalyst

60 s lean / 10 s rich

T = 435°C

Propylene

- NOx Conversion (%)
- Lambda
- T = 435°C
- NOx
- Lambda

Ethylene

- NOx Conversion (%)
- Lambda
- T = 435°C
- NOx
- Lambda

Concentration (ppm)

- Propylene
- CO
- Ethylene
- Formaldehyde
- Acetaldehyde
- Propane
- MeOH
- n-octane
- Toluene

Lean/Rich Cycling over SCR Catalyst

60 s lean / 10 s rich

T = 435°C

- NOx Conversion (%)
- Lambda
- T = 435°C
- NOx
- Lambda

Concentration (ppm)

- Propylene
- CO
- Ethylene
- Formaldehyde
- Acetaldehyde
- Propane
- MeOH
- n-octane
- Toluene

Lean/Rich Cycling over SCR Catalyst

60 s lean / 10 s rich

T = 435°C

- NOx Conversion (%)
- Lambda
- T = 435°C
- NOx
- Lambda

Concentration (ppm)

- Propylene
- CO
- Ethylene
- Formaldehyde
- Acetaldehyde
- Propane
- MeOH
- n-octane
- Toluene
NOx Conversion over Cu-zeolite SCR Catalyst During Lean-rich Cycling: C₃H₆ and C₂H₄ as Rich Phase Reductants

**SCR catalyst only:**
Lean (60 s): 300 ppm NO, 8% O₂, 5% CO₂, 5% H₂O, N₂ as balance; Rich (5 s): 300 ppm NO, 3333 ppm C₃H₆ or 5000 ppm C₂H₄, O₂ as indicated, 5% CO₂, 5% H₂O, N₂ as balance

- Cycle-averaged NOx conversion is higher than theoretical value if NOx is only reduced during rich phase => hydrocarbon storage + lean phase NOx reduction
- NOx conversion is sensitive to O₂ content of feed
Steady State NOx Conversion over Cu-zeolite SCR Catalyst

Conditions: 300 ppm NO, 5% CO₂, 5% H₂O, N₂ balance, GHSV = 30,000 h⁻¹

- Propylene and ethylene show moderate activity for NOx reduction over SCR catalyst under steady-state and cycling conditions
- NOx conversion is sensitive to O₂ content of feed
Breakthrough curves for C₃H₆ adsorption on Cu-CHA

Arrhenius plot of Henry’s constant values obtained from Langmuir isotherm model

- Maximum C₃H₆ loading (72 °C) = 3.6 wt%
- Magnitude of heats of adsorption consistent with chemi- and physisorption; chemisorption is indicated to be strong
- TPD experiments (Cu-CHA and Cu-leached samples): desorption peak at 250 °C due to propene adsorbed on Cu²⁺; desorption peaks at 150 °C and 330 °C due to propene adsorbed on (non-Cu) acidic sites in zeolite
- In addition to propene, many other desorbed species are observed: C₂H₂, C₂H₄, C₂H₆, C₄H₈, CO, CO₂, H₂O, etc.
Spatiotemporal Analysis of NOx Reduction by NH₃ & C₃H₆ over Cu-chabazite During Lean/Rich Cycling

- Bench-reactor experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>NH₃ Lean (60 s)</th>
<th>NH₃ Rich (5 s)</th>
<th>C₃H₆ Lean (60 s)</th>
<th>C₃H₆ Rich (5 s)</th>
<th>NH₃ + C₃H₆ Lean (60 s)</th>
<th>NH₃ + C₃H₆ Rich (5 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO (ppm)</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>O₂ (%)</td>
<td>8</td>
<td>1</td>
<td>8</td>
<td>1</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>C₃H₆ (ppm)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3333</td>
<td>0</td>
<td>3333</td>
</tr>
<tr>
<td>NH₃ (ppm)</td>
<td>0</td>
<td>300</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>300</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>H₂O (%)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>N₂ (%)</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balace</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

- Total flow: 13.7 L/min (equivalent to 30K SV for 3-in core: 1L)
- Temperature: 200, 250, 300, 350, 400, 450 °C

- Spatiotemporal resolution of reactions
NOx Reduction by NH$_3$

- Total consumption of NH$_3$ with near stoichiometric NO$_x$ reduction within 1$^{st}$ ¼ catalyst at all temps.

- NOx reduction occurs both in rich & lean phases
- Greater portion of NOx reduction in lean phase at lower temperatures
  - Due to lower reduction rate & higher NH$_3$ storage
Significant NOx Reduction by C₃H₆ Above 250 °C

- Up to ~20% NOx conversion
- Best performance at 350 °C
- Entire length used except at 400-450 °C

- NOx reduction occurs both in rich & lean phases (3 “regimes” at 350, 400, 450 °C)
- Greater portion of NOx reduction in lean phase at 300 °C than at 450 °C
  - Due to lower reduction rate & higher C₃H₆ storage (see peak tails)
NH₃ Could be Surface Intermediate

Temperature ramp (200 → 500 °C) after C₃H₆ cycling at 450 °C → 200 °C; catalyst was purged with O₂, H₂O and CO₂ at 200 °C before the TPD

- High-T release of NH₃ suggests its formation, storage & usage on surface only
  - Could explain "3rd" NOx reduction regime (peak in lean phase) observed during C₃H₆ cycling at 350, 400, 450 °C

Purge at 200 °C until C₃H₆ close to zero
Effects of NH$_3$ & C$_3$H$_6$ on NOx Reduction are Additive

- Spatial profiles of NH$_3$ & C$_3$H$_6$ utilization virtually unaffected by co-feeding
### Bench-reactor experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>C₃H₆</th>
<th>NH₃ + C₃H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>¹⁵N¹⁸O (ppm)</strong></td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td><strong>O₂ (%)</strong></td>
<td>8</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td><strong>C₃H₆ (ppm)</strong></td>
<td>0</td>
<td>0</td>
<td>3333</td>
</tr>
<tr>
<td><strong>NH₃ (ppm)</strong></td>
<td>0</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td><strong>CO₂ (%)</strong></td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>H₂O (%)</strong></td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>Ar (%)</strong></td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

- Total flow: 6.9 L/min
- Catalyst length: 0.75 in
- Temperature: 350 °C

Note: higher NO, NH₃ concentrations & lower flow rate used to facilitate MS analysis
$^{15}$N$^{18}$O Experiments Performed to Probe the Chemistry of NH$_3$ Intermediate (cont.)

- **Gas effluent analysis**
  - Mass spectrometer (EI, quadrupole)
  - Monitored mass-to-charge ratios (m/z):
    - Reductants: 24 (C$_2$H$_4$), 28 (CO, C$_2$H$_4$), 29 & 30 (aldehydes), 41 (C$_3$H$_6$)
    - O$_2$: 34 ($^{18}$O$^{16}$O)
    - NO: 31 ($^{15}$N$^{16}$O major component at outlet)
    - N$_2$: 29 ($^{15}$N$^{14}$N), 30 ($^{15}$N$_2$)

- **Cross-sensitivity issues have been considered**

- $^{15}$N$_2$
- Rich phase
- m/z 29
- m/z 30
- m/z 29 & 30 can represent both nitrogen and aldehydes
- Aldehyde-attributable signals were subtracted

\[ m/z \ 29 \text{ and } 30 \text{ can represent both nitrogen and aldehydes} \]

\[ m/z \ 29 \text{ and } 30 \text{ can represent both nitrogen and aldehydes} \]
C\textsubscript{3}H\textsubscript{6} Contributes to NH\textsubscript{3} Formation but Inhibits NH\textsubscript{3}-NO Reaction

- 2 regimes of \textsuperscript{15}NO reduction during NH\textsubscript{3} cycling
  - Rich phase (I); early lean phase (II)
- 3 regimes of \textsuperscript{15}NO reduction during C\textsubscript{3}H\textsubscript{6} cycling
  - Rich phase (I); early lean phase (II); mid lean phase (III; starts when HC's are depleted)
- Regimes I & II of \textsuperscript{15}NO reduction during C\textsubscript{3}H\textsubscript{6} cycling lead exclusively to \textsuperscript{15}NH\textsubscript{3}
  - Third regime (III) utilizes stored \textsuperscript{15}NH\textsubscript{3} producing \textsuperscript{15}N\textsubscript{2}
- Adsorbed hydrocarbons slow kinetics of NH\textsubscript{3} utilization (i.e., \textsuperscript{15}N\textsuperscript{14}N formation)
  - cf. unaffected NH\textsubscript{3} storage capacity & additive effect on cycle-averaged NO conversion
Mitigation of H₂S Emissions by Cu-CHA SCR Catalyst
Desulfation Comparison: LNT-only vs. LNT-SCR

Ford Laboratory Data

Cu-CHA SCR catalyst virtually eliminates H₂S emissions produced by LNT during rich high-temperature desulfation (H₂S from LNT converted to SO₂) – more detail in SAE 2009-01-0285 (L. Xu et al.)
N$_2$O Reduction Over Cu-CHA SCR Catalyst

Cycle-averaged N$_2$O conversion over SCR catalyst during 60 s lean/5 s rich cycling:

Lean: 300 ppm NO, 8% O$_2$, 5% CO$_2$, 5% H$_2$O, N$_2$ as balance;
Rich: 300 ppm NO, 1% H$_2$ or 1% CO or 3333 ppm C$_3$H$_6$ as reductant, 5% CO$_2$, 5% H$_2$O, N$_2$ as balance;
GHSV = 30,000 h$^{-1}$

- H$_2$ best reductant for N$_2$O
- No reductant breakthrough from LNT observed at ≥400 °C, hence N$_2$O conversion tails off (implies that N$_2$O decomposition must be occurring)
N$_2$O Reduction Over Cu-CHA SCR Catalyst

Comparison of gas composition behind LNT and SCR catalysts during lean-rich cycling (1% C$_3$H$_6$ as reductant, 360 s lean, 30 s rich; 375 °C)

- As expected NOx and N$_2$O breakthrough LNT catalyst before NH$_3$ and C$_3$H$_6$
- Significant conversion of NOx, NH$_3$, C$_3$H$_6$ and N$_2$O over SCR catalyst
Comparison of N₂O concentrations behind LNT & SCR catalysts (360 s lean, 30 s rich):

- Increased N₂O formation over LNT when using CO as reductant, compared to H₂ (consistent with Abdulhamid et al. and LePhuc et al.)
- For CO, N₂O formation observed at L-R and R-L transition (consistent with Elizundia et al.)
- Some N₂O conversion occurs before reductant has broken through, implying N₂O decomposition

N\textsubscript{2}O Reduction Over Cu-CHA SCR Catalyst: Steady-state Continuous Flow (1)

Feed: 100 ppm N\textsubscript{2}O, 5% CO\textsubscript{2}, reductant as shown, bal. N\textsubscript{2}; GHSV = 30,000 h\textsuperscript{-1}

- H\textsubscript{2} best reductant, followed by NH\textsubscript{3}
- N\textsubscript{2}O reduction not inhibited by water; v. slight inhibition of decomposition reaction
- Slight promoting effect with water for reduction using CO or C\textsubscript{3}H\textsubscript{6}; implies in situ formation of H\textsubscript{2} via WGS or steam reforming
N₂O Reduction Over Cu-CHA SCR Catalyst: Steady-state Continuous Flow (2)

- N₂O decomposition is weakly promoted by NO, e.g.: N₂O + NO → N₂ + NO₂
- Effect appears to be catalytic, rather than stoichiometric (e.g., may facilitate migration of adsorbed O through NO₂ intermediates, enhancing the recombination of O atoms)*

LNT-SCR System Aging

Cycle-averaged NOx conversion for BASF LNT and LNT-SCR systems

Feed: lean (60 s): 500 ppm NO, 8% O2, 5% CO2, 5% H2O, balance N2; rich (5 s): 2.5% CO, 5% CO2, 5% H2O, balance N2. GHSV = 60,000 h⁻¹.

- After aging, deterioration in LNT NOx conversion is observed; based on analytical data, this can be attributed to accumulation of residual sulfate in washcoat and Pt-Ba phase segregation (→ decreased NOx storage capacity)
- After aging, NOx conversion over SCR catalyst is increased, due to increased LNT selectivity to NH3 and increased NOx slip available for reaction
- Hence, SCR catalyst helps to compensate for deterioration in LNT NOx conversion
The 150 °C Challenge: Non-thermal Plasma-Assisted NOx Storage-Reduction on Perovskite LNT Catalysts

• Limiting factors for LNT operation at low temperatures are ability to:
  (i) store NOx
  (ii) regenerate storage sites
  (iii) reduce released NOx

• Concept:
  - apply perovskites for (i)
  - apply non-thermal plasma for (ii) and (iii)*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO\textsubscript{x} storage capacity (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 °C</td>
</tr>
<tr>
<td>Pt/30BaO/Al\textsubscript{2}O\textsubscript{3}</td>
<td>86.9</td>
</tr>
<tr>
<td>LaMn\textsubscript{0.9}Fe\textsubscript{0.1}O\textsubscript{3}</td>
<td>380.5</td>
</tr>
</tbody>
</table>

500 ppm NO, 8% O\textsubscript{2}, N\textsubscript{2} bal., 50 min, GHSV = 30,000 h\textsuperscript{-1}

* Production of H\textsubscript{2}-rich gas for LNT regeneration using plasmatron fuel reformer:
Comparison of First Cycle and Cycle-averaged NOx Storage Capacities for Fully Formulated LNT Catalysts

- LNT performance severely limited at 150 °C by ability to regenerate NOx storage sites

Non-thermal Plasma-Assisted NOx Storage-Reduction: Experimental Details

H₂ or Ar non-thermal plasma applied in rich phase

Discharge power = 20 w

Effluent gases analyzed using MS

NOx Conversion Under Lean-Rich Cycling w/o NTP: $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$

- Lean (10 min): 500 ppm NO, 8% $\text{O}_2$, bal. Ar
- Rich (2 min): 1% $\text{H}_2$, bal. Ar; GHSV = 10,000 h$^{-1}$
- Catalyst pre-treatment in 1% $\text{H}_2$ at 500 °C for 1 h

- Low rich phase NOx reduction activity of $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ responsible for poor NOx conversion under lean-rich cycling
NOx Conversion Under Lean-Rich Cycling with NTP: LaMn$_{0.9}$Fe$_{0.1}$O$_3$

N$_2$ and NOx profiles (T = 30 °C)
Solid line: H$_2$ plasma; dotted: Ar plasma

- 90% NOx conversion obtained at 30 °C for LaMn$_{0.9}$Fe$_{0.1}$O$_3$ under these conditions

Summary (1)

- Reactor studies have shown that a hydrocarbon-based NOx reduction pathway (ethylene and propylene studied) can operate on a Cu-chabazite SCR catalyst in parallel with the NH$_3$-SCR pathway.
- The contribution of hydrocarbons to NOx reduction is most evident under conditions of low NH$_3$ availability.
- NH$_3$ is formed as an intermediate in NOx reduction by propene on the SCR catalyst.
- The presence of propene slows the kinetics of (co-fed) NH$_3$ utilization by NOx on the SCR catalyst, but doesn’t affect cycle-averaged NH$_3$ utilization (60 s lean/5 s rich cycles) except at very high concentrations.
- Propene adsorbs strongly in the Cu-chabazite catalyst; at high temperatures, propene is converted to a variety of products (via oligomerization, cracking, oxidation, etc.).
Summary (2)

• The synergy of coupled LNT-SCR systems results in significant operational benefits:
  - higher system NOx conversion due to ability of SCR catalyst to utilize NH$_3$ and HCs for NOx reduction
  - lower NH$_3$ and HC emissions
  - lower H$_2$S and N$_2$O emissions
  - ability to compensate for decreased LNT activity after aging (NOx reduction increasingly shifted towards SCR catalyst)

• The use of NTP, combined with perovskites possessing high NOx storage capacity, represents a promising approach for low temperature NOx storage-reduction
Acknowledgements

• Funding:
  Department of Energy, Vehicle Technologies Program

• Project partners:
  ORNL
  Ford Motor Co.
  University of Houston: M. Harold
  BASF: C.Z. Wan

• Dalian University of Technology