Development of Optimal Catalyst Designs and Operating Strategies for Lean NOx Reduction in Coupled LNT-SCR Systems

Mike Harold, PI
University of Houston
June 10, 2010

ACE029

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Overview

TIMELINE
- Start: Oct. 1, 2010
- End: Sept. 30, 2012
- 10% complete

BUDGET
- Total project funding
  - DOE: $2,217,317
  - UH & partners: $687,439
- Funding received
  - FY10: $637,728

BARRIERS/TARGETS
- Reduce NOx to < 0.2 g/bhp-h for heavy-duty diesel by 2015
- Reduce PM to < 0.01 g/bhp-h for heavy-duty diesel by 2015
- Increase truck efficiency by 20% over current levels by 2015

PARTNERS
- U. Houston (lead)
- Center for Applied Energy (U. Kentucky)
- Ford Motor Company
- BASF Catalysts LLC
- Oak Ridge National Lab
LNT/SCR Research: Observations

- Synergistic benefits of LNT/SCR have been demonstrated
- Most previous studies show increased NOx conversion by adding SCR unit downstream of LNT
- Mechanisms of LNT/SCR synergies not understood or characterized
- Understanding captured in quantitative models will lead to optimal LNT/SCR designs & operating strategies
  - Reduced PGM, improved fuel utilization
Goal: Identify the NOx reduction mechanisms operative in LNT (Lean NOx Traps) and *in situ* SCR (Selective Catalytic Reduction) catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies.

Impact: Progress towards goal will accelerate the deployment of a non-urea NOx reduction technology for diesel vehicles.
NSR/SCR Catalyst Architectures

Several catalyst formulations & architectures to be evaluated in this project
Collaborative Project Team: Fundamentals to Applications

- **University of Houston**
  - Mike Harold (PI), Vemuri Balakotaiah, Dan Luss
  - Catalytic engineering; NOx storage & reduction, DPF research, Diesel emissions

- **University of Kentucky - Center for Applied Energy**
  - Mark Crocker (CoPI)
  - Catalytic materials; Lean NOx reduction & catalysis research

- **Oak Ridge National Laboratory**
  - Jae-Soon Choi
  - Extensive R&D in emission aftertreatment

- **BASF Catalysts LLC (formerly Engelhard Inc.)**
  - C.Z. Wan, Stan Roth
  - International leader in emission catalysts
  - LNT work builds off UH – BASF collaborations

- **Ford Motor Company**
  - Bob McCabe, Mark Dearth, Joe Theis
  - OEM provides path to application
  - UH & CAER/UK have had close collaborations with Ford
Approach: Team Participants

- **UH**
  - Kinetic Data
    - LNT & SCR mechanism & kinetics (BSR3, TAP)
    - LNT-SCR segmented performance & optimization (BSR4, engine dyno)
    - LNT & SCR microkinetic modeling & parameter estimation
    - LNT-SCR segmented & double-layer reactor modeling
    - LNT-SCR system optimization & integration (engine dyno, BSR4)

- **CAER**
  - Performance Data
    - Catalyst formulation & characterization
    - LNT ammonia generation (BSR1)
    - LNT-SCR serial & double-layer (BSR)
    - LNT-SCR aging (BSR)

- **BASF Catalysts**
  - Catalysts
    - Catalyst synthesis
    - LNT & SCR catalyst expertise

- **Ford**
  - Performance Data
    - Desulfation & durability testing (BSR2, chassis dyno)
    - LNT, SCR, LNT-SCR performance & application expertise
    - LNT-SCR systems integration (chassis dyno)

- **CAER**
  - Spatio-Temp. Data
    - Catalyst characterization
    - LNT ammonia generation (SpaciMS)
    - LNT-SCR mechanism (DRIFTS)
    - LNT-SCR serial & double-layer performance (SpaciMS)

- **CAER**
  - DRIFTS Data
    - LNT-SCR segmented & double-layer reactor modeling

- **ORNL**
  - Catalyst characterization
    - LNT ammonia generation (SpaciMS)
    - LNT-SCR mechanism (DRIFTS)
    - LNT-SCR serial & double-layer performance (SpaciMS)

- **UH**
  - Reports, Publications, Presentations, Graduates

- **BASF Catalysts**
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    - LNT-SCR system optimization & integration (engine dyno, BSR4)
Project Deliverables: Phase 1

- Identify the main NO\textsubscript{x} conversion mechanisms in LNT-SCR systems
- Determine LNT catalyst composition effects and operating conditions for maximizing \textit{in situ} ammonia generation, supported by model predictions
- Establish the kinetics of primary reactions during NO\textsubscript{x} storage and reduction and ammonia-based SCR
## Schedule of Tasks: Phase 1

<table>
<thead>
<tr>
<th>Phase 1 Tasks</th>
<th>Year 1</th>
<th>Year 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1: Project management &amp; planning</td>
<td>Q1</td>
<td>Q2</td>
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<tr>
<td>1.2: Reactor study of non-NH$_3$ NO$_x$ reduction mechanism</td>
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<td>1.3: DRIFTS study of non-NH$_3$ NO$_x$ reduction mechanism</td>
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<td>1.4: TAP study of NO$_x$ reduction with H$_2$/CO/C$_3$H$_6$ on LNT</td>
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<td>1.5: Kinetics study of NO$_x$ storage &amp; reduction with H$_2$/CO/C$_3$H$_6$ on LNT:</td>
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<td>1.5.1: Steady-state kinetics of reactions on LNT</td>
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<td>1.5.2: NO$_x$ storage and NO oxidation on LNT</td>
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<td>1.6: Parametric study of LNT NO$_x$ reduction selectivity</td>
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<td>Q1</td>
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<td>1.7: Development of microkinetic models</td>
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<td>1.8: Development of low-dimensional models</td>
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<td>1.9: Phase 1 reporting</td>
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<td>Q2</td>
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*(Red indicates in progress; ■ indicates complete)*
## Schedule of Tasks: Phase 2

<table>
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<th>Phase 2 Tasks</th>
<th>Year 2</th>
<th>Year 3</th>
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<tbody>
<tr>
<td></td>
<td>Q 1</td>
<td>Q 2</td>
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<tr>
<td>2.1: Spatiotemporal study of LNT NO(_x) reduction selectivity</td>
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<tr>
<td>2.2: Isotopic TAP study of NO(_x) reduction on LNT &amp; SCR</td>
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<tr>
<td>2.3: Transient kinetics of NO(_x) reduction on LNT &amp; SCR</td>
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<tr>
<td>2.4: Kinetics of transient NO(_x) reduction w/ NH(_3) on SCR</td>
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<td>2.5: Examine effect of PGM/ceria loading on LNT-SCR</td>
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<td>2.6: Prepare double layer LNT-SCR catalysts</td>
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<tr>
<td>2.7: Spatiotemporal study of LNT-SCR performance</td>
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<tr>
<td>2.8: Sulfation-desulfation study of LNT-SCR system</td>
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<tr>
<td>2.9: Modeling and simulation studies</td>
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<tr>
<td>2.10: Phase 2 reporting</td>
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Project Approach & Tools

Premise: Systematic approach and state-of-art tools leads to fundamental understanding & optimized designs

- Catalyst synthesis & characterization
- Bench reactors
- FTIR, QMS, CIMS
- SpaciMS
- TAP reactor
- Dynamometers
Non-Ammonia NOx Reduction Mechanism
(Ford; Tasks 1.2, 2.7)

Lab reactor data suggest a non-NH$_3$ reduction mechanism

- **Enhanced conversion from SCR cat at temps below 225°C and above 450°C**
  (where little or no NH$_3$ is formed or expected to store on the SCR cat)
- **Data suggest an additional non-ammonia NOx conversion mechanism over the SCR catalyst.**

Lab data: 70K simulated 3-mode Lab aging; 60sL/5sR eval. cycles
Vehicle Testing: Steady-Speed

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


Before LNT

After LNT

After SCR

NH₃ produced cannot explain extra NOx conversion by SCR
Experimental Results (Task 1.2; Ford)

- No NH$_3$ observed between LNT/SCR in some cases: This rules out NH$_3$-SCR due to NH$_3$ storage (and no lean LNTNH$_3$ production!).
- No R-NO observed between LNT/SCR: This rules out nitromethane production on the LNT and storage on the SCR.
- SCR reduces NO and NO$_2$ for 100-300 sec after 2-5 sec rich period: Indicates a stored or in situ reactant.
- NOx reduction over the SCR requires periodic rich purge: Reductants required to create reactive species in LNT.
- N-containing Reductant is produced on LNT, and it gives no signal in FID and NOx analyzers:

**HCNO is likeliest possibility.**

Some N-containing Species produced by LNT, as evidenced by NOx remake post LNT

Production favored by lower temperatures and reduced oxidation/storage performance of LNT

![Cyanuric Acid](attachment:cyanuric_acid.png)

cyanuric acid
HNCO Observed in Lab Reactor Under Lean/Rich Cycling Conditions (no H₂O; CO₂)

Formation of HNCO (M/Z 43) with Ethylene

- HNCO ppm
- NH₃ ppm
- Ethylene ppm
- Propene ppm
- NO ppm
- NO₂ ppm

HNCO Observed in Lab Reactor Under Lean/Rich Cycling Conditions (no H₂O; CO₂)
Reactor Studies at UK CAER

- **LNT-SCR studies:**
  - reproduce non-NH$_3$ NOx conversion route observed by Ford (using non-proprietary LNT catalyst)
  - identify optimal experimental conditions for subsequent *in situ* DRIFTS studies

- Low PGM-loaded LNT used, with Cu-zeolite SCR catalyst

- Gas sampling at three positions

- **SpaciMS studies (Ford, ORNL):**
  - gain insights into the factors controlling NH$_3$ emissions from LNT catalysts: underlying chemistry, effect of process parameters, effect of catalyst composition
NOx and NH₃ Conversion in LNT-SCR System: Evidence for non-NH₃ NOx Conversion Pathway (Tasks 1.2, 1.6)

Rich phase reductant:
1% CO, 0.3% H₂

Observations first made by Ford confirmed at UK CAER:
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
## NOx Conversion in the LNT-SCR System: Results for Different Reductants (Task 2.7)

<table>
<thead>
<tr>
<th>Reductant</th>
<th>Total NOx conversion over SCR catalyst (%)</th>
<th>NOx conversion over SCR catalyst during lean phase (%)</th>
<th>NOx conversion over SCR catalyst during rich phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO/H₂/C₂H₄</td>
<td>6.9</td>
<td>5.8</td>
<td>1.1</td>
</tr>
<tr>
<td>CO/H₂/C₃H₆</td>
<td>15.3</td>
<td>5.9</td>
<td>9.6</td>
</tr>
<tr>
<td>CO/H₂</td>
<td>3.6</td>
<td>3.45</td>
<td>0.15</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.3</td>
<td>2.4</td>
<td>0.9</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>8.0</td>
<td>0.8</td>
<td>7.2</td>
</tr>
</tbody>
</table>

*CO/H₂/C₃H₆ as reductant, lean-rich cycling: 233 °C*

When propene is added as rich phase reductant, NOx conversion over SCR catalyst mainly occurs in rich phase (as opposed to lean phase for conventional NH₃ route)
SpaciMS Study of NH₃ Evolution in LNT Catalysts (1): Degreened Catalyst, Low OSC (Task 1.6)

NO evolution:
NO concentration peaks near front of catalyst:
- NOx storage mainly in front portion
- NOx released to gas phase subsequently undergoes consumption (to some degree) downstream

NH₂ evolution:
NH₃ concentration peaks near middle of catalyst:
- possible correlation with H₂ (from prior work)
- NH₃ released to gas phase subsequently undergoes consumption (to some degree) downstream
NH₃ Evolution in LNT (UH; Task 1.6)

Catalyst: Pt (2.2 wt.%)/BaO (20 wt.%)
300 °C, 60 s storage; 10 s regeneration (1.5% H₂)
LNT Modeling (UH; Tasks 1.7, 1.8)

- LNT reactor models completed for Pt/BaO, \( \text{H}_2 \) as reductant
- Microkinetic formulation: storage & reduction
- Global kinetic model formulation accounts for particle size effects, \( \text{NH}_3/\text{N}_2\text{O}/\text{N}_2 \) selectivity
NH$_3$ SCR on Fe-Zeolite (UH; Task 2.4)

500 ppm NO, 500 ppm NH$_3$, 5% O$_2$

Washcoat:
- 50μm
- Fe: 4 wt.%
- Ti: 1.5% wt.%
- Al: 4.5% wt.%
- Si: 38% wt.%

- Steady-state & transient tests & intrinsic kinetics
- Fe- & Cu-zeolite catalysts: provided & synthesized
NH₃ SCR Kinetics on Fe-Zeolite

**Standard SCR:**

\[ 4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \]

**Kinetic Rate form:**

\[-R_{\text{NO}} = Ae^{-E/RT}\left[\text{NO}\right]^1\left[\text{NH}_3\right]^{-0.3}\left[\text{O}_2\right]^{0.56}\]

\[ E \sim 42 \text{ kJ/mol} \]

**SCR rate:** positive order in NO & \(O_2\), inhibited by NH₃
Activities Planned: 4QFY10, FY11

- Spatio-temporal LNT data to be collected for comparison to global model with focus on NH₃
- TAP study of SCR, NSR with H₂ & CO
- In situ DRIFTS study at ORNL: identification of possible CₐHₐNₐOₐ species formed on LNT/SCR catalysts
- Complete LNT-SCR reactor studies, including parametric study of NH₃ formation over model LNT catalysts varying in ceria content
- Isotopic ¹⁵NO bench & TAP reactor experiments
- Development of kinetic & reactor models
  - SCR microkinetic model & SCR reactor with comparison to data
  - Integration of LNT & SCR global kinetic based reactor models
Summary

- Good progress on several fronts
  - Non-NH₃ SCR mechanism important
  - Conditions for NH₃ generation identified from spatio-temporal data
  - SCR kinetics for Fe-zeolite
  - LNT micro & global kinetics & reactor models

- Next steps to focus on LNT/SCR data & modeling, DRIFTS & TAP studies