CLEERS Coordination & Joint Development of Benchmark Kinetics for LNT & SCR

Agreements:

• Coordination of Cross-Cut Lean Exhaust Emission Reduction Simulation (8745)
  Stuart Daw, Vitaly Prikhodko, Charles Finney

• Joint Development of Benchmark Kinetics for LNT & SCR (8746)
  Jae-Soon Choi, Josh Pihl, Bill Partridge, Kalyana Chakravarthy, Todd Toops, Michael Lance, Stuart Daw

Pl: Stuart Daw
Presenter: Jae-Soon Choi
Oak Ridge National Laboratory

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Overview

Timeline

- Project start date:
  - CLEERS Coordination (8745) FY00
  - LNT & SCR Kinetics (8746) FY00

- Project end date & percent complete:
  - All ongoing

Budget

- Project funding for FY09/FY10
  - CLEERS Coordination (8745): $200K/$200K
  - LNT & SCR Kinetics (8746): $450K/$500K

- Funding request for FY11
  - Similar to FY10

Barriers

- Fuel penalty
  - Regeneration & desulfation of emission controls require extra fuel consumption

- Cost of aftertreatment
  - High cost inhibits market acceptance of diesel & lean-gasoline

- Durability
  - At present, large built-in margin required

Partners

- Informal but close collaboration w/ CLEERS Focus Group members & DOE Diesel Crosscut Team
  - > 20 institutions
  - Nat’l labs: SNL, PNNL
  - Industry: GM, Ford, Cummins, DDC, Navistar, Delphi, Umicore …
Objectives

Enable robust & energy efficient lean emission control technologies by Coordinating & conducting emissions controls simulation research

Current development of lean-burn aftertreatment is highly empirical & requires fundamental insights to significantly improve system performance & reduce cost

- Identify and prioritize R&D needs within industry, and coordinate DOE research efforts (CLEERS Coordination)
- Develop detailed technical data required to simulate energy efficient emission controls (LNT & SCR Kinetics)
  - Experiments: specialized measurements under relevant conditions to provide new insights into key LNT and SCR chemistry and kinetics
  - Modeling: consolidate new insights into LNT and SCR models that relate device and catalyst properties to fuel efficiency and emissions performance

Research targets chosen based on the latest CLEERS poll & reviewer comments
- SCR: types & interactions of surface species, HC poisoning
- LNT: sulfur impact, NH₃ mechanism (growing interest with respect to NH₃ slip control or coupled LNT-SCR system)
Milestones

• FY2009 milestones completed
  ✓ 8745: Organized 12th CLEERS public workshop
  ✓ 8746: Published LNT model and results for systems simulation

• FY2010 milestones on target for Sept. 2010 completion
  ✓ 8745: Organized 2010 CLEERS public workshop
    – 8746: Publish joint results with PNNL on SCR catalyst kinetics
**Approach:** Prioritize/Coordinate/Perform/Disseminate
Lean Exhaust Emissions Research

**DOE Diesel Cross-Cut Team**
Caterpillar, Cummins, Chrysler, Detroit Diesel, DOE-OVT, Ford, General Motors, Navistar, U.S. Army TARDEC, U.S. EPA, Volvo

**CLEERS Planning Committee**
- Wei Li (GM)
- Stuart Daw (ORNL)
- Louise Olsson (Chalmers)
- Chris Rutland (UW)
- Houshun Zhang (DDC)

**Technology Focus Groups**
- DPF, LNT, SCR
- Monthly teleconferences
- Selected membership

**Website (www.cleers.org)**
- General information
- Meeting announcements
- Shared data

**Workshops**
- Public
- Annual in Detroit area
- Presentations on website

**Experiments (LNT & SCR)**
- Bench/micro/DRIFTS reactors
- Specialized diagnostics (SpaciMS)
- Characterization (Microscopy, TPR)

**Modeling/Simulation (LNT)**
- Microkinetic-based model
- Global model
- LNT lean/rich cycling
- Sulfation impact on performance

**CLEERS Reference Catalysts**

**Collaboration w/ PNNL**
Lee, Tonkyn, Devarakonda

**Collaboration w/ SNL**
Larson

**New insights, data & models relevant to development of robust, energy-efficient, & cost-effective emission controls**
Technical Accomplishments

• CLEERS Coordination (8745)
  – Organized 13th (2010) CLEERS Workshop
  – Coordinated monthly Focus Group teleconferences
  – Coordinated efforts to address 2008-2009 R&D priority survey and leverage ORNL, PNNL, SNL unique capabilities
  – Proposed draft protocol for transient SCR catalyst characterization

• LNT & SCR Kinetics (8746)
  – Continued DRIFTS HC poisoning analysis of CLEERS reference urea-SCR catalyst
  – Collaborated with PNNL on SCR modeling
  – Resolved S spatio-temporal details on CLEERS reference LNT catalyst with HR-EPMA, microscopy, DRIFTS, TPR, SpaciMS, and high-speed FTIR
  – Initiated detailed investigation of LNT NH₃ selectivity (reductant types, temperatures, sulfation; bench reactor, SpaciMS, high-speed FTIR, DRIFTS)
  – Began incorporating NH₃ results in global LNT models
  – Continued SNL collaboration micro-kinetic LNT modeling (lean/rich cycling, S)
Result Highlights: CLEERS Coordination (1/3)

- ORNL continued established coordination roles

- CLEERS website
- Monthly teleconferences
  - Group telecon (20-30 domestic + int’l participants)
  - Presentations of very recent technical results
  - Host rotates among DPF, LNT, SCR Focus Groups
- Workshop #12, April 28-30, 2009, UM Dearborn
  - > 110 attendees (OEMs, suppliers, software companies, nat’l labs, universities)
  - OBD industry panel included in response to R&D gaps analysis
- Workshop #13, April 20-22, 2010, UM Dearborn
  - About 90 attendees (OEMs, suppliers, software companies, nat’l labs, universities)
  - Industry panel on engine-aftertreatment systems and vehicle simulations
- Preliminary SCR transient catalyst lab protocol
  - Presented and discussed at public workshop
- CLEERS LNT model for system simulations
  - Demonstrated and published

12th CLEERS Workshop
- In collaboration with PNNL, ORNL proposed a lab protocol for transient SCR catalyst characterization

- Monolith core reactor measurements with specified inlet transient sequence
- Provides key information needed for constructing accurate SCR device models at minimum time (~24 hrs) and expense
- Specifically reveals:
  - NH\textsubscript{3} storage and release
  - NH\textsubscript{3} and NO oxidation
  - NO SCR kinetics (and NH\textsubscript{3}/NO impact)
  - NO + NO\textsubscript{2} SCR kinetics
- Presented at the CLEERS Workshop and in the CLEERS Focus Groups
- Undergoing experimental validation and utilization for systems simulations

Result Highlights: CLEERS Coordination (2/3)

Specified reactor inlet transients

- T (°C)
- O\textsubscript{2} (%)
- NH\textsubscript{3} (ppm)
- NO (ppm)
- NO\textsubscript{2} (ppm)

(time (minutes))
**Result Highlights: CLEERS Coordination (3/3)**
- ORNL models are improving understanding of lean emissions control options on fuel economy

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**Example simulation of PHEV (see VSS017 talk)**
(PSAT modeling with simplified CLEERS SCR and LNT models)

**Parameters:**
- Diesel engine w & w/o NO\(_x\) control (LNT vs. SCR)
- SCR with stoichiometric ratio NH\(_3\) to NO\(_x\)
- 1450 kg vehicle
- 5 UDDS cycles from cold start
- 100% initial charge in 5 kWhr battery

**Results:**

<table>
<thead>
<tr>
<th>Diesel + SCR</th>
<th>Diesel</th>
<th>Diesel + LNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Economy (mpg)</td>
<td>Tailpipe NO(_x) (g/mile)</td>
<td>Fuel Economy (mpg)</td>
</tr>
<tr>
<td>136.3</td>
<td>0.16 (77% red)</td>
<td>136.4</td>
</tr>
</tbody>
</table>

- 2% fuel penalty for LNT (higher for more NO\(_x\) removal)
- SCR almost eliminates direct fuel penalty
- But SCR has extra NH\(_3\) emissions (0.068g/mile)
- Proposed mechanism for toluene poisoning of Fe zeolite SCR catalyst based on surface spectroscopy

(1) 350ppm NH₃: numerous spectral features due to adsorbed NH₃

Note: all steps include 14% O₂, 4.5% H₂O, 5% CO₂

Insights shared with modeling teams at PNNL & ORNL
Result Highlights: SCR Research (1/2)

- Proposed mechanism for toluene poisoning of Fe zeolite SCR catalyst based on surface spectroscopy

1. 350 ppm NH₃: numerous spectral features due to adsorbed NH₃
2. + 350 ppm NO: surface NH₃ decreased due to consumption by SCR reaction

Note: all steps include 14% O₂, 4.5% H₂O, 5% CO₂

Insights shared with modeling teams at PNNL & ORNL
Result Highlights: SCR Research (1/2)

- Proposed mechanism for toluene poisoning of Fe zeolite SCR catalyst based on surface spectroscopy

(1) 350 ppm NH₃: numerous spectral features due to adsorbed NH₃
(2) + 350 ppm NO: surface NH₃ decreased due to consumption by SCR reaction
(3) + 50 ppm toluene: SCR reaction poisoned, surface NH₃ increases

note: all steps include 14% O₂, 4.5% H₂O, 5% CO₂

Insights shared with modeling teams at PNNL & ORNL
**Result Highlights: SCR Research (2/2)**

- ORNL is integrating multiple sources of data into SCR modeling

  - Detailed model with PNNL (coding assistance & DRIFTS insights)
  - Complementary global model for systems simulations
    - Based on published model catalyst data (Cu-ZSM5)
    - Will be updated with CLEERS SCR protocol data and DRIFTS results

**Global model features:**

- NH\textsubscript{3} adsorption/desorption
- 3 SCR reactions
  - NO, NO\textsubscript{2}, “fast”
- NO, NH\textsubscript{3} oxidation reactions
- N\textsubscript{2}O not tracked for simplicity
- Future plans
  - HC poisoning effects
  - O\textsubscript{2} effect on NO SCR
  - LNT-SCR systems

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**Points from experiments by Olsson et.al, Applied Catalysis B: Environmental 81(2008) 203-217. Lines from ORNL simulation.**
Result Highlights: LNT Research (1/5)
- In-depth characterization confirmed link between commercial LNT composition & sulfur chemistry

CLEERS LNT (lean GDI, Umicore) characterized with microscopy, HR-EPMA, TPR

<table>
<thead>
<tr>
<th>Domain</th>
<th>Composition</th>
<th>S content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-rich</td>
<td>Ba (high), Ce/Zr, Pt, Pd</td>
<td>7.3</td>
</tr>
<tr>
<td>Ce/Zr-rich</td>
<td>Ba (low), Ce/Zr, Pt, Pd</td>
<td>2.1</td>
</tr>
<tr>
<td>Al-rich</td>
<td>Al, Rh, Pd</td>
<td>2.4</td>
</tr>
<tr>
<td>Mg/Al-rich</td>
<td>Mg/Al, Pt, Ce</td>
<td>1.2</td>
</tr>
</tbody>
</table>

corroborates previous conjectures

Ba sulfation is vigorous leading to plug-like poisoning of NOx storage sites

Sulfation of Ce/Zr, Al, Mg/Al is less efficient but significant “S-trap” delaying Ba sulfation
**Result Highlights: LNT Research (2/5)**

- Improved spatial & temporal resolution of gas analysis confirms sulfur - NH$_3$ correlation

**Spatial resolved new data (SpaciMS)**
before vs. after CLEERS LNT sulfation at 300 °C (bench)

**Previously proposed conceptual model**

- Plug-like S poisoning of NO$_x$ storage sites displaces active NO$_x$ storage/reduction downstream
- As a result, length of OSC-only zone (downstream of active NSR zone) gets shorter
- More NH$_3$ (slipping from active NSR zone) manages to escape LNT without being oxidized by OSC
- Started in-depth study of NH$_3$ mechanisms

- NH$_3$ important for stand-alone LNT (slip control) & LNT-SCR
  - Recent ORNL chassis study of a European lean GDI (09 BMW) shows significant NH$_3$ slip can occur

- Current LNT models have limited NH$_3$ capability
  - Generally not tracking NH$_3$ profiles
  - Recent addition of 2-step mechanism: NO$_x$ + H$_2$ $\rightarrow$ NH$_3$; NH$_3$ + NO$_x$ $\rightarrow$ N$_2$

- S study (see previous 2 slides) highlights importance of spatiotemporal reactions & surface species

- This FY, we initiated systematic study of NH$_3$ on CLEERS LNT
  - Spatiotemporal resolution of reaction distributions
    - Bench reactor, HS-FTIR (temporal), UEGO (temporal), SpaciMS (spatial)
    - Type of reductant (e.g., HC impact), temperature
  
  - Transient NH$_3$ surface chemistry
    - DRIFTS reactor
    - NH$_3$ interaction with catalyst surface (e.g., OSC)
  
  - Complementary to U Houston DOE project
    - Focused on coupled LNT-SCR synergy mechanisms
    - Catalyst formulation effects
Result Highlights: LNT Research (4/5)

- Initial results reveal some key NH$_3$ features to be captured by models

Bench reactor (CLEERS LNT)
60/5-s lean/rich cycling

- Wide NH$_3$ peaks
  significant NH$_3$ formation behind regen front

- N$_2$O at rich $\rightarrow$ lean
  indicate NH$_3$ storage & oxidation

**DRIFTS (Pt/Ba/Al$_2$O$_3$)**

- NH$_3$ storage on surface
- NH$_3$ oxidation by
  - OSC (during regeneration)
  - O$_2$ (inception of subsequent lean)
- NH$_3$ storage as nitrates indicates
  possible axial redistribution of NO$_x$ via NH$_3$
Result Highlights: LNT Research (5/5)

- LNT models are being used to better understand NH₃ & S chemistry and evaluate system impact

  - Further SNL collaboration on microkinetic model (see ACE035 talk)
    - Implemented lean/rich cycling
    - Initial work on sulfation/desulfation
  - Developed a global model to enable faster simulations than microkinetic model
    - Experimental findings used to improve NH₃ prediction

Global model features:
- Catalytic reactions on Pt sites
  - No storage
  - Global rate expressions
  - Inhibition terms where necessary
- NOₓ storage on fast (near Pt) and bulk BaCO₃ sites
  - Carbonates, peroxides, nitrites, nitrates, bulk nitrates
  - Oxygen storage on CeO₂
- NOₓ release rate adjusted using experimental data → better NH₃ match
- Currently isothermal

CLEERS LNT, 60/5-s lean/rich cycling, 300 C

![Graph showing cycle-integrated value vs fractional LNT length for NOₓ and NH₃ comparison between model and experiment.](graph.png)
Collaborations

• Partners
  – Universities: Kentucky, Houston, ICT Prague (summer research by Dr. Kočí at ORNL), Chalmers (students from Prof. Olsson’s group)
  – Industry: Cummins, Navistar, Ford, Umicore, BASF, other CLEERS Focus Group members and DOE Diesel Crosscut Team

• Technology Transfer
  – 18+ publications & presentations (dissemination of DOE-funded research outcome via high visibility forums: NAM, SAE, int’l journals etc.)
  – SCR lab protocol publicly proposed
  – LNT & SCR models used for DOE Vehicle & System HEV/PHEV Simulations (FY10 FreedomCAR Highlight)
  – Data, systems impact guidance for PNNL & SNL activities
Future Work

• CLEERS Coordination (8745)
  – Planning Committee, Focus Groups, Workshop & website
  – Synchronizing ORNL-PNNL-SNL R&D
  – Priority Survey in 2011 (every 2 years)
  – Basic data & model exchange between CLEERS & other VTP projects

• LNT & SCR Kinetics (8746)
  – LNT kinetics, durability (major focus on NH₃ chemistry)
    • Bench reactor studies (reductant type, HC impact)
    • Spatiotemporal analysis (SpaciMS, high-speed FTIR, DRIFTS)
    • Model NH₃ spatiotemporal profiles (with SNL)
    • Model LNT sulfation (with SNL)
    • CLEERS reference catalyst vs. latest European lean GDI (09 BMW)
  – Urea-SCR kinetics (HC poisoning)
    • CLEERS lab protocol implementation
    • DRIFTS surface analysis with reference catalysts (Fe vs. Cu)
    • PNNL collaboration
Summary

• **Relevance**
  – Assist DOE in coordinating & conducting R&D enabling development of energy & cost effective lean emissions control technologies

• **Approach**
  – Planning Committee, Focus Groups, website, Workshops, polling, Crosscut updates, data & model exchanges
  – Multi-scale lab R&D on commercial & model LNT & urea-SCR catalysts under relevant conditions (modeling & experiments)

• **Technical Accomplishments**
  – Monthly Focus meetings, website, 12th & 2010 Workshops, Crosscut reports, systems implementation of CLEERS data & models
  – Fundamental understanding and modeling of practically relevant urea-SCR & LNT catalysts

• **Collaborations**
  – Non-proprietary collaborations among industry, national labs, universities, and foreign institutions through CLEERS organizational structure
  – Collaboration with other VTP projects (e.g., DOE-system simulations, U. Houston)
  – Extensive publications/presentations

• **Plans for Next Fiscal Year**
  – Planning Committee, Focus Groups, Crosscut reports, website, Workshops, priority poll, VTP leveraging
  – LNT modeling of NH₃, N₂O & HC impact via spatiotemporal chemistry
  – NH₃-SCR modeling supported by DRIFTS and CLEERS lab protocol