Overview

Timeline
- Status: On-going core R&D
- Originated FY03 with DPF
- Now also includes LNT, SCR and DOC technologies

Budget
- FY10 funding - $750K
- FY11 funding allocation $750K
  - Split between SCR, LNT, DOC and DPF focus areas

Barriers
- Limitations on:
  - available modeling tools
  - chemistry fundamentals
  - knowledge of material behavior
- Effective dissemination of information
- Technical “Valley of Death”

Partner
- Diesel Crosscut Team
- 21CT partners
- USCAR partners
- Oak Ridge National Lab
Goal and Relevance

Goal and Relevance

CLEERS PNNL Subprogram Goal

Working closely with our National Lab partners, the CLEERS industrial/academic team and in coordination with our CRADA portfolio, PNNL will…

…provide the practical & scientific understanding and analytical base required to enable the development of efficient, commercially viable emissions control solutions and modeling tools for ultra high efficiency vehicles.

VT program goals are achieved through these project objectives:

- interact with technical community to indentify relevant technological gaps
- understand fundamental underlying mechanisms and material behavior
- develop analytical and modeling tools, methodologies, and best practices
- apply knowledge and tools to advance technologies leading to reducing vehicle emissions while improving efficiency

Specific work tasks in support of the objectives are arrived at through:

- focus group industrial monthly teleconferences, diesel x-cut meetings
- yearly workshops and surveys
- submission of SOW to the VT office
Technical Milestones & Approach

- The overall performance measure of the project is inextricably linked to the interests of industry
  - PNNL CLEERS activities have resulted in the formation of new CRADAs
  - Tremendous success of the annual workshops
  - Strong participation in the monthly teleconferences

- Specific performance measures are developed with the industrial/academic partners and captured in SOW
  - Specific technical targets and major milestones are described in our AOPs and annual reports to VT

- Approach - “Science to Solutions”
CLEERS activity

Integrated Systems – John Lee

- DPF subtasks* – Mark Stewart
- SCR subtasks* – John Lee
- LNT subtasks – Chuck Peden

*PNNL-led subteam

**Past activities

CRADA activities

DPF – DOW Automotive (Stewart)**
SCR/DPF – PACCAR (Rappe)
SCR, HC – Ford Motor Company (Peden, Lee)
SCR, DOC – General Motors (Peden)
LNT – Cummins Inc. (Peden)

Oxidation Catalysts

- General Motors (Lee)
- SDC Materials (Herling)
- Caterpillar (Rappe)**
FY2010/2011 Scope Objectives

► Selective Catalytic Reduction (SCR)
  - Update our SCR model for the state-of-the-art Cu SCR catalyst, and develop kinetics models to describe the performance degradation due to the competitive adsorption and catalyst aging
  - Conduct detailed characterization of the Cu SCR catalyst with emphasis on the active sites and its deactivation

► Lean NOx Trap (LNT)
  - Complete the investigation of CO₂ and H₂O effects on BaO morphology changes and NOx storage properties
  - Fundamental studies of novel high-temp LNT catalyst materials

► Diesel Particulate Filter (DPF)
  - Evaluate the accuracy of unit collector model with respect to nano-sized particulates, and improve the accuracy of micro-scale model for prediction of soot-catalyst contact
  - Characterize soot chemistry and structure relevant to exhaust system performance and regeneration
Technical Accomplishments Outline

- **SCR**
  - Developed single site kinetic models to describe the effects of competitive adsorption on NOx reduction on Fe SCR catalyst.
  - Currently developing Cu SCR model with ORNL, and conducting detailed characterization of the state-of-the-art Cu SCR catalyst with emphasis on the active sites.

- **LNT**
  - Demonstration of significantly enhanced high temperature performance for a K/MgAl₂O₄ LNT material.
  - Fundamental studies of complex morphology changes in K-based LNT materials have been initiated.

- **DPF**
  - Currently evaluating the accuracy of unit collector model with respect to nano-sized particulates.
  - Recently collected soot from HDD engine at MTU for characterization of soot chemistry and structure.
Selective Catalytic Reduction
Effect of Hydrocarbon on SCR Reactions

- The effects of HC on Fe SCR catalyst examined using model HC species for combustion products and unburned fuel
- Detrimental effects of toluene & n-dodecane on SCR reactions
- Models developed to investigate the effects of HC on SCR reaction pathways quantitatively

Feed Conditions
175 ppm NO
175 ppm NO₂
350 ppm NH₃
14% O₂
2% H₂O
50 ppm toluene (350 C1)
29 ppm dodecane (350 C1)
29k h⁻¹
Overview of PNNL 1-D SCR Model

- Gas phase, surface phase concentrations and NH$_3$ storage as states
- Coded as ‘C’ S-functions and developed in Matlab/Simulink
- Optimized and validated using steady state and transient reactor data

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<th>No</th>
<th>Reaction Name</th>
<th>Reaction</th>
<th>Reaction Rate</th>
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<td>NH$_3$ Adsorption</td>
<td>NH$_3$ + S $\rightarrow$ NH$_3^*$</td>
<td>$R_1 = k_1 C_{s,NH3}(1 - \theta) \Omega$</td>
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<td>2</td>
<td>NH$_3$ Desorption</td>
<td>NH$_3^*$ $\rightarrow$ NH$_3$ + S</td>
<td>$R_2 = k_2 \theta \Omega$</td>
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<td>Fast SCR</td>
<td>2NH$_3$+NO+NO$_2$ $\rightarrow$ 2N$_2$+3H$_2$O</td>
<td>$R_3 = k_3 C_{NO} C_{NO2} \theta \Omega$</td>
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<td>Standard SCR</td>
<td>4NH$_3$+4NO+O$_2$ $\rightarrow$ 4N$_2$+6H$_2$O</td>
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<td>NO$_2$-SCR</td>
<td>4NH$_3$+3NO$_2$ $\rightarrow$ 3.5N$_2$+6H$_2$O</td>
<td>$R_5 = k_5 C_{NO2} \theta \Omega$</td>
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<td>6</td>
<td>NH$_3$ Oxidation</td>
<td>2NH$_3$+3/2O$_2$ $\rightarrow$ N$_2$+3H$_2$O</td>
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<td>NO-NO$_2$ Oxidation</td>
<td>NO+1/2O$_2$ $\rightleftharpoons$ NO$_2$</td>
<td>$R_7 = k_{7,a} C_{NO} C_{O2}^{1/2} - k_{7,b} C_{NO2}$</td>
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Modeling Competitive Adsorption

• Single site storage model was first developed, and parameters were obtained from the Langmuir isotherms.

• Assuming the adsorbates, such as NH₃, NO, NO₂, H₂O and hydrocarbons (toluene, n-dodecane), competing for the same active site, single site kinetics for each species and the respective surface coverage are defined as follows:

\[
\frac{d\theta_i}{dt} = \frac{1}{\Omega_i} \left[ k_{ads,i} (1 - \theta_i - \sum_{j=1}^{N-1+P} \theta_j) c_{s,i} \Omega_i - k_{des,i} \theta_i \Omega_i - \sum_{k=1}^{M} n_{i,k} r_{i,k} \right] 
\]

\[
\varepsilon \frac{\partial c_{g,i}}{\partial t} = -\varepsilon u \frac{\partial c_{g,i}}{\partial x} - \beta_i A_g \left( c_{g,i} - c_{s,i} \right) 
\]

\[
(1 - \varepsilon) \frac{\partial c_{s,i}}{\partial t} = \beta_i A_g \left( c_{g,i} - c_{s,i} \right) + \sum_k r_{i,k} n_{i,k} 
\]
CA Model Validation: NH₃, H₂O, Dodecane

- Competitive adsorption (CA) model development using data for NH₃ vs. H₂O, NH₃ vs. HC

- CA model validation for full competitive adsorption of NH₃, H₂O, and dodecane
CLEERS Cu SCR Model Development

- Commercial Cu SCR catalyst evaluation
  - Cu SCR being used by most OEMs in North America
  - Lab reactor testing currently being conducted at ORNL using the CLEERS Transient reactor test protocol

- PNNL’s 1-D Cu SCR catalyst model
  - Same strategy used for the Fe SCR catalyst model
  - Cu catalyst model being developed entirely in Matlab/Simulink
  - Autonomie being considered as platform to share CLEERS SCR catalyst model with the others

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<th>NO₂ (ppm)</th>
<th>NH₃ (ppm)</th>
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<th>H₂O (%)</th>
<th>CO₂ (%)</th>
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<td>10</td>
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State-of-the-art Cu SCR Catalyst Research

First open literature studies of the latest Cu SCR catalyst
- The current production Cu SCR catalyst is based on CHA zeolite.
- Cu-SSZ-13 prepared and evaluated for various SCR reactions

Detailed characterization of active sites in progress
- TPD, TPR of model Cu-zeolite catalysts
- In situ XRD and EXAFS experiments at Brookhaven’s NSLS
Lean NOx Traps
FY2010/2011 Scope Objectives

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  - Update our SCR model for the state-of-the-art Cu SCR catalyst, and develop kinetics models to describe the performance degradation due to the competitive adsorption and catalyst aging
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- Lean NOx Trap (LNT)
  - Investigate CO\textsubscript{2} and H\textsubscript{2}O effects on BaO morphology changes and NOx storage properties
  - Fundamental studies of novel high-temp LNT catalyst materials

- Diesel Particulate Filter (DPF)
  - Evaluate the accuracy of unit collector model with respect to nano-sized particulates, and improve the accuracy of micro-scale model for prediction of soot-catalyst contact
  - Characterize soot chemistry and structure relevant to exhaust system performance and regeneration
Approach

- Higher temperature NOx reduction performance required for:
  - Difficult to meet “not to exceed” regulations during desulfations
  - Possible use of LNTs for lean-gasoline applications

- PNNL/Cummins/JM CRADA focusing on degradation of possible materials for next-generation high temperature LNTs.
- CLEERS studies are addressing more fundamental issues of these potential new LNT materials related to composition, morphology, and chemical reaction kinetics and mechanisms.
- For these studies, PNNL has prepared a range of materials based on literature and prior CLEERS work at PNNL.
• K-based LNTs known to exhibit higher temperature performance
• Recent literature reports suggest titania (TiO$_2$) may be a better support for K-based LNTs than alumina (Al$_2$O$_3$)
• Prior CLEERS studies on Ba-based LNTs at PNNL have suggested MgAl$_2$O$_4$ as a promising support material for high temperature application

![Graph showing NOx uptake over temperature for different supports](image)

- Superior activity of MgAl$_2$O$_4$-supported LNT relative to Al$_2$O$_3$- and TiO$_2$-supported samples over all temperatures.
- Moreover, maximum NOx uptake activity at a considerably higher temperature of 450 °C.
K-loading effects on MgAl$_2$O$_4$ support materials

- We’re not aware of prior systematic studies of K-loading.
- Negligible MgAl$_2$O$_4$ contribution in NOx uptake at high temperature.
- Drastic difference between 5 wt% and 10 wt%.
- Higher loading than 10 wt% does not improve the activity.
Significant Morphology Changes During Operation of Ba-Based LNTs Were Observed in our Prior CLEERS Studies

\[ \text{BaO nanoparticles} \]

\[ \text{Heat} \]

\[ \text{Ba(NO}_3\text{)}_2 \text{ particles + thin Ba(NO}_3\text{)}_2 \text{ layer} \]

\[ \text{NO}_2 \text{ adsorption at 400-600K} \]

Similar to Ba, FTIR Spectral Changes Consistent with Multiple K-oxide Phases

FTIR spectra of NO$_2$ adsorbed on K(2 or 10)/Al$_2$O$_3$ samples

2 wt% K: mostly bidentate nitrates $\rightarrow$ surface nitrates?

10 wt% K: ionic nitrates and bidentate nitrates $\rightarrow$ surface and bulk nitrates?
Complex Morphology Changes in K/Al$_2$O$_3$

Morphology change of K phase during decomposition and formation of nitrate

- Heating above 150°C
  - $\text{H}_2\text{O}$
  - $\text{Al}_2\text{O}_3$

- Heating above 300°C
  - Amorphous

- Decomposition to NO$_2$ and NO

Synchrotron XRD at the NSLS is being used to study the complex morphology changes in K-based LNTs
Diesel Particulate Filter
Approach

- Conduct bench reactor soot experiments
  - Soot oxidation with NOx correlated by surface area
  - HC Absorption
- Examine soot nano-structure using TEM and advanced image analysis techniques
- Improve pore-scale filter dynamics tools through:
  - Characterization of necessary microstructure resolution and sample size for accurate predictions in various media
  - Validation and enhancement of particle capture mechanics
  - Validation of particle motion Brownian dynamics algorithm
- Collect structural data for filter substrates using:
  - Micro/nano X-ray computed tomography
  - Porosimetry
- Carry out fundamental single cell filtration experiments using reproducible lab-generated aerosols
Numerous pore-scale DPF simulations have been carried out to date using the Lattice-Boltzmann method.

Pore networks have been resolved down to a few microns.

Qualitative features in back-pressure, deposit morphology, and soot penetration into filter walls have been reproduced.

Insight into pore-scale mechanisms has assisted in the development of systems and new materials.
Recent studies suggest requirements for quantitative pore-scale simulations:

- Sintered granular materials (SiC) are easier to simulate than cordierite
- Cordierite may require resolutions < 1 um and domain sizes of over 1 mm (>0.5E+9 computational cells)

Adjustment of lattice-Boltzmann parameters may allow lower resolutions at the expense of shorter time-steps

Fortunately, cost and availability of massively parallel computational resources are rapidly becoming more favorable

→ Precise quantitative performance predictions from pore-scale simulations may be just around the corner
Kinetic Measurements & Surface Area

- Bench reactor soot experiments (in progress)
  - Soot oxidation w/ NOx correlated by surface area
  - HC adsorption

![Graph showing reaction rate vs. temperature](image1.png)

![Graph showing specific surface area vs. percent oxidized](image2.png)

Surface area measurement by in situ BET
Conclusion & Future Work
Conclusions

**SCR**
- Developed single site kinetic models to describe the effects of competitive adsorption on NOx reduction on Fe SCR catalyst
- Currently developing Cu SCR model using data obtained by CLEERS transient reactor protocol with ORNL
- First open literature investigation of the state-of-the-art Cu SCR catalyst with emphasis on the active sites

**LNT**
- Mg/Al$_2$O$_4$ identified as a very promising support material for K-based LNTs in high-temperature applications
- Initial structural studies of K-based LNTs indicate very complex morphology changes

**DPF**
- Recently collected soot from HDD engine at MTU for characterization of soot chemistry and structure relevant to exhaust system performance and regeneration
Future Work

**SCR**
- Update the kinetics for Cu SCR model with ORNL’s data, and develop kinetics models to describe the performance degradation due to the competitive adsorption and catalyst aging.
- Continue to conduct detailed characterization of the Cu SCR catalyst with emphasis on the active sites and its deactivation.

**LNT**
- Complete studies of CO₂ and H₂O effects on BaO morphology changes and NOx storage properties.
- Continue fundamental studies of morphology changes and NOx uptake mechanisms of novel high-temp LNT catalyst materials.
- Investigate the formation and stability of PGM particles (also relevant to DOC, TWC).

**DPF**
- Evaluate the accuracy of unit collector model with respect to nano-sized particulates, and improve the accuracy of micro-scale model for prediction of soot-catalyst contact.
- Characterize soot chemistry and structure relevant to exhaust system performance and regeneration.
Acknowledgements

- **PNNL**
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