Overview

► Timeline
  ■ Status: On-going core R&D
  ■ Originated FY03 with DPF

► Budget
  ■ FY09 funding - $750K
  ■ FY10 funding allocation $750K
    ▪ Split between LNT, SCR 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

VT program goals are achieved through these project objectives:

- interact with technical community to identify 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

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.
Technical Milestones & Approach

**Approach - “Science to Solutions”**

**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
CLEERS activity

Integrated Systems - Herling

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

*PNNL led subteam

CRADA activities

- DPF – DOW Automotive (Stewart)
- SCR/DPF – PACCAR (Rappe)
- SCR – Ford Motor Company (Peden)
- SCR – General Motors (Peden, Lee)
- LNT – Cummins Inc. (Peden)
- Oxidation (HCCI) – Caterpillar (Rappe)
FY2009/2010 Scope Objectives

▶ SCR
- Investigate the competitive adsorption effects on NH3 storage under controlled lab reactor conditions
- Develop kinetic models to characterize competitive adsorption and inhibition, and to describe the impact on SCR performance quantitatively

▶ LNT
- Optimization of catalyst morphology via controlled synthesis.
- Mechanisms of CO2 and H2O promotion of desulfation
- Characteristics (performance and poisoning) of ceria-supported LNT materials
Technical Accomplishments Outline

- **Selective Catalytic Reduction**
  - Characterized the effects of H2O and HC on SCR reaction
  - Develop and validate models for H2O and toluene storage
  - Developed single site kinetic models to describe the inhibition effects on NH3 sorption and NOx reduction

- **Lean NOx Trap Fundamentals**
  - Prior conclusions concerning morphology changes in LNT materials during operation
  - Ultra-high field NMR spectroscopy and ultra-high resolution TEM studies of the binding of Ba and Pt to washcoat alumina surfaces

- **Conclusions & Future Work**
Selective Catalytic Reduction
Effect of Hydrocarbon on NOx Reduction

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

- No effect of ethylene, propane
- Detrimental effects of toluene, dodecane
- More pronounced effect on NO-SCR
- No effect on NO₂-SCR
Overview of PNNL 1-D SCR Model

- Gas phase, surface phase concentrations and NH₃ storage as states
- Coded as ‘C’ S-functions and developed in Matlab/Simulink
- Optimized and validated using steady state and thermal transient reactor data

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction Name</th>
<th>Reaction</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH₃ Adsorption</td>
<td>NH₃ + S → NH₃⁺</td>
<td>( R₁ = k₁ Cₛ,\text{NH₃}(1 - \theta) \Omega )</td>
</tr>
<tr>
<td>2</td>
<td>NH₃ Desorption</td>
<td>NH₃⁺ → NH₃ + S</td>
<td>( R₂ = k₂ \theta \Omega )</td>
</tr>
<tr>
<td>3</td>
<td>Fast SCR</td>
<td>2NH₃+NO+NO₂ → 2N₂+3H₂O</td>
<td>( R₃ = k₃ Cₙo CₙO₂ \theta \Omega )</td>
</tr>
<tr>
<td>4</td>
<td>Standard SCR</td>
<td>4NH₃+4NO+O₂ → 4N₂+6H₂O</td>
<td>( R₄ = k₄ Cₙo \theta \Omega )</td>
</tr>
<tr>
<td>5</td>
<td>NO₂-SCR</td>
<td>4NH₃+3NO₂ → 3.5N₂+6H₂O</td>
<td>( R₅ = k₅ CₙO₂ \theta \Omega )</td>
</tr>
<tr>
<td>6</td>
<td>NH₃ Oxidation</td>
<td>2NH₃+3/2O₂ → N₂+3H₂O</td>
<td>( R₆ = k₆ CₙO₂ \theta \Omega )</td>
</tr>
<tr>
<td>7</td>
<td>NO-NO₂ Oxidation</td>
<td>NO+1/2O₂ ⇄ NO₂</td>
<td>( R₇ = k₇,₁ Cₙo CₙO₂^{1/2} - k₇,₂ CₙO₂ )</td>
</tr>
</tbody>
</table>
Effect of H$_2$O on SCR Reactions

H$_2$O Storage Model

Effect of H$_2$O on NO Oxidation

Model for H$_2$O Inhibition of NO Oxidation
Hydrocarbon Storage Model: Toluene

<table>
<thead>
<tr>
<th>$T (^\circ C)$ / $C$ (ppm)</th>
<th>50</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>100</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>150</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Test Matrix

Typical Adsorption Test

$1/n_{st} = \frac{1}{n_{st,eq}} = \frac{1}{N_{total}} + \frac{1}{K(T)c_{s,C7H8}N_{total}}$

$\dot{n}_{C7H8,in} - \dot{n}_{C7H8,out}$

$\int_{0}^{t_{eq}}(\dot{n}_{C7H8,in} - \dot{n}_{C7H8,out})dt$

Storage rate parameters are obtained through approximation of Langmuir isotherms.
Toluene Inhibition on NO and NH$_3$ Oxidation

**NH$_3$ Oxidation Test**
Feed: 350 ppm NH$_3$, 14% O$_2$, 50 ppm toluene (350 C1)

**NO Oxidation Test**
Feed: 350 ppm NO, 14% O$_2$, 25 ppm toluene (175 C1)

**Model Validation on Temperature Ramps**

**Arrhenius Plot and Model Validation**
Lean NOx Trap Fundamentals
NOx Storage/Reduction (NSR) Catalysis

Lean Conditions

NO, NO2, O2 → NO2(g) → NO2(g) → Pt → NO2 → NO, NO2, O2

Rich Conditions

HC, CO, H2 → NO2 (g) → NO2 (g) → Pt → NO2 → NO, NO2, O2

N2, CO2, H2O → NO2 (g) → NO2 (g) → Pt → NO2 → NO, NO2, O2

γ-Al2O3 → Nitrate → NOx Storage Cycle

γ-Al2O3 → Nitrate → NOx Reduction Cycle

Lean Conditions

Rich Conditions

NOx Storage Cycle

NOx Reduction Cycle
Morphology Changes During Operation Indicate an Important Role for the BaO/Alumina Interface

BaO nanoparticles

Heat

Ba(NO$_3$)$_2$ particles + thin Ba(NO$_3$)$_2$ layer

NO$_2$ adsorption at 400-600K

Introduction

- Surface structures and chemistry of gamma-alumina are not easily studied – even their bulk structures remain a topic of some controversy because of low crystallinity and small particle sizes.

- Bulk alumina has Al$^{3+}$ cation sites in tetra- and octa-hedral coordination. What about coordination of surface aluminum atoms?

Two Stable $\gamma$-$\text{Al}_2\text{O}_3$ Surfaces


Use of one-of-a-kind Ultra-High Field NMR in the Environmental Molecular Science Lab at PNNL

- Penta-coordinate Al$^{+3}$ ions readily observable in γ-Al$_2$O$_3$;
- Are these species are located at the alumina surface?

Lewis acidic 5-fold Al sites on \(\gamma\)-\(\text{Al}_2\text{O}_3\) surfaces are nucleation sites for catalytic phases!

Addition of a catalytic phase, BaO, quantitatively 'titrates' 5-fold Al sites.

\[ \begin{align*}
\text{Ba}(2\%)/\gamma\text{-Al}_2\text{O}_3 \\
\text{Ba}(1\%)/\gamma\text{-Al}_2\text{O}_3 \\
\text{Ba}(0.5\%)/\gamma\text{-Al}_2\text{O}_3 \\
\gamma\text{-Al}_2\text{O}_3
\end{align*} \]

5-fold sites are fully titrated at \(\sim 4\) weight % loading of BaO on \(200\, \text{m}^2/\text{gm}\ \gamma\text{-Al}_2\text{O}_3\).

The titration results are consistent with expected distribution of $\gamma$-$\text{Al}_2\text{O}_3$ surfaces.

- 4 weight % loading of BaO sufficient to titrate all 5-fold Al$^{+3}$ sites.
- Assuming that BaO forms perfect 2D clusters or domains on the 200 m$^2$/g $\gamma$-$\text{Al}_2\text{O}_3$ substrate, 1 ML of BaO will be reached at ~25% weight loading.

Thus, ~16% ($4 \div 25$) of the alumina surface consists of 5-fold Al$^{+3}$ sites.
\(\gamma-Al_2O_3(100)\) surfaces are estimated to be \(\sim 17\%\) of the total surface area.

\(\gamma-Al_2O_3(110)\) - \(\sim 70-83\%\)

\(\gamma-Al_2O_3(111)\) - stable?

Additional evidence for reaction only on (100) surfaces obtained from low-energy ion scattering (LEIS) and high-resolution STEM.
Ultra-high resolution STEM (aberration-corrected) shows BaO monomers at low loading 2%BaO/γ-Al₂O₃

A: no BaO
B: BaO monomer decorate the facet boundary
C: fairly uniform dispersion of BaO
Line scans 1,2: confirms the single BaO

2%BaO/γ-Al₂O₃

Ultra-high resolution STEM also shows that Pt can be monatomically dispersed at low loading. However, Pt ‘clusters’ on Al₂O₃ at a loading where the Pt/5-fold Al site ratio is much less than 1. Why??

DFT Calculations Identify Bonding Orientation for PtO Clusters on γ-Al₂O₃(100)

Conclusion & Future Work
Conclusions: SCR Scope

- Characterized the effects of H2O and hydrocarbons on SCR reaction pathways over Fe-zeolite catalyst
  - No effect of ethylene and propane on NOx reduction
  - Detrimental effects of H2O, toluene and n-dodecane on Standard SCR through suppressed NO oxidation & NH3 adsorption
  - Smaller effect on Fast SCR, and no effect on NO2-SCR reactions

- Developed models to describe the inhibition effects of H2O and toluene on NOx reduction kinetics
  - Storage models were developed using Langmuir isotherms.
  - A single site kinetic model was developed and validated to predict the effects of H2O and toluene on NO oxidation and NH3 oxidation.
Conclusions: LNT Scope

- Interactions of LNT catalytic phases with the washcoat support material, alumina, have been studied
  - 5-fold Al$^{+3}$ surface structures identified in $^{27}$Al NMR spectra are active ‘Lewis acid’ sites for adsorption of reactant and catalyst precursor species
  - Both Ba and Pt are shown to prefer anchoring at these surface sites

- Studies of the effects of CO$_2$ and H$_2$O on performance and desulfation of model Ba-based LNTs have continued
  - The presence of CO$_2$ promotes the removal of sulfur species, especially at temperatures below 500 °C
  - This behavior is largely attributed to a suppression of the formation of refractory BaS phases

- Ceria as a support material for Ba-based LNTs
  - These LNT catalysts display distinct advantages but appear to lack the ability to fully desulfate because of strong interactions between ceria and sulfur oxides
Future Work

► Complete the kinetic modeling of NH$_3$ oxidation, NO oxidation and other SCR reactions on Fe-zeolite catalyst
► Investigate the competitive adsorption kinetics on a model Cu-zeolite SCR catalyst through experiments and modeling
► Investigate the effects of catalyst aging on kinetic parameters and physicochemical properties of a model Cu-zeolite catalyst
► Thermal transient reactor testing of model & commercial Cu-zeolite SCR catalyst
► Isocynanic acid reagent studies
  ■ Steady state kinetic modeling of HNCO hydrolysis and adsorption on Fe-zeolite
  ■ Transient reactor modeling based on HNCO injection
Future Work (con’t)

- Fundamental studies of novel high temperature LNT formulations
- Complete studies of CO$_2$ and H$_2$O effects on performance and desulfation of Ba-based LNT materials
- Continue development of micro-scale DPF simulation tools, including detailed comparison to granular unit-collector theory
- Fundamental filtration experiments with repeatable lab-generated particulates and current DPF substrates
Acknowledgements

- **PNNL**
  Shelley Carlson, Maruthi Devarakonda, Tom Gallant, Do Heui Kim, Ja Hun Kwak, Gary Maupin, George Muntean, Ken Rappe, Nat Saenz, Janos Szanyi, Russ Tonkyn, Diana Tran, Alla Zelenyuk

- **ORNL**
  Stuart Daw, Todd Toops, Josh Pihl and support from the ORNL team

- **Umicore**
  Owen Bailey and support for SCR catalyst materials

- **DOE Vehicle Technologies Program**
  Gurpreet Singh and Ken Howden
Backup Slides
In addition to \( \text{NH}_3 \) adsorption and desorption on catalyst surface,

\[
\text{NH}_3 \text{ oxidation: } \ 2\text{NH}_3 + \frac{3}{2}\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}
\]

\[
\text{NO oxidation: } \ \text{NO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{NO}_2
\]

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

\[
\text{NO}_2\text{-SCR: } \ 4\text{NH}_3 + 3\text{NO}_2 \rightarrow \frac{7}{2}\text{N}_2 + 6\text{H}_2\text{O}
\]

\[
\text{Fast SCR: } \ 2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\]
## List of Kinetic Parameters

<table>
<thead>
<tr>
<th></th>
<th>$A_{\text{ads}}$</th>
<th>$A_{\text{des}}$</th>
<th>$E_{\text{des}}$ (kJ/mol)</th>
<th>$\gamma$ (-)</th>
<th>$\Omega$ (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>83.9</td>
<td>2.0E5</td>
<td>70</td>
<td>0.368</td>
<td>46.3</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5.5</td>
<td>1.0E5</td>
<td>73</td>
<td>5.853</td>
<td>51.1</td>
</tr>
<tr>
<td>Dodecane</td>
<td>48.3</td>
<td>2.7E6</td>
<td>76</td>
<td>0.956</td>
<td>53.4</td>
</tr>
</tbody>
</table>
# Test Conditions

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_x$</td>
<td>350 ppm</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>350 ppm</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>0 or 5 %</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>14 %</td>
</tr>
<tr>
<td><strong>Hydrocarbon</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4$ &amp; $\text{C}_3\text{H}_8$ – combustion products</td>
<td></td>
</tr>
<tr>
<td>Toluene – aromatic fuel component</td>
<td></td>
</tr>
<tr>
<td>n-dodecane – long chain HC fuel component</td>
<td></td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td>0 – 5%</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>balance</td>
</tr>
<tr>
<td><strong>Space velocity</strong></td>
<td></td>
</tr>
<tr>
<td>29k hr⁻¹ for steady state tests</td>
<td></td>
</tr>
<tr>
<td>44k hr⁻¹ for transient tests</td>
<td></td>
</tr>
</tbody>
</table>
5-fold Al-atoms display 'chemical' characteristics of being surface cations.

5-fold Al cations increase at the expense of 6-fold cations after high temperature annealing.

5-fold cations disappear and octahedral Al increases after exposure to H$_2$O.

Effect of Dodecane on NOx Reduction

- Decreased NOx reduction during temp-down ramp
- More pronounced effect on Standard SCR
- No effect on NO\textsubscript{2}-SCR

Feed Conditions
- 175 ppm NO
- 175 ppm NO\textsubscript{2}
- 350 ppm NH\textsubscript{3}
- 14% O\textsubscript{2}
- 2% H\textsubscript{2}O
- 29 ppm dodecane (350 C1)
H₂O Inhibition Modeling

Effect of H₂O on SCR Reactions

Effect of H₂O on NO Oxidation

H₂O Storage Model

Model for H₂O Inhibition of NO oxidation
Effects of HCs under Transient Conditions
Effect of Toluene on NO Oxidation

- More pronounced inhibition effect during temp-up ramp
- Severe inhibition in the presence of H₂O

350 ppm NO, 14% O₂, 25 ppm toluene, 2% H₂O
**In-situ TEM observation of morphological changes in Ba(NO₃)₂ upon heating**

Characteristics: particle shrinks, with a linear shrinkage of ~31%

Theoretical value: 32%

BaO maintains overall morphology of ‘precursor’ Ba(NO$_3$)$_2$ but as a collection of small particles.

Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk' Ba(NO₃)₂ morphologies present.

Observed practical implications of the Ba-phase morphology.

- From TPD experiments, the “monolayer” morphology is found to decompose at lower temperature in vacuum and in a reducing atmosphere than “bulk” nitrates.
- “Monolayer” Ba-phase is also easier to ‘de-sulfate’.
- Formation of a high-temperature (deactivating?) BaAl$_2$O$_4$ phase requires BaO coverages above 1 monolayer.
- Morphology model at least partially explains relatively small use of Ba species (often <20%) in storing NOx during typical lean-rich cycling.
Decomposition of $\text{Ba(NO}_3\text{)}_2$ precursor requires a 500 °C calcination.

'Wet impregnation' of $\gamma$-$\text{Al}_2\text{O}_3$ with an aqueous $\text{Ba(NO}_3\text{)}_2$ solution; dried at 125 °C.

Large $\text{Ba(NO}_3\text{)}_2$ crystallites.

Calcined in dry air at 500 °C.

In-situ time-resolved XRD.

BaO nanoparticles on a BaO monolayer.
**CO₂ Promotion of Desulfation of Model LNTs**

<table>
<thead>
<tr>
<th></th>
<th>Pt-Ba(20)/Al₂O₃</th>
<th>Pt-Ba(8)/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfated</td>
<td>2.81</td>
<td>2.85</td>
</tr>
<tr>
<td>Desulfated with H₂</td>
<td>0.50</td>
<td>0.11</td>
</tr>
<tr>
<td>Desulfated with H₂/CO₂</td>
<td>0.30</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**H₂ TRPX spectra:**

- Pt-BaO(20)/Al₂O₃ without (a) and with (b) CO₂.
- Pt-BaO(8)/Al₂O₃ without (c) and with (d) CO₂.
TR-XRD diffractograms of pre-sulfated Pt-BaO(20)/Al₂O₃ obtained during the temperature ramping in the presence of both H₂ and CO₂.

510 °C – 800 °C

630 °C – 690 °C
Synchrotron Time-Resolved XRD During Desulfation – Pt-BaO(8%/Al₂O₃)

TR-XRD diffractograms of pre-sulfated Pt-BaO(8)/Al₂O₃ obtained during the temperature ramping in the presence of both H₂ and CO₂.

510 – 800 °C

Intensity (Arb. Units)

2 theta (degree)

510 °C
610 °C
710 °C
800 °C for 1 min
800 °C for 9 min

BaSO₄