Low-Temperature Hydrocarbon/CO Oxidation Catalysis in Support of HCCI Emission Control

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Pacific Northwest National Laboratory
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Overview

Timeline
- Start – February 2005
- Finish – February 2009
- 100% Complete

Budget
- Total Project Funding
  - DOE – $1,350K
  - CRADA
- Funding received in FY08
  - $350K
- Funding received in FY09
  - $350K

Barriers
- LTC HC & CO emissions
- High exhaust gas temp. requirements
- Catalyst fundamentals

Partner
- Caterpillar, Inc.
- CRADA
  - Work-in-kind contribution
- Project lead
  - Dr. Ronald Silver
Objectives

Develop low-temperature HC & CO oxidation catalysts to enable HCCI application

Specifications to vendors:

- **HC oxidation**: 90% at 175°C and higher
- **HC light-off**: 50% at < 150°C
- **CO oxidation**: 99% at higher temperatures
- **CO light-off**: 50% at < 150°C

Akin to the cold start problem, except the exhaust never reaches light-off temperatures on commercial catalysts.
Milestones & Approach

► Milestones for the past two years of effort
- Complete bench-scale assessment of transients
  - Completed
- Complete optimization of monolithic formulations
  - Completed
- Complete steady-state and transient engine testing
  - Completed

► Approach
- Catalyst formulation, characterization & screening
- Assess monolith-supported catalysts
- Bench scale transient studies
- Catalyst scaling for engine testing
- Engine testing: steady-state and transient
- Correlation between bench & engine scale
Addition of praseodymium (Pr) enhances low-temperature REDOX capacity of the CeO$_2$ catalyst, improving the low-temperature oxidation capacity.

**Ce$_x$Pr$_{1-x}$O$_2$ System Investigations:**

Varying Pr levels in Pd/CeO$_2$ system

Improvements needed to improve paraffinic activity of the system.
Technical Accomplishments – FY08/09

2%Pt/Ce\textsubscript{0.9}Pr\textsubscript{0.1}O\textsubscript{2} system: Catalyst pretreatments investigated in an attempt to improve activity of system.

Surface pre-sulfation significantly improves propane activity of the system.
2%Pt/Ce$_{0.9}$Pr$_{0.1}$O$_2$ system

Effect of different catalyst pretreatments: TPR results

Features:
- 100°C – Pt-oxide reduction
- 350°C – surface ceria/praseodymia reduction
- 440°C – sulfated ceria/praseodymia species
- 700°C – bulk ceria reduction

► (NH$_4$)$_2$SO$_4$ & H$_2$SO$_4$ pretreatment improve reducibility of Pt-oxide species
► Formation of new sulfated feature at 440°C
Technical Accomplishments – FY08/09

2%Pt/Ce$_{0.9}$Pr$_{0.1}$O$_2$ system

Effect of different catalyst pretreatments: BET results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$</td>
<td>46.20</td>
<td>0.2374</td>
<td>173.1</td>
</tr>
<tr>
<td>2%Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$-H$_2$SO$_4$</td>
<td>45.87</td>
<td>0.2829</td>
<td>184</td>
</tr>
<tr>
<td>2%Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$-(NH$_4$)$_2$SO$_4$</td>
<td>44.91</td>
<td>0.2697</td>
<td>184.2</td>
</tr>
<tr>
<td>2%Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$-HNO$_3$</td>
<td>51.26</td>
<td>0.06717</td>
<td>14.73</td>
</tr>
<tr>
<td>2%Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$-ammonia</td>
<td>47.29</td>
<td>0.2304</td>
<td>185</td>
</tr>
</tbody>
</table>

► Textural properties of system (SA, PV, PS) relatively unaffected by pre-sulfation of catalyst surface.
Technical Accomplishments – FY08/09

2\%Pt/Ce_{0.9}Pr_{0.1}O_{2} system

Effect of different catalyst pretreatments: XPS results

- S^{6+} identified at ~169 eV, indicating sulfate feature.
- Relative ratio of peaks at 529, 532 eV indicates more oxygen shifted to higher binding energy, likely indicating presence of a SO_{4}^{2-} feature.
Technical Accomplishments – FY08/09

2%Pt/Ce$_{0.9}$Pr$_{0.1}$O$_2$ system

Effect of different catalyst pretreatments: XPS results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt$^{2+}$ (%)</th>
<th>Pt$^{4+}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$</td>
<td>57.5</td>
<td>42.5</td>
</tr>
<tr>
<td>Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$-$\text{H}_2\text{SO}_4$</td>
<td>47.1</td>
<td>52.9</td>
</tr>
<tr>
<td>Pt/Pr$<em>{0.1}$Ce$</em>{0.9}$O$_2$-$\text{(NH}_4\text{)}_2\text{SO}_4$</td>
<td>43.5</td>
<td>56.5</td>
</tr>
</tbody>
</table>

- Pt state affected by sulfation.
- Effect of SO$_4^{2-}$ strong electron-withdrawing capacity.
2%Pt/Ce$_{0.9}$Pr$_{0.1}$O$_2$ system

Proposed ‘improved’ propane oxidation mechanism

Propane adsorption – hydrogen extraction generally accepted as the rate determining step in the process.
2%Pt/CexCo1-xO2 system interrogation: Co employed in an attempt to improve paraffinic activity of the system.

C3H8 activity of system improved with blending of small amounts of Co into CeO2 system.
Technical Accomplishments – FY08/09

2%Pt/CexCo1-xO2 system interrogation: BET results

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Co0.1Ce0.9O2</td>
<td>75.81</td>
<td>0.2665</td>
<td>152.3</td>
</tr>
<tr>
<td>Pt/Co0.3Ce0.7O2</td>
<td>48.67</td>
<td>0.1934</td>
<td>123.6</td>
</tr>
<tr>
<td>Pt/Co0.5Ce0.5O2</td>
<td>37.60</td>
<td>0.2008</td>
<td>123.2</td>
</tr>
<tr>
<td>Pt/Co0.9Ce0.1O2</td>
<td>9.727</td>
<td>0.03715</td>
<td>24.98</td>
</tr>
<tr>
<td>Pt/Co3O4</td>
<td>1.567</td>
<td>0.08406</td>
<td>28.8</td>
</tr>
</tbody>
</table>

- Textural properties remain intact with blending of small amount of Co into CeO₂ system (10%).
- Larger amounts of Co result in moderate to significant structural changes.
Technical Accomplishments – FY08/09

2%Pt/\text{Ce}_x\text{Co}_{1-x}\text{O}_2 \text{ system interrogation: SEM studies}

- Small amount of Co (10%) shows surface effects only
- Significant morphological differences with larger amounts of Co
Technical Accomplishments – FY08/09

2%Pt/CexCo1-xO2 system interrogation: XRD analyses

- CeO2 peaks (◊) remain relatively strong through 50% Co blending.
- Appearance of platinum peaks (*) indicates strong Pt agglomeration with larger (>50%) amounts of Co blended into system.
Technical Accomplishments – FY08/09

2%Pt/CexCo1-xO2 system interrogation:
Platinum particle size

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt/C3O4</th>
<th>Pt/C0.9Co0.1O2</th>
<th>Pt/C0.5Ce0.5O2</th>
<th>Pt/C0.3Ce0.7O2</th>
<th>Pt/C0.1Ce0.9O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (nm)</td>
<td>39.9</td>
<td>37.9</td>
<td>22.4</td>
<td>N. A.</td>
<td>N. A.</td>
</tr>
</tbody>
</table>

- Pt metal remains well dispersed with moderate amounts of Co blended into the CeO2 system.
- Significant metal agglomeration obvious with larger amounts of Co as indicated in XRD analyses.
Technical Accomplishments – FY08/09

2%Pt/CexCo1-xO2 system interrogation:
TPR investigations of supports only

- Co feature reduced from 397°C to 324°C with larger amounts of ceria in the sample. Surface ceria feature at 500°C improved in the presence of Co to ~280°C with 10% Co.
- Indicates strong synergistic effects between metals.
Technical Accomplishments – FY08/09

2%Pt/CexCo1-xO2 system interrogation:
TPR investigations of catalysts

- Ce/Co combined samples promote Pt reduction at lower temperature (100°C/132°C).
- Ceria promotes improved Co reduction from 310°C to 241°C, analogous to support only interaction. Surface ceria feature captured there with small to moderate Co amounts in catalyst.
PNNL & Caterpillar® diesel oxidation catalysts
- 2.47 L each
- 25% total flow: 35K/hr to 122K/hr SV

Catalyst Supplier oxidation catalyst
- 17 L
- 100% total flow: 13K/hr to 26K/hr SV.
6-inch Monolith Brick Coating Details

6 inch diameter 5 ¾ inch height. 1159 gram weight, washed by acetone, 2-propanol, 10% HNO₃, and rinsed with D.I. H₂O to pH >5. Dried in air.

Slurry:

Ce₀.₉Pr₀.₁O₂ was prepared by calcination of Pr(NO₃)₃ and Ce(NO₃)₃ aqueous solution in air at 650°C for 4 hours

Aqueous slurry of 12 wt% Ce₀.₉Pr₀.₁O₂ was prepared by ball-mill

Coating:

Dipped dried brick into slurry followed by drying in vacuum oven at 70°C. Same procedure was repeated 3 times to get ~20 wt% loading. Brick was then calcined at 450°C for 4 hours.

2 wt% Pd coating:

Pd was coated on Ce₀.₉Pr₀.₁O₂ loaded brick using 4 wt% Pd(NH₃)₄(NO₃)₂ aqueous solution via wetness impregnation method followed by vacuum drying at 80°C and calcination at 450°C for 4 hours.
Normalizing for Space Velocity

Caterpillar Engine Testing

Normalizing for space velocity (assuming 1st order kinetics and mass transfer limitation)
Allows comparison of PNNL/CAT catalysts to SV of a commercial supplier catalyst at total flow

\[ \eta(\xi) = 1 - \left[1 - \eta(\xi_0)\right]^\frac{\xi_0}{\xi} \]

\( \eta \) = fractional NOx conversion efficiency
\( \xi \) = space velocity (SV) of interest
\( \xi_0 \) = reference SV at which conversion efficiency is known
Engine Testing

Carbon Monoxide (CO) Results

Supplier catalyst: 240% precious metal loading vs. PNNL catalyst.

$T_{50}^{\text{CO}}$ target (150°C) nearly reached with PNNL catalyst!
Engine Testing

Ethylene ($C_2H_4$) Results

Neither sample exhibited good $C_2H_4$ activity.
Engine Testing

Unburned Fuel (>C₅) Results

PNNL catalyst reached $T_{90\text{HC}} @ <240^\circ\text{C}$.
Catalyst supplier did not achieve $T_{90\text{HC}}$ until almost $350^\circ\text{C}$!
Highly thermally-conductive pellet loaded with catalyst powder inside inconel 600 device. Nickel 200 resistive wire heater encapsulated by double-glass insulation. Two thermocouples, one inside pelleted support, one outside housing.

U.S. Heavy Duty Federal Test Procedure (FTP)
Temperature control achieved using external/internal thermocouples in conjunction with predictive algorithm driving the heater profile against a constant cooling load.
Transient Testing – HCCI

Assumptions:

- Heavy Road Idle (IdleHR) – 150°C
- HCCI Idle (IdleHCCI) – 125°C
- Heavy Road High Speed/High Load (HLHR) – 450°C
- HCCI High Speed/High Load (HLHCCI) – 325°C

\[
HCCI\ Transient = IdleHCCI + (HR\ Transient - IdleHR) \cdot \frac{HLHCCI - IdleHCCI}{HLHR - IdleHCCI}
\]
Transient Testing – HCCI

Transient Engine Temperature Profiling

- U.S. Heavy-Duty FTP
- HCCI FTP (estimate)

Temperature, °C

Time, minutes

Pacific Northwest
NATIONAL LABORATORY
Transient Testing – HCCI

>95% CO destruction over the entire transient cycle
Transient Testing – HCCI

>56% oxidation of 250 ppm NO over the entire transient cycle
Examined feasibility of formulation \((\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_2)\) for contact soot oxidation.

Compared soot oxidation of Ce/Pr formulation to commercial supplier formulation.
Ce$_{0.8}$Pr$_{0.2}$O$_2$ provides significant enhancement of soot oxidation over soot alone and 2%Pd metal.
3:1 Mass Ratio Catalyst:Soot Mixture

Ce$_{0.8}$Pr$_{0.2}$O$_2$ provides significant enhancement of soot oxidation over commercial soot oxidation catalyst.
Summary

- Paraffin oxidation activity improved in systems via surface sulfation and via incorporation of small amounts of Co.
- Engine testing at Caterpillar, results are very promising.
- Transient testing has shown good transient CO oxidation capacity and good NO oxidation activity.
- Potential for contact soot oxidation applicability.

Targets

- CO light-off: 50% CO oxidation at 150°C
  - Successful in achieving CO light-off at well less than 100°C.
- CO oxidation: 99% at higher temperatures
  - Successful in achieving complete CO oxidation at 100°C and less.
- HC light-off: 50% HC oxidation at 150°C.
  - Successful in achieving C₂H₄ light-off at less than 100°C.
  - Have gotten C₃H₈ light-off to less than 300°C.
- HC oxidation: 90% HC oxidation at 175°C.
  - Successful in achieving >90% C₂H₄ oxidation at <100°C.
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