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

Ken Rappé
Pacific Northwest National Laboratory

May 19, 2009

acep_03_rappe

iic Institute for Interfacial Catalysis
Control of Chemical Transformations for a Secure Energy Future

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Overview

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

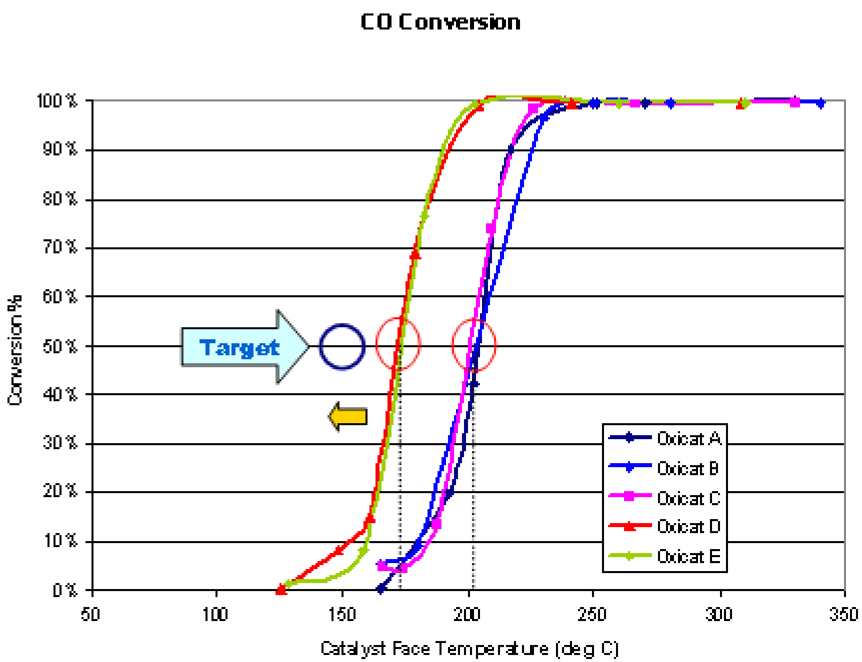
Budget
- Total Project Funding
  - DOE – $1,350K
  - CRADA
- Funding received in FY08
  - $350K
- Funding received in FY09
  - $350K

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

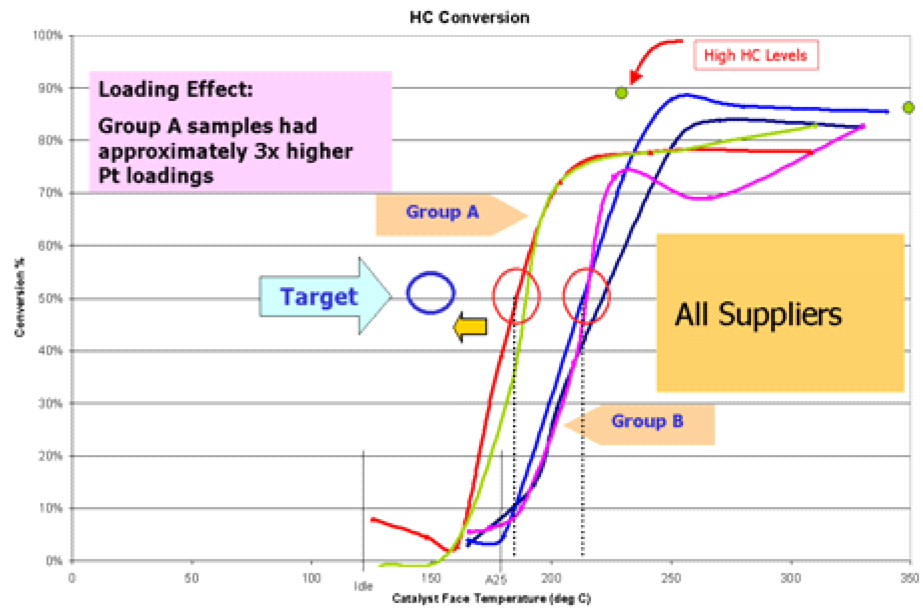
Develop low-temperature HC & CO oxidation catalysts to enable HCCI application



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.

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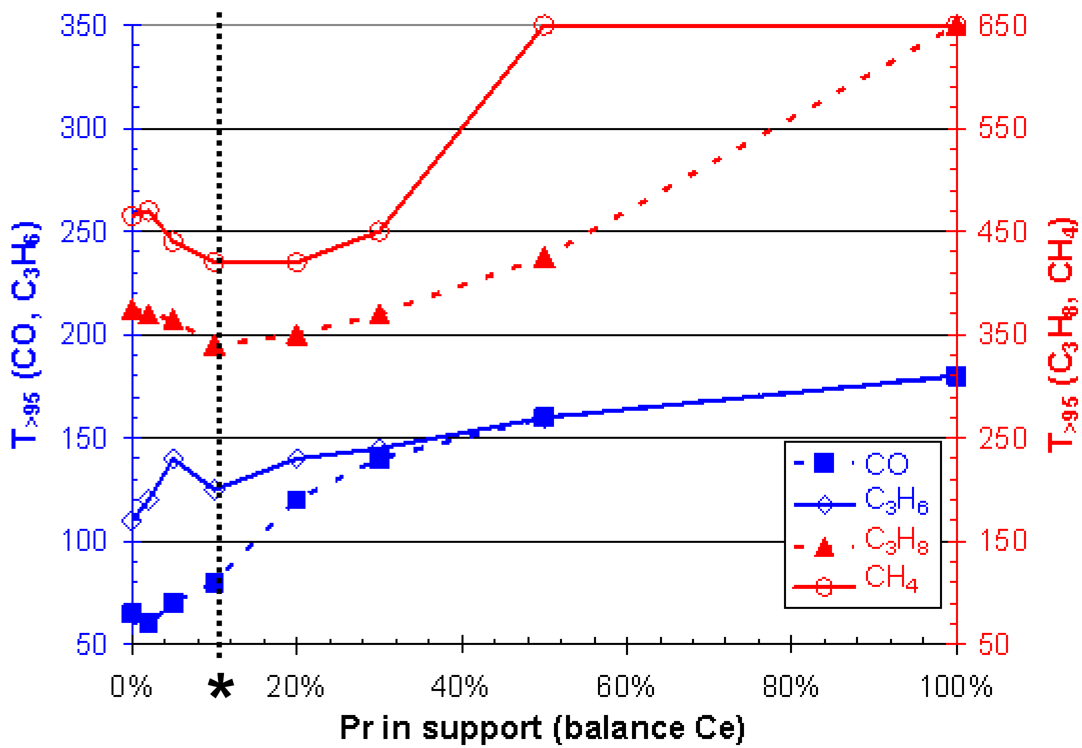
Milestones & Approach

- 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

Technical Accomplishments – Review

Addition of praseodymium (Pr) enhances low-temperature REDOX capacity of the CeO_2 catalyst, improving the low-temperature oxidation capacity.



$Ce_xPr_{1-x}O_2$ System Investigations:

Varying Pr levels in Pd/CeO_2 system

- Improvements needed to improve paraffinic activity of the system.

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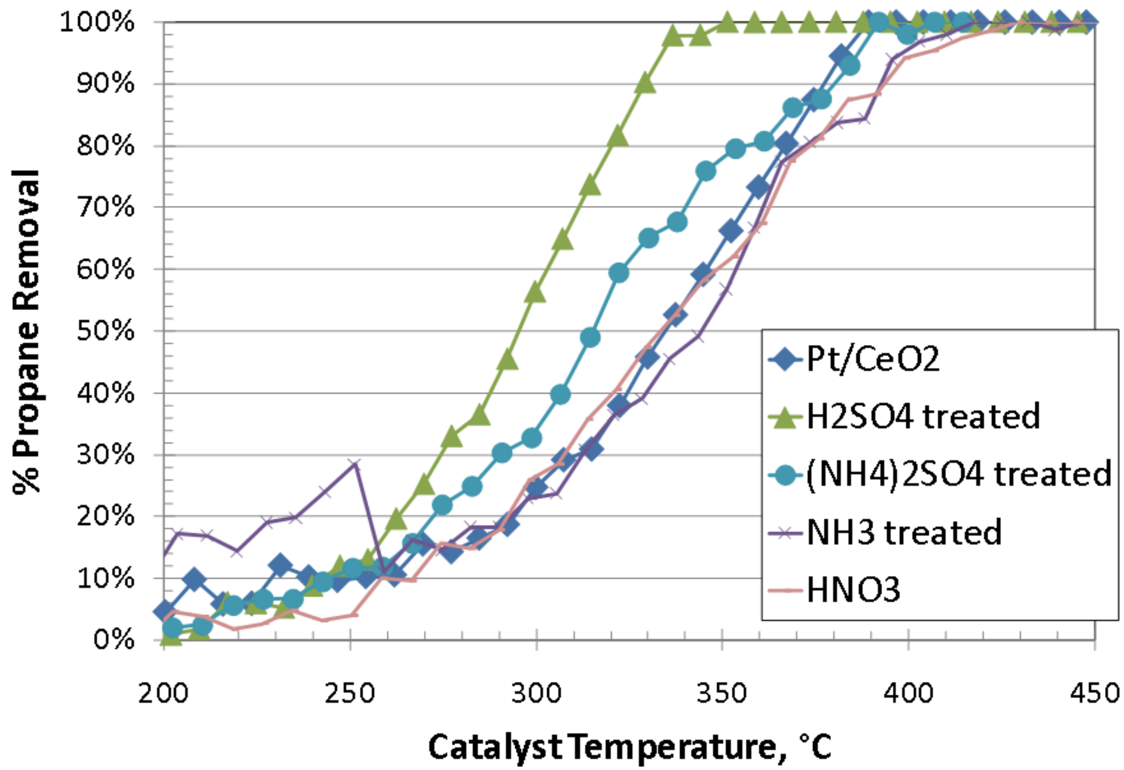
Technical Accomplishments – FY08/09

$2\%Pt/Ce_{0.9}Pr_{0.1}O_2$ system: Catalyst pretreatments investigated in an attempt to improve activity of system.



- Surface pre-sulfation significantly improves propane activity of the system.

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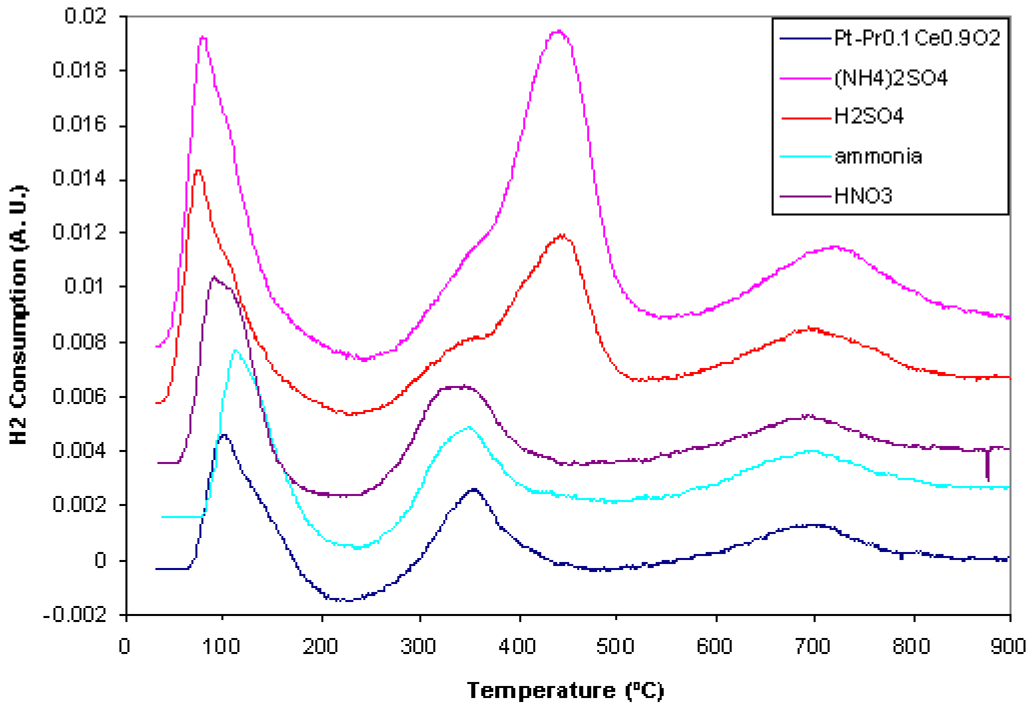
Technical Accomplishments – FY08/09

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

- $(NH_4)_2SO_4$ & H_2SO_4 pretreatment improve reducibility of Pt-oxide species
- Formation of new sulfated feature at 440°C

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Technical Accomplishments – FY08/09

2%Pt/$Ce_{0.9}Pr_{0.1}O_2$ system
Effect of different catalyst pretreatments: BET results

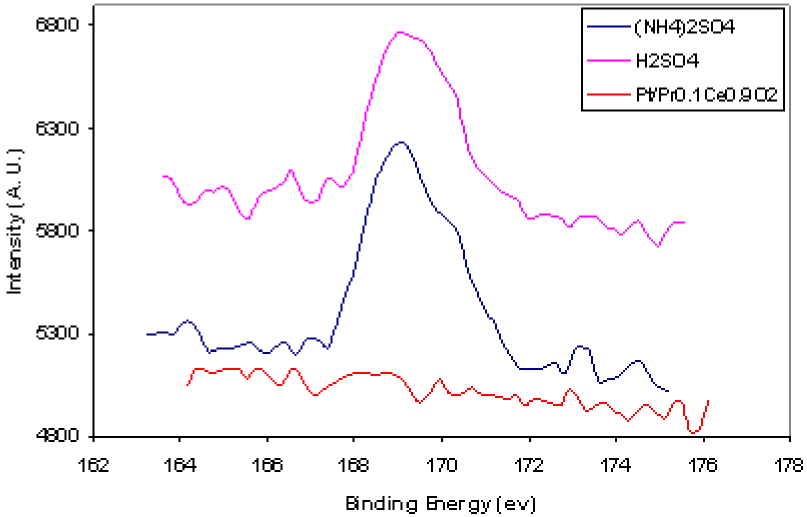
Catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (A)
2%Pt/$Pr_{0.1}Ce_{0.9}O_2$	46.20	0.2374	173.1
2%Pt/$Pr_{0.1}Ce_{0.9}O_2$-H_2SO_4	45.87	0.2829	184
2%Pt/$Pr_{0.1}Ce_{0.9}O_2$-$(NH_4)_2SO_4$	44.91	0.2697	184.2
2%Pt/$Pr_{0.1}Ce_{0.9}O_2$-HNO_3	51.26	0.06717	14.73
2%Pt/$Pr_{0.1}Ce_{0.9}O_2$-ammonia	47.29	0.2304	185

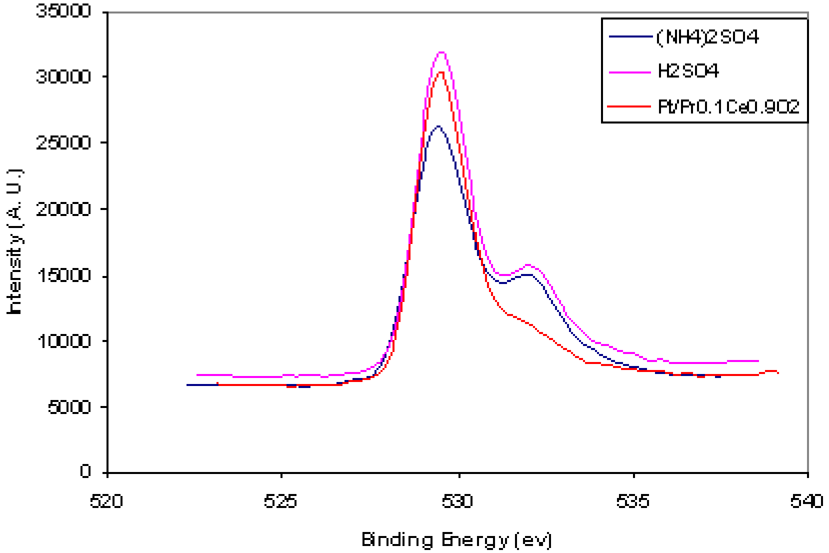
- Textural properties of system (SA, PV, PS) relatively unaffected by pre-sulfation of catalyst surface.

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.

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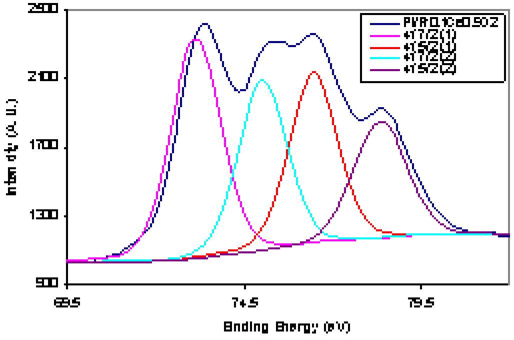
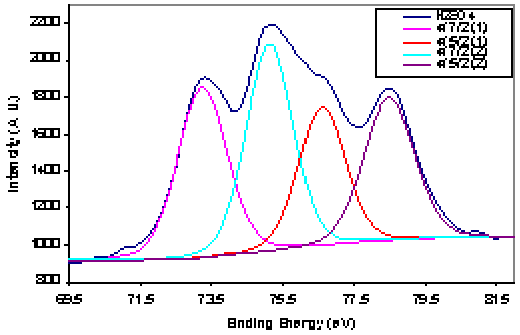
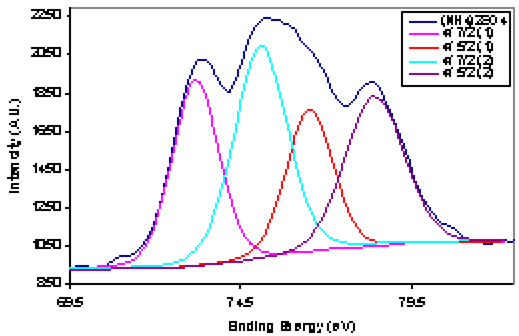
Technical Accomplishments – FY08/09

2%Pt/$Ce_{0.9}Pr_{0.1}O_2$ system

Effect of different catalyst pretreatments: XPS results







Catalyst	Pt^{2+} (%)	Pt^{4+} (%)
Pt/$Pr_{0.1}Ce_{0.9}O_2$	57.5	42.5
Pt/$Pr_{0.1}Ce_{0.9}O_2$-H_2SO_4	47.1	52.9
Pt/$Pr_{0.1}Ce_{0.9}O_2$-$(NH_4)_2SO_4$	43.5	56.5

- Pt state affected by sufation.
- Effect of SO_4^{2-} strong electron-withdrawing capacity.

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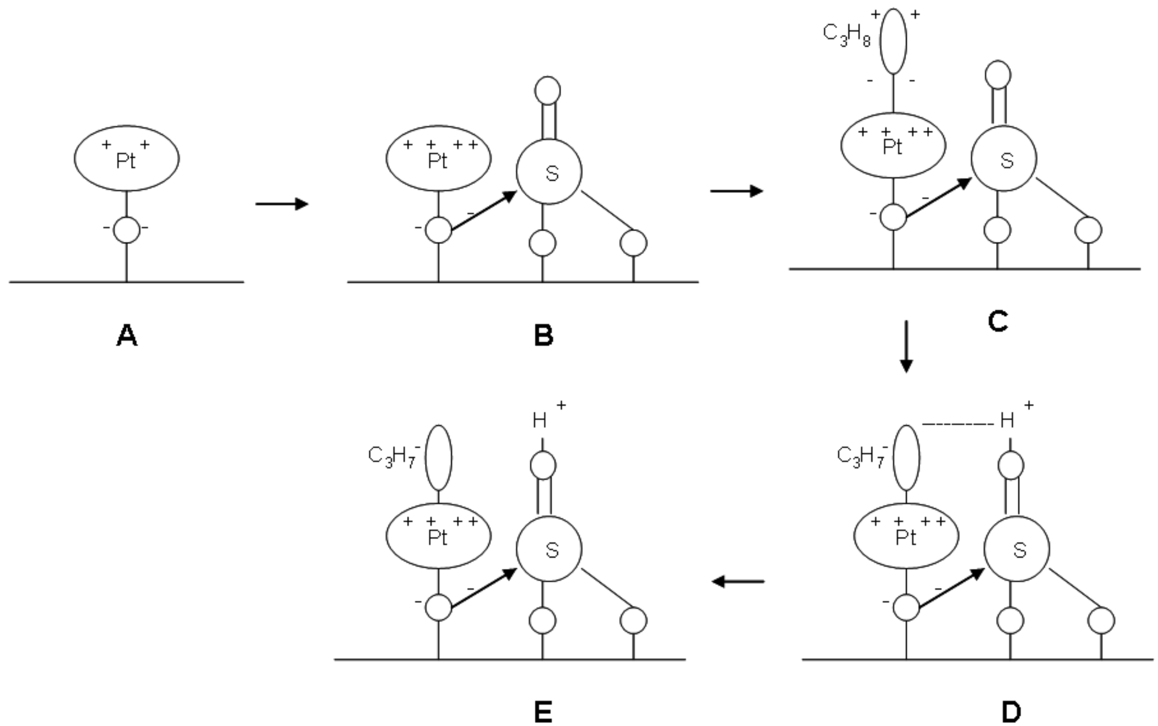
Technical Accomplishments – FY08/09

2%Pt/$Ce_{0.9}Pr_{0.1}O_2$ system

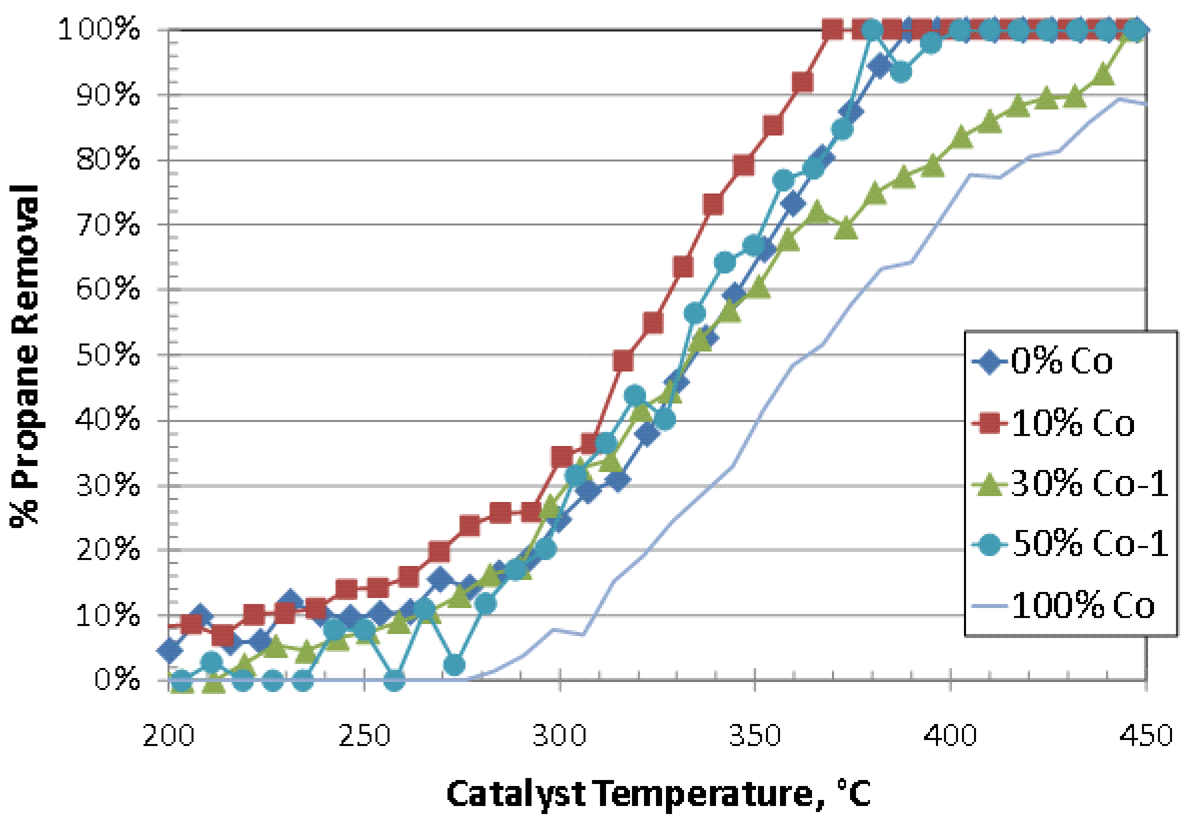
Proposed 'improved' propane oxidation mechanism



- Propane adsorption – hydrogen extraction generally accepted as the rate determining step in the process.

Technical Accomplishments – FY08/09

2%Pt/$Ce_xCo_{1-x}O_2$ system interrogation: Co employed in an attempt to improve paraffinic activity of the system.



- C_3H_8 activity of system improved with blending of small amounts of Co into CeO_2 system

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Technical Accomplishments – FY08/09

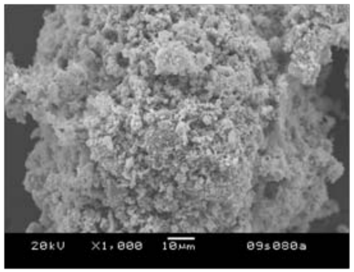
2%Pt/$Ce_xCo_{1-x}O_2$ system interrogation: BET results

Catalyst name	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (A)
Pt/$Co_{0.1}Ce_{0.9}O_2$	75.81	0.2665	152.3
Pt/$Co_{0.3}Ce_{0.7}O_2$	48.67	0.1934	123.6
Pt/$Co_{0.5}Ce_{0.5}O_2$	37.60	0.2008	123.2
Pt/$Co_{0.9}Ce_{0.1}O_2$	9.727	0.03715	24.98
Pt/Co_3O_4	1.567	0.08406	28.8

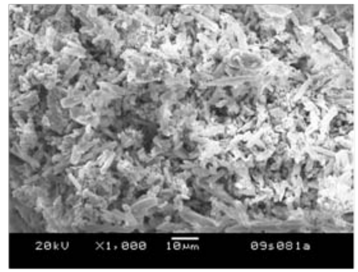
- Textural properties remain intact with blending of small amount of Co into CeO_2 system (10%).
- Larger amounts of Co result in moderate to significant structural changes

Technical Accomplishments – FY08/09

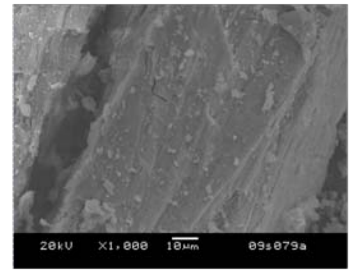
2%Pt/$Ce_xCo_{1-x}O_2$ system interrogation: SEM studies



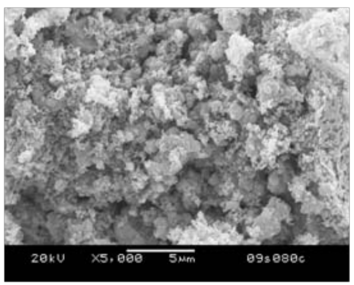
Pt/Co_3O_4



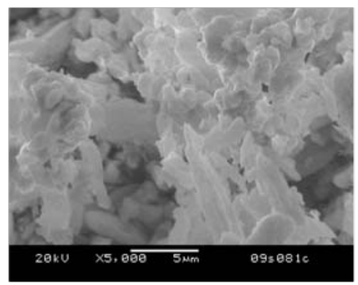
$Pt/Co_{0.3}Ce_{0.7}O_2$



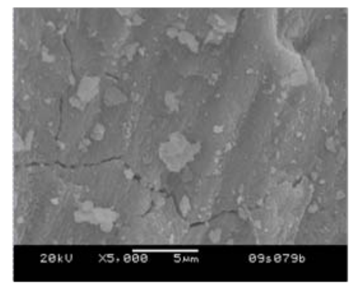
$Pt/Co_{0.1}Ce_{0.9}O_2$



Pt/Co_3O_4



$Pt/Co_{0.3}Ce_{0.7}O_2$



$Pt/Co_{0.1}Ce_{0.9}O_2$

- Small amount of Co (10%) shows surface effects only
- Significant morphological differences with larger amounts of Co

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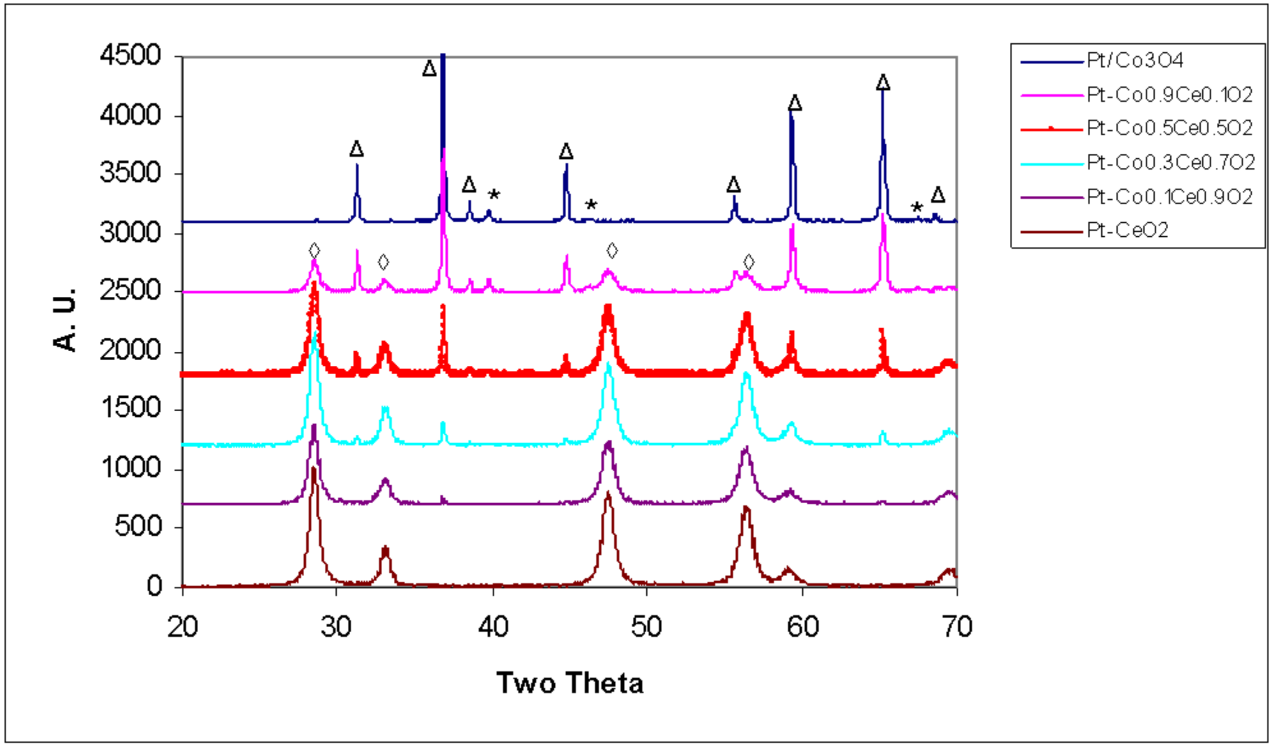
Technical Accomplishments – FY08/09

2%Pt/$Ce_xCo_{1-x}O_2$ system interrogation: XRD analyses



- CeO_2 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.

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Technical Accomplishments – FY08/09

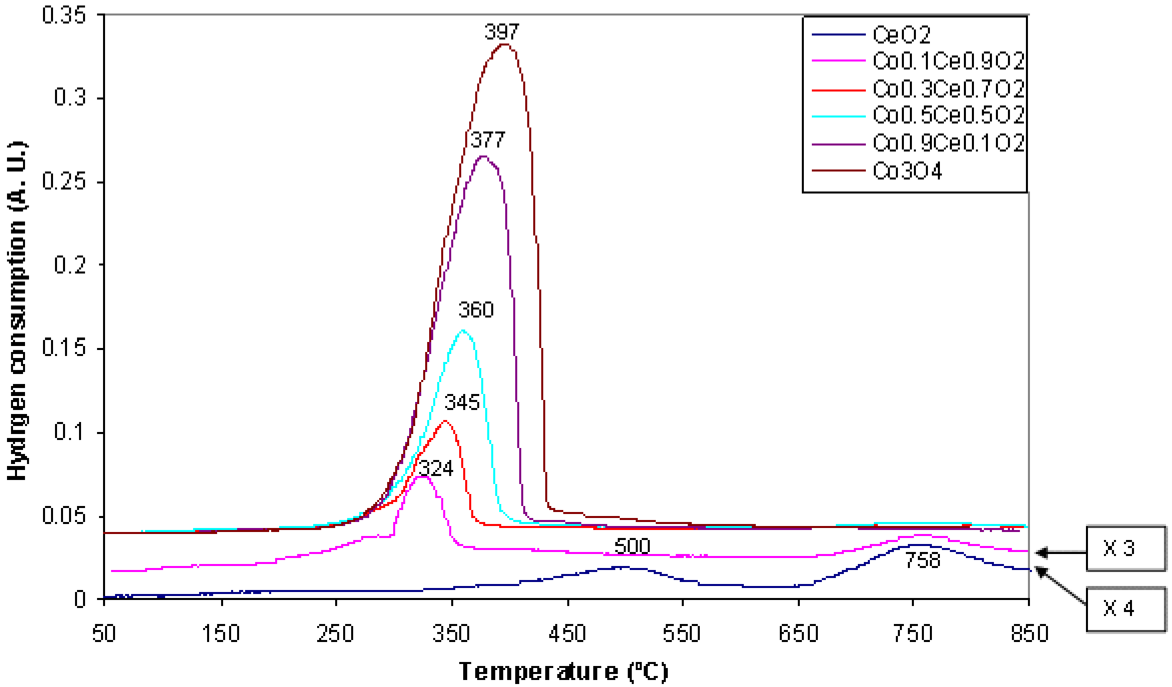
2%Pt/$Ce_xCo_{1-x}O_2$ system interrogation: Platinum particle size

Catalyst	Pt/Co_3O_4	Pt/$Co_{0.9}Co_{0.1}O_2$	Pt/$Co_{0.5}Ce_{0.5}O_2$	Pt/$Co_{0.3}Ce_{0.7}O_2$	Pt/$Co_{0.1}Ce_{0.9}O_2$
Pt (nm)	39.9	37.9	22.4	N. A.	N. A.

- Pt metal remains well dispersed with moderate amounts of Co blended into the CeO_2 system.
- Significant metal agglomeration obvious with larger amounts of Co as indicated in XRD analyses.

Technical Accomplishments – FY08/09

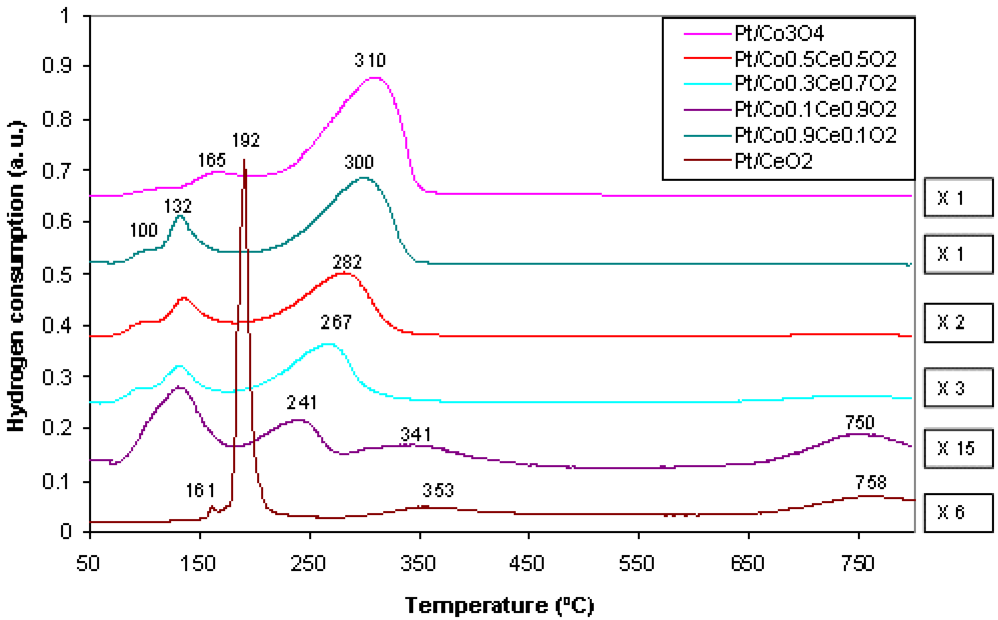
2%Pt/$Ce_xCo_{1-x}O_2$ system interrogation: TPR investigations of supports only



- 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/$Ce_xCo_{1-x}O_2$ 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.

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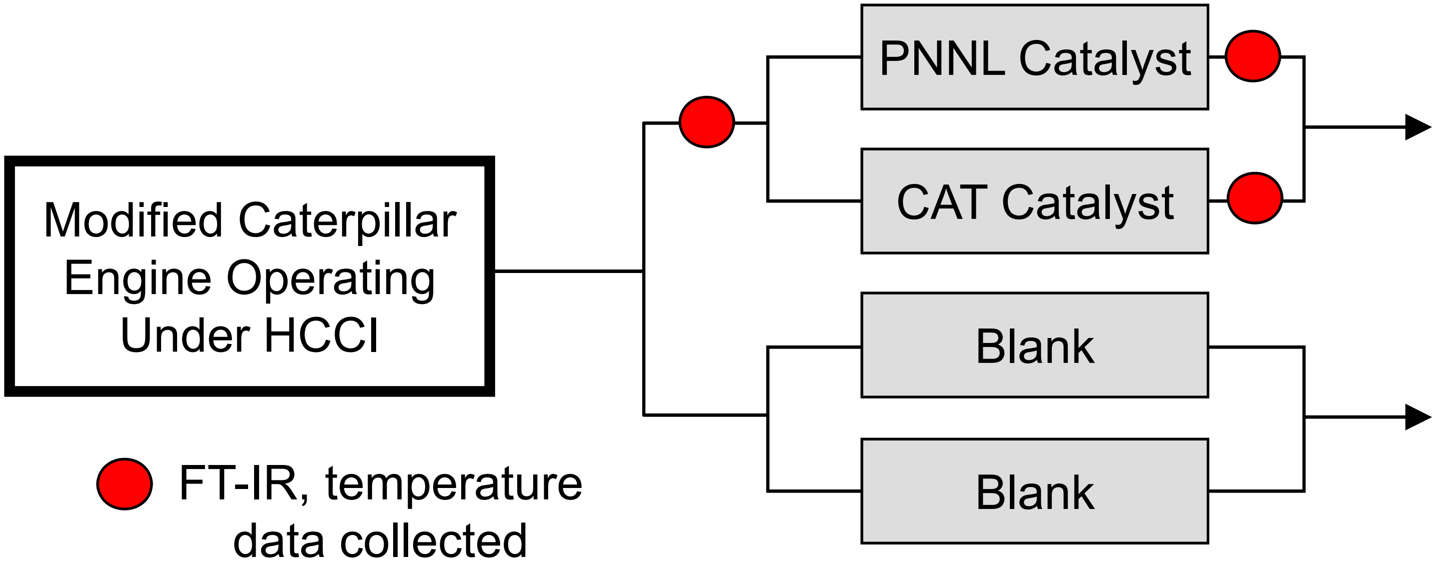
Engine Testing at Caterpillar



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.

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6-inch Monolith Brick Coating Details

6 inch diameter 5 ¾ inch height. 1159 gram weight, washed by acetone, 2-propanol, 10% HNO_3, and rinsed with D.I. H_2O to pH >5. Dried in air.

Slurry:

$Ce_{0.9}Pr_{0.1}O_2$ was prepared by calcination of $Pr(NO_3)_3$ and $Ce(NO_3)_3$ aqueous solution in air at 650°C for 4 hours

Aqueous slurry of 12 wt% $Ce_{0.9}Pr_{0.1}O_2$ 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 $Ce_{0.9}Pr_{0.1}O_2$ loaded brick using 4 wt% $Pd(NH_3)_4(NO_3)_2$ 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

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

η = fractional NOx conversion efficiency

ξ = space velocity (SV) of interest

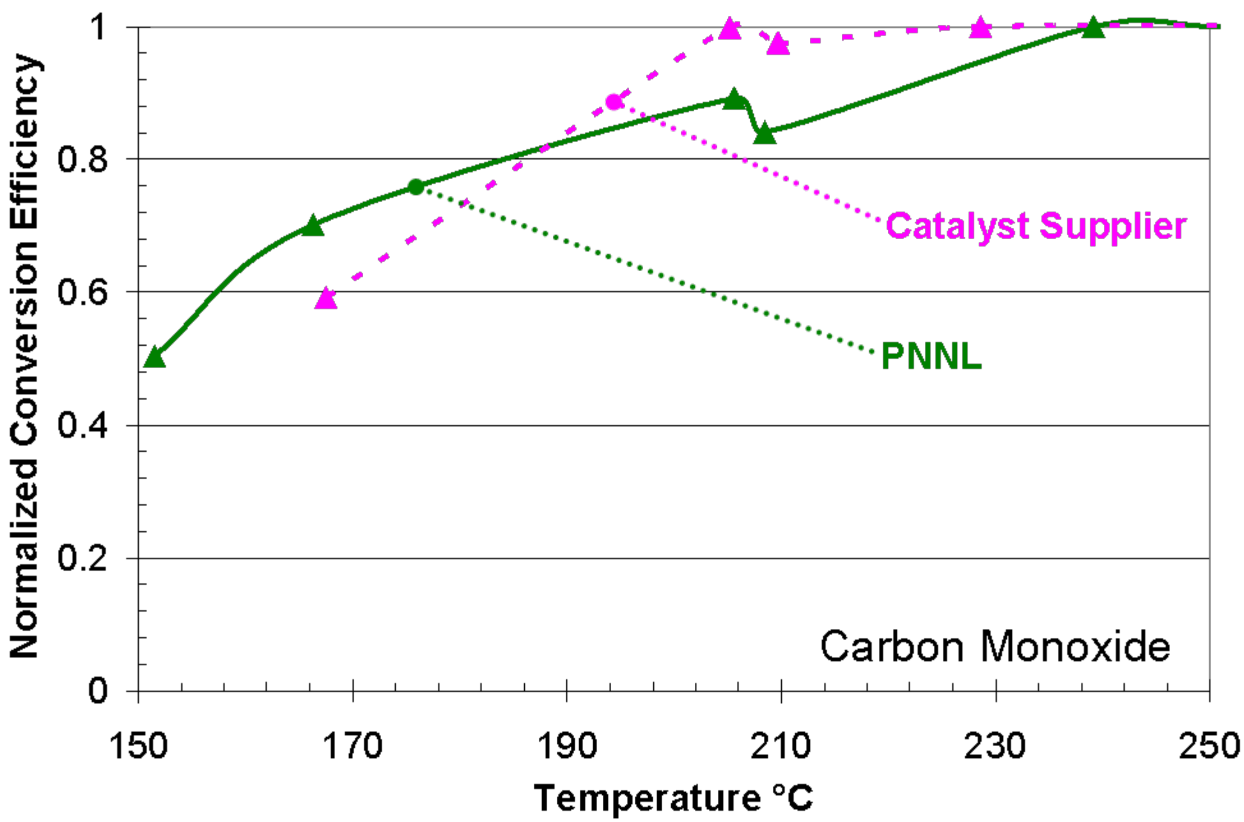
ξ_0 = reference SV at which conversion efficiency is known

Engine Testing

Carbon Monoxide (CO) Results

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

T_{50}CO target (150°C) nearly reached with PNNL catalyst!



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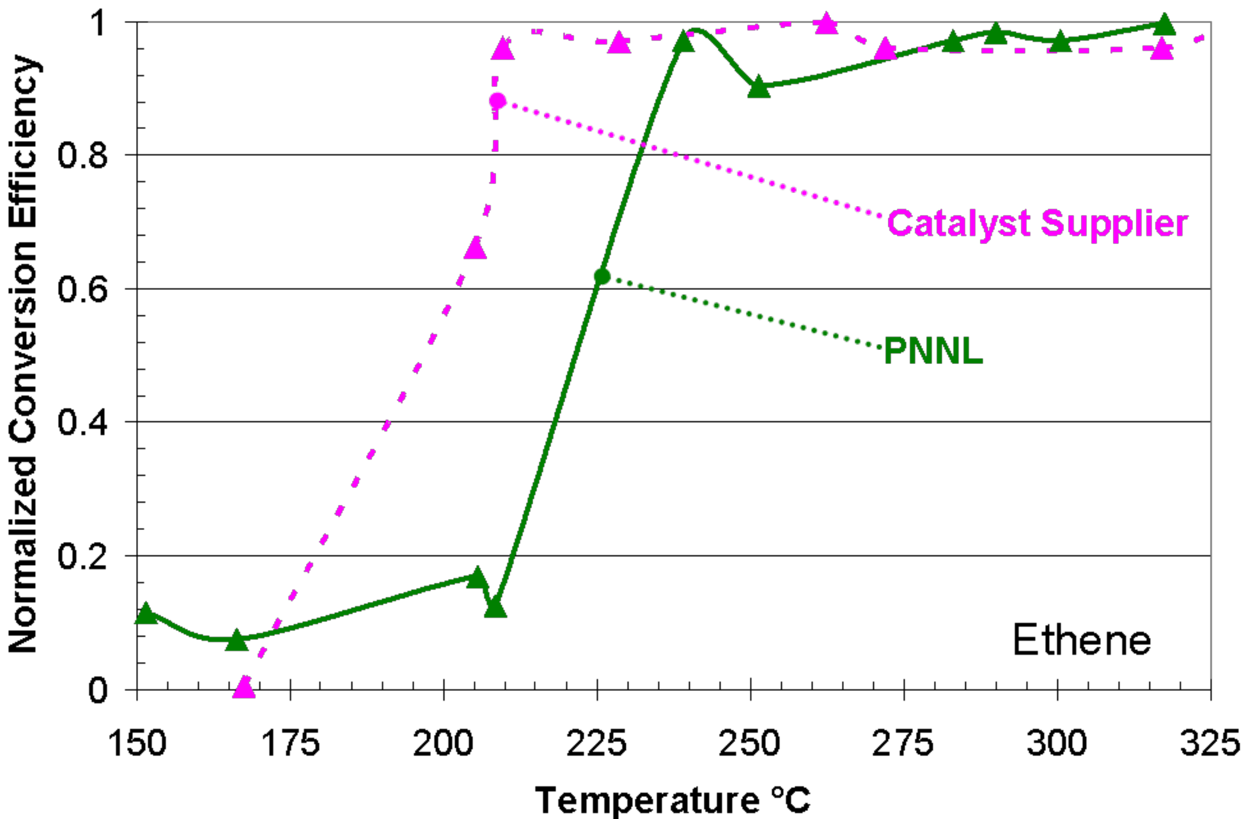
Engine Testing

Ethylene (C_2H_4) Results

Neither sample exhibited good C_2H_4 activity.

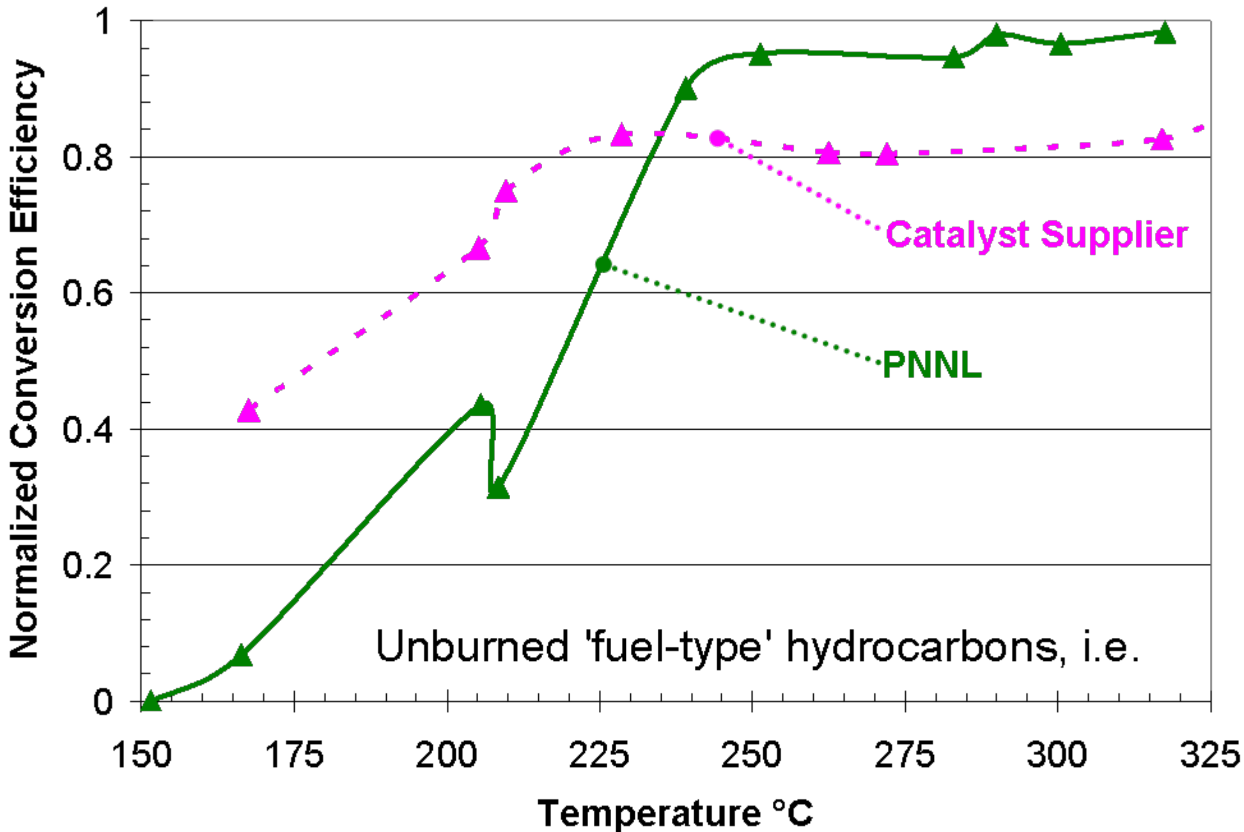


Engine Testing

Unburned Fuel (>C_5) Results

PNNL catalyst reached T_{90}HC @ <240°C.

Catalyst supplier did not achieve T_{90}HC until almost 350°C!



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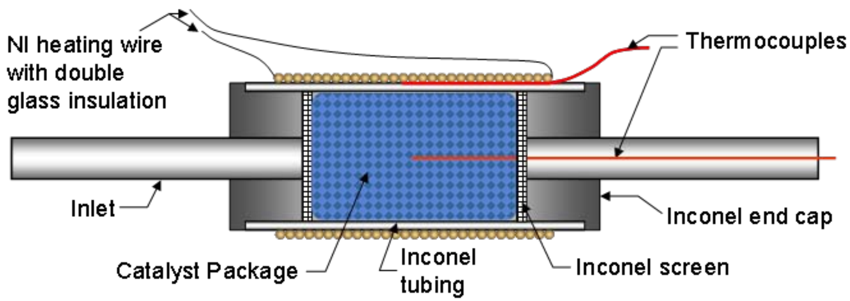
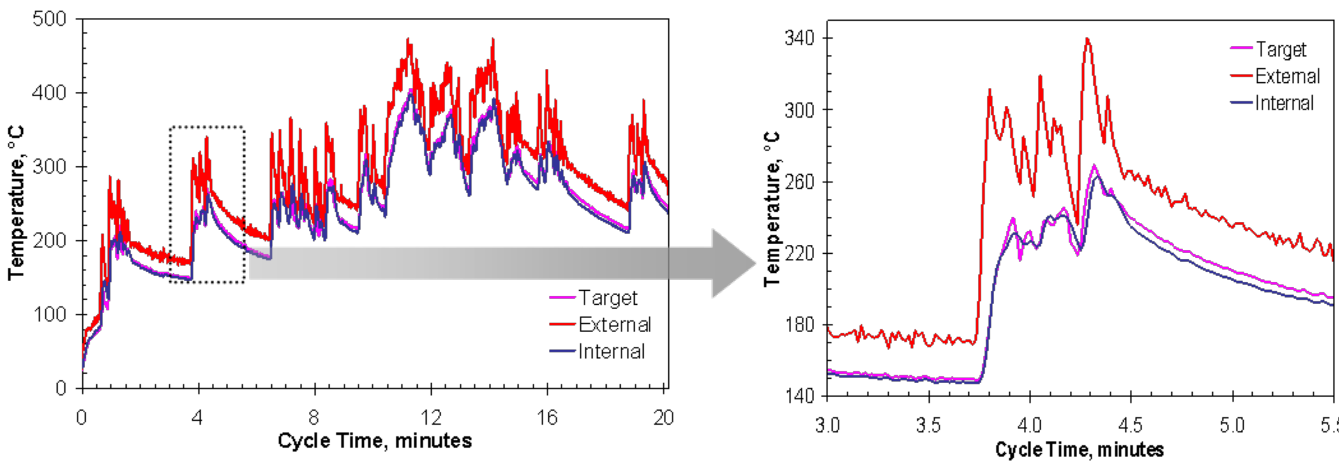
Transient Testing

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>U.S. Heavy Duty Federal Test Procedure (FTP)</u>

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

$$HCCI\,Transient = IdleHCCI + \left(HR\,Transient - IdleHR\right)\cdot\frac{HLHCCI - IdleHCCI}{HLHR - IdleHCCI}$$

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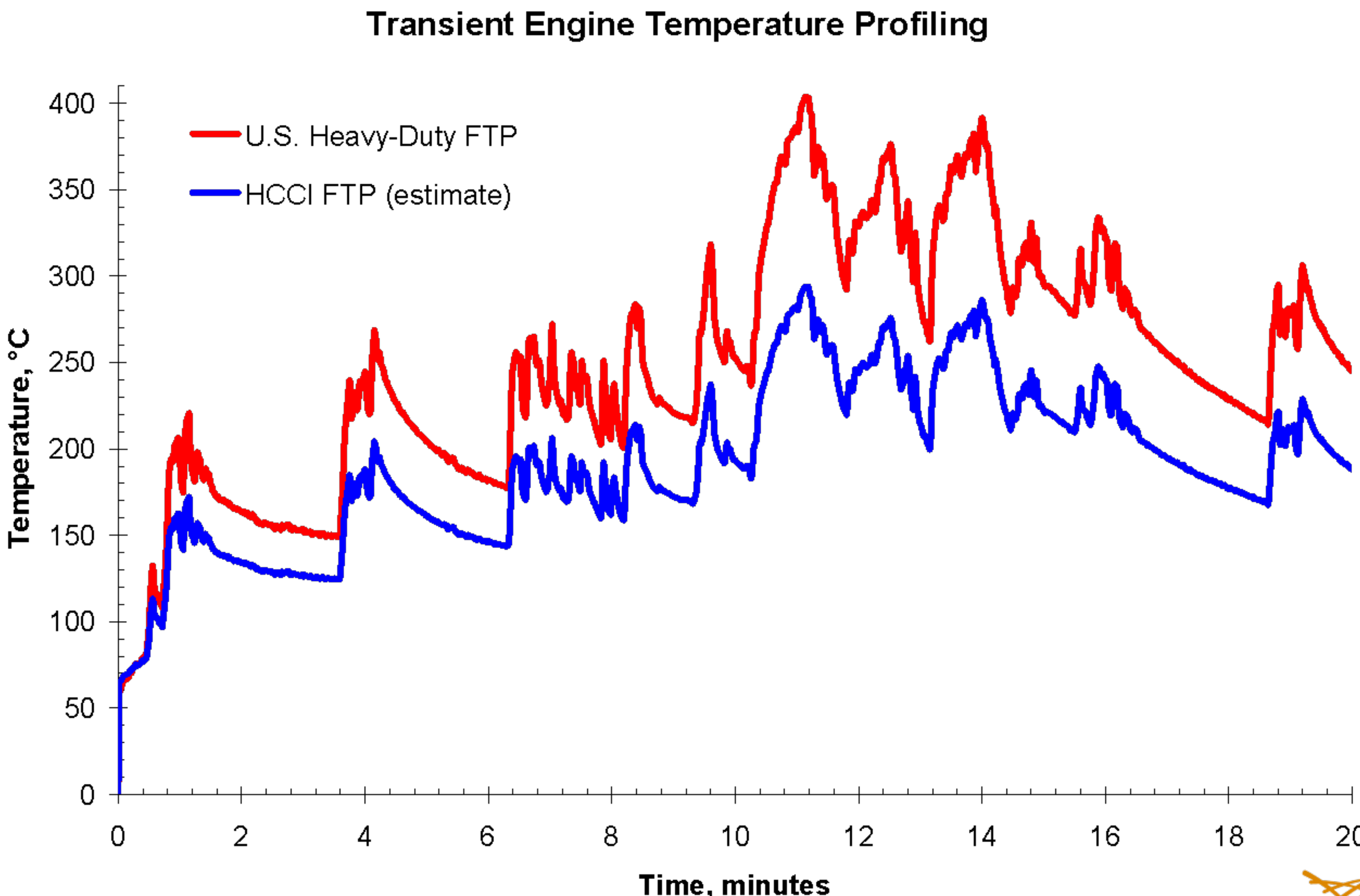
Transient Testing – HCCI



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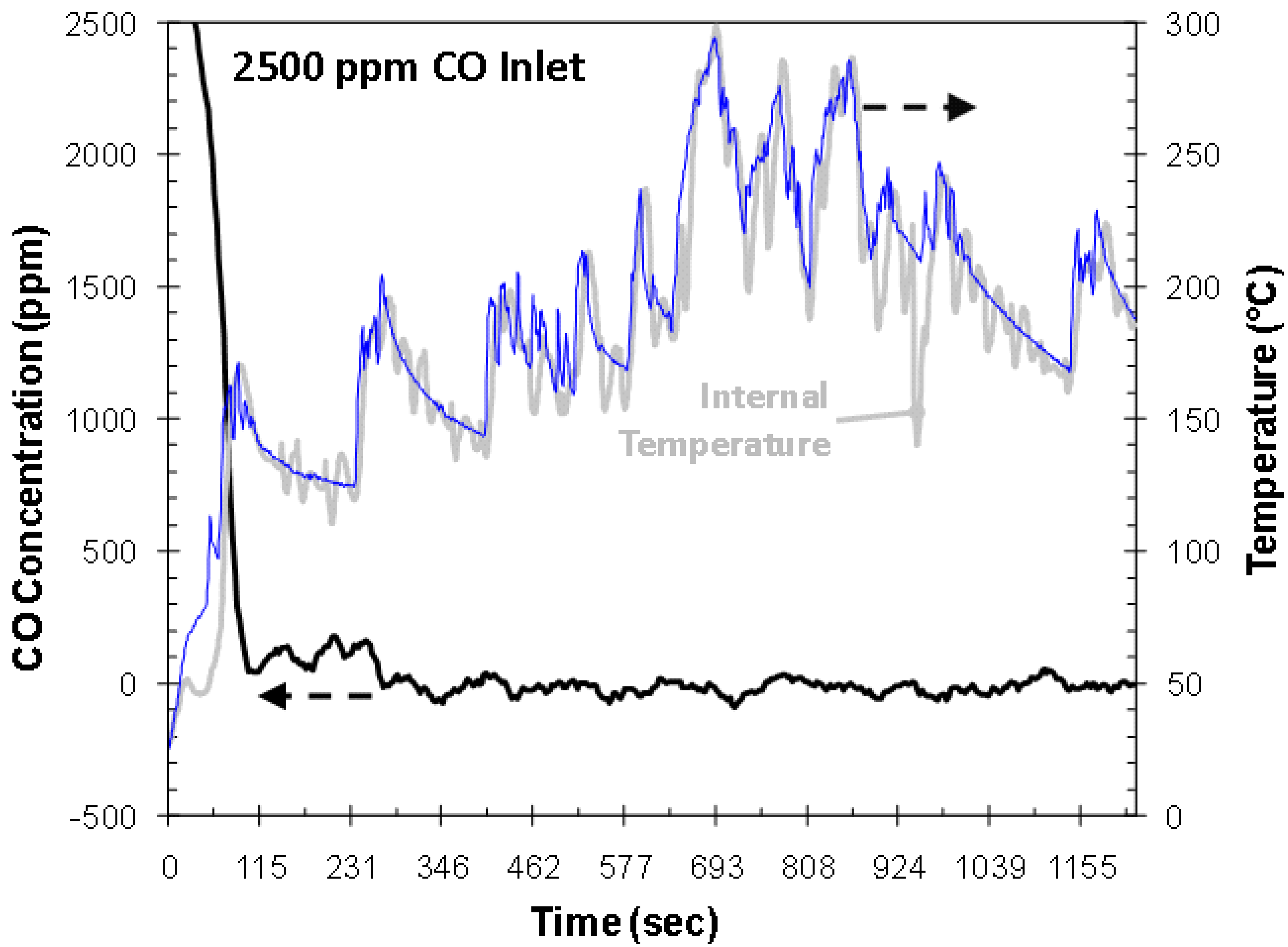
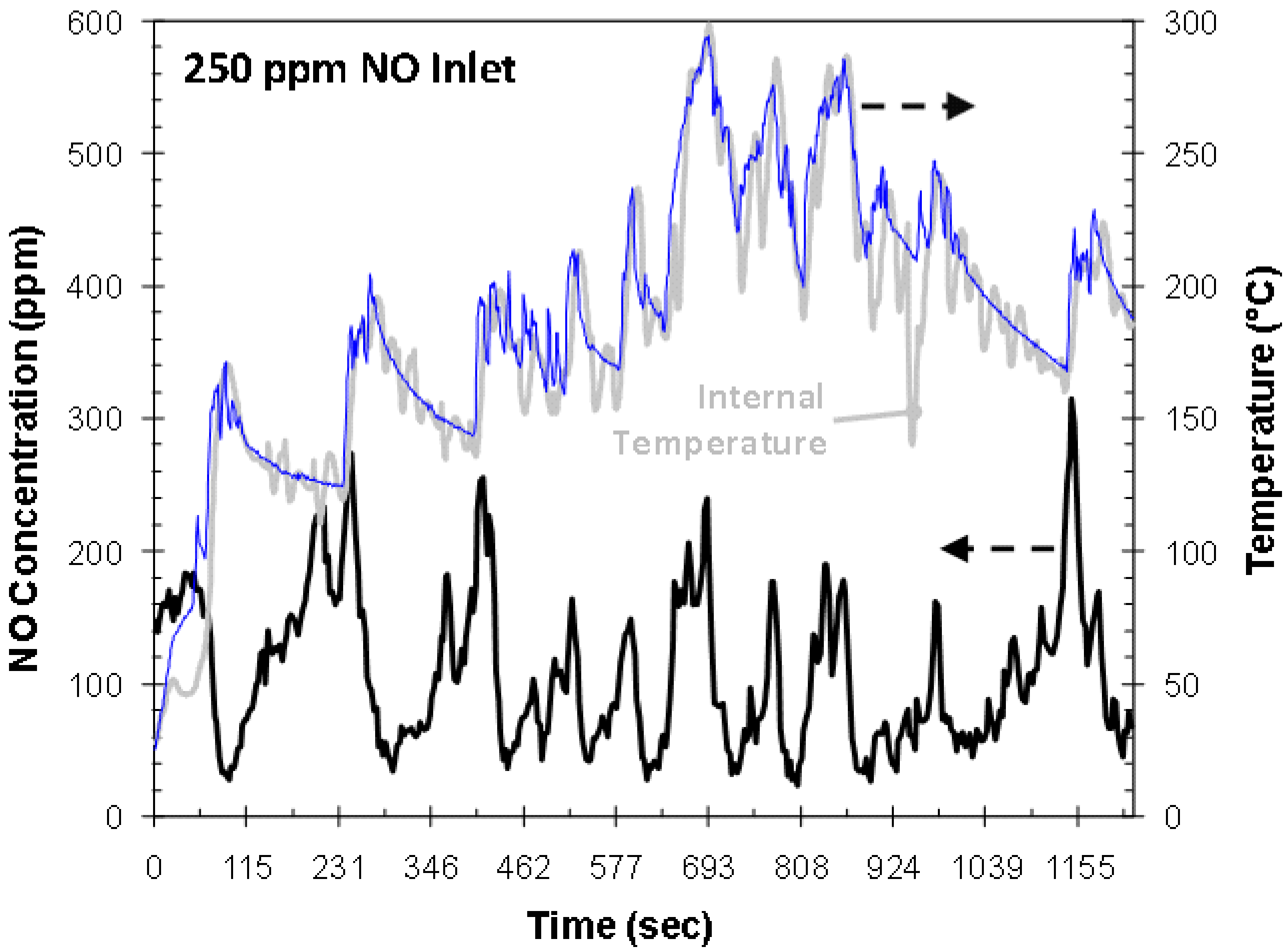
Transient Testing – HCCI



- >95% CO destruction over the entire transient cycle

Transient Testing – HCCI



- >56% oxidation of 250 ppm NO over the entire transient cycle

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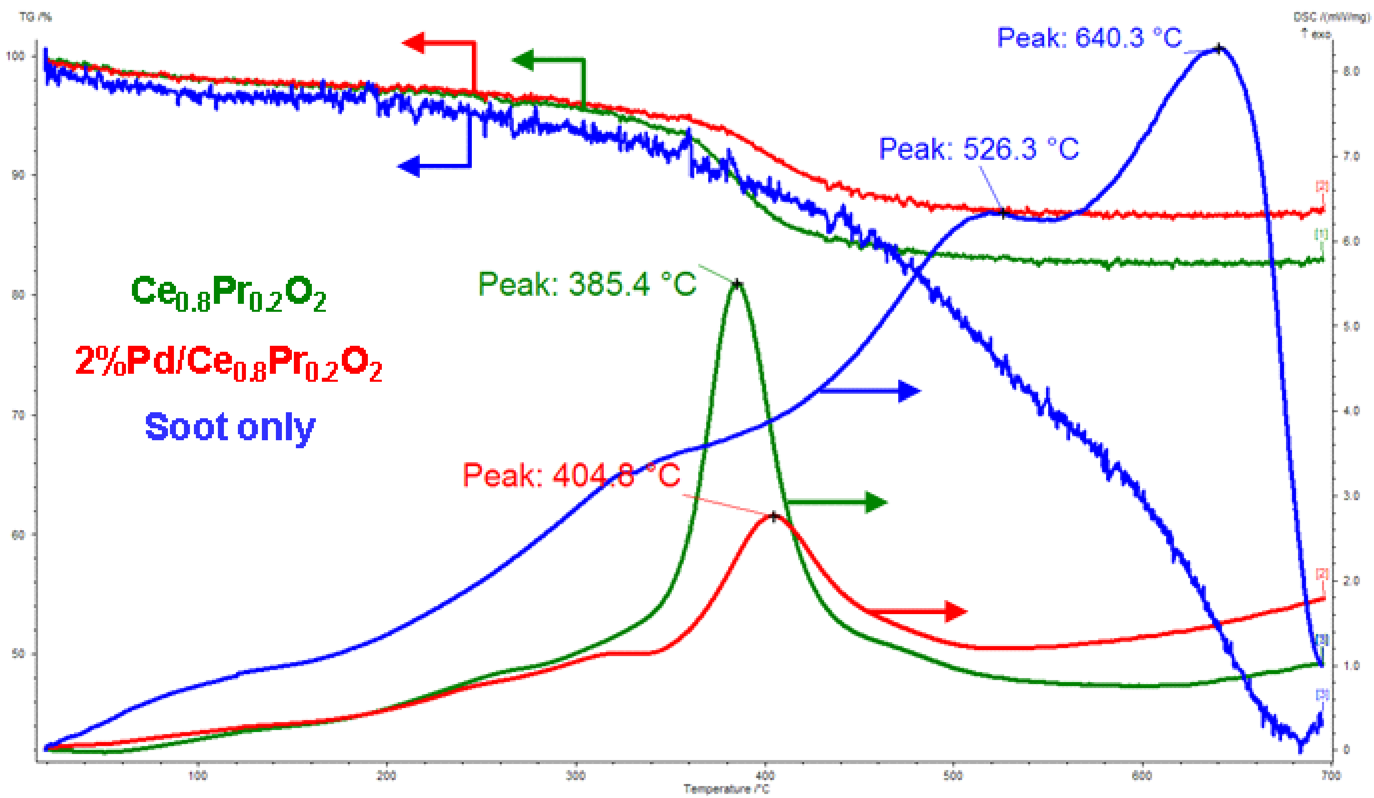
Soot Oxidation Feasibility Investigations

- Examined feasibility of formulation ($Ce_{0.8}Pr_{0.2}O_2$) for contact soot oxidation.
- Compared soot oxidation of Ce/Pr formulation to commercial supplier formulation

3:1 Mass Ratio Catalyst:Soot Mixture



- $Ce_{0.8}Pr_{0.2}O_2$ provides significant enhancement of soot oxidation over soot alone and 2%Pd metal

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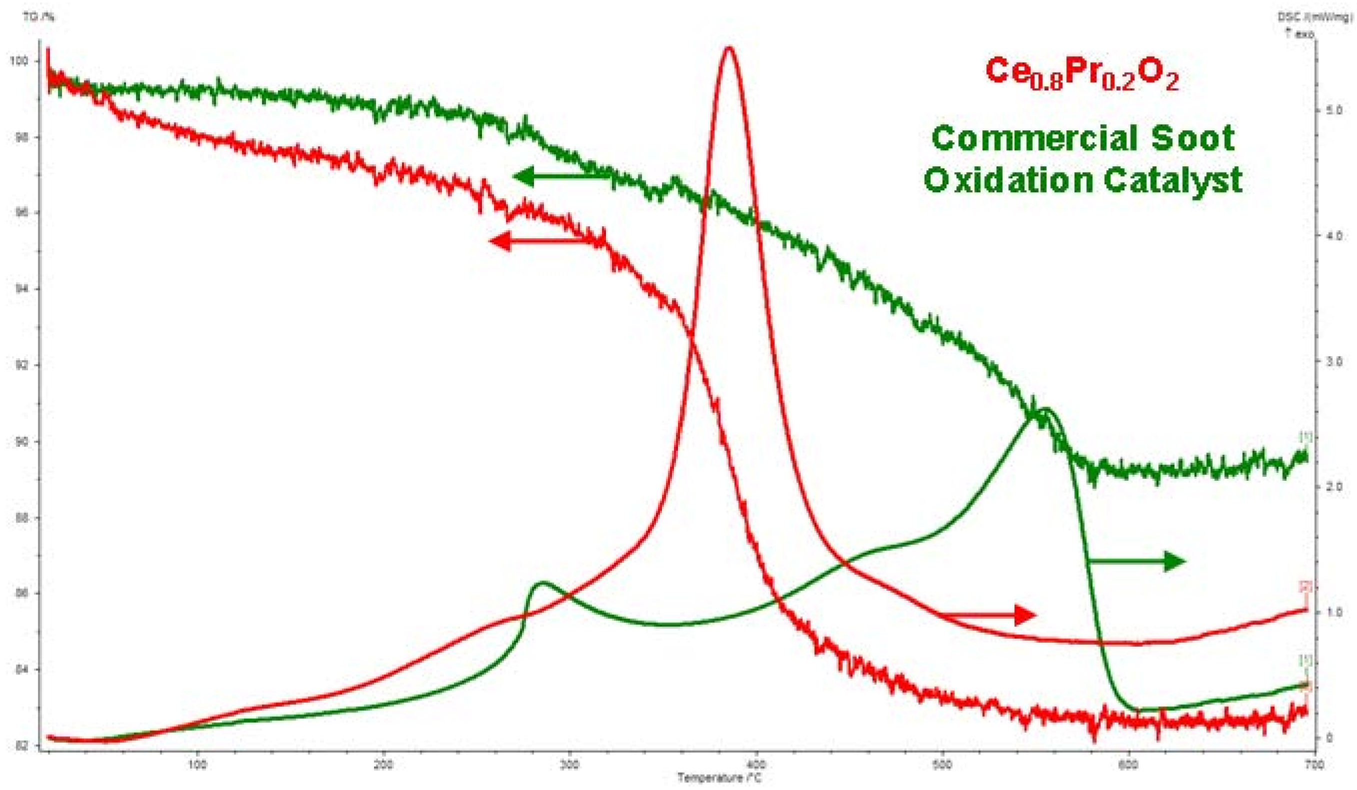
3:1 Mass Ratio Catalyst:Soot Mixture



- $Ce_{0.8}Pr_{0.2}O_2$ provides significant enhancement of soot oxidation over commercial soot oxidation catalyst.

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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 C_2H_4 light-off at less than 100°C.
    - Have gotten C_3H_8 light-off to less than 300°C.
  - HC oxidation: 90% HC oxidation at 175°C.
    - Successful in achieving >90% C_2H_4 oxidation at <100°C.

Acknowledgments

Ron Silver, Tom Paulson, Colleen Eckstein
– Caterpillar, Inc.

Ken Howden
– DOE OFCVT

U.S. Department of Energy
Energy Efficiency and Renewable Energy
FreedomCAR & Vehicle Technologies Program

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