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

CRADA: PNNL – Caterpillar

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14th DEER (Diesel Engine-Efficiency & Emissions Research) Conference
Dearborn, Michigan
August 5, 2007

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

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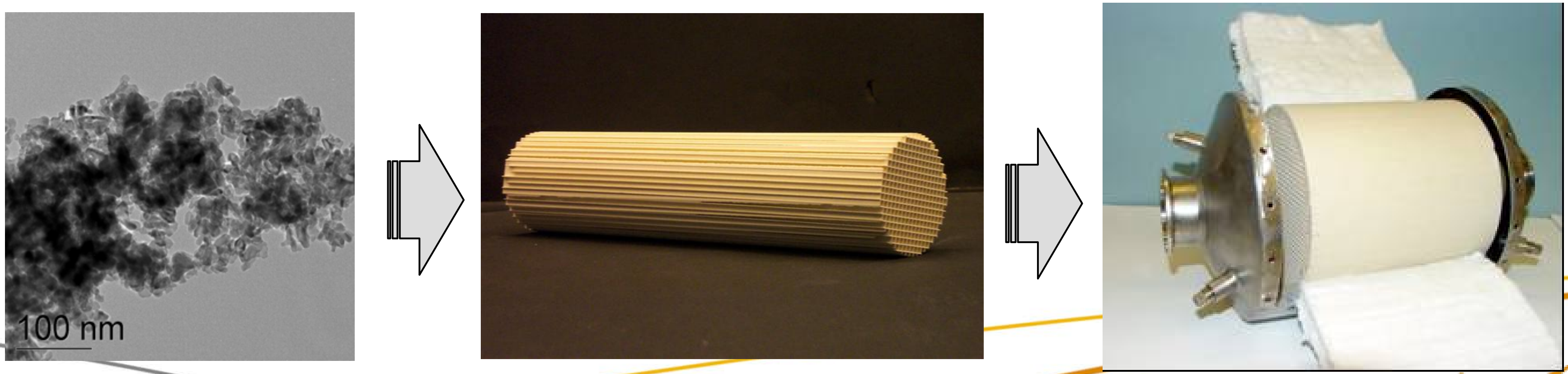
Overview

Low-Temperature Oxidation Catalysts for HCCI Emissions Control

- HCCI shows promise for meeting future HD NO_x limits (Duffy *et al*., DEER 2004)
  - Major hurdles: high hydrocarbon CO emissions
  - Low exhaust temperatures below typical light-off
- Program initiated Summer 2004 (at PNNL) to survey work in low temperature oxidation (CO) and propose roadmap



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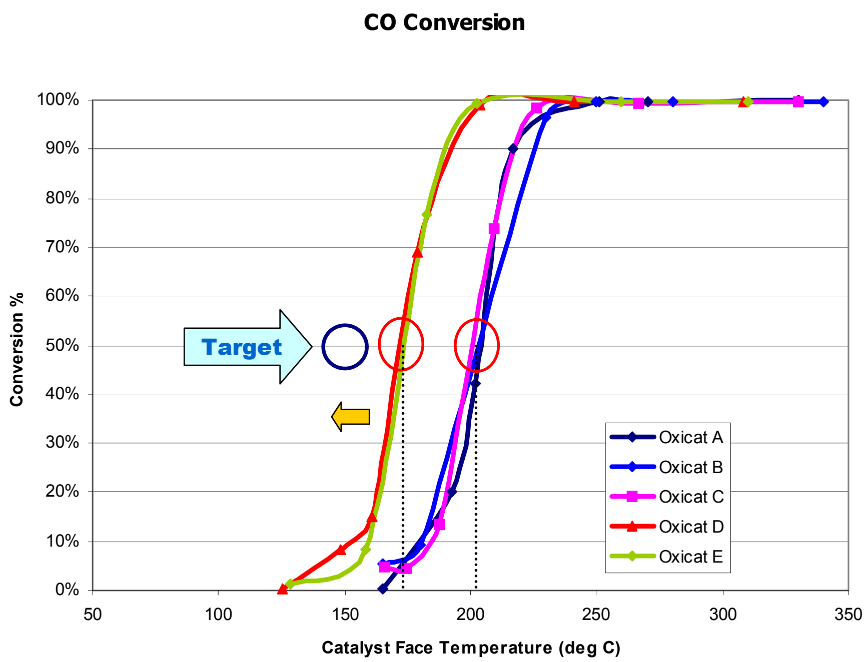
Objectives

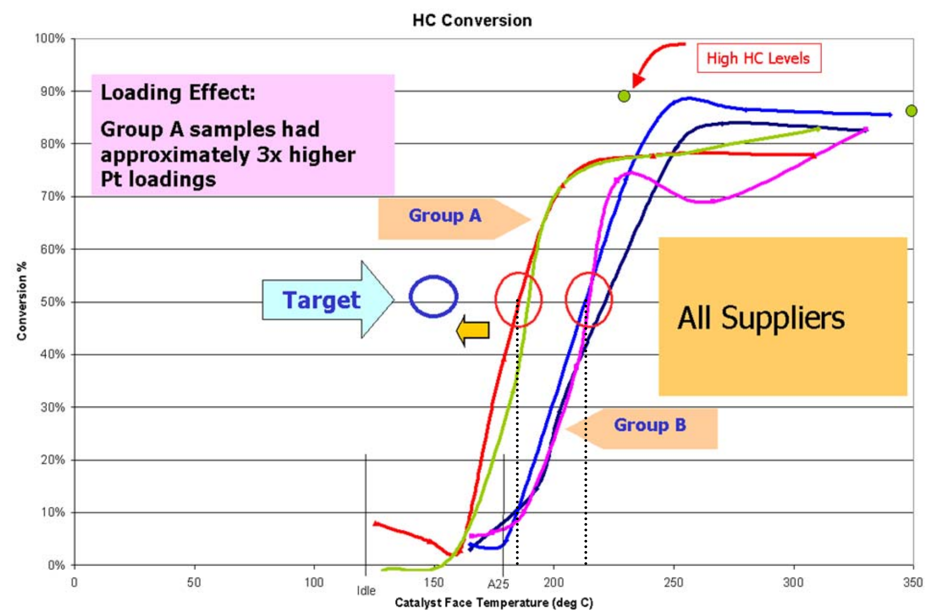
Develop low-temperature HC & CO oxidation catalysts to enable HCCI application



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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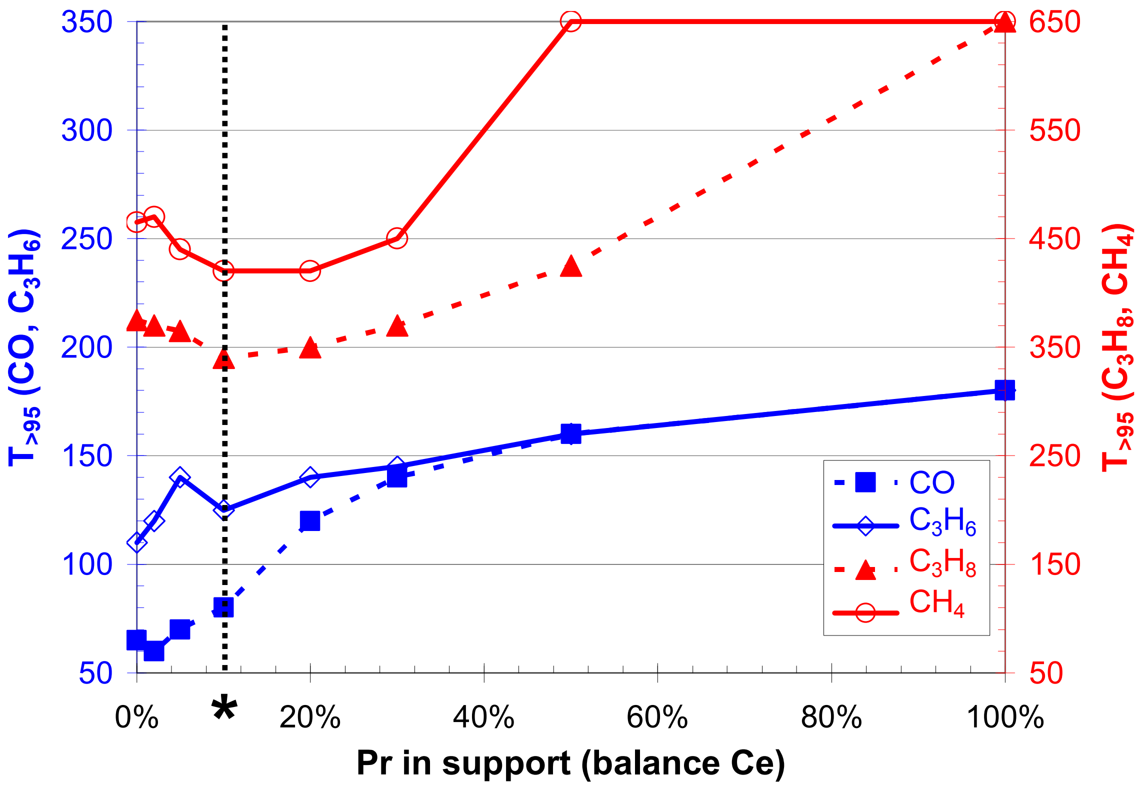
Review

$Ce_xPr_{1-x}O_2$ System Investigations

Addition of transition metals praseodymium (Pr) and terbium (Tb) believed to enhance low-temperature REDOX capacity of the CeO_2 catalyst, improving the low-temperature oxidation capacity.

Ferrer, V. et al *Catal. Today* **2005**, *107-108*, 487-492

Logan, A. D. et al *J. Mater. Res*. **1994**, *9*, 468-475



Varying Pr levels in Pd/CeO_2 System

Pd source: $Pd(NH_3)_4(NO_3)_2$

Ce/PrO_2 source: $Ce/Pr(NO_3)_3 \cdot 6H_2O$

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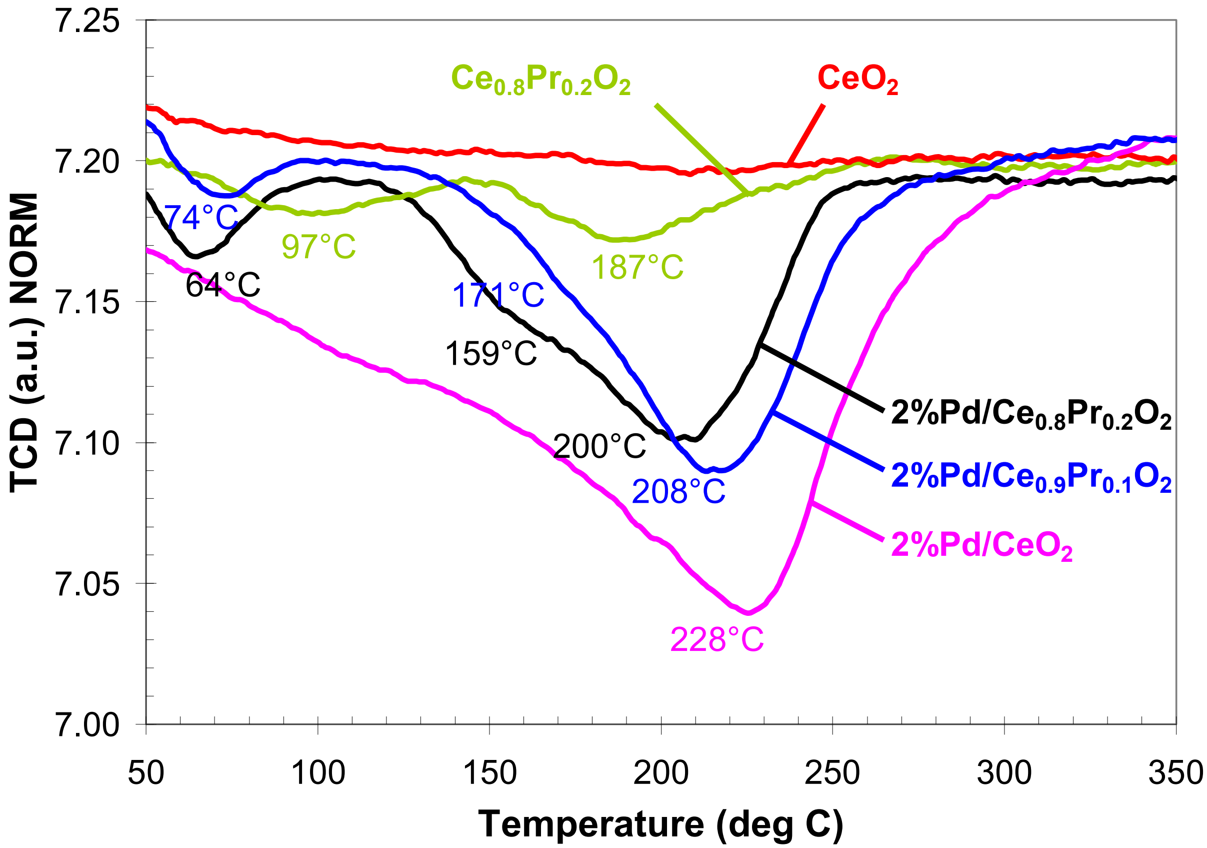
Review

$Ce_xPr_{1-x}O_2$ System Characterization Efforts TPO Investigations of Pd Catalysts



Shoulder at 159-171°C is due to Pr, and more noticeable upon ↑ Pr.

200-228°C is Pd oxidation. *Increased* Pr *decreases* T required to facilitate Pd-interaction with support; i.e. Pd is more readily oxidized as Pr increases.

This is seen again by Pd oxidation at 64-74°C.

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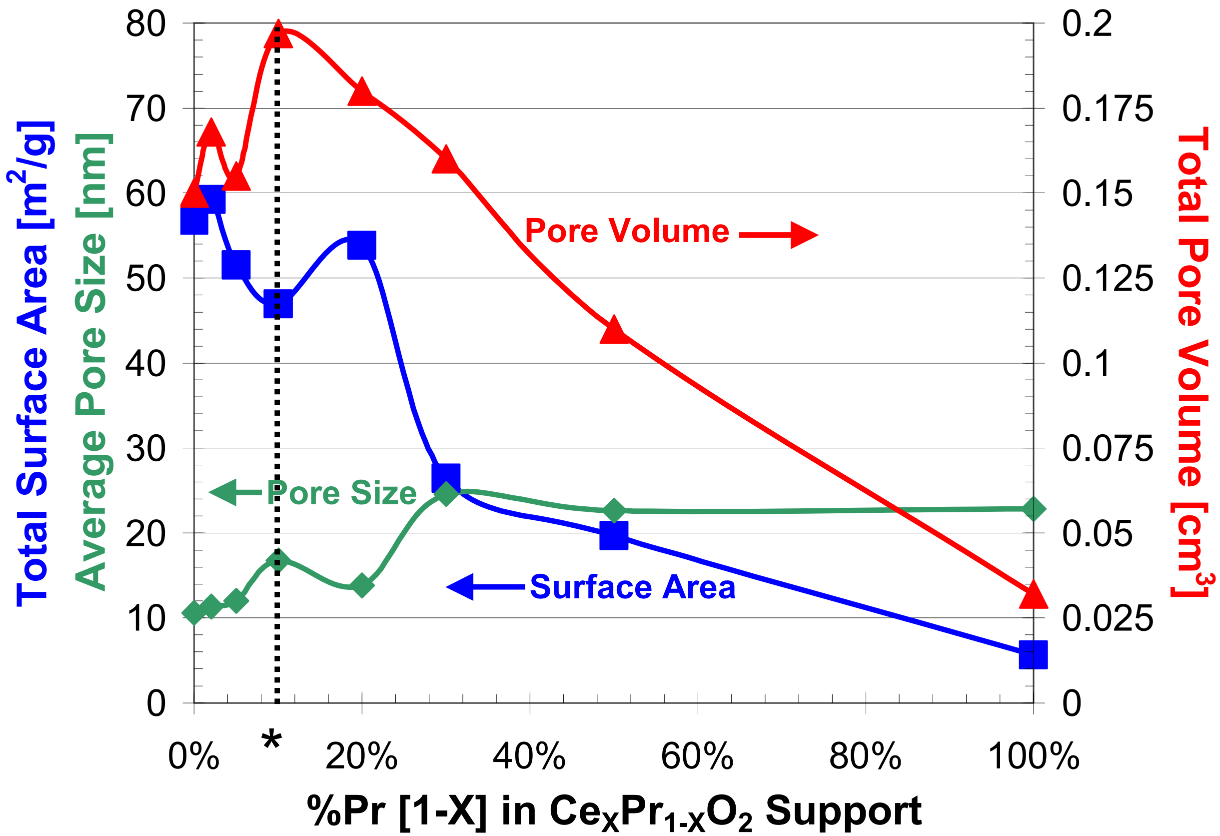
Review

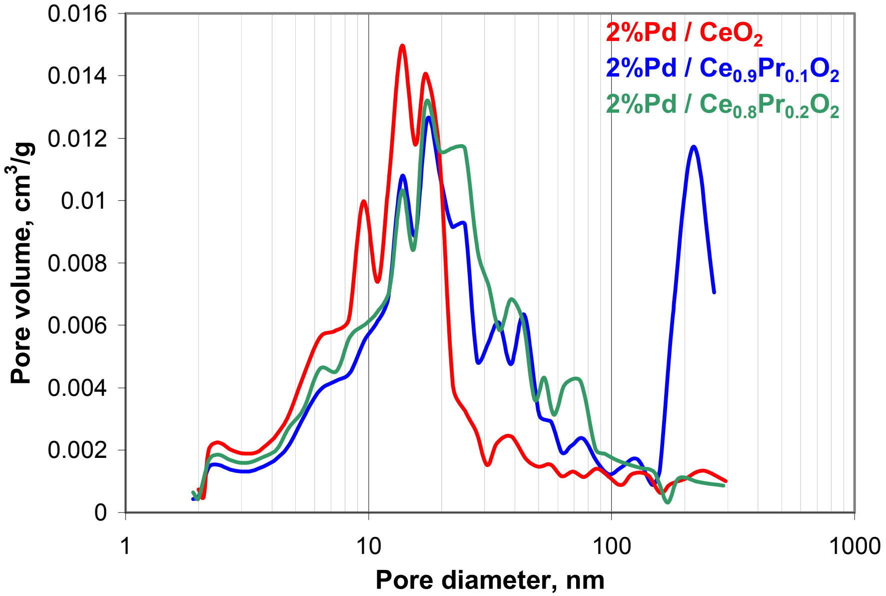
$Ce_xPr_{1-x}O_2$ System Characterization Efforts
BET Investigations of Pd Catalysts

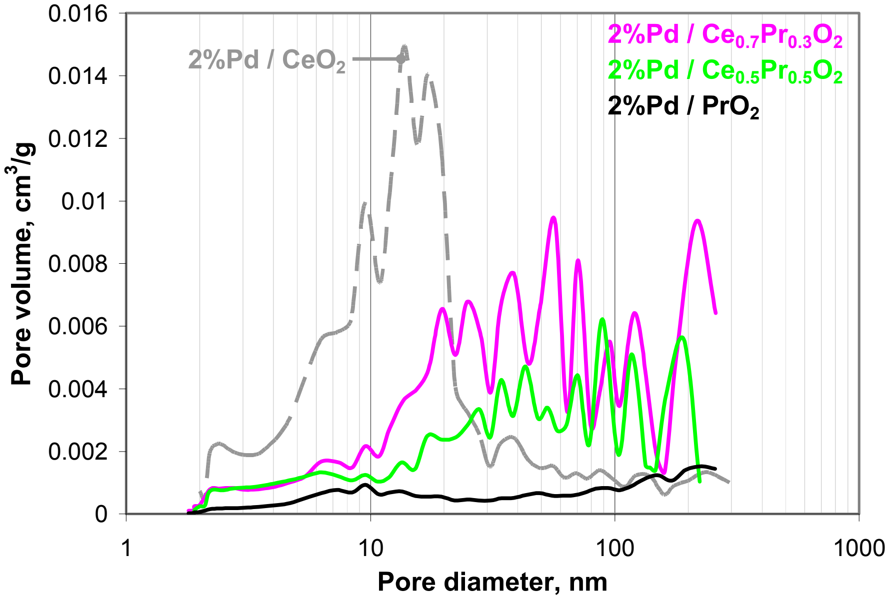
- Small amounts of Pr (0-20%) believed to not reduce surface area of CeO_2
- Larger amounts (>20%) impact the surface up to 100% PrO_2 with surface area <10 m^2/g



Review

$Ce_xPr_{1-x}O_2$ System Characterization Efforts
Pore Distribution Investigations of Pd Catalysts





- 10%-20% Pr brings in larger (≥ 20nm) pores, shifts maxima slightly to larger pores asymmetrically.
- >20% significantly decreases maxima, drastic broadening of the peak towards larger pore sizes asymmetrically.

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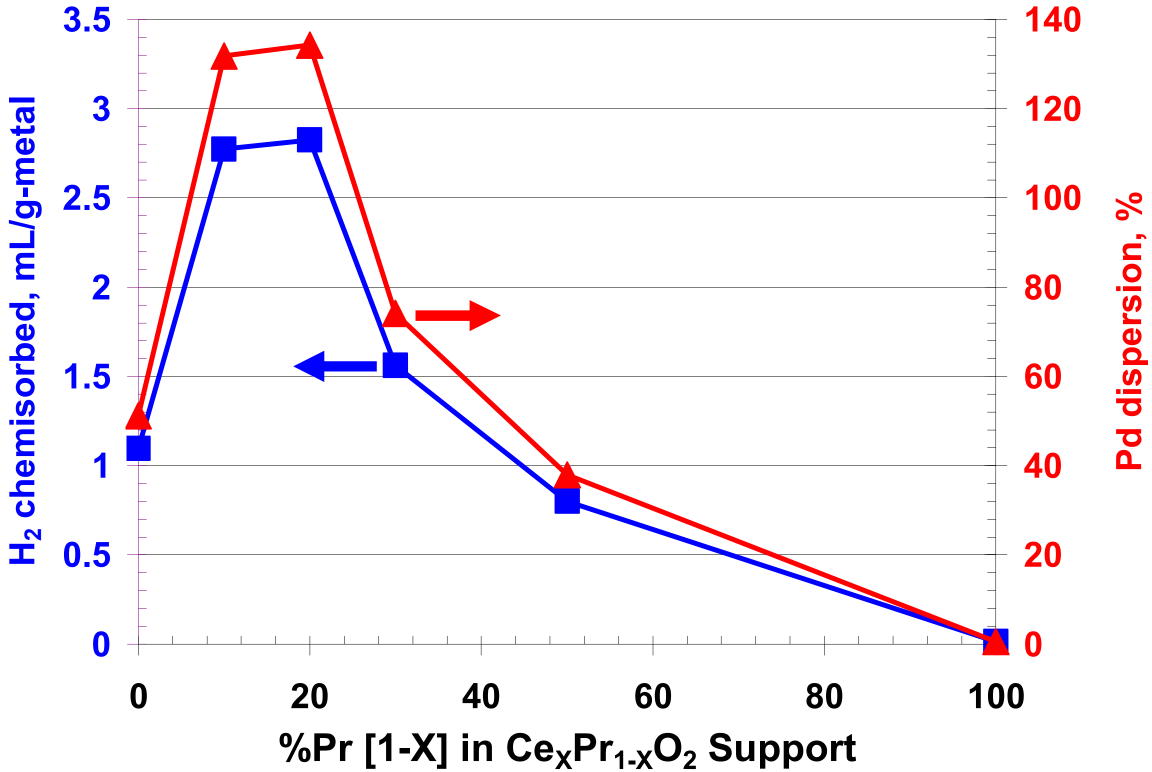
$Ce_xPr_{1-x}O_2$ System Characterization Efforts
Metal Dispersion Investigations of Pd Catalysts

Increased synergy of Pd with support at 10-20% Pr loading; ‘spill-over’ effect* results in >100% effective dispersion.

*Gatica, J. et al *J. Phys. Chem. B* **2001**, *105*, 1191-1199



Optimal metal-support interaction at 10-20% Pr loading.

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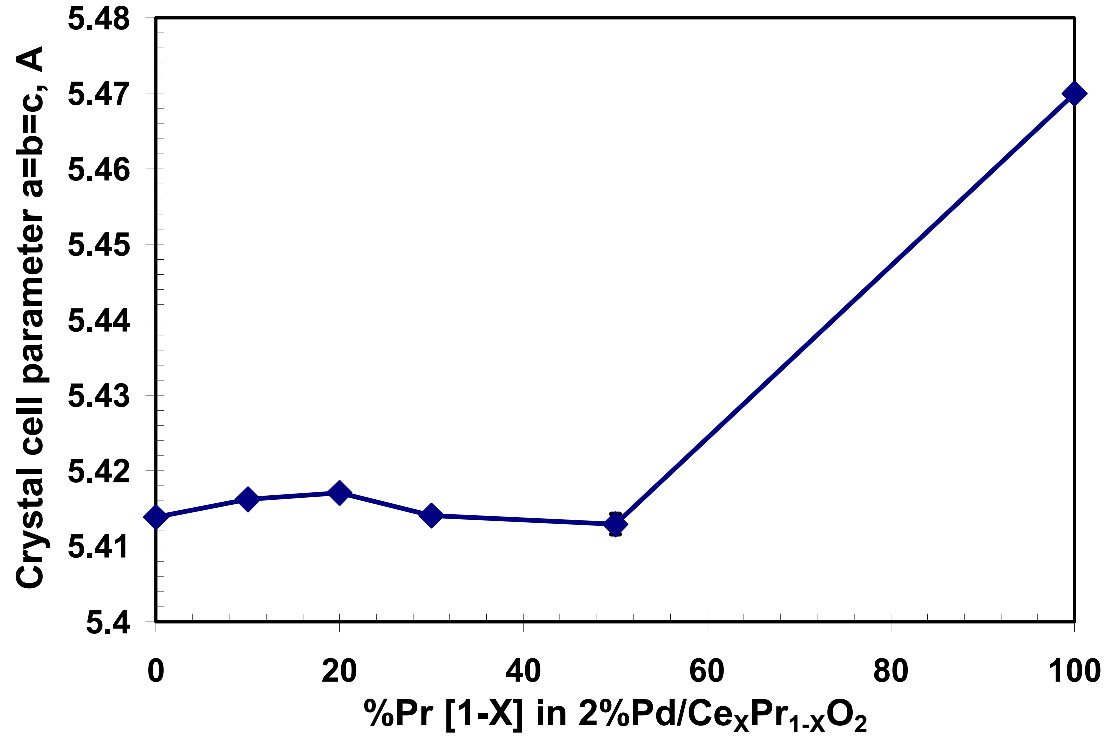
$Ce_xPr_{1-x}O_2$ System Characterization Efforts
Crystal Cell Parameter of Pd Catalysts



10%-20% Pr results in ‘swelling’ of the crystal structure.

This is lost with >20% Pr.

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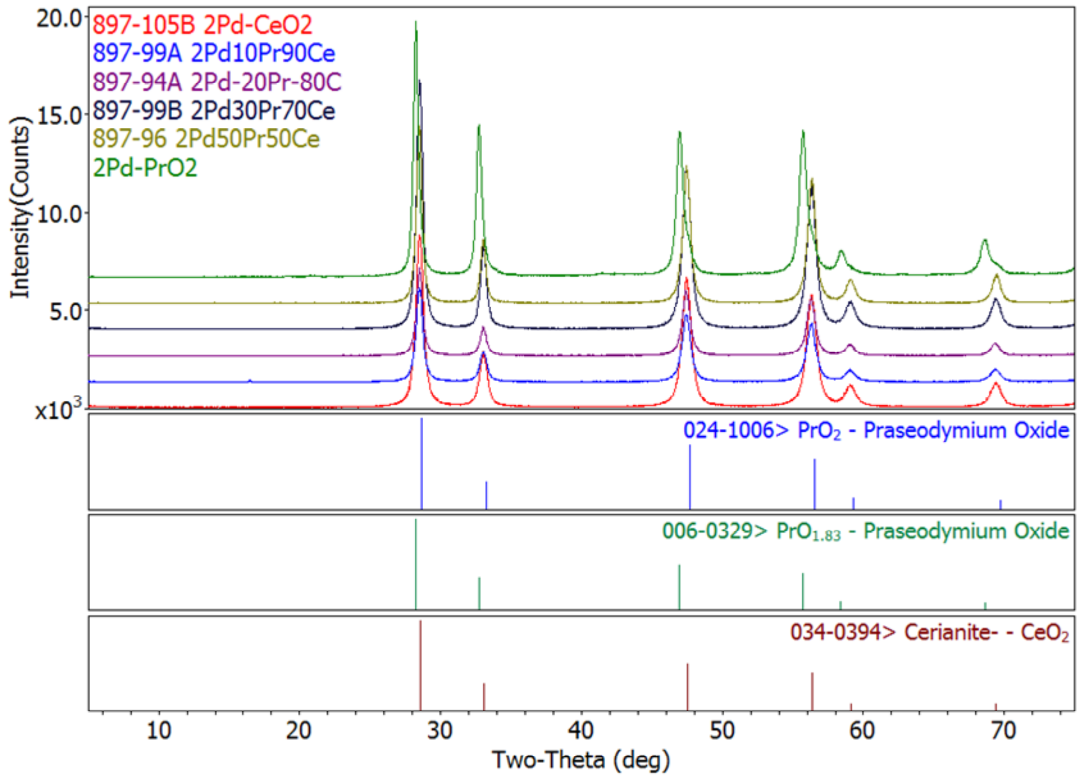
$Ce_xPr_{1-x}O_2$ System Characterization Efforts
XRD Pattern of Pd Catalysts



Pr blends into support as PrO_2; Pr_6O_{11} ultimately forms

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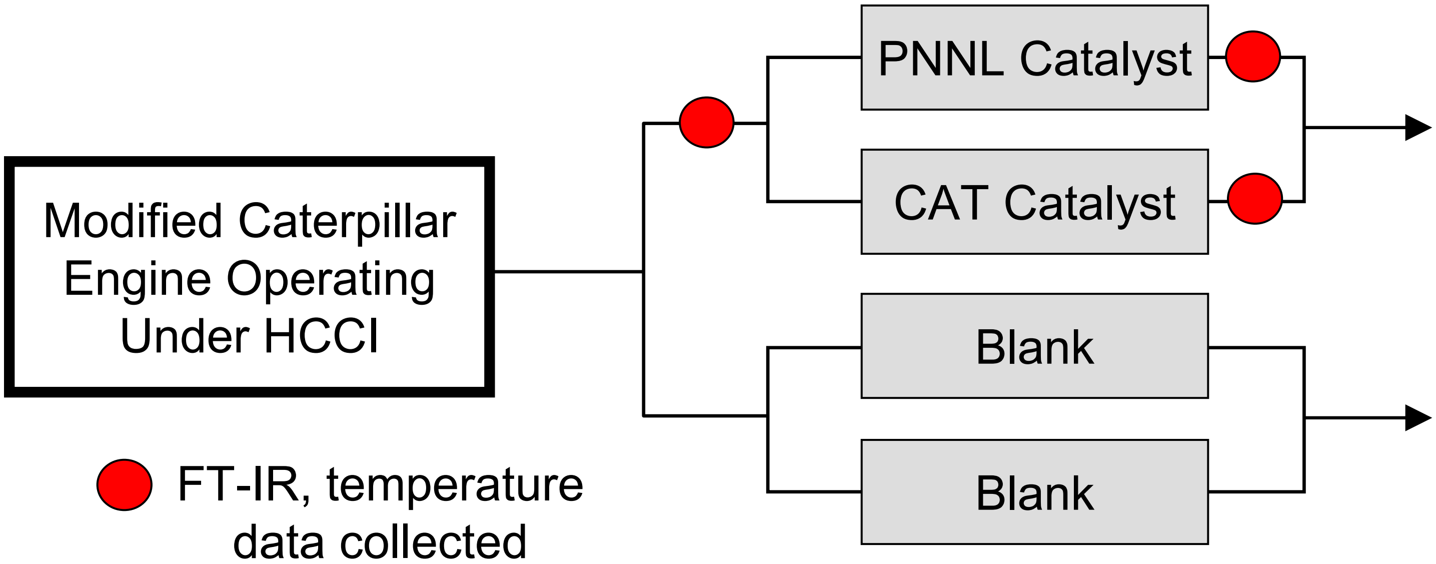
Engine Testing at Caterpillar



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.

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

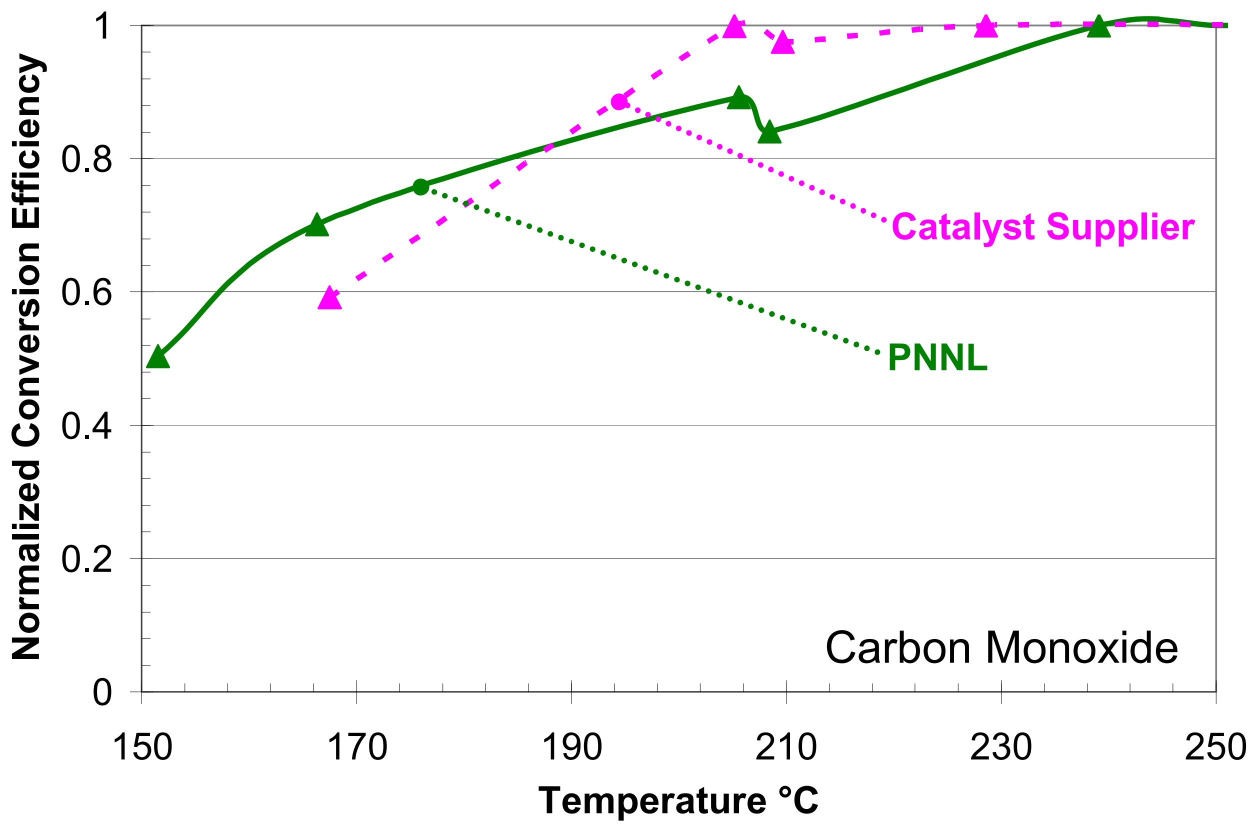
ξ_0 = reference SV at which conversion efficiency is known

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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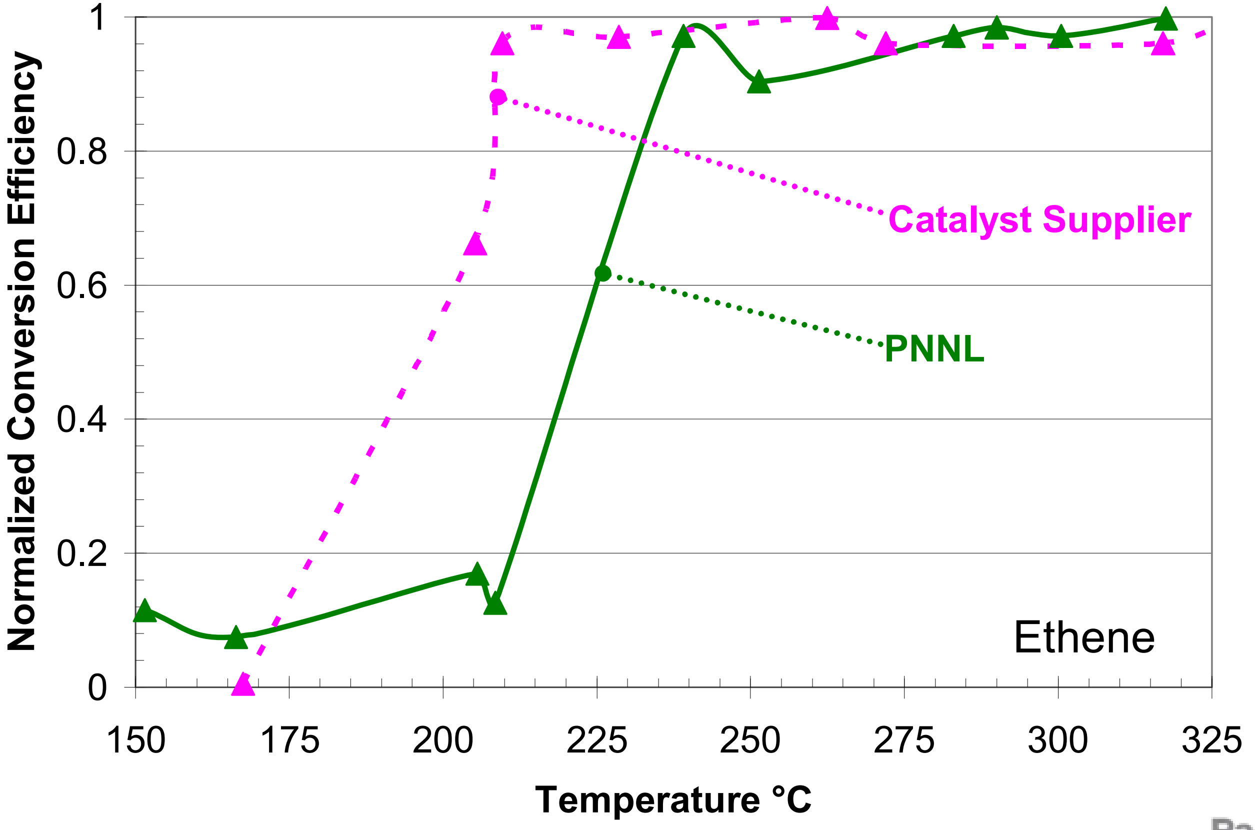
Engine Testing

Ethylene (C_2H_4) Results

Neither sample exhibited good C_2H_4 activity.



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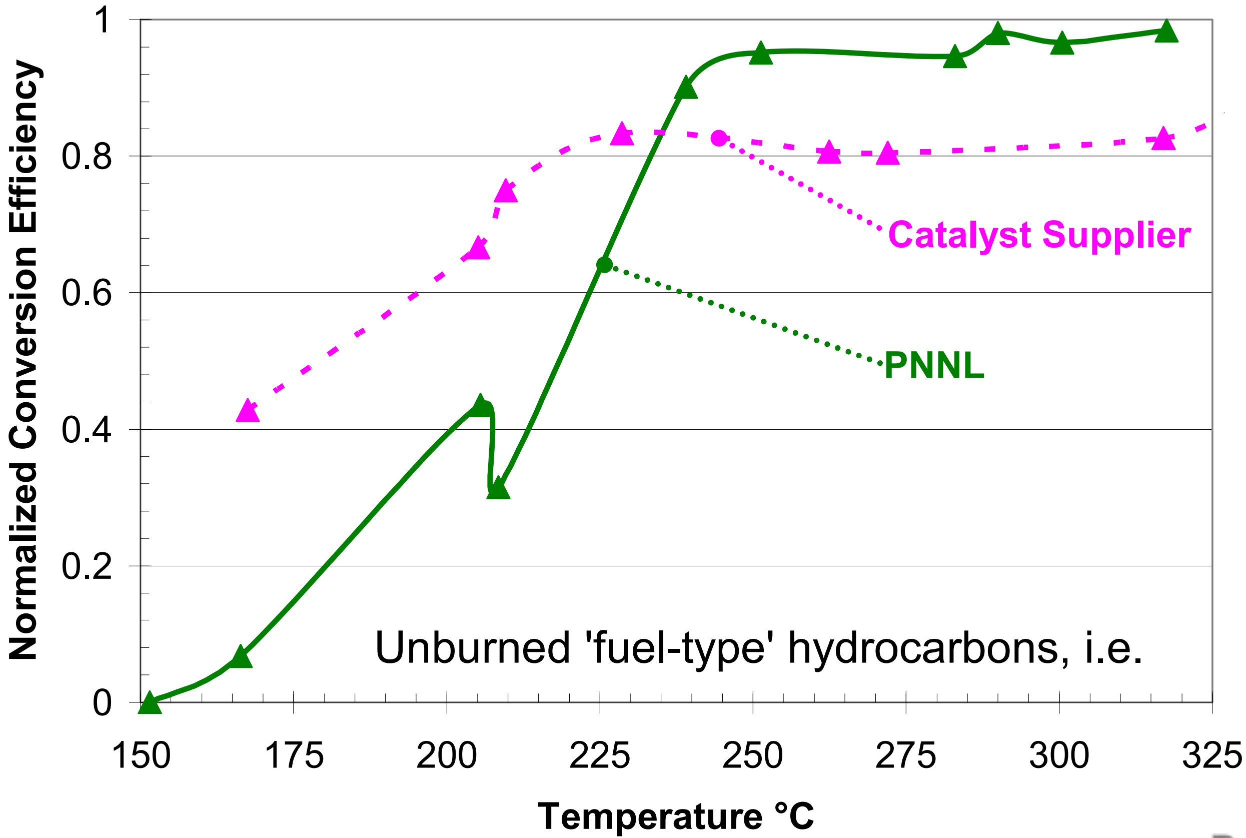
Engine Testing

Unburned Fuel (>C_5) Results

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

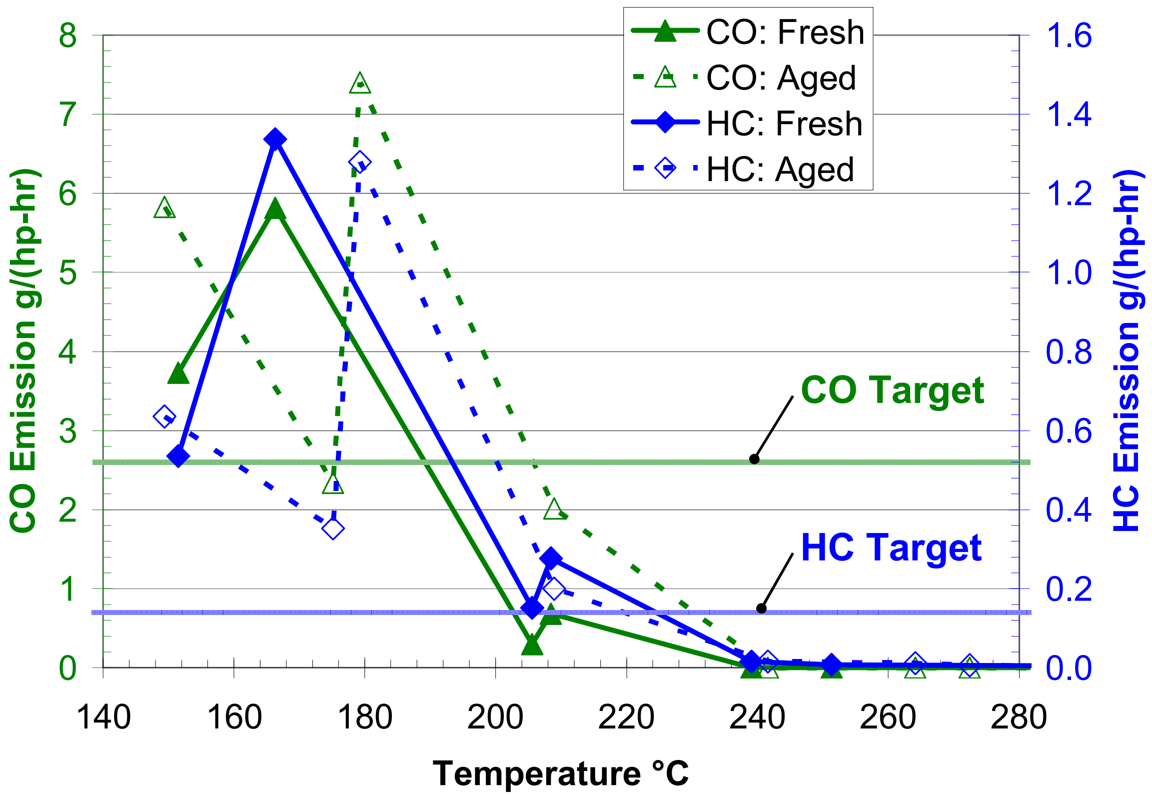
Catalyst supplier did not achieve T_{90}HC until almost 350°C!



Engine Testing

PNNL Emissions Target Analysis

Emission	Target Level g/(hp-hr)
HC	0.14
CO	2.6



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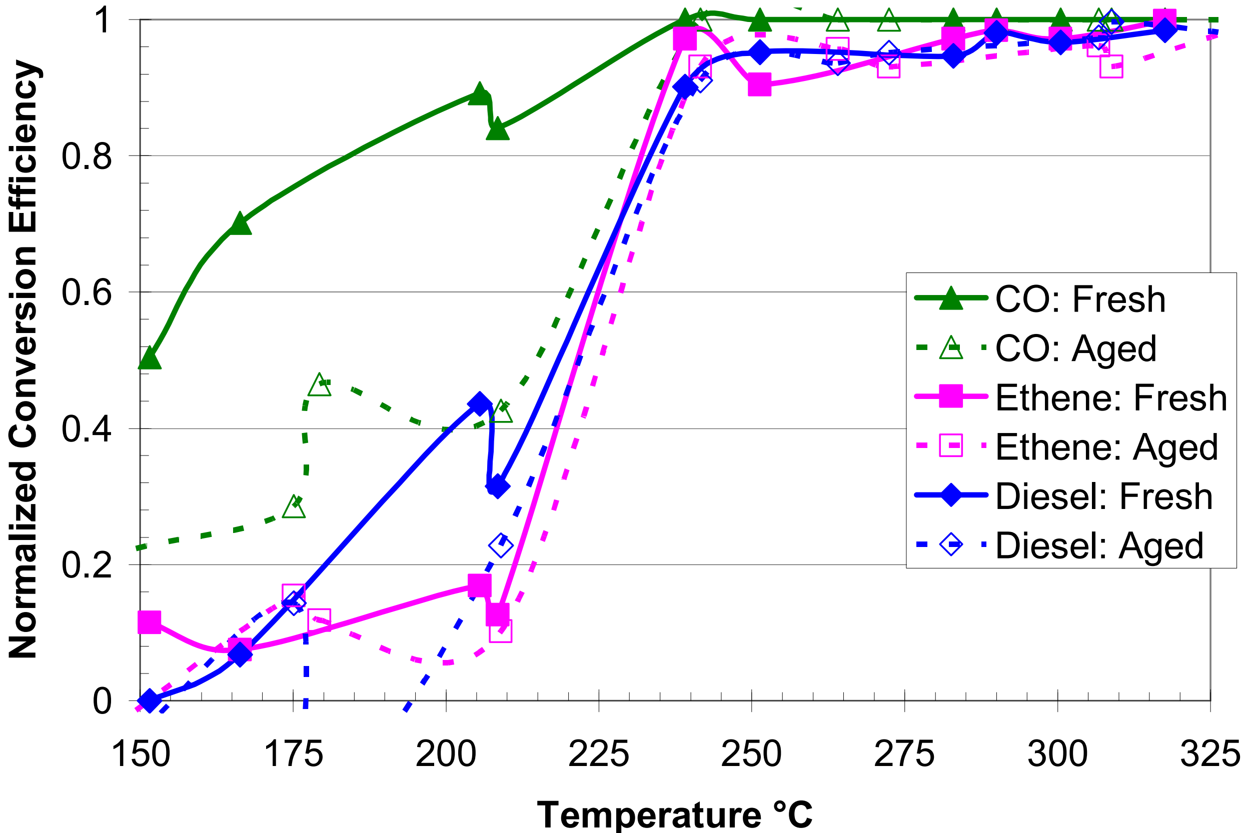
Engine Testing

PNNL Fresh vs. Aged Results

Following fresh catalyst testing (11 point test array, repeated 3 times), catalyst aged on engine by exposing to 450°C/4 hours.



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Summary

- Engine test conducted at Caterpillar on HCCI configured engine.
- Testing allowed comparison of vendor-supplied catalyst to PNNL-formulated catalyst.
- Vendor supplied catalyst contained 2.4 times the metal loading density versus PNNL catalyst.
- PNNL catalyst nearly achieved T_{50}(CO) target.
- PNNL catalyst achieved T_{90}(HC) target at <240°C. Supplier catalyst required almost 350°C.
- Good aging results on engine.

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Acknowledgments

Tom Paulson, Dennis Endicott, Christie Ragle
– Caterpillar, Inc.

Ken Howden
– DOE OFCVT

U.S. Department of Energy
Energy Efficiency and Renewable Energy
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