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

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CRADA: PNNL – Caterpillar
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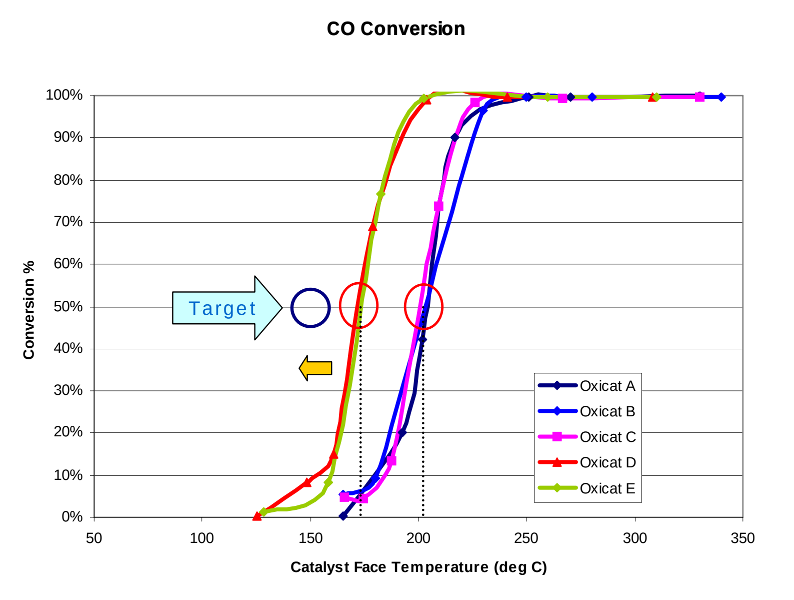
Purpose of Work/Barriers

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

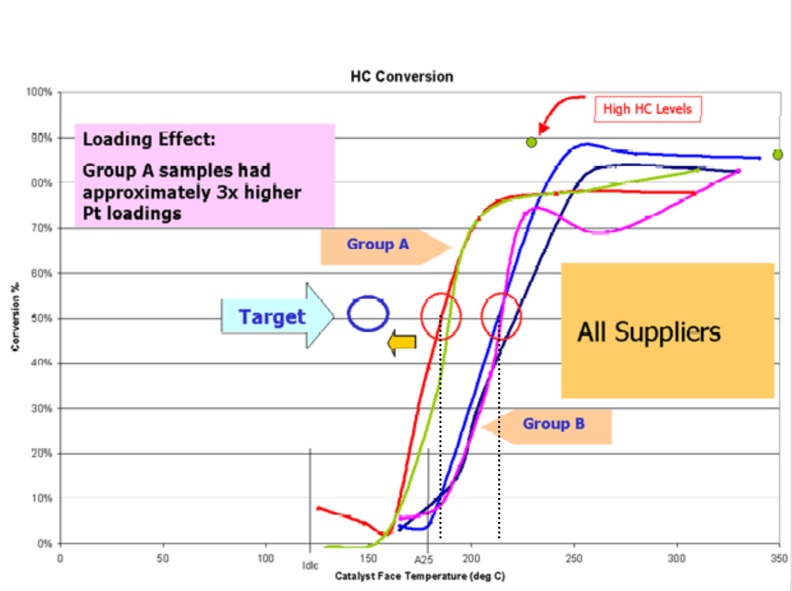
- HCCI shows promise for achieving increased fuel efficiency and meeting future HD NO_x limits. Barriers include:
  - High hydrocarbon (up to 2000 ppm C_1) and CO emissions (0.1-0.4%).
  - Low exhaust temperatures are below typical light-off for standard oxy-cats.



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

Specifications (CAT to vendors):

HC light-off: 50% at < 150°C
CO light-off: 50% at < 150°C



FY07 Merit Reviewer Comments

Comment 1: Hard to compete with Suppliers wrt formulations.

To date, suppliers response has been to increase metal loading. This is the battle: metal loading versus novel formulation.

Comment 2: Higher aging temperatures needed.

Extended aging at 450°C; examining failure modes up to 650°C

Comment 3: Limited tech transfer & collaboration with Suppliers.

Caterpillar is intimately involved with Suppliers on their side of the CRADA. They have run numerous engine tests with Supplier catalysts.

Comment 4: Need more justification for selection of metals.

Previous reviews have demonstrated the screening of numerous blended systems incorporating γ-Al_2O_3, CeO_2, SnO_2, PrO_2, & TbO_2.

Teaming Strategy – Industry Collaboration

Work Scope:

- **PNNL**: Catalyst development & characterization, flow bench studies
- **Caterpillar**: Exhaust characterization, engine testing, catalyst formulation, catalyst aging studies

PNNL team working very closely with Caterpillar team

- Technical exchange meetings: WebEx
- Ron Silver, Svetlana Zemskova (Caterpillar, Advanced Materials Technology)

Caterpillar engine characterization efforts: vendor-supplied catalysts

Re-formulated HCCI HC/CO vendor-supplied catalysts

Approach

- ✓ **Completed effort**
- ➢ **Current effort**
- ⮙ **Future effort**

FY07 Project Tasks

	Task	
✓	Literature mining to identify potential targets	PNNL
✓	Catalyst formulation, characterization, screening	PNNL/CAT
➢	Assess monolith-supported catalysts	PNNL/CAT
➢	Catalyst scaling for engine testing	PNNL/CAT
➢	Engine testing [SS & transient]	CAT
⮙	Correlation between bench & engine scale	PNNL/CAT

Milestones

- Complete bench-scale assessment of catalyst systems
- Complete optimization of monolithic formulations
- Complete steady-state & transient engine testing

Approach to Low-Temperature Materials Investigations

1 In-depth data mining efforts identified numerous materials warranting screening

→

2 Materials screening efforts identified candidates warranting further investigation: ***CeO_2 & multi-component CeO_2 systems***

3 Detailed system interrogation identified optimum CeO_2 form & CeO_2/metal sources

→

4 Insertion of transition metal into CeO_2-matrix examined to enhance low-T REDOX capacity: ***Pr identified***

5 In-depth physical characterization of $Ce_xPr_{1-x}O_2$-system catalysts to develop structure-activity relationships

→

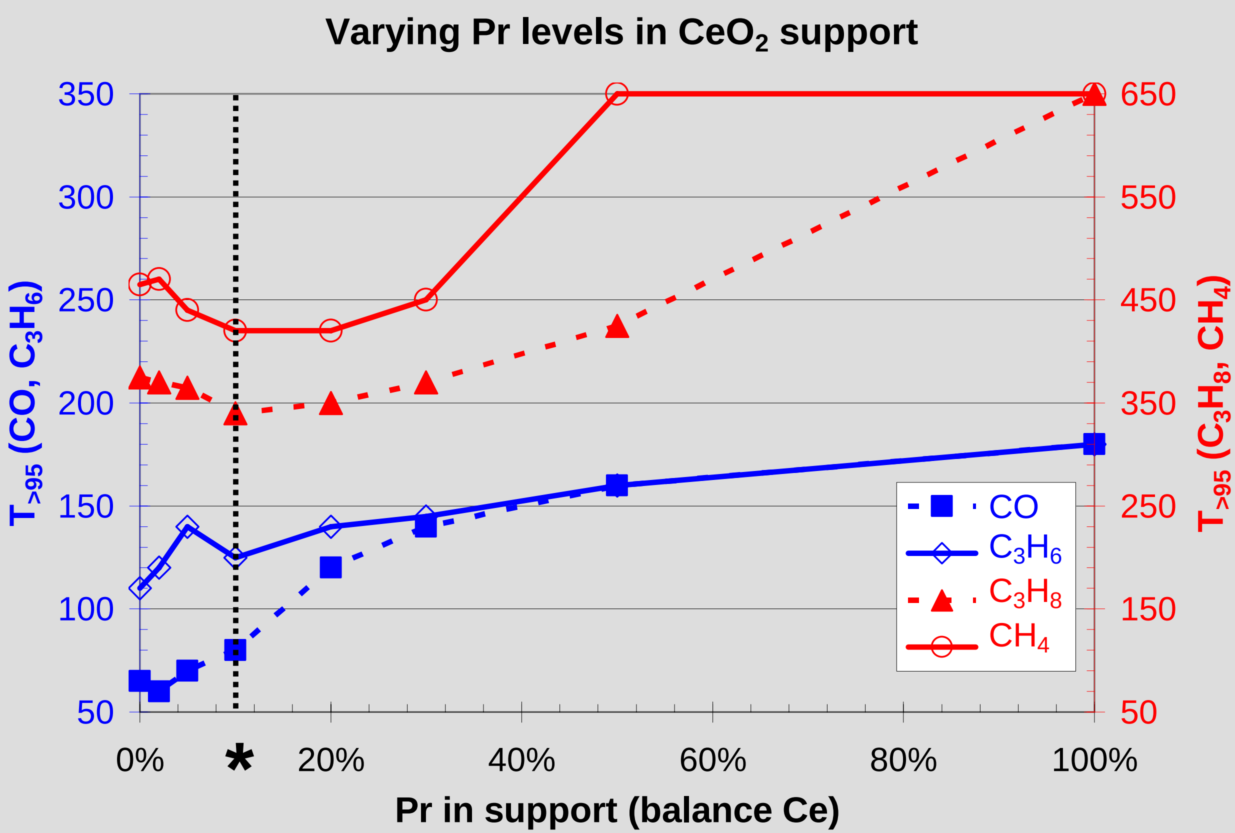
6 $Ce_xPr_{1-x}O_2$-system catalysts examined in core configuration and hydrothermal aging effects

7 Investigation of metal combinations with $Ce_xPr_{1-x}O_2$-system to improve hydrocarbon activity of the catalyst system, including blending of Ag, Mo, Va, Ga, In with Pt & Pd

Technical Accomplishment Summary

2%Pd/$Ce_xPr_{1-x}O_2$ 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

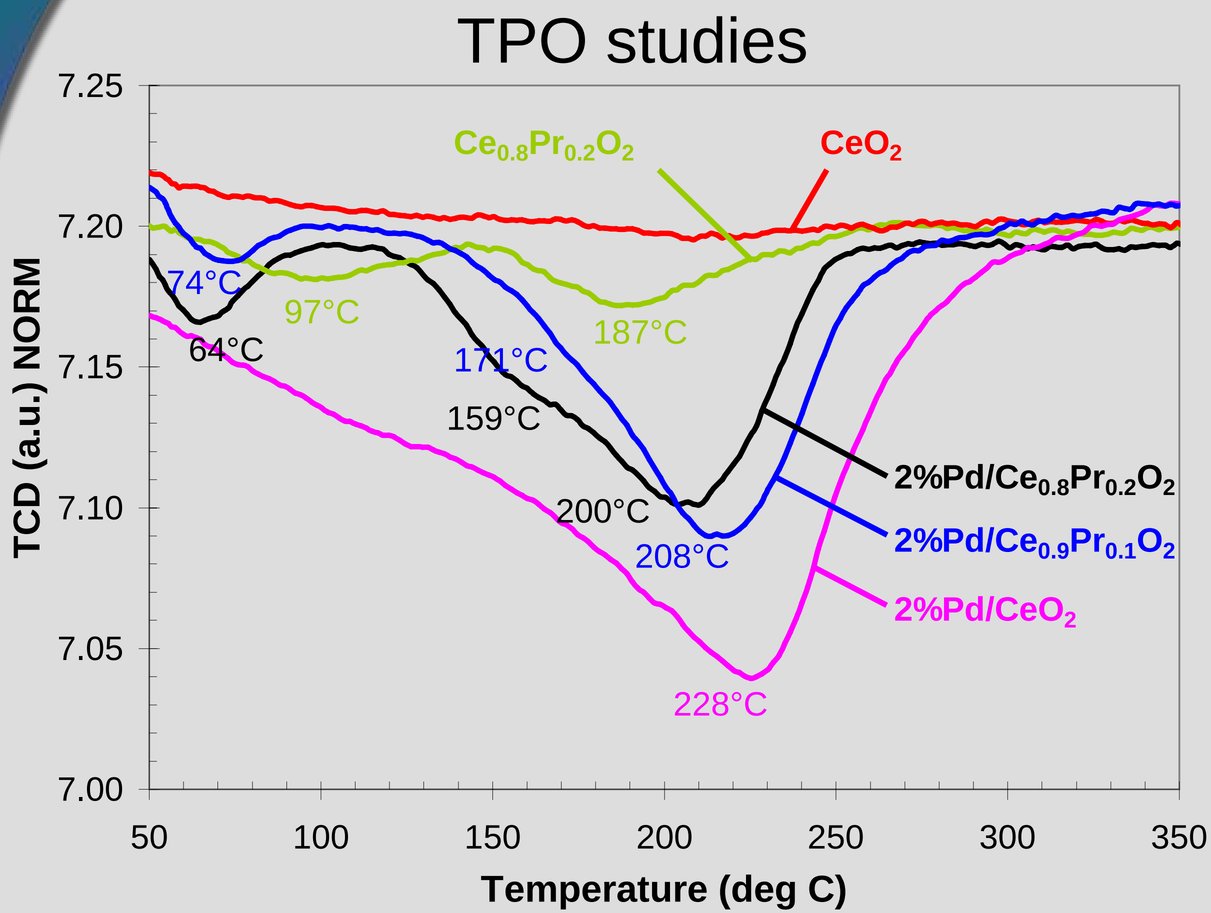
X = 1 [CeO_2], 0.98, 0.95, 0.9, 0.8, 0.7, 0.5, 0 [PrO_2]

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

Ce/PrO_2 source: decomposition of Ce & $Pr(NO_3)_3 \bullet 6H_2O$ solutions

Technical Accomplishment Summary

2%Pd/$Ce_xPr_{1-x}O_2$ System Investigations



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

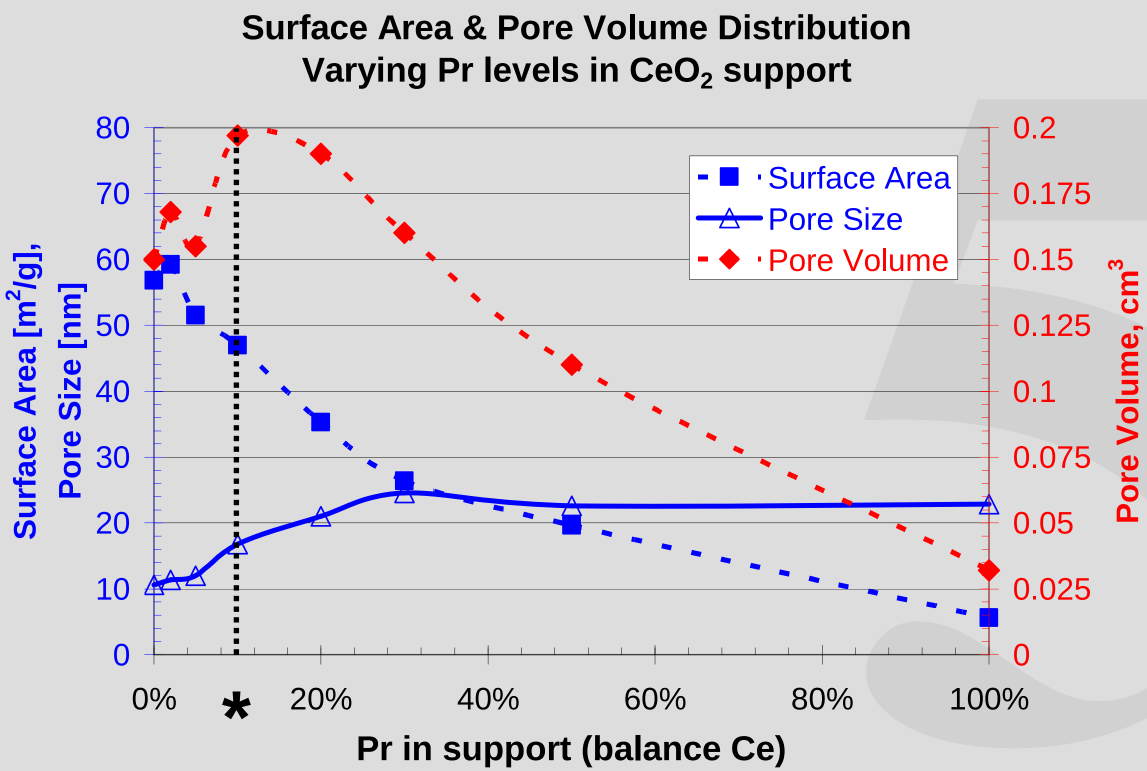
This is seen again by Pd oxidation at 64-74°C.

200-228°C is Pd oxidation and more readily oxidized as Pr ↑ (i.e. ↑ Pr increased interaction of Pd with CeO_2 support).

Technical Accomplishment Summary

$2\%Pd/Ce_xPr_{1-x}O_2$ System: BET Results

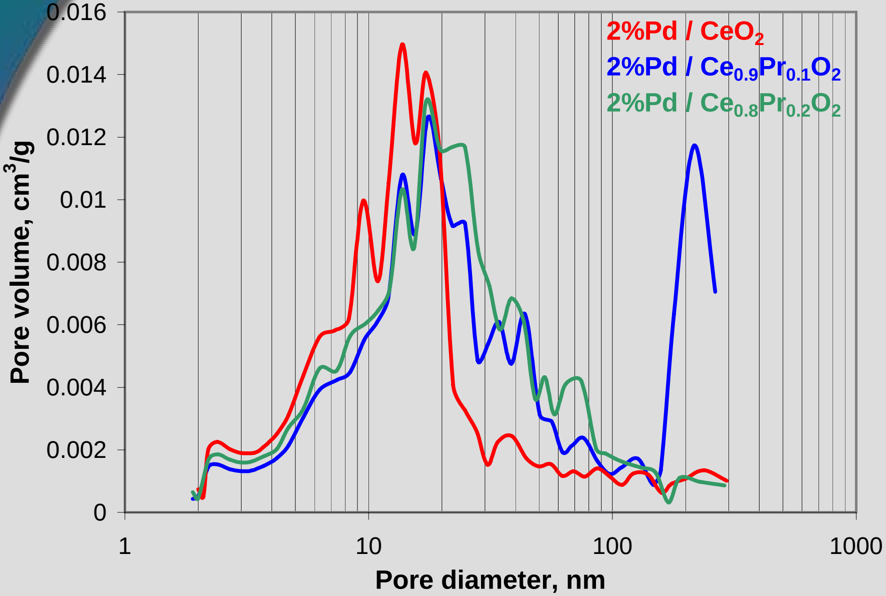
Total pore volume reaches maximum (*) at 10% Pr.

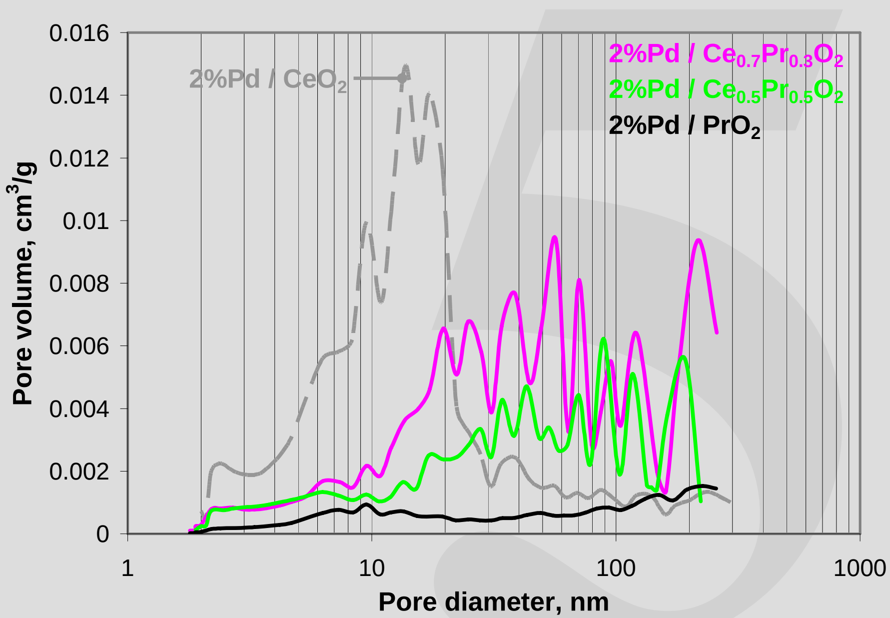


- Small amounts of Pr (0-20%) believed to not reduce surface area of CeO_2, larger amounts (>20%) impact the surface up to 100% PrO_2 with surface area <10 m^2/g.

Technical Accomplishment Summary

2%Pd/$Ce_xPr_{1-x}O_2$ System: Pore Distribution





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

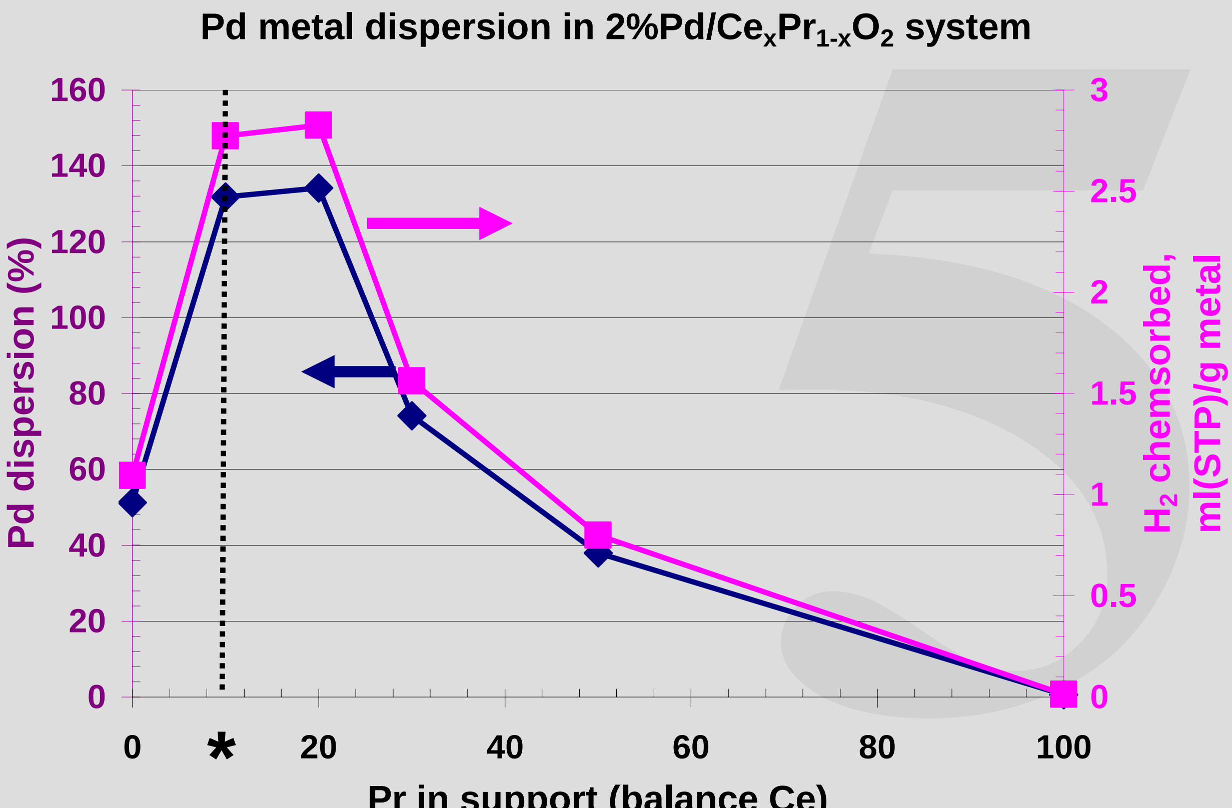
Technical Accomplishment Summary

2%Pd/$Ce_xPr_{1-x}O_2$ System: Pd Dispersion

Effective Pd dispersion maximized at 10-20% Pr loading in $Ce_XPr_{1-X}O_2$ support.

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.

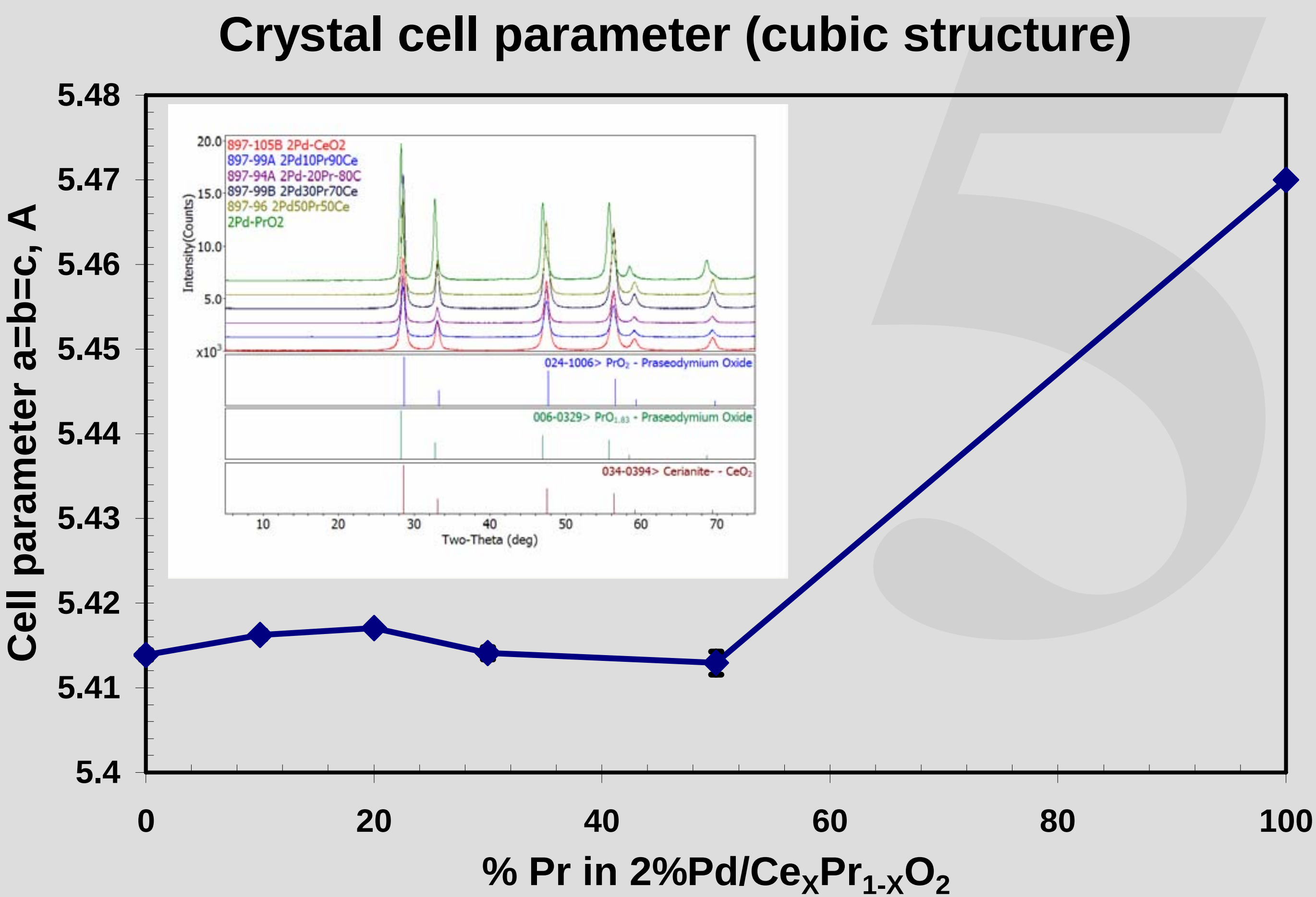
Technical Accomplishment Summary

2%Pd/$Ce_xPr_{1-x}O_2$ System: XRD Analyses

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

This is lost with >20% Pr.

Structure similar to PrO_2 would account for no XRD shift from 10-50% Pr.

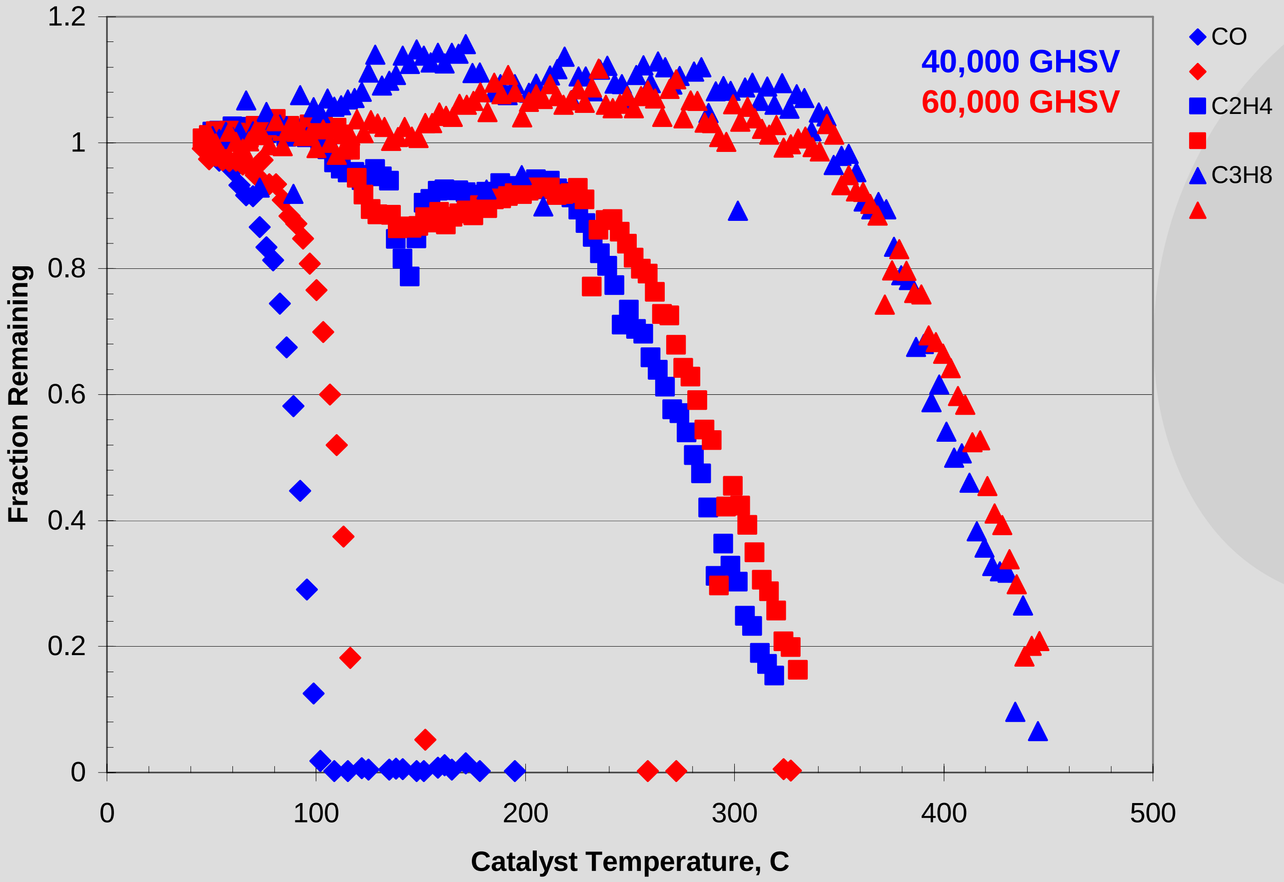


Technical Accomplishment Summary

2%Pd/$Ce_{0.9}Pr_{0.1}O_2$ – 25mm OD x 40mm L core

Metal & Ce/Pr slurry blended prior to coating core.

Results correlate well with powder test bench.

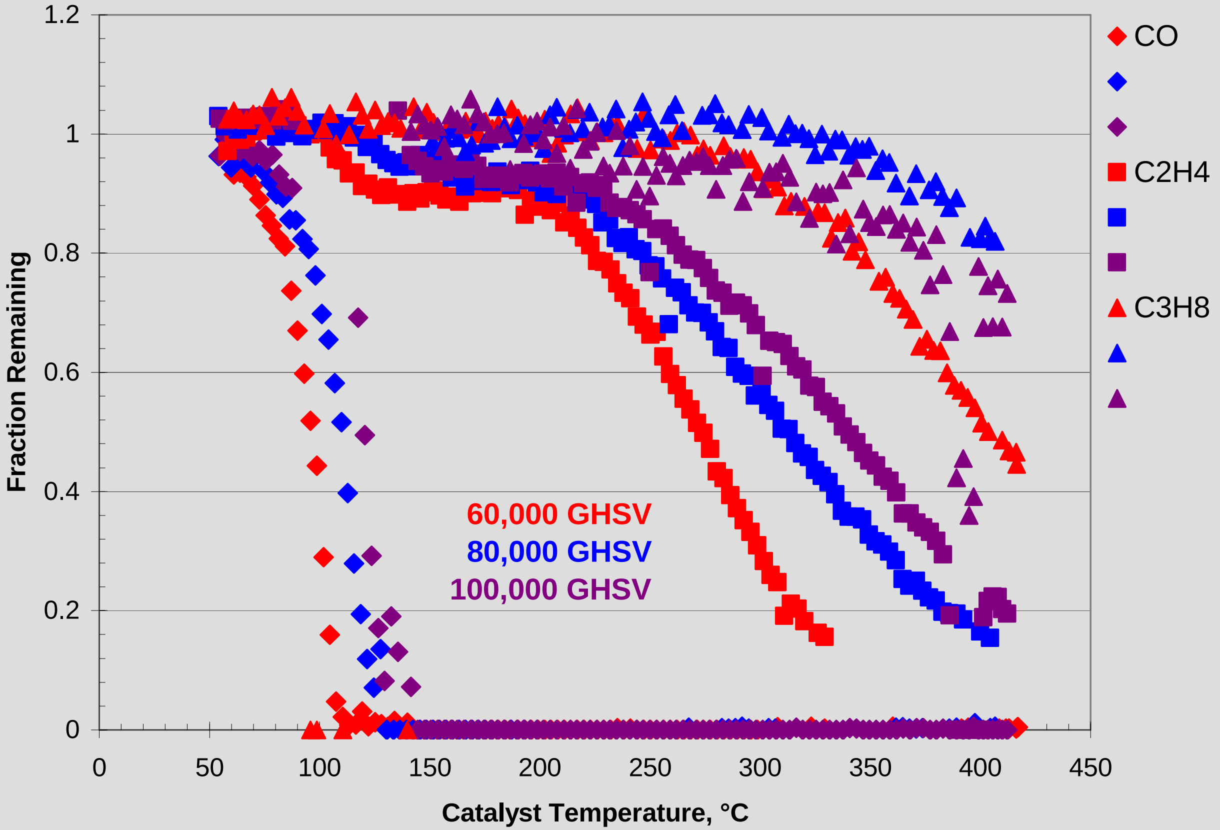


Technical Accomplishment Summary

2%$Pd/Ce_{0.9}Pr_{0.1}O_2$ – 25mm OD x 40mm L core

Metal deposited following Ce/Pr slurry core coating.

Results indicate metal should be blended into slurry prior to core coating.



Same catalyst and preparation technique as employed with catalyst brick supplied to Caterpillar for engine testing.

Technical Accomplishment Summary

2%Pd/$Ce_{0.8}Pr_{0.2}O_2$ System Investigations

- Currently executing metal investigations to improve upon hydrocarbon activity of the system.
- Studies will investigate the blending of Ag, Mo, Va, Ga, & In with Pt & Pd.

Engine Testing

- Caterpillar currently engine testing several newly reformulated vendor supplied catalysts.
- PNNL supplied catalyst brick to Caterpillar for testing in this effort. Tests are ongoing.

Future Work

Continue preparations of monolith coated catalysts, and evaluation of activity.

Evaluate metal systems to improve hydrocarbon activity of formulations.

Continue assessment of durability of monolith-supported formulations via hydrothermal aging (10%H_2O/air 450°C 100 hours).

Evaluate results of on-going engine testing, continue catalyst development for future engine testing

Summary

Identified CeO_2 system as promising area for investigation. Results of incorporating Pr into support has improved activity of catalyst formulations.

Employing characterization tools (BET, TPO/TPR, XRD etc.) for evaluation of catalyst formulations and assessment of structure-property activity relationships.

Currently testing of core-configured catalysts. Caterpillar to provide comparison to vendor supplied formulations.

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

21ST CENTURY TRUCK PARTNERSHIP

21CTP Technical Goal: Demonstrate low-temperature CO/HC oxidation to enable HCCI application

Project Objectives

Develop novel catalyst formulations to achieve low temperature CO and hydrocarbon oxidation in HCCI engine emissions, providing a key enabling technology for HCCI applications.

FY 2007 Focus

- Complete screening activities; continue catalyst characterizations
- Down select formulations to 2-3 targets
- Begin catalyst monolith assessments; prepare for engine test

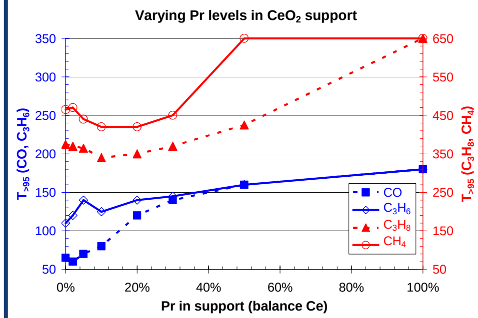
Planned Duration

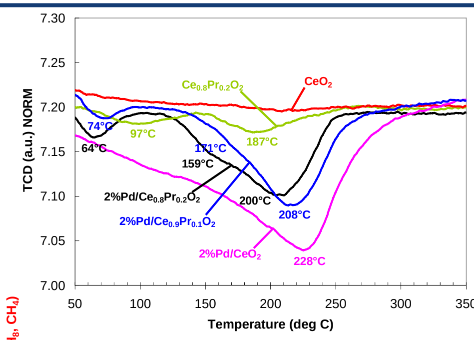
February 2005 to February 2008

DOE Funding/Industry Cost Share (50%)

FY05:\$400K FY06: \$350K FY07: \$350K

Catalyst test results investigating the addition of Pr to the Pd/CeO_2 system; indicating improvement in paraffin activity





TPO investigations showing Pd more readily oxidized with increased Pr loading (increased interaction with CeO_2 support).

Principal Investigators

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Accomplishments (all FY06 milestones achieved)

- *Caterpillar completed current HCCI exhaust hydrocarbon speciation. Bench scale hydrocarbon surrogates adjusted based upon analysis of results. – Dec 2006*
- *Procedure developed for monolith catalyst coating; currently testing initial cores for verification – May 2007*
- *Catalyst screening narrowed to ~2 primary targets (Pt, Pd/CeO_2); pursuing promising formulations – Nov 2006*

Significant Future Milestones

- *Complete optimization of monolithic formulations – Aug 2007*
- *Steady-state and transient engine testing – 2008*

Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
WR #####/#####	Advanced Combustion	Emission Control	Applied Research	06-18