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

CRADA: PNNL – Caterpillar

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Institute for Interfacial Catalysis
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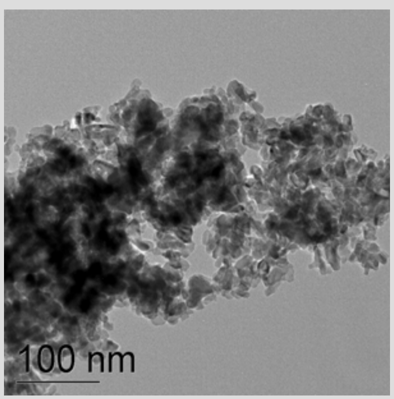
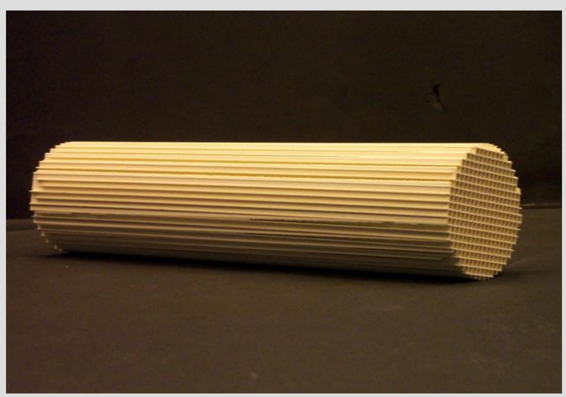
Overview

Low-Temperature Oxidation Catalysts for HCCI Emissions Control

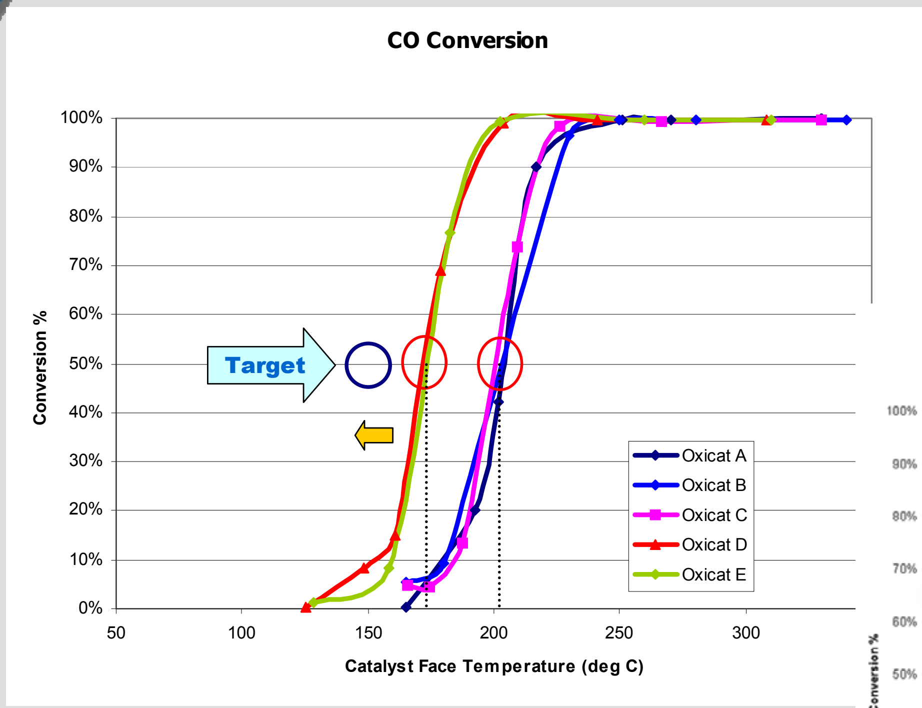
- HCCI shows promise for meeting 2010 HD NO_x limits (Duffy *et al*., DEER 2004)
  - One of the major hurdles with implementation is high hydrocarbon (up to 2000 ppm C_1) and CO emissions (0.1-0.4%)
  - Low exhaust temperatures are below typical light-off for standard oxidation catalysts
- Program initiated Summer 2004 (at PNNL) to survey work in low temperature oxidation (CO) and propose roadmap





Objectives

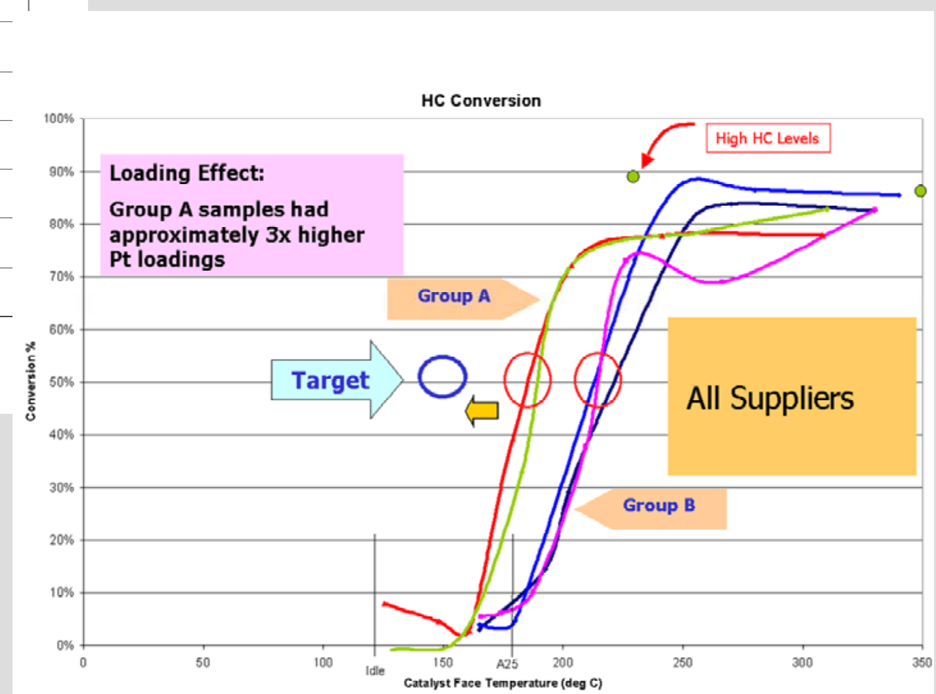
Develop low-temperature HC & CO oxidation catalysts to enable HCCI application



Specifications to vendors:

HC oxidation: 90% at 175^{o}C and higher
HC light-off: 50% at < 150^{o}C

CO oxidation: 99% at higher temperatures
CO light-off: 50% at < 150^{o}C



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

Technical Summary

Low Temperature CO/HC Oxidation Catalyst Literature Survey

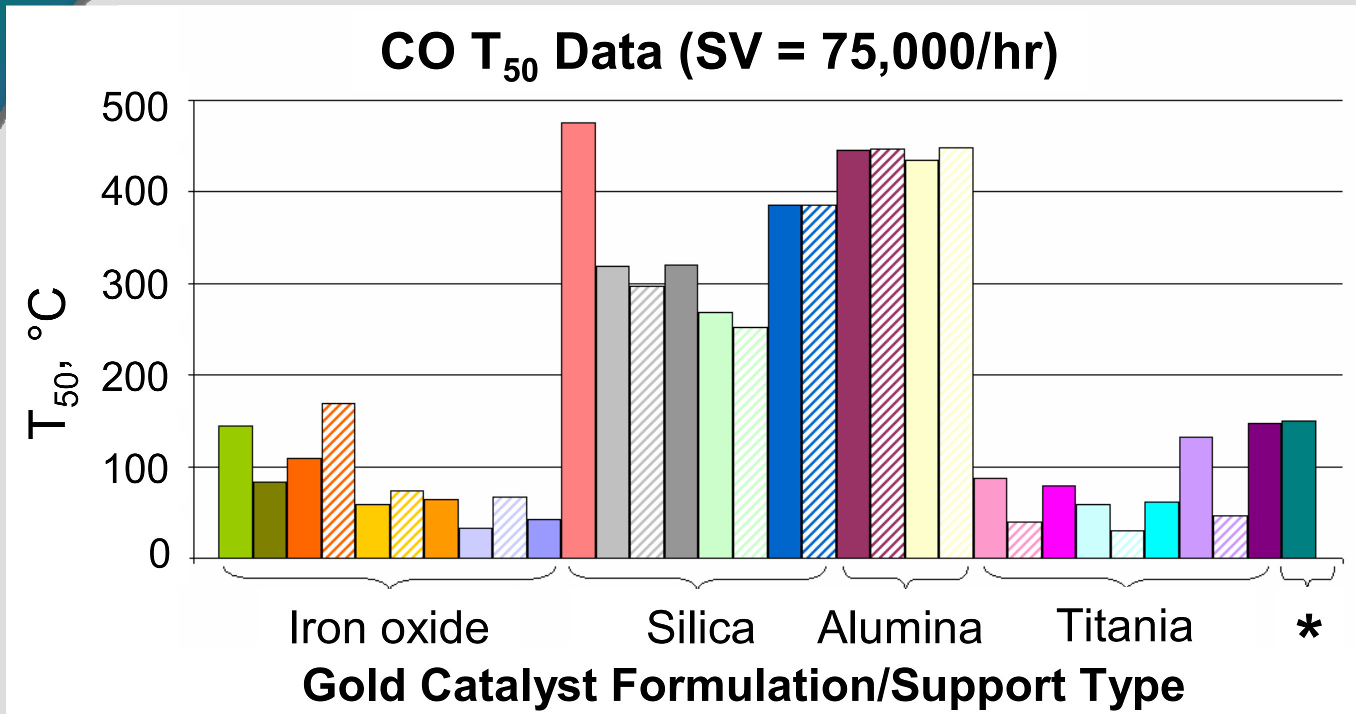
- Multi-component Pt systems
- Nano-phase Au systems
- Other PGM (e.g. Pd, Ru)
- Non PGM (e.g. Co, Cu, Ag, Sn)

Extensive catalyst synthesis & screening efforts (>75 formulations to date):

- **Supports**
  - Engelhard γ-Al_2O_3, Aldrich SnO_2, Davison SiO_2
  - Multiple CeO_2 formulations
  - Multiple $Ce_XSn_YO_2$, $Ce_XPr_YO_2$, $Ce_XTb_YO_2$ blends
  - CeO_2/γ-Al_2O_3 sequential formulations
  - Other supports employed: ZnO_2, ZrO_2, Ce-Y zeolite, ZSM-5
- **Metals**
  - Predominantly Pt- & Pd-based; multiple Rh & Ru formulations also interrogated
  - Multi-component formulations combining PGMs Pd, Pt, Rh, Ru, & non-PGMs Mn, Co, Ni
  - Multi-component Pt/Sn, Pt/Ce, & Pd/Ce on γ-Al_2O_3 and CeO_2

Technical Summary

Nano-Phase Gold (Au) Catalyst Investigations

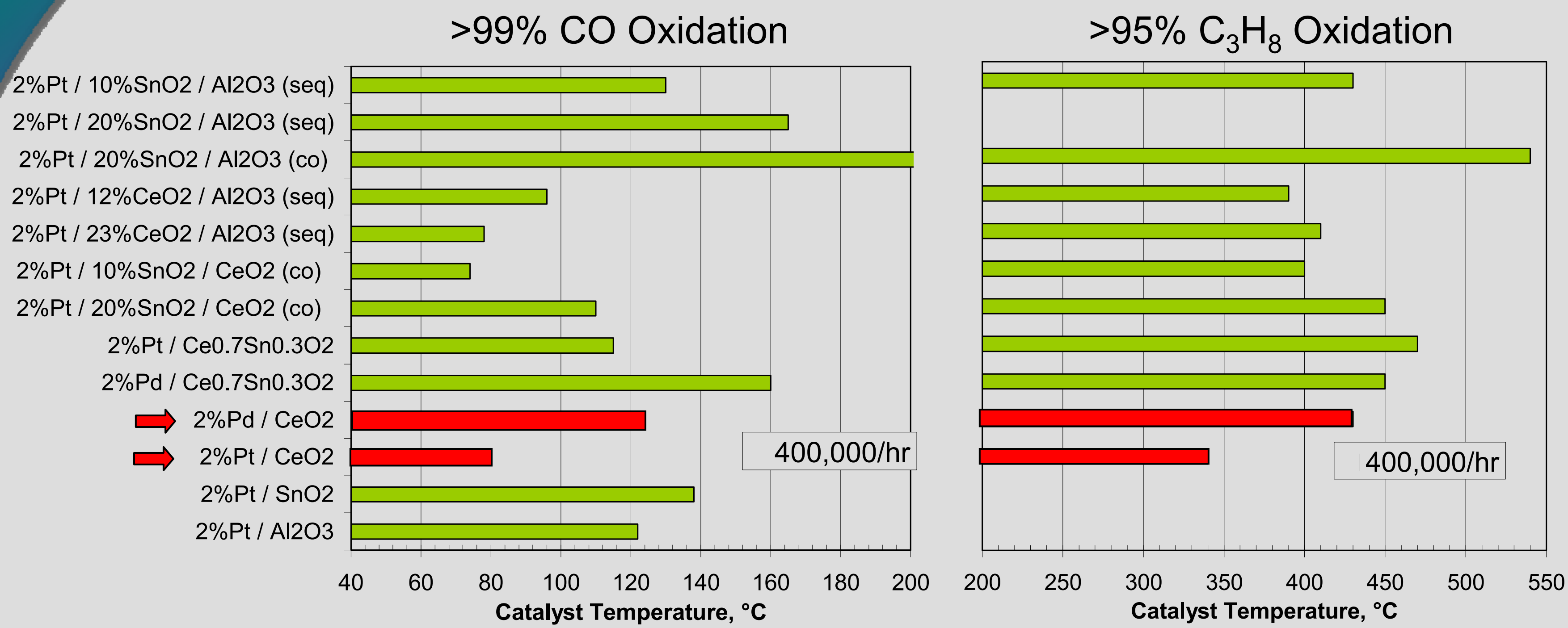


Testing currently in progress to evaluate durability and suitability for monolith coating.

- Extensive literature search assisted in narrowing selection for study.
- Four (4) 1-5% Au catalyst supports interrogated; *2%Pt/γ-Al_2O_3 tested & shown for comparison.
- Various formulations include variables such as precursor materials, preparation/drying conditions and calcination temperature.

Technical Summary

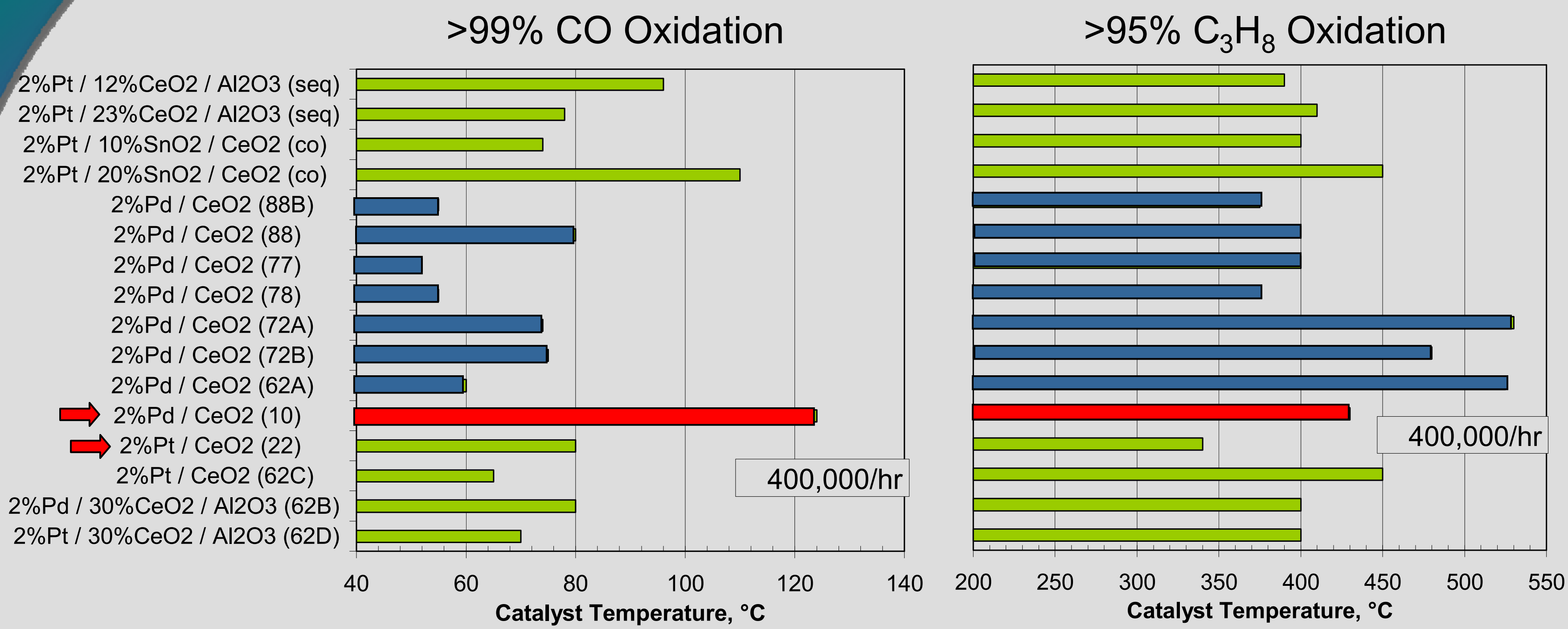
Initial Screening Efforts – CO, C_3H_6, C_3H_8 & CH_4 investigated



- Completed screening activities on initial catalyst formulations.
- GHSV 400K shown; 200K & 800K GHSV also characterized.
- Targeted activity achieved for CO.
  - 50% oxidation at < 150°C; 99% oxidation at higher temperatures
- **Pt/CeO_2 & Pd/CeO_2** systems show promise, warrant further investigation

Technical Accomplishment Summary – PNNL

Target system: Pd/CeO_2 – CO & C_3H_8 activity shown



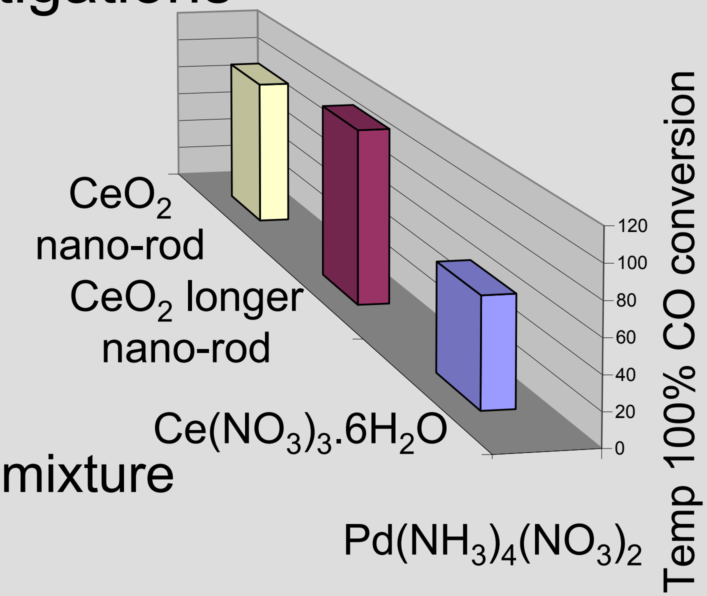
- GHSV 400K hr^{-1} shown; 200K & 800K hr^{-1} also characterized
- Screening efforts include additional **10+ Pd/Pt CeO_2**–based formulations
- Excellent low-temperature activity achieved with re-formulated **Pd/CeO_2** system; showing improvement with C_3H_8 activity

Technical Accomplishment Summary

2%Pd/CeO_2 System

Summary of Pd- and Ce-source investigations

- Pd-source:
  - ✓ $Pd(NO_3)_2$
  - ✓ $Pd(NH_3)_4(NO_3)_2$
  - Pd-acetyl acetonate (PdACAC)



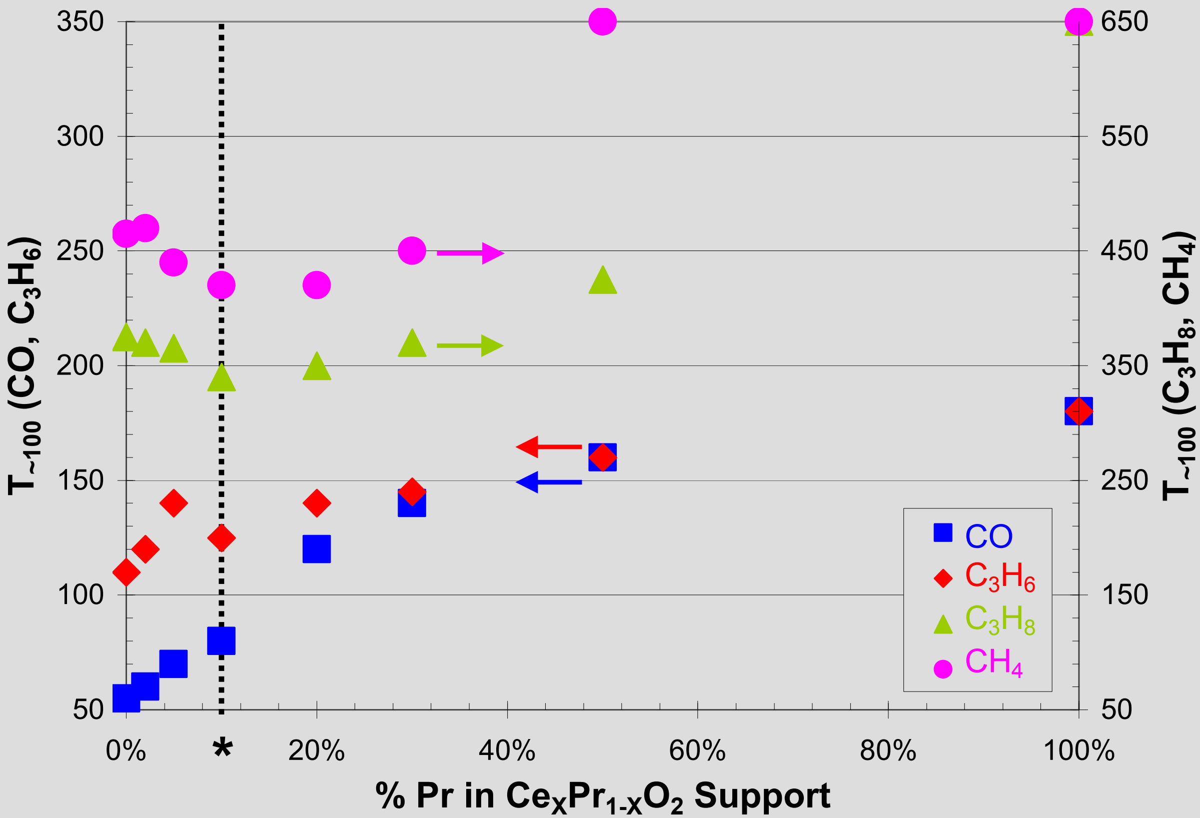
- Ce-source:
  - Calcination of CeO_2 sol and surfactant mixture
  - ✓ Decomposition of $Ce(NO_3)_3•6H_2O$
  - Calcination of CeO_2 nano-rod solution
  - Calcination of CeO_2 *longer* nano-rod solution

- Significant improvements made in low temperature activity [T_{99}(CO)~60°C]; need to improve higher temperature HC activity (e.g. C_3H_8).

Technical 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

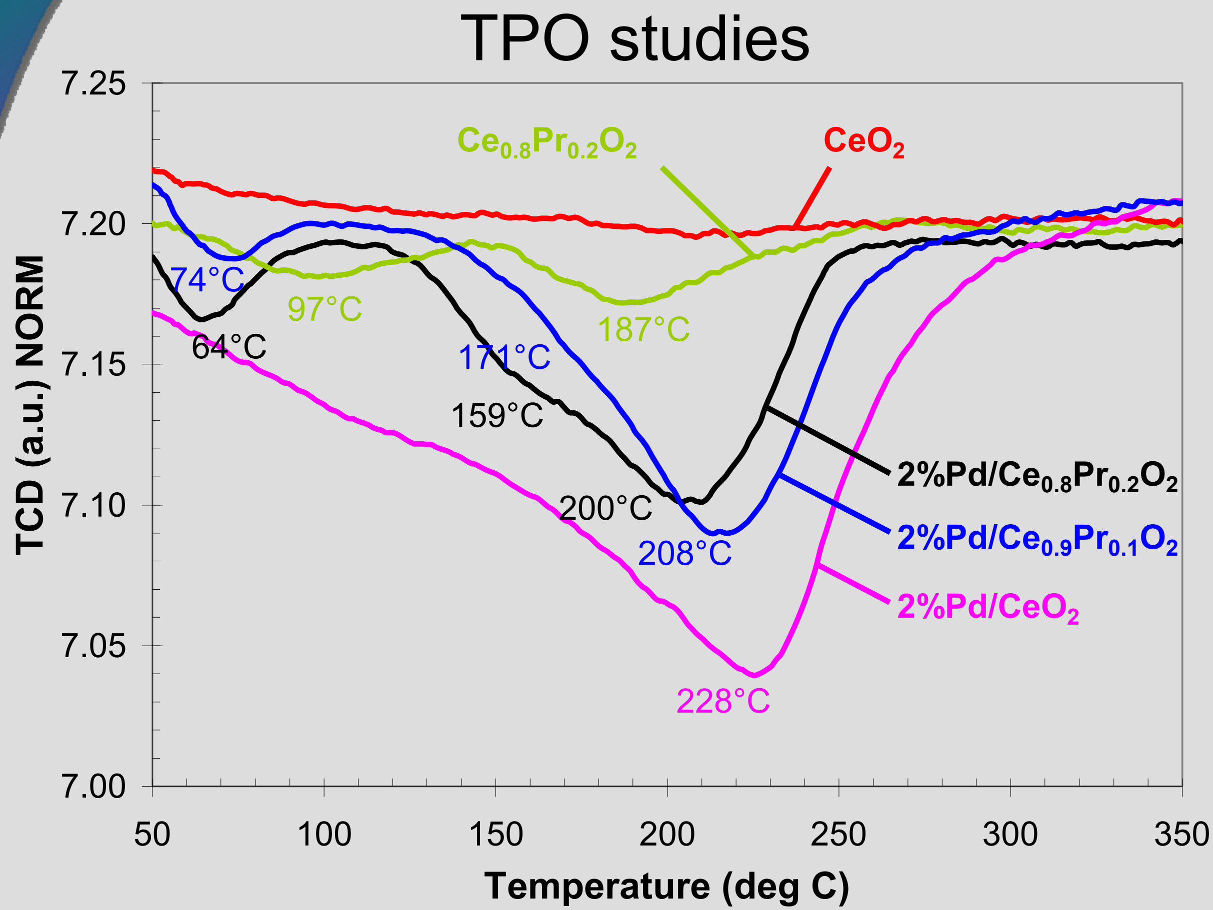
X = 1 [CeO_2], 0.98, 0.95, 0.9, 0.8, 0.7, 0.5, 0 [PrO_2]

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

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

Technical 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.

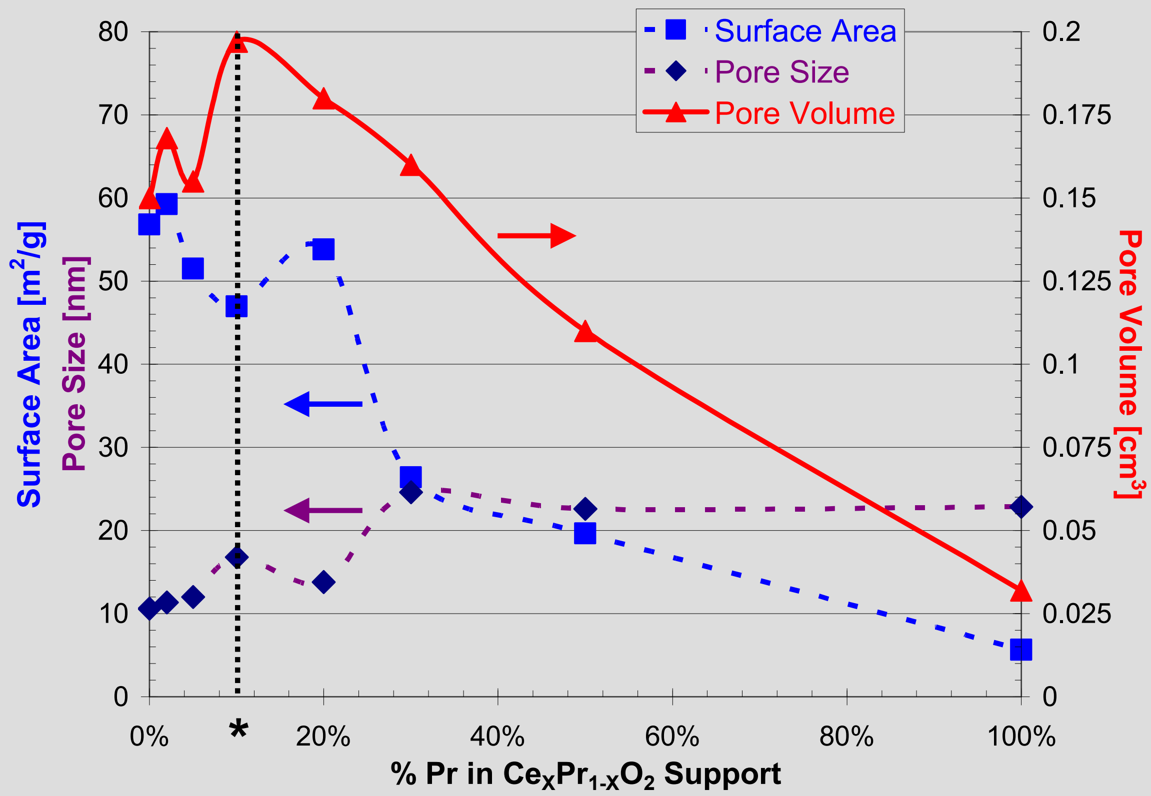
This is seen again by Pd oxidation at 64-74°C.

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

Technical Summary

2%Pd/$Ce_XPr_{1-X}O_2$ System: BET Results

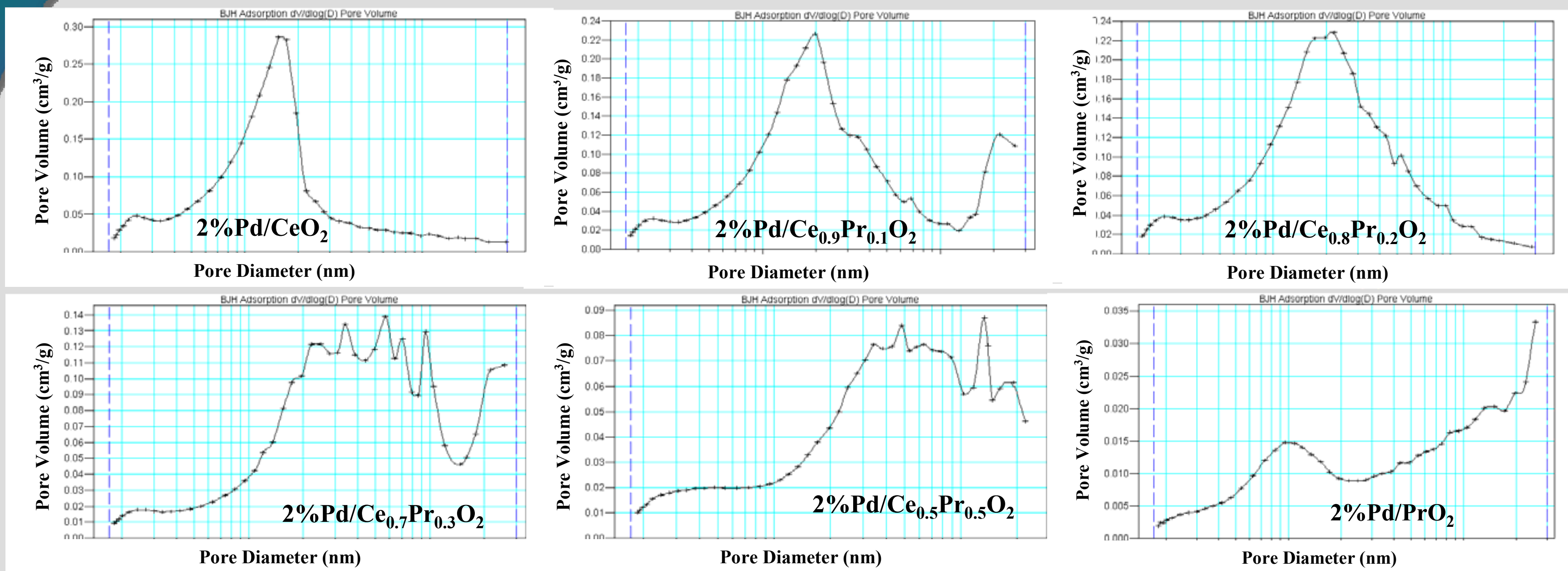
Total pore volume reaches maximum (*) at 10% Pr.



- 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 Summary

2%Pd/$Ce_XPr_{1-X}O_2$ System: Pore Distribution



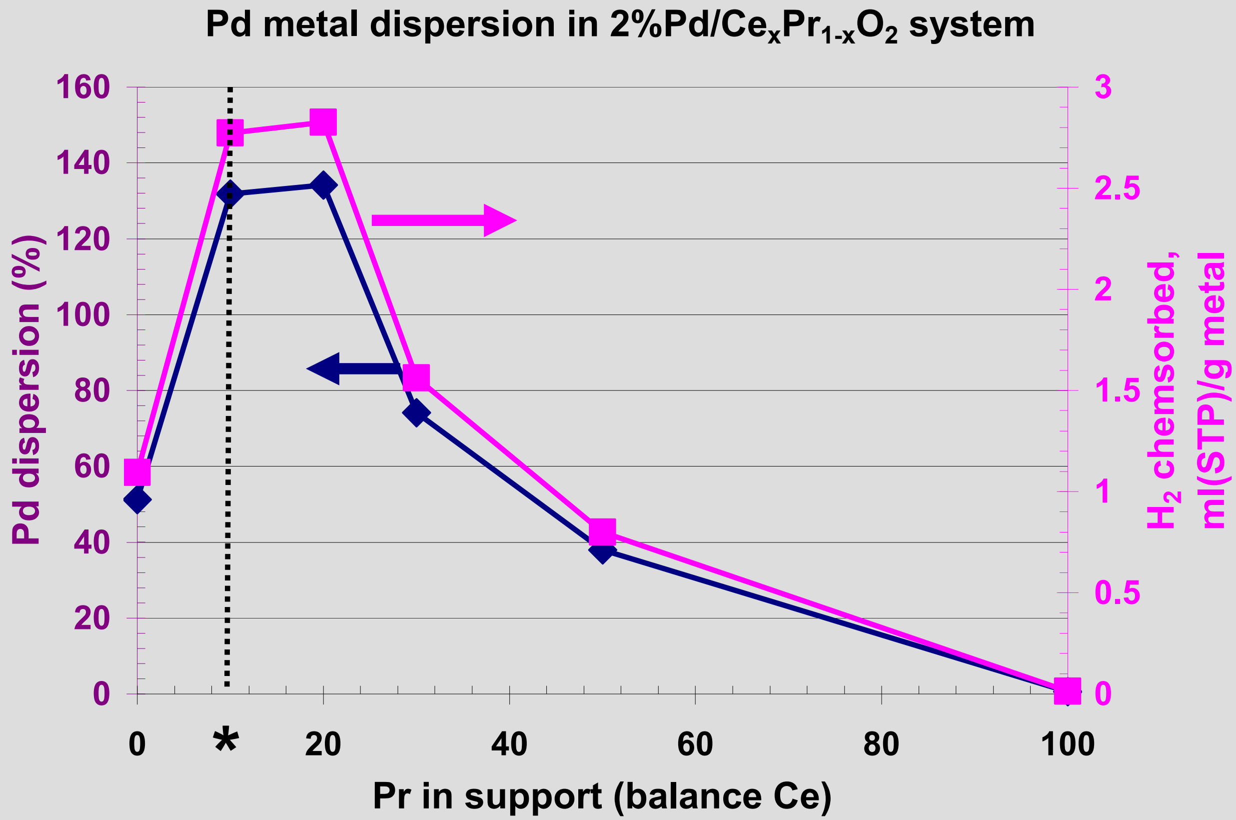
- 10%-20% Pr brings in larger (≥ 20nm) pores, shifts the maxima slightly to larger pores asymmetrically.
- >20% significantly decreases the maxima with drastic broadening of the peak towards the larger pore sizes asymmetrically.

Technical 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

De Leitenburg, C. et al *J. Cat.* **1997,** *166*, 98-107

Eriksson, S. et al *Appl. Cat. A: Gen.* **2007,** *326,* 8-16

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

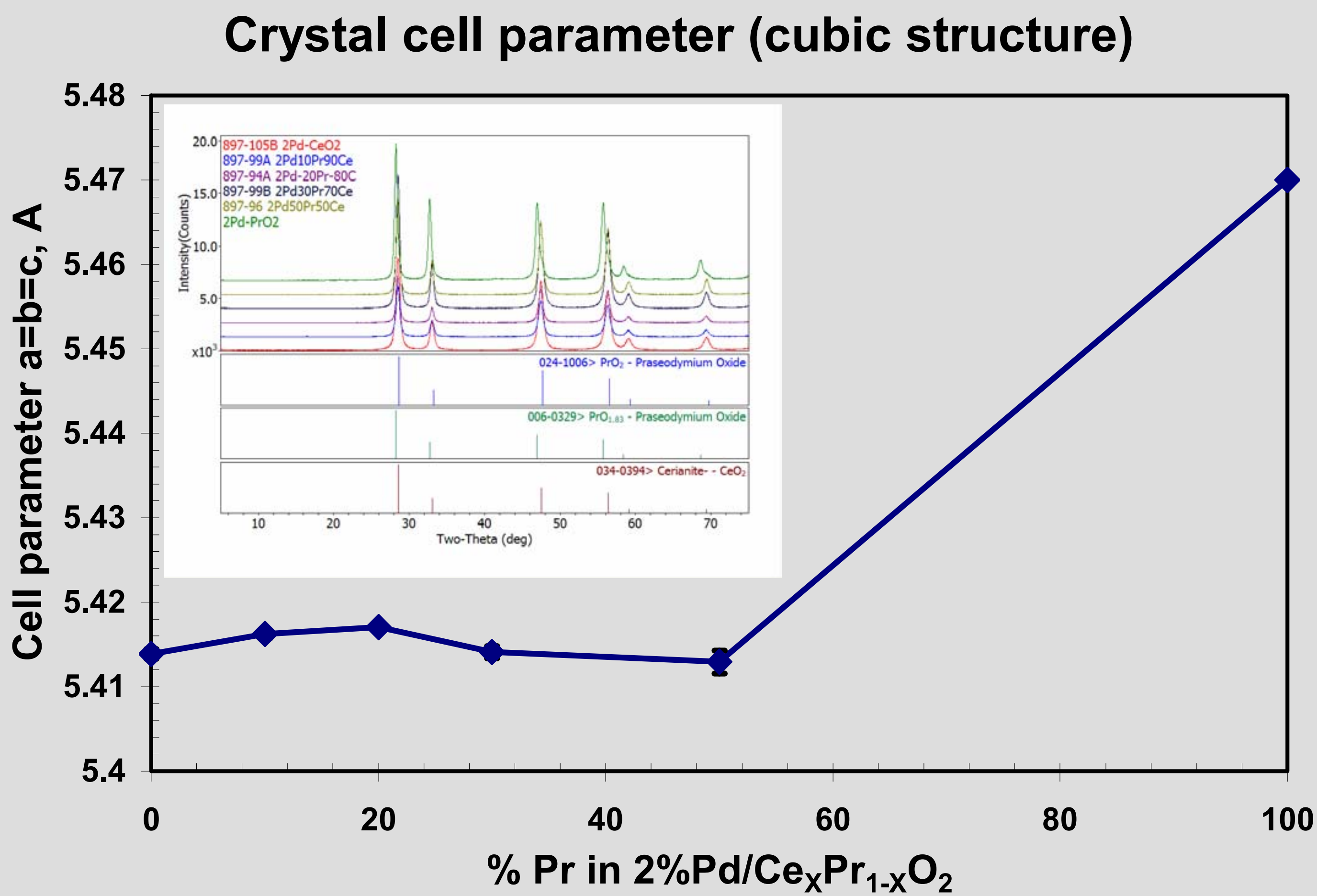
Technical Summary

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.

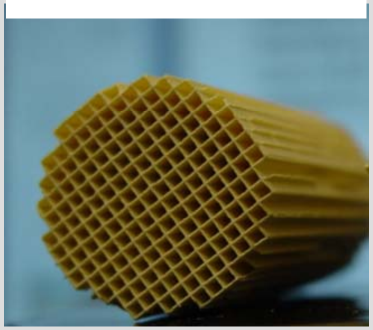
Structure similar to PrO_2 (versus $PrO_{1.83}$) would account for no XRD shift from 10-50% Pr.



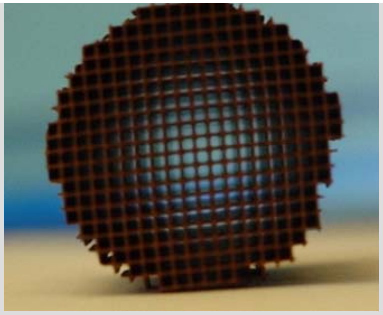
Technical Summary

Catalyst core test efforts – preliminary results

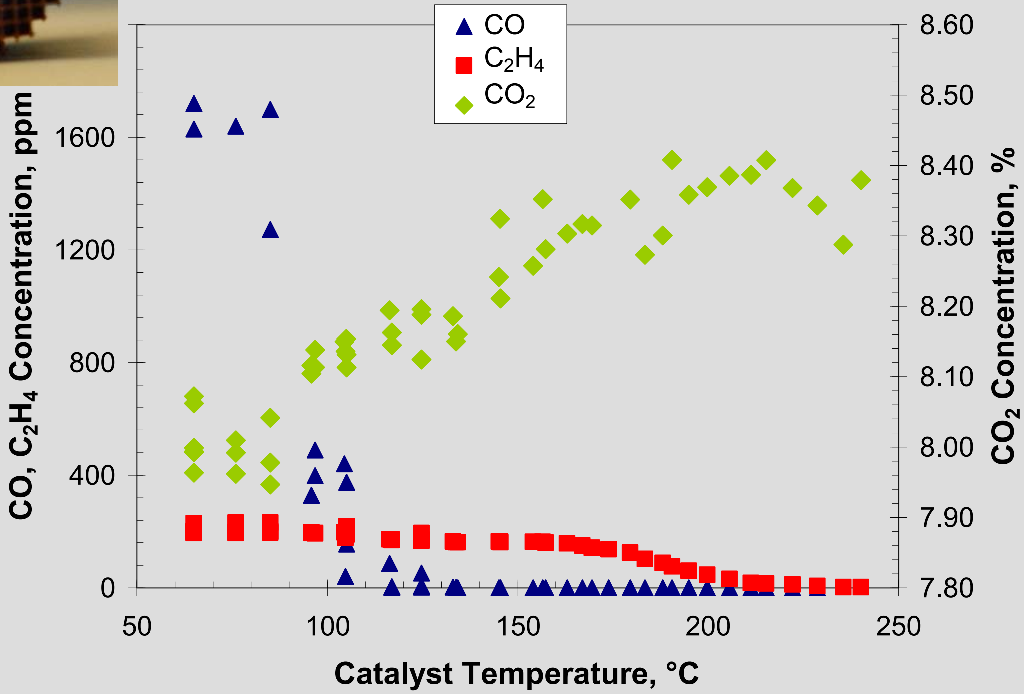
uncoated



22.2 wt% coated



- CO activity very similar to 200,000 hr^{-1} on powder catalyst; powder & core bench correlate well with one another.
- CO target <150°C achieved



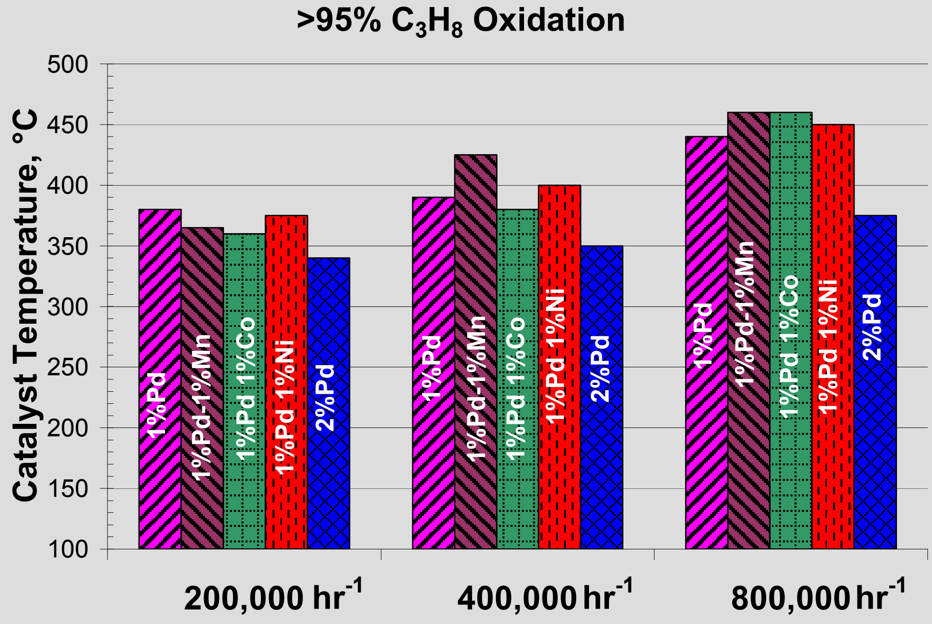
- Core test bench on-line
- Currently testing first cores
  - 2%Pd / $Ce_{0.8}Pr_{0.2}O_2$
  - 2.0 g catalyst on 9.0 g core (22.2 wt%)
  - Catalyst thickness ~77µm (ρ ~ 1.3 g/cm^3)
  - SV = 25,000/hr

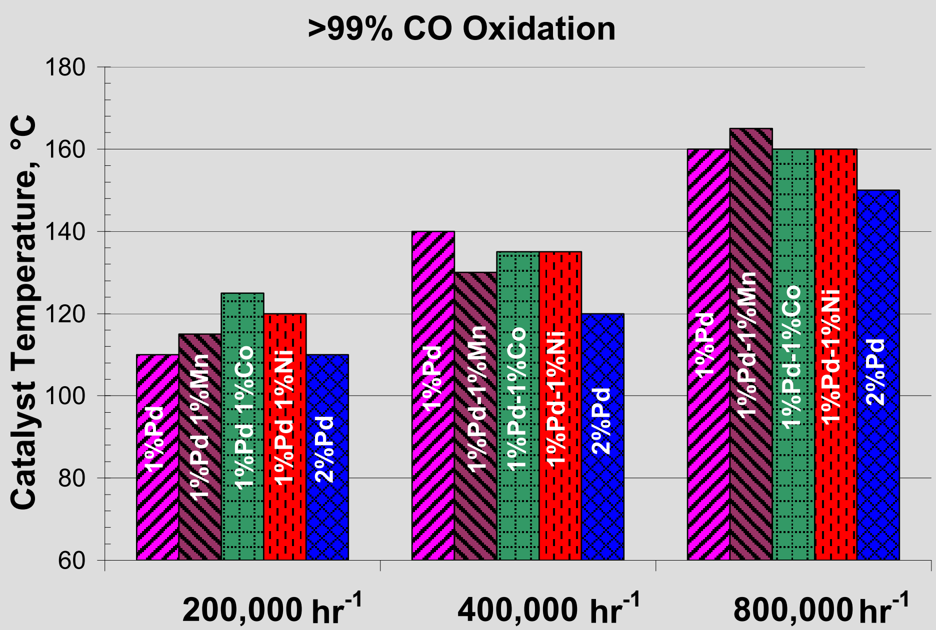
Technical Summary

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

Non-PGMs

- Investigation into replacing PGM with a non-PGM (Mn, Co, Ni).





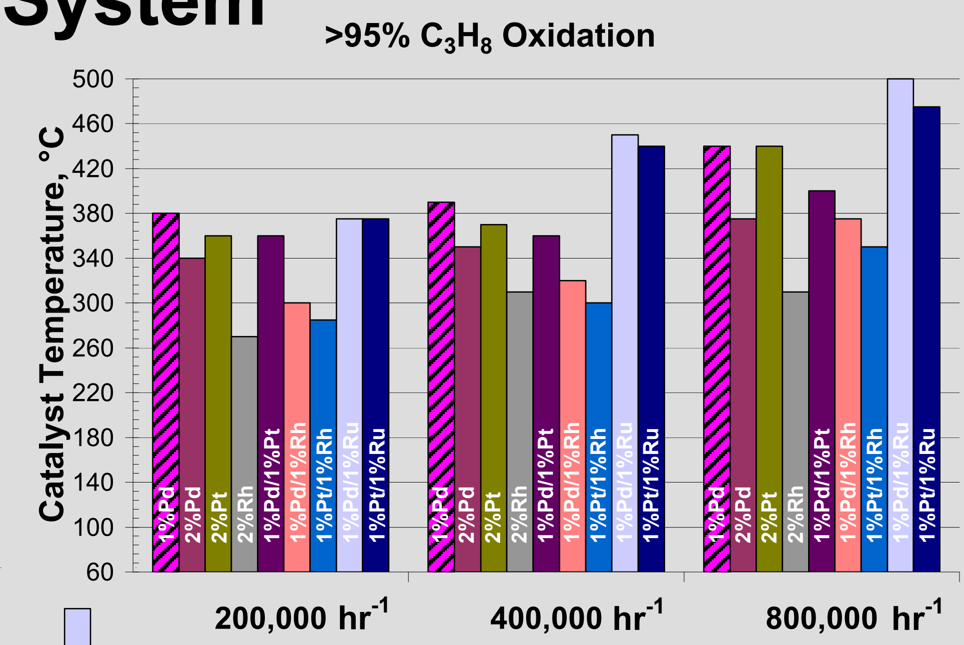
- No significant improvement.
- This represents just a glimpse; not comprehensive.

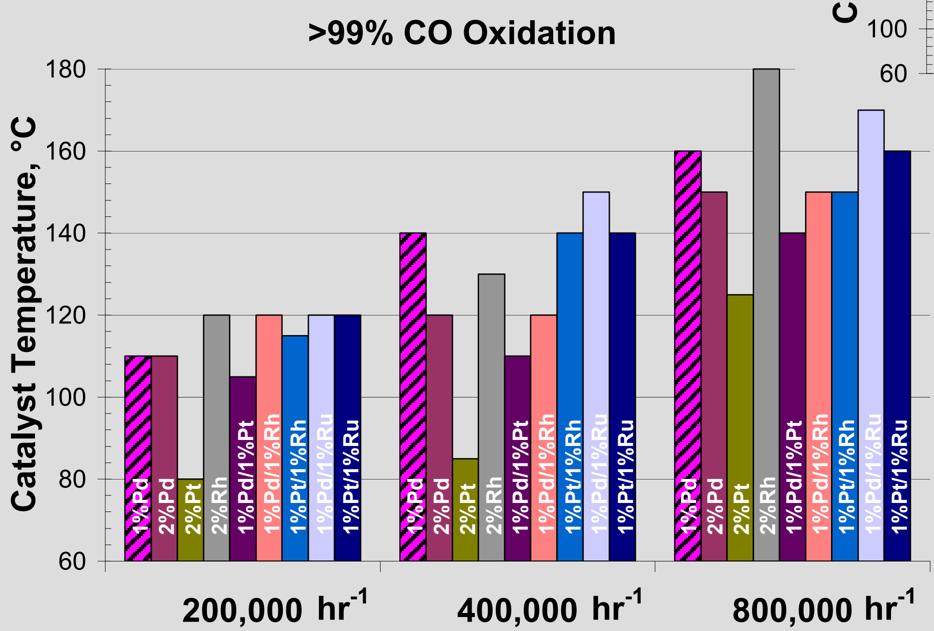
Technical Summary

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

Other-PGMs

- Investigation into the effect of other PGMs, including Pt, Rh, Ru.





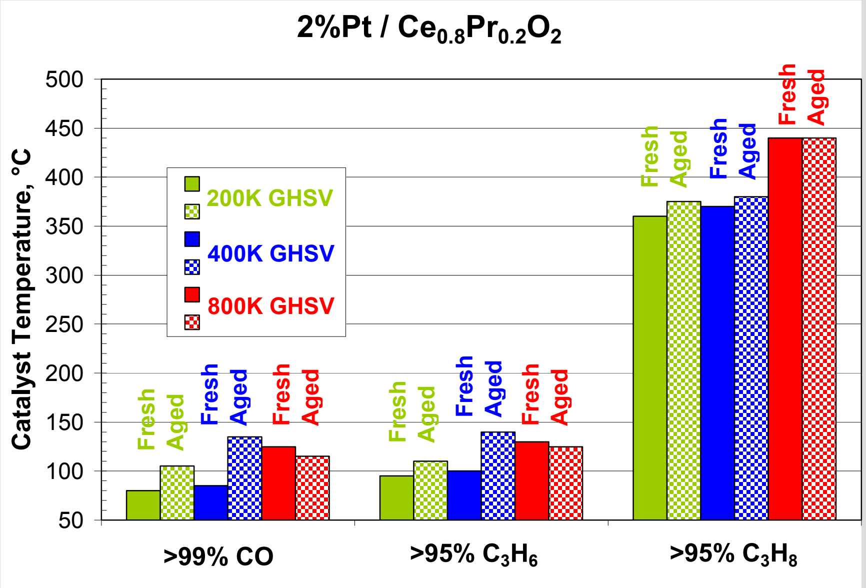
- Pt excellent for CO, olefin oxidation.
- Rh excellent for paraffin oxidation.
- Pt/Rh catalyst is promising.

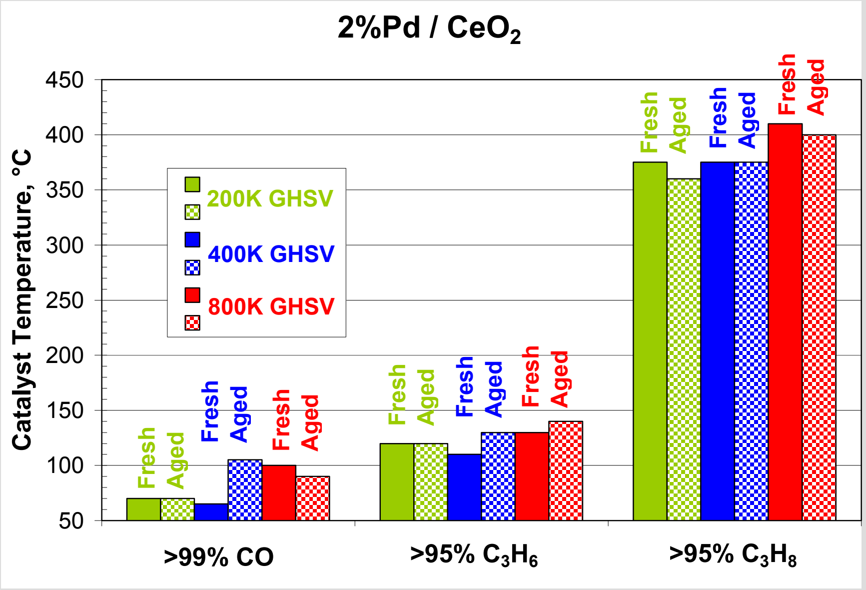
Technical Summary

2%Pd/$Ce_XPr_{1-X}O_2$ System:

Preliminary Durability Investigations

- Results of hydrothermal aging tests.
- Samples aged in 10% H_2O in air at 350°C for 100 hours.





- Effect of aging:
  - Minimal effect on Pd.
  - Slight deactivation of Pt.

Summary

Identified CeO_2 system as promising area for investigation. Results of incorporating Pr into support has decreased the temperature required for activity.

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

Blending in of 10% to 20% Pr ‘swells’ the oxide crystal structure; >20% Pr appears to cause loss of smaller pores (<20nm) and loss of surface area.

Increased synergy of precious metal with 10% to 20% Pr blended into the CeO_2 support.

Beginning core-configured investigations.

Acknowledgements

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– DOE OFCVT

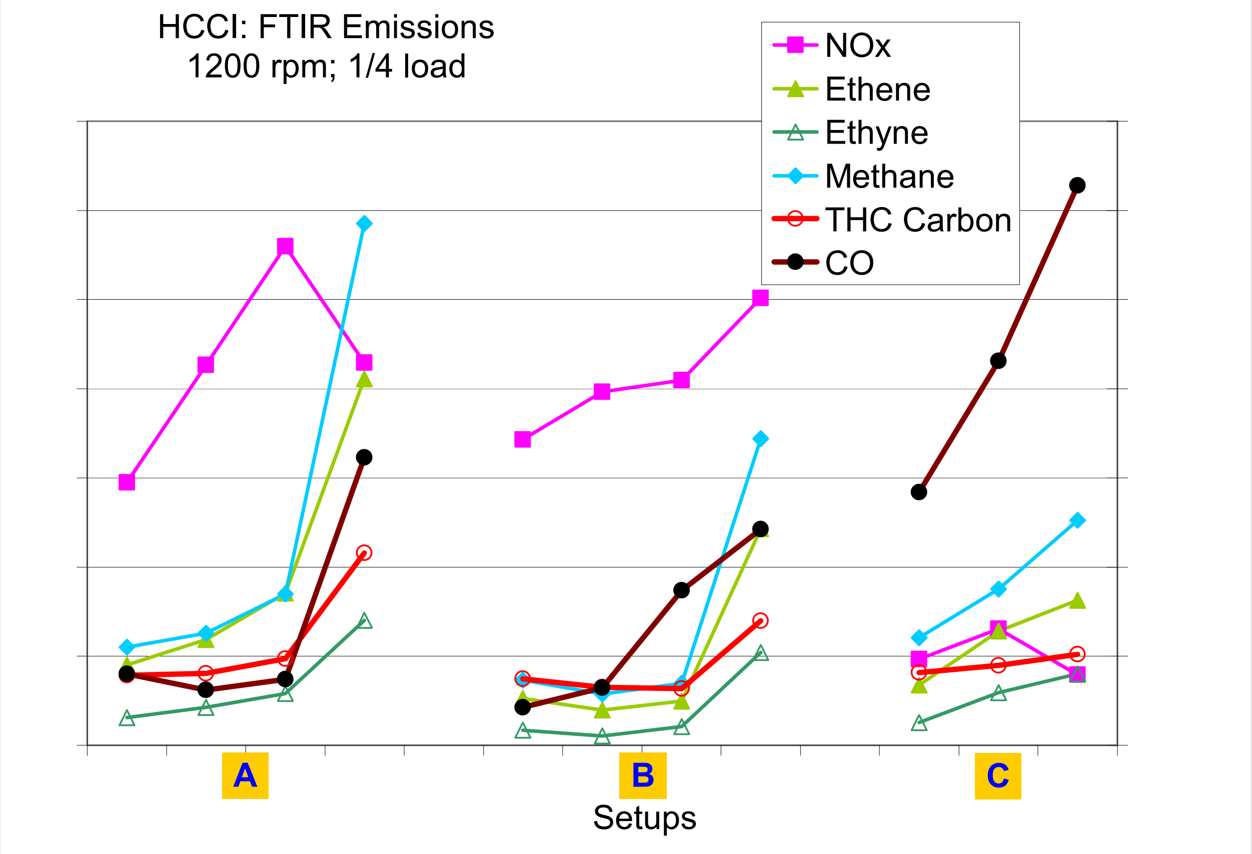
U.S. Department of Energy
Energy Efficiency and Renewable Energy
FreedomCAR & Vehicle Technologies Program

Appendix

HCCI emission hydrocarbon speciation efforts

Caterpillar speciation efforts complete for HCCI exhaust characterization.
Vendor supplied catalysts tested.

Trade-off:
NO_x versus CO levels



Cat ID and composition	88C, 2Pd-CeO_2	99A, 2Pd-$Pr_{0.1}Ce_{0.9}O_2$	94A 2Pd-$Pr_{0.2}Ce_{0.8}O_2$	99B 2Pd-$Pr_{0.3}Ce_{0.7}O_2$	96 2Pd-$Pr_{0.5}Ce_{0.5}O_2$	97 2Pd-$Tb_{0.5}Ce_{0.5}O_2$
BET, m^2/g	56.8	47.0	53.8	26.4	19.7	5.94
Pore volume, cc/g	0.15	0.20	0.18	0.16	0.11	0.05
Pore size, nm	10.6	16.8	13.8	24.6	22.6	31.7