Investigation of Low Temperature Emissions Control Catalysts to Enable Fuel-Efficient Engine Commercialization

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May 1, 2014
CLEERS workshop

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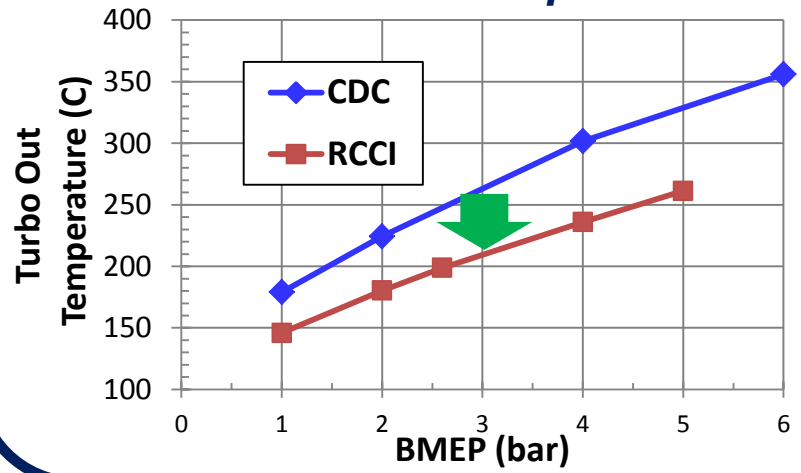
Project focused on emissions control to enable combustion-modes identified in USDRIVE roadmap

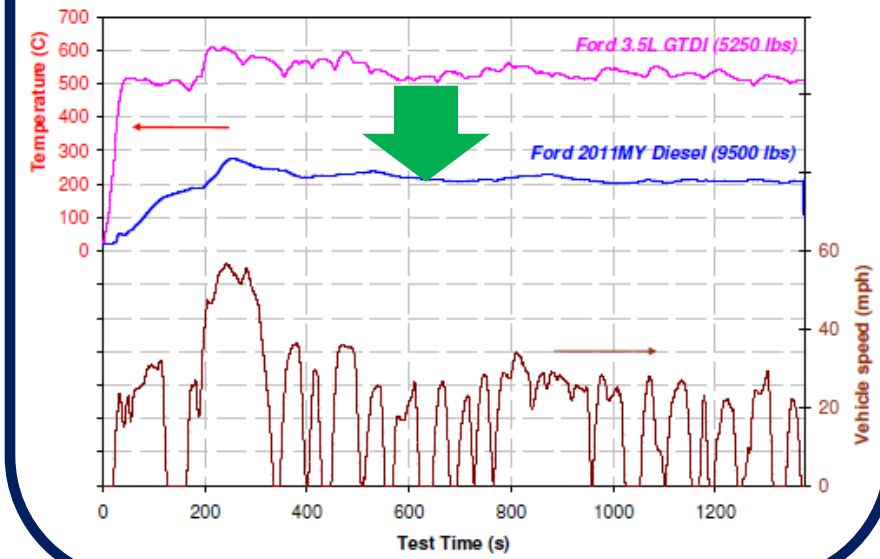
Enable emission compliance and thereby commercialization for:

- **Low Temperature Combustion (LTC)**
- **Dilute Gasoline Combustion**
- **Clean Diesel Combustion (CDC)**

Higher efficiency of LTC (RCCI) lowers exhaust temperatures



Diesel exhaust temperatures lower than gasoline over drive cycle



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Turbos lower gasoline exhaust temperature

Diesel graph: C. Lambert, "Future Directions in SCR Systems", 2012 CLEERS workshop, 05/01/2012.
Turbo: http://www.autoblog.com/2012/10/03/turbo-sales-to-accelerate-by-80-could-make-up-40-of-global-of/

Challenge and advance novel approaches for low temperature emission control

- This project is "high risk-high reward" by design

Catalyst Development:

1. **Develop novel materials**
2. **Modify modern catalysts**
3. **Investigate new approaches**

- *Challenge innovative catalysts under engine-relevant conditions (with multiple pollutants)*
- *Further understanding of catalyst and trap approaches at low temperatures*
- *Define and enable durability to thermal and poisoning processes*

Goal:
Catalyst and trap materials with >90% conversion at 150ºC

Innovate

Challenge

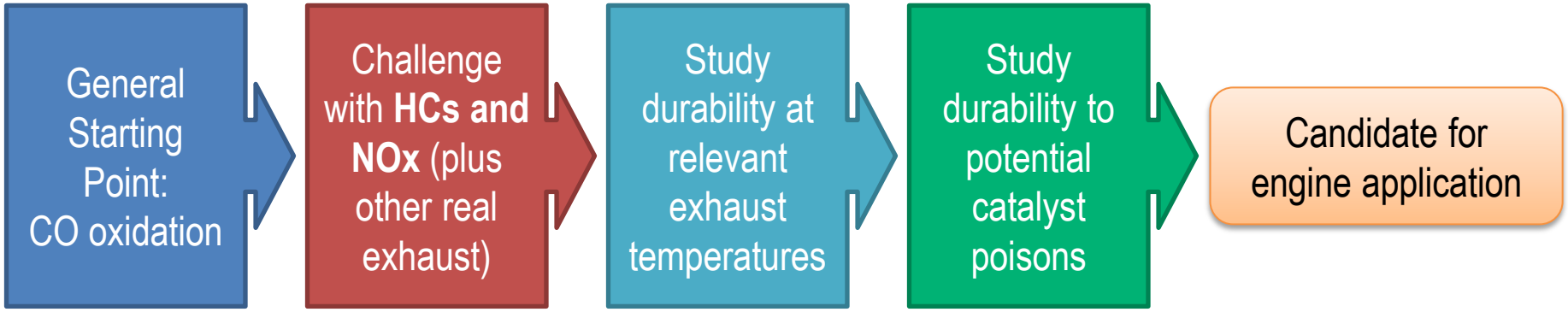
Understand

Begin with catalysts and materials in literature, BES program, and suggested by industry

Cost-effective and thermally stable materials durable to multiple pollutants

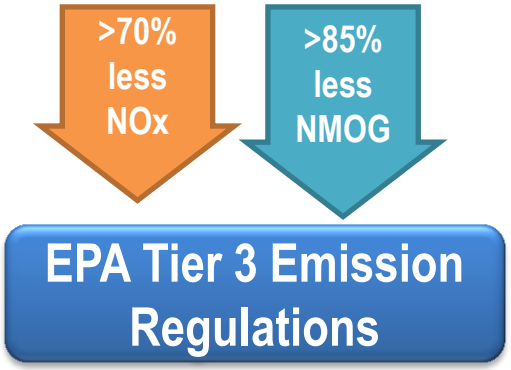
Systematic approach to evaluate novel catalysts and modifications to established technology

Strategy ultimately aims to achieve EPA Tier 3 compliance



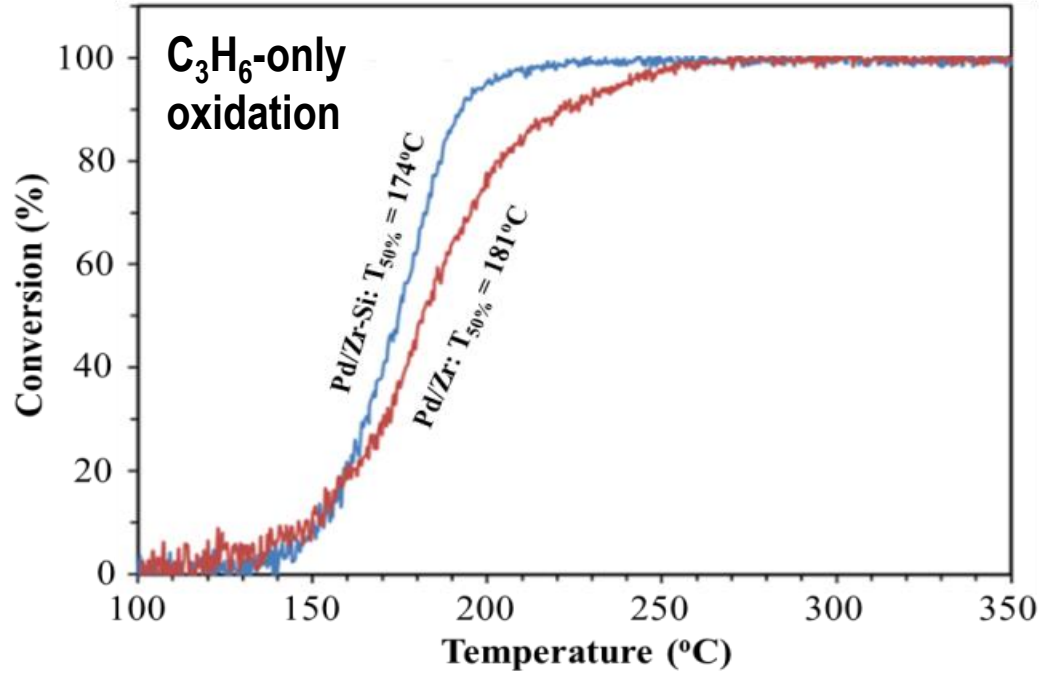
Relative to oxidation catalysts…

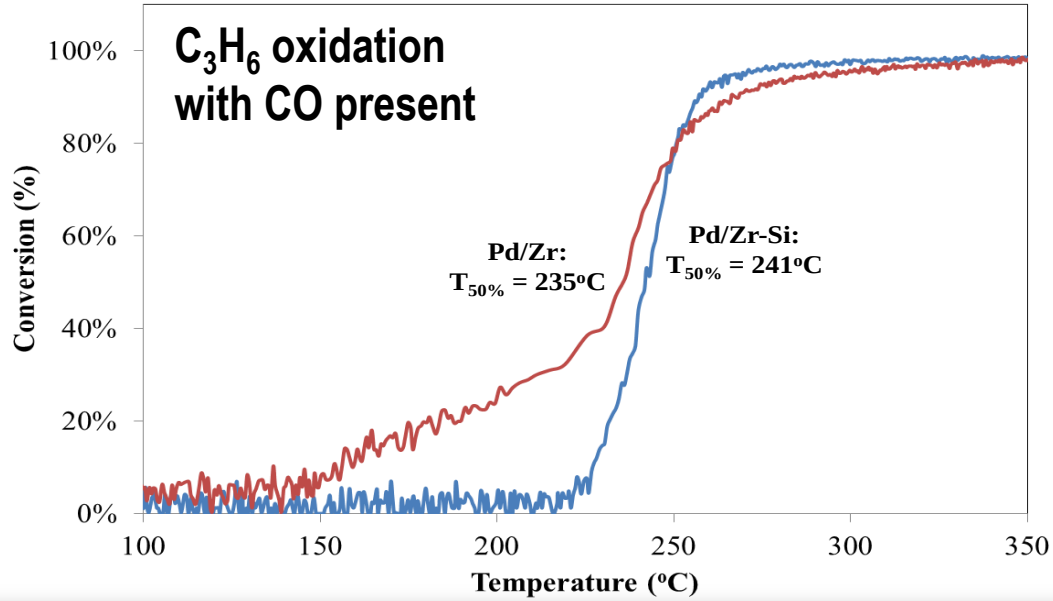
- CO oxidation is common metric in literature/BES program, but… EPA Tier 3 calls for dramatic reductions in HC and NOx
- Focusing HC and NOx is important, but mitigating CO can help these reactions



CO has similar impact on HC reactivity

- HC shown to impact CO-oxidation…what about the inverse?
- Without CO:
  - The HC light-off temperature of the Pd/Zr-Si and Pd/Zr catalysts are 174 and 181°C
- With CO
  - the light off temperatures increased to 241 and 235°C.
- CO is not a primary focus but, its reactivity is important for the overall performance





Technical areas of study

- **Investigation of innovative Au@Cu (core@shell) catalyst for oxidation**

Au@Cu System

- Modification of conventional support materials with PGM-based catalysts to achieve high surface area support with better activity

Support Study

- PGM-free catalyst study, Cu-Ce-Co

PGM-Free Catalyst

- Study of trapping materials

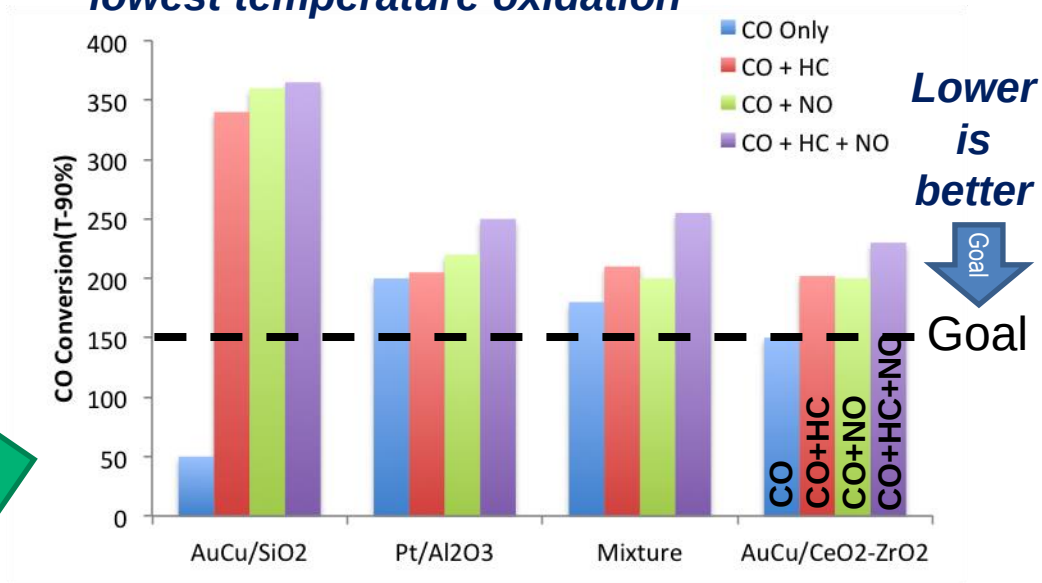
Traps

Au@Cu supported on ceria-zirconia gives best durability and oxidation performance

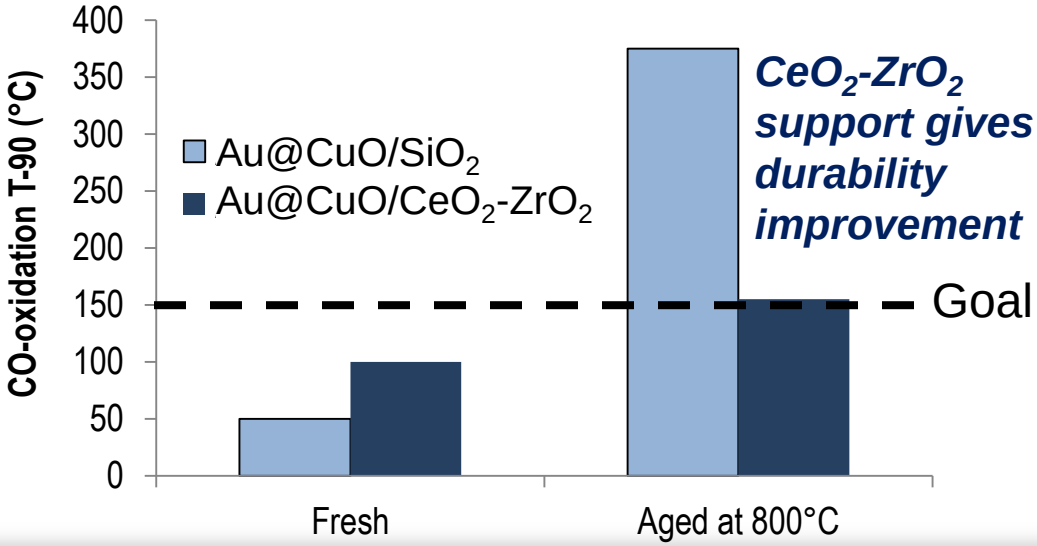
Status of Au@Cu studies:

- CO oxidation occurs at very low temperature…as long as no NO+HC
- 90% Oxidation of HCs and CO at 150°C is difficult
  - Both Au@Cu/SiO_2 and Pt/Al_2O_3 show impact from NO and HCs
- **CeO_2-ZrO_2 support lowers oxidation temperature**

T-90 shows Au@Cu on CeO_2-ZrO_2 gives lowest temperature oxidation



- **CeO_2-ZrO_2 support improves durability**
  - 90% conv. achieved w/ 16h 800°C aging for CO oxidation
- Sulfur poisoning also problematic with Au@Cu



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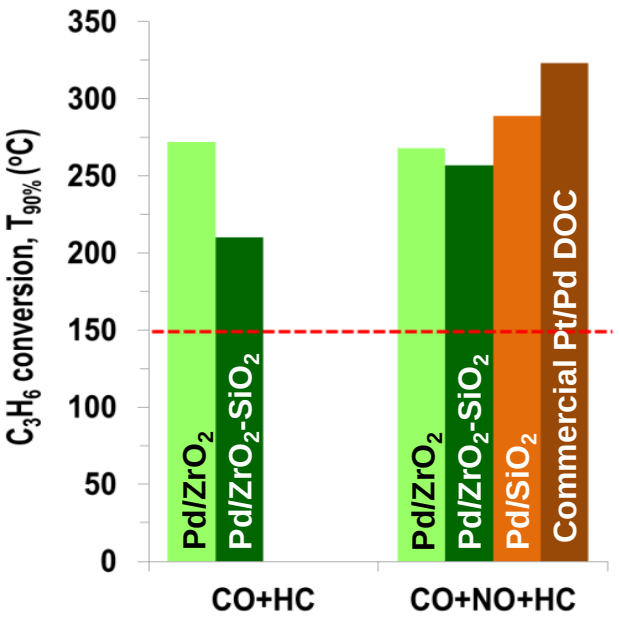
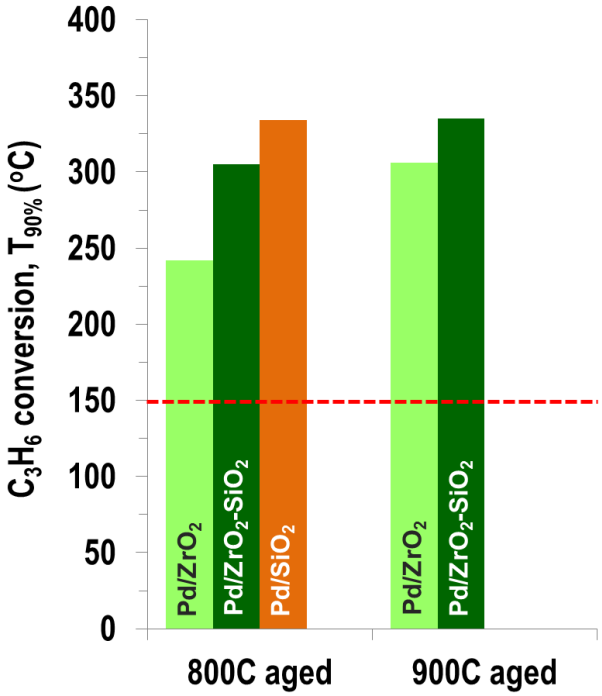
Effort also investigating more traditional pathways to emissions control: support modification with PGM

- **First approach: optimize support for Pd catalysts by combining high acidity of ZrO_2 with high surface area of SiO_2; coated SiO_2 with ZrO_2**
- **ZrO_2 coating introduces surface acidity:**
  - Favorable for Pd dispersion, HC oxidation, and S tolerance
  - High acidity: benefit on HC oxidation vs. high basicity: high sulfur adsorption
- **Pd/ZrO_2-SiO_2 shows better performance for HC oxidation**
  - $T_{90\%}$ in CO+NO+HC
  - Commercial DOC 323°C
  - Pd/ZrO_2-SiO_2: 257°C
- **After aging at 800°C, Pd/Zr shows excellent stability**
  - Increase in T90 observed on Pd/ZrO_2-SiO_2
  - improved zirconia adherence necessary





Reaction Conditions: 0.4% ppm CO / 0.05% ppm NO / 0-0.1% C_3H_6 +10% O_2 + 5% H_2O in Ar, W/F = 0.19 g·h mol^{-1}, GHSV of Pd/ZrO_2 = 150,000 hr^{-1}

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PGM-Free Catalyst

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Traps

Intriguing non-precious metal catalyst

Applied Catalysis A: General 451 (2013) 282–288

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Influence of calcination temperature on the structure and catalytic performance of CuO_x-CoO_y-CeO_2 ternary mixed oxide for CO oxidation

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[b] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
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- Ternary mixed oxide with aqueous synthesis
- Durability not fully vetted…nor activity in presence of HC+NO

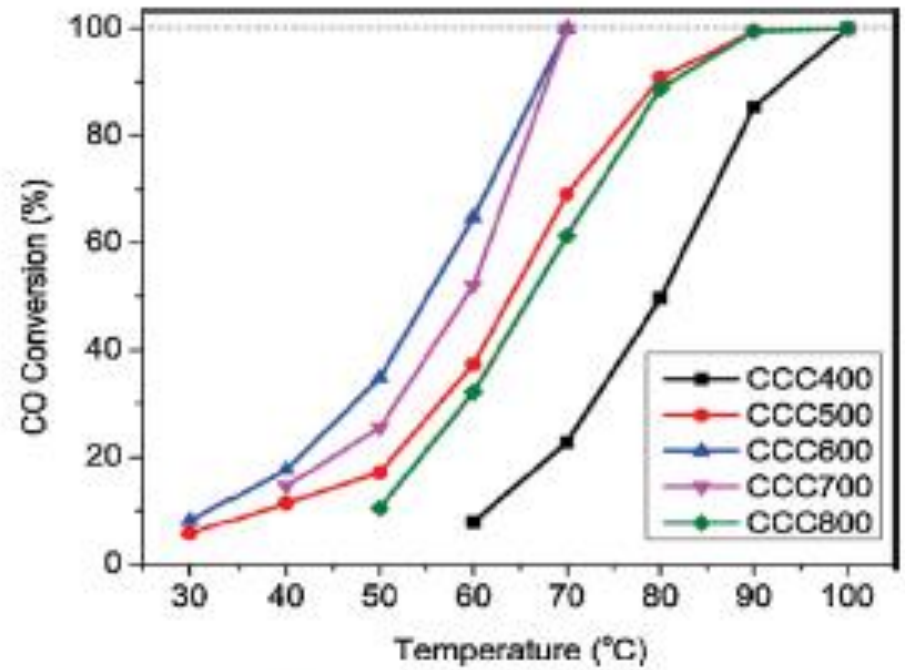
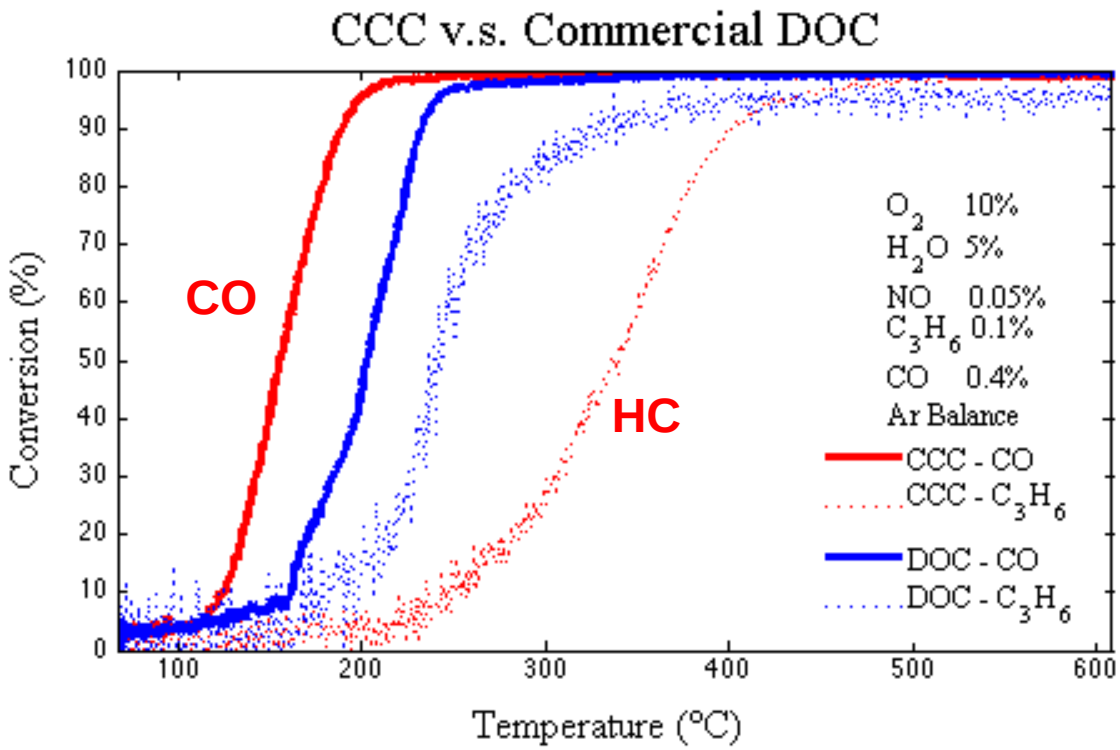


Fig. 1. CO conversion over the catalysts heated at different temperature. Reaction condition: catalyst 50 mg, flow rate 40 ml/min, 1 vol% CO balance in air.

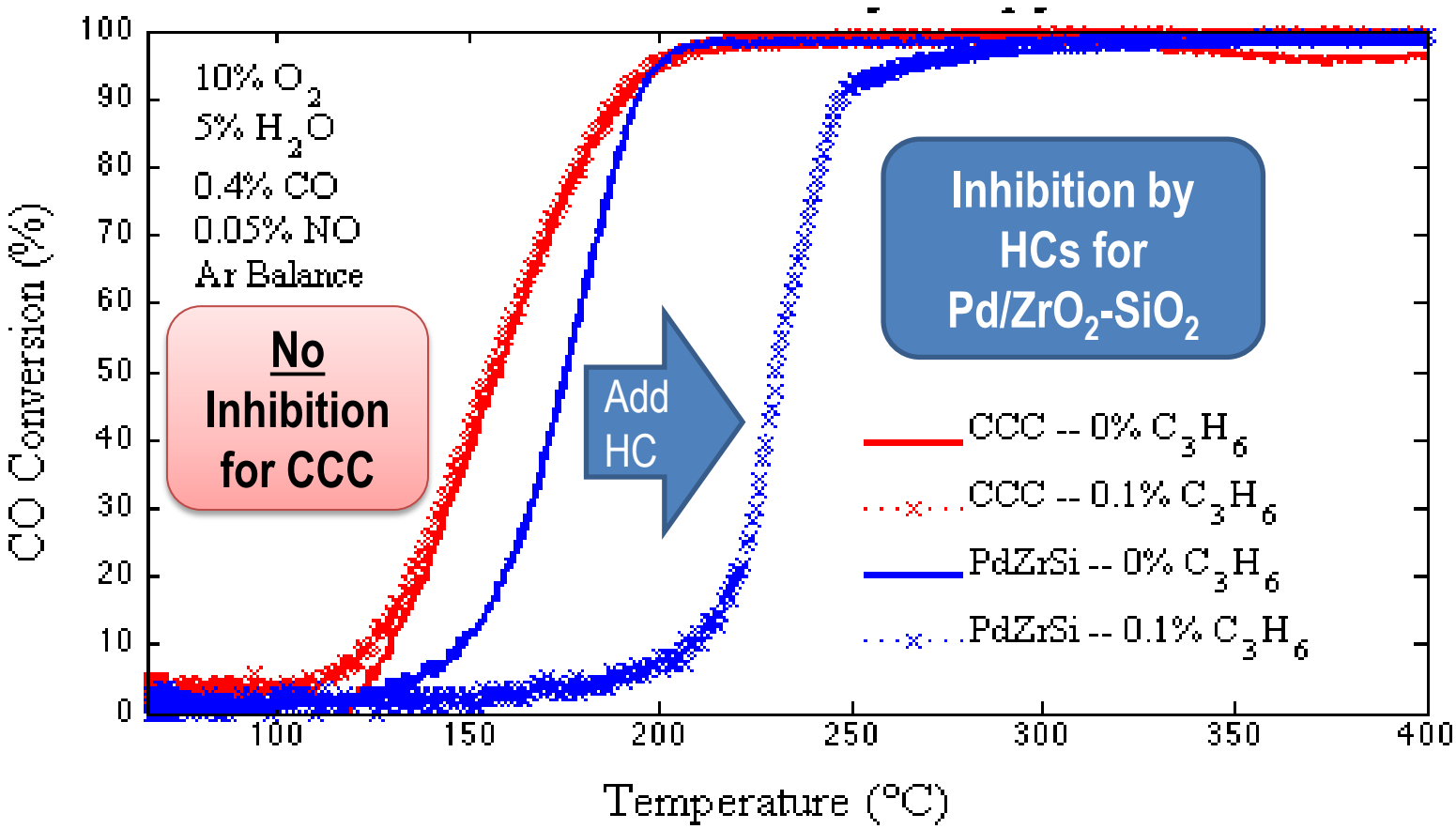
PGM-free CuO_x-CoO_y-CeO_2 catalyst oxidizes CO below 200°C in presence of HC

- Co-precipitated CuO_x, CoO_y, and CeO_2 (CCC) ternary oxide
- PGM-Free CCC (red) **outperforms commercial catalysts** currently used in DOC (blue) washcoats for oxidation of CO
  - hydrocarbon oxidation still relatively high



HC inhibition NOT observed on CuO_x-CoO_y-CeO_2

- CO oxidation inhibition by propylene is readily seen on platinum group metal (PGM) catalysts; Pd/ZrO_2-SiO_2 catalyst shown here (blue)
- **However…no inhibition observed for CCC catalyst** (red)



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Support Study

- PGM-free catalyst study, Cu-Ce-Co

PGM-Free Catalyst

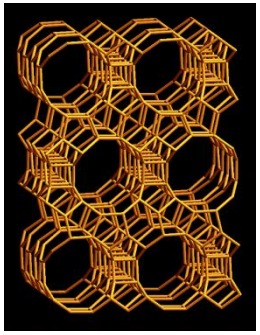
- **Study of trapping materials**

Traps

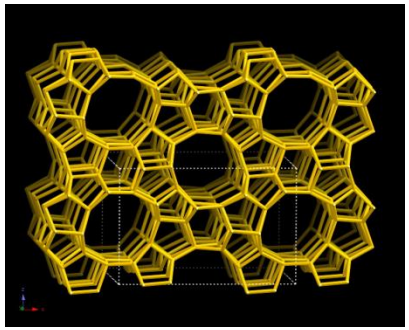
Baseline HC-trap materials selected to determine key controlling factors

- Zeolites chosen based on industry feedback and literature survey
  - Most studied materials in academic settings
  - Components of actual commercial technology (conventional ICEs)

Beta (12-ring pore)



ZSM-5 (10-ring pore)



Large and medium pore structures allow easy HC transport

Zeolite type	SiO_2/Al_2O_3 molar ratio	Nominal cation form	Surface area (m^2/g)
Beta	25	H^+	680
Beta	25	Ag^+	NM
Beta	300	H^+	620
Beta	300	Ag^+	NM
ZSM-5	30	H^+	405
ZSM-5	30	Ag^+	NM
ZSM-5	280	H^+	400
ZSM-5	280	Ag^+	NM

- Systematic variation of key zeolite properties
  - Pore structure (Beta vs. ZSM-5)
  - Acidity (low vs. high SiO_2/Al_2O_3)
  - Cation type (H^+ vs. Ag^+) *5 wt% Ag loading obtained for both zeolite types (low SiO_2/Al_2O_3 cases)*

In progress

- Investigating performance trends will give Information necessary for designing HC-traps tailored to advanced ICEs

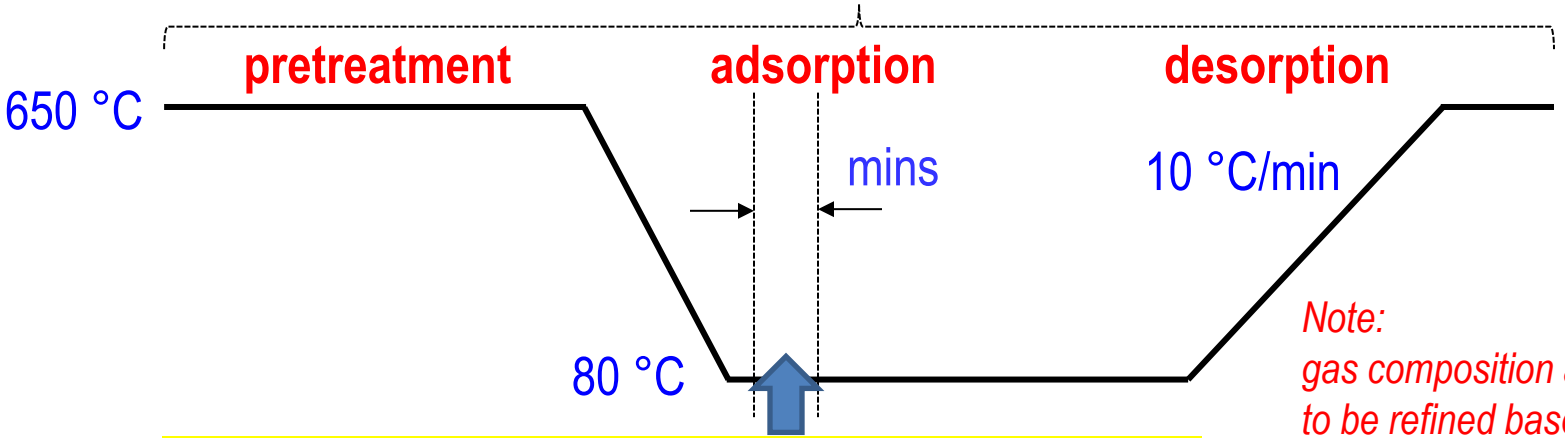
Simple laboratory protocol being employed for HC-trap will incorporate Low Temperature Protocol when defined

- Controlled lab microreactor study to determine key performance values
  - HC storage capacity and rate
  - HC release temperature and rate
  - NO and CO impact
  - Thermal aging impact (650 to 800 °C)

As a function of

zeolite type
acidity
cation type and loading

Base gas: 10% O_2, 5% H_2O, 5% CO_2

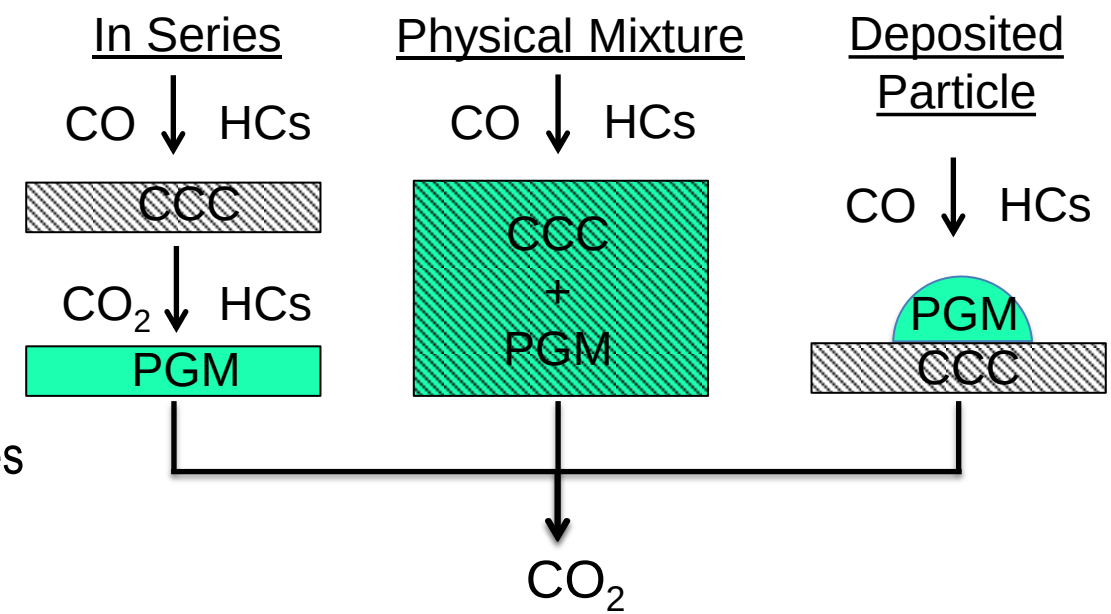


500 ppm HC (C1 basis), 200 ppm NO, 200 ppm CO

Note:
gas composition and temperature to be refined based on other on-going ORNL VTO projects on advanced combustion engines (e.g., RCCI)

Future work

- **<u>Support Study:</u> increase accessible area of the coated ZrO_2 layer on SiO_2 for durability and acidity; ceria-zirconia**
- **<u>PGM-Free Catalyst:</u> investigate the potential of utilizing CCC resistance to HC inhibition to improve HC oxidation over PGM catalysts**
  - Study combinations of CCC and PGM catalysts in attempt to reduce CO inhibition of HC oxidation over PGM catalyst
  - J.-Y. Luo, et al. paper* on CuO-CeO_2 and Co_3O_4-CeO_2 suggests separate active sites for CO and HC oxidation



- **<u>Traps:</u> Complete the planned basic characterization and reactor evaluation of baseline zeolite-based HC trap materials**
  - Characterization: ICP, BET, porosity, NH_3-TPD
  - Reactor evaluation: HC storage and TPD

*Reference: J.-Y. Luo, M. Meng, Y.-Q. Zha, L.-H. Guo, *J. Phys. Chem. C.* **2008**, *112*, 8694.

Summary

Objective: Develop emission control technologies that perform at low temperatures (<150ºC) to enable fuel-efficient engines with low exhaust temperatures to meet emission regulations

Relevant To All ACEC Tech Team Combustion Techniques

Novel Concepts → *Innovate* → *Challenge* → *Understand* → *Real Conditions*

Au@Cu System	Lower CO oxidation temperature, but NO+HCs and S are issues
Support Study	Improving support chemistry; seeking more ZrO_2 coverage; also include ceria-zirconia
PGM-Free Catalyst	Low cost catalyst with no CO-HC inhibition - seeking to utilize lack of inhibition
Traps	Experimental design complete, studies beginning

ADDITIONAL SLIDES

Presentations and Publications

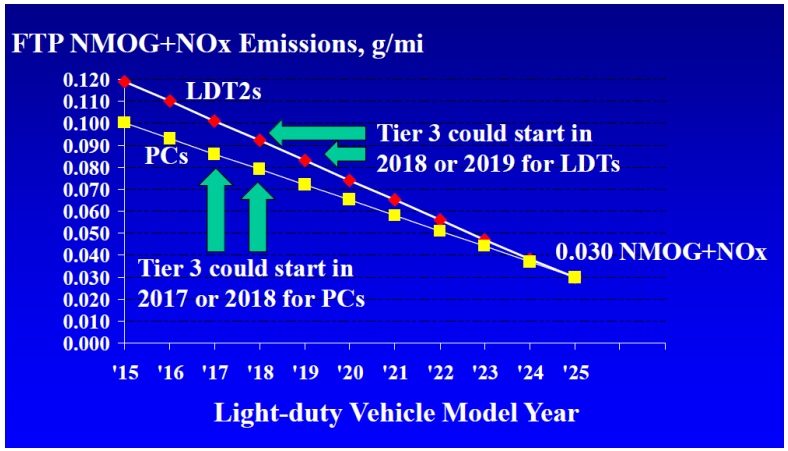
- **Presentations and Publications:**
  - J. Chris Bauer, Todd J. Toops, Yatsandra Oyola, James E. Parks II, Sheng Dai, Steven H. Overbury, "Catalytic activity and thermal stability of Au–CuO/SiO2 catalysts for the low temperature oxidation of CO in the presence of propylene and NO", *Catalysis Today* **231** (2014) 15–21.
  - Mi-Young Kim, Jae-Soon Choi, Todd J. Toops, Andrew Binder, James E Parks II, Viviane Schwartz, Jihua Chen, Cyril Thomas, "Developing novel Pd oxidation catalysts using ZrO_2-SiO_2 supports", poster presentation at the *2014 CLEERS Workshop*, Dearborn, Michigan, April 29th - May 1st, 2014.
  - Mi-Young Kim, Jae-Soon Choi, Todd J. Toops, Viviane Schwartz, Jihua Chen, Eun-Suk Jeong, Sang-Wook Han, "CO oxidation over Pt/SiO_2 and Pd/SiO_2 catalysts: Impact of ZrO_2 and TiO_2 coating on low-temperature activity, hydrothermal stability and sulfur tolerance", oral presentation at the *12th Annual Symposium of the Southeastern Catalysis Society*, Asheville, North Carolina, September 30, 2013.
  - Mi-Young Kim, Jae-Soon Choi, Todd J. Toops, Viviane Schwartz, Eun-Suk Jeong, Sang-Wook Han, Jihua Chen, "Low temperature CO oxidation over Pt, Pd on SiO_2 by surface modification with ZrO_2 and TiO_2 – Impact on hydrothermal stability and sulfur tolerance", oral presentation at the *1st Annual ORNL Postdoc Research Symposium*, Oak Ridge, Tennessee, July 18, 2013.
- **Relevant BES-based publications:**
  - Zhi-Gang Liua,, Song-Hai Chai, Andrew Binder, Yuan-Yuan Li, Lin-Tao Ji, Sheng Dai, "Influence of calcination temperature on the structure and catalytic performance of CuOx-CoOy-CeO_2 ternary mixed oxide for CO oxidation", *Applied Catalysis A: General* **451** (2013) 282– 288.
  - J. Chris Bauer, David Mullins, Meijun Li, Zili Wu, E. Andrew Payzant, Steven H. Overbury, and Sheng Dai "Synthesis of silica supported AuCu nanoparticle catalysts and the effects of pretreatment conditions for the CO oxidation reaction" *Phys. Chem. Chem. Phys.* 2011, *13*, 2571-2581.

Objectives

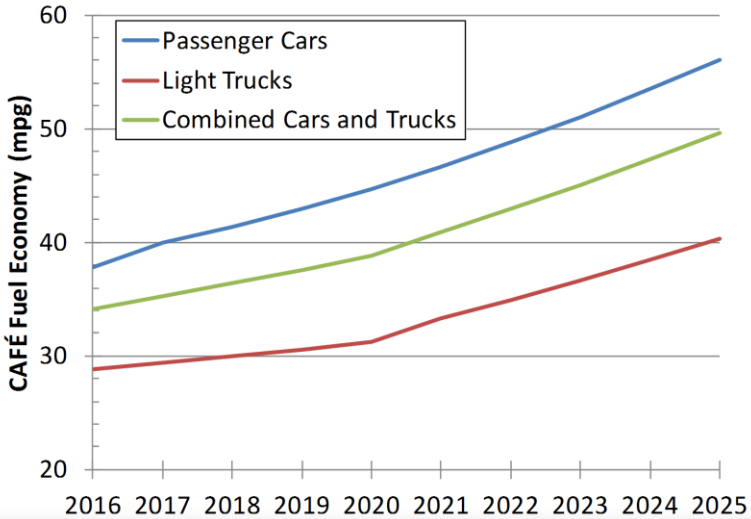
Develop durable emission control technologies that perform at low temperatures (<150ºC) to enable fuel-efficient engines with low exhaust temperatures to meet regulations

- Identify advancements in catalysis that will enable commercialization of advanced combustion engine vehicles
  - Advanced combustion engines have greater efficiency and consequently lower exhaust temperature conditions
- At low temperatures, catalysis is challenging
- Perform research on strategies to improve low temperature catalysis for emission control
  - ~90% conversion at 150°C or lower
- Investigate "trap" material technologies that would temporarily store emissions
  - Released and converted later under periodic high temperature conditions

Emissions



Fuel Economy



Top: J.Kubsh, "Light-duty Vehicle Emission Standards", 01/10/2013.
Bottom: C. DiMaggio, "ACEC Low Temperature Aftertreatment Program", 06/21/2012.

Summary of Technical Accomplishments

- **Completed support investigation of innovative Au@Cu (core@shell) catalyst for oxidation**
  - Found CeO_2-ZrO_2 support gives improved oxidation ***and*** better durability
  - Sulfur a concern

Au@Cu System

- **Successfully added ZrO_2 to SiO_2 support for Pd catalyst to achieve high surface area support with better activity**
  - High activity in both CO and C_3H_6 oxidation due to acidity generated
  - Promising for sulfur tolerance
  - Characterized the accessible area of ZrO_2 layer on SiO_2 (critical for durability)

Support Study

- **Demonstrated catalyst with no PGM based on Cu-Ce-Co**
  - CO low temperature oxidation not inhibited by HCs
  - HC oxidation temperature relatively high
  - Projected cost of catalyst is very low

PGM-Free Catalyst

- **Initiated study of trapping materials**
  - New activity in project
  - Experimental design based on discussion with industry

Traps

Remaining Challenges

General Starting Point: CO oxidation → Challenge with **HCs and NOx** (plus other real exhaust) → Study durability at relevant exhaust temperatures → Study durability to potential catalyst poisons → Candidate for engine application

Au@Cu System	NOx OK, but HCs problematic	ZrO_2-CeO_2 improves durability to 800°C	Sulfur problematic	*Effort idle for now*
Support Study	Lower CO and HC oxidation	ZrO_2-SiO_2 durability can be improved	*Next step: increase coverage of ZrO_2 on SiO_2*	
PGM-Free CCC Catalyst	CO oxidation not inhibited by HCs, but HC oxidation poor	*Durability and resistance to poisons yet to be investigated*		
Traps	*Effort just beginning; lots of remaining work*			

Au-only catalyst supported on ceria-zirconia also shows good stability

- Even with low weight loading high activity shown with unaged sample
  - W/F = 0.25 g*h/mol
    - SV = ~95,000 h^{-1}
  - $T_{50\%}$ = 50°C
  - $T_{90\%}$ = 94°C
- Activity drops after aging at 800°C, but is still very high
  - $T_{50\%}$ = 103°C
  - $T_{90\%}$ = 182°C