Low Temperature Emission Control to Enable Fuel-Efficient Engine Commercialization

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Advanced Combustion Engines Program
U.S. Department of Energy

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Project Overview

Timeline

• Year 1 of 3-year program*
• Builds on previous R&D in FY13-FY15

Budget

• FY2016: $400k (Task 1*)

*Task 1: Low Temperature Emission Control
Part of large ORNL project “Enabling Fuel Efficient Engines by Controlling Emissions” (2015 VTO AOP Lab Call)

Partners

• Low Temperature Aftertreatment Sub-Team of US DRIVE Advanced Combustion and Emission Control Tech Team
• Johnson Matthey (Haiying Chen)
• BES-funded scientists
• NSF-funded scientists/students
• University of South Carolina
• Karlsruhe Institute of Technology

Barriers

• From DOE Vehicle Technologies Multi-Year Program Plan (2011-2015)
  – 2.3.1.B: Lack of cost-effective emission control
  – 2.3.1.D: Durability
• Overall, addressing emission compliance barrier to market for advanced fuel-efficient engine technologies
Objectives and Relevance

Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations

Goal: 90% Conversion at 150°C

- Greater combustion efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent

Higher efficiency engines have lower exhaust temperatures*

Emissions standards getting more stringent

Fuel Economy Standards
54.5 mpg CAFE by 2025

>70% less NOx
>85% less NMOG
70% less PM

EPA Tier 3 Emission Regulations
2017-2025 (phased in)

*Reactivity Controlled Compression Ignition (RCCI) [a Low Temperature Combustion mode] vs. Conventional Diesel Combustion (CDC)
Relevance: Guiding Documents Define Needs

- 2015 CLEERS Industry Priorities Survey
- USDRIVE “The 150ºC Challenge” Workshop Report
- USDRIVE ACEC Tech Team Roadmap (2013)

Identified Needs Addressed:
- Lower temperature CO and HC oxidation
- Low temperature NOx reduction
- Cold start emission trapping technologies
  - Especially passive NOx adsorbers
- Reduced PGM
- Better durability
- Promote innovative catalytic solutions via partnering with DOE BES programs

Relative to all combustion approaches cited in ACEC Tech Team Roadmap:

- Low Temperature Combustion (LTC)
- Dilute Gasoline Combustion
- Clean Diesel Combustion (CDC)
**Approach:** employ low temperature protocols to evaluate novel catalysts

- Protocols finalized in June 2015 by the Low Temperature Aftertreatment Sub-Team of the US DRIVE Advanced Combustion and Emission Control Team

- Full file at: www.CLEERS.org

### LTC-D: Low Temp. Combustion Diesel

- Total HC: 3000 ppm
- C₂H₄: 1667 ppm
- C₃H₆: 1000 ppm
- C₃H₈: 333 ppm
- CO: 2000 ppm
- NO: 100 ppm
- H₂: 400 ppm
- H₂O: 6 %
- CO₂: 6 %
- O₂: 12 %
- Balance N₂

### Powder Catalyst Requirements

- Reactor ID 3-13 mm
- Catalyst particle size ≤ 0.25 mm (60 mesh)
- Catalyst bed L/D ≥ 1
- Space velocity
  - 200-400 L/g-hr
  - For 0.1 g sample, flow 333-666 sccm
Approach: identify candidates through independent research and collaborations with NSF- and BES-funded scientists

- Initial data* from U. South Carolina shows good CO and propylene (not shown) activity
  - simple conditions, not full protocol
  - MC: MnO$_x$-CeO$_2$
  - SMC: SnO$_2$-MnO$_x$-CeO$_2$
  - Also evaluated with 1% Pd

- Through a collaboration, catalysts evaluated under LTC-D protocol

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  - In general, hydrocarbon activity is promising
    - Improves further with Pd addition

- Protocols helping to elucidate strengths and weaknesses of catalysts being evaluated

Collaborations

• DOE Basic Energy Sciences Program
  – Sheng Dai and Steve Overbury (ORNL), Center for Nanophase Material Science (ORNL)

• CLEERS
  – Dissemination of data; presentation at CLEERS workshop

• Academia
  – University of South Carolina
    • Professors John Regalbuto, Jochen Lauterbach and Erdem Sasmaz
  – International collaborations
    • UPMC, France (Dr. Cyril Thomas) & CNU, Korea (Prof. Sang-Wook Han), Karlsruhe Institute of Technology

• Industry
  – USCAR/USDRIVE ACEC Tech Team Catalyst Sub-Team
    • low temperature evaluation protocols
  – Catalyst and washcoat suppliers
    • Johnson Matthey: Industry input from Haiying Chen
    • Solvay: alumina-based supports provided for PGM support studies at USC (Barry Southward)

• Other DOE-funded FOA Projects
    • Catalysts being investigated for stoichiometric applications
  – UCONN-led project: Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation
Milestones

• FY15 Milestones:
  – {Key SMART milestone} Investigate individual roles of the components in the CuCoCe ternary oxide and potential synergies with standard emissions control components (12/31/2014) **complete**
  – Identify candidate materials for NH$_3$ SCR catalysts that are active at low temperatures (9/30/2015) **complete**
    • Intended as an identification of catalysts being studied in the literature and through fundamental studies, not as an experimental campaign
    • Identified MnOx-based catalysts to be the only materials to show significant activity below 150°C…as low as 110-120°C [1,2]; concerns regarding thermal durability.

• FY16 Milestones: **on track**
  – Report on evaluation of CCC+PGM emissions control studies including implementation of full ACEC low temperature protocol (9/30/2016).

Technical Accomplishments

• PGM-free mixed metal oxides
  – Identified new mixed metal oxide candidate (USC) that has improved HC activity (Sn-Mn-Ce and Mn-Ce)
  – Measured sulfur tolerance of CCC while also exploring mitigation strategies with PGM

• Support modifications for enhanced PGM activity
  – New core@shell technique employed to maximize ZrO₂ surface for PGM catalysis shown to yield improved activity especially for THC
  – Successfully implemented nano-on-nano technique with Pd dispersed on nanoparticles of Ce-Zr dispersed on Al₂O₃; high activity observed, approaching targets for some gases

• Trapping materials
  – Determined key attributes of silver-alumina HC trap; deep ion exchange and low Si:Al
  – Demonstrated NO adsorption on Pd/ZSM-5; impact of pretreatment temperature
Mixed metal oxide has shown interesting chemistry and some promise without PGM

• CuO$_x$-CoO$_y$-CeO$_z$ (CCC) promising for CO oxidation
  – Interfacing crystalline regions of Co$_3$O$_4$ and CeO$_2$
  – Cu in lattices of both Co$_3$O$_4$ and CeO$_2$ evenly
  – CO oxidation unaffected by HC

• Need additional catalyst for low-temp. HC oxidation
  – Aids HC oxidation over Pt/Al$_2$O$_3$ in physical mixture
Inclusion of PGM improves sulfur tolerance and sulfur removal of CCC

• Employed ACEC protocol for sulfur poisoning
  – Flow 5 ppm SO₂ at 300°C for 5 hours
  – 200 L/g-hr (GHSV ~300,000 h⁻¹)
    • Dense catalyst results in small volume
• Significant deactivation observed if Pt/Al₂O₃ not included
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- Significant deactivation observed if Pt/Al$_2$O$_3$ not included
- After sulfation, ramp under LTC-D conditions to investigate full reactivity
- Desulfation attempted at 600°C under cycling lean and rich conditions
  - 10% O$_2$ and 1% H$_2$
  - 30 seconds each, 30 minutes total
- Results show the presence of Pt help protect/recover activity of the catalysts
  - Unclear if CCC has role as desulfated evaluation behaves similar to Pt/Al$_2$O$_3$
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ZrO₂ support has shown excellent activity with Pd catalyst; efforts to improve ongoing

• Pd/ZrO₂ has good activity, excellent thermal durability, good S tolerance
• Goal: further improve activity and sulfur tolerance
  – Support ZrO₂ on high surface area SiO₂
• Initial effort not successful as Pd/ZrO₂ still more active
  – not a monolayer; 15% coverage of SiO₂ surface
  – Pd dispersed on both ZrO₂ and SiO₂

New synthesis technique successfully creates ZrO$_2$ shell around SiO$_2$ core

- Able to synthesize a complete shell around SiO$_2$ core using new technique SiO$_2$@Pd/ZrO$_2$
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  - Pd (1 wt%) deposition solely on ZrO$_2$ outer shell

This research was performed, in part, using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities.
New synthesis technique successfully creates ZrO₂ shell around SiO₂ core

- Able to synthesize a complete shell around SiO₂ core using new technique SiO₂@Pd/ZrO₂
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- While employing ACEC low temperature protocols improved activity shown with this technique

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  – Pd (1 wt%) deposition solely on ZrO₂ outer shell
• While employing ACEC low temperature protocols improved activity shown with this technique
• Robust after aging at 900°C for 10h
  – Improved initial dispersion technique still needed

DG = Degreened

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Targeted PGM deposition on Ce-Zr nanoparticles also investigated

- Starting with CeZr nanoparticles, ~5 nm, anchor them to high surface area supports
  - In this instance Al₂O₃, but SiO₂ also possible

- Target Pd deposition on preferred supported metal oxide
  - nano-particles of PGM on nano-particles of Ce-Zr
  - Controlling pH enables targeted deposition

- It is possible...

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Pd/Ce-Zr/Al$_2$O$_3$ catalysts show promise

- Good activity being observed
  - Degreened, 4wt.% Pd/Ce-Zr/Al$_2$O$_3$
    - Pd nano-particles on Ce-Zr nano-particles
  - Also, tolerant to hydrothermal aging
    - THC oxidation improves after 900°C
- However, meeting 150°C target still challenging, especially for C$_2$H$_4$ & C$_3$H$_8$
Technical Accomplishments

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Ion-exchanging and Ag loading key factors in HC adsorption in the presence of H$_2$O

Base gas: 10% O$_2$ and 5% H$_2$O

650 °C pretreatment

80 °C adsorption

3 mins

10 °C/min desorption

500 ppm HC (C$_1$ basis), 200 ppm NO, 200 ppm CO

- NO does not adsorb significantly
- C$_3$H$_6$ adsorption requires **ion-exchanged sites** in the zeolite
- Higher Ag loading results in higher C$_3$H$_6$ adsorption/desorption
- Release is complicated
Release profile indicates significant reactivity of stored HC and varies with Ag loading.

Stored C\textsubscript{3}H\textsubscript{6} is released as:
- CO $\rightarrow$ BEA-zeolite
- CO, C\textsubscript{3}H\textsubscript{6} $\rightarrow$ 1 wt.% Ag/BEA
- CO, C\textsubscript{3}H\textsubscript{6}, CO\textsubscript{2}, ethylene, formaldehyde $\rightarrow$ 5 wt.% Ag/BEA

**Adsorption Conditions:**
C\textsubscript{3}H\textsubscript{6}: 167 ppm, O\textsubscript{2}: 10%, H\textsubscript{2}O: 5%, NO: 200 ppm, Total Flow: 300 sccm, SV: 90,000 h\textsuperscript{-1}

**Desorption Conditions:**
O\textsubscript{2}: 10%, H\textsubscript{2}O: 5%, Ar balance
Release profile indicates significant reactivity of stored HC and varies with Ag loading.

- $\text{C}_3\text{H}_6$ is released mainly as HCs followed by smaller amounts of $\text{CO}_2$ and CO.
- The desorption T of $\text{C}_3\text{H}_6$ is lower for lower Ag loading.
Pd/ZSM-5 stores both NO and HC; pretreatment temperature affects NO release

- Pd/ZSM-5 key attribute is the ability to store both NO and HCs
- NO release profile affected by pretreatment
  - Materials characterization needed to explain effect
- HC capture is similar to Ag-BEA
  - Release profile data incomplete
CCC also shows the ability to store and release NO at low temperatures while flowing full simulated exhaust streams:

- **Stoich** = 188 µmol/g_{catalyst}
- **Lean** = 111 µmol/g_{catalyst}

*Preliminary data*
Remaining Challenges

- **PGM-free mixed metal oxides**
  - Overall activity needs to be improved, especially for hydrocarbons
  - Sulfur tolerance needs to be improved and strategies for removal need to be identified

- **Support modifications for enhanced PGM activity**
  - Overall activity needs to be improved, especially for $C_2H_4$ and $C_3H_8$
  - Sulfur tolerance has not been demonstrated on new samples

- **Trapping Materials**
  - Trapping efficiency needs to be improved for both NO and HC
  - Demonstration of effectiveness when mixed with oxidation catalysts has not been shown

Future Directions

- Identify and increase active sites on CCC through systematic synthesis; expand collaboration w/USC (Sn-Mn-Ce oxide)
- Investigate S interactions in physical mixture w/ PGM catalyst; find minimum PGM needed to mitigate S impact
- Initial dispersion of PGM to be improved; new techniques (precursor, pH, reduction step); **Begin Pt + Pd + Rh studies**
- Implement ACEC S protocol for new samples; initial samples showed good recovery at low temperatures
- Increase active sites w/ higher loadings and more complete ion-exchange
- Explore effectiveness with best catalysts from other areas; implement new ACEC trapping protocols (when published)
Responses to 2015 Reviewers (3)

- **Approach (3.67/4.0):** steps taken are logical ...process and techniques of evaluating the material are excellent ...[need to] expose the candidate catalysts to hydrothermal aging and sulfur poisoning ... exhaust approach and test protocol critical to move into practical application

- **Technical Accomplishments (3.33/4.0):** very high caliber work ... new approach delivering results, good start ... begun the SCR work but show no plans or data ... findings have been very insightful ... more involvement from catalyst suppliers would be sensible ... sulfur exposure on the CCC catalysts

- **Collaborations (3.33/4.0):** collaborators have the needs covered, excellent ... more regular technical interactions with industrial partners ... reaching out to additional catalyst suppliers could be beneficial

- **Future plans (3.33/4.0):** future work was clear and consistent with the remaining challenges and the overall target path.... sound technical path forward ... sulfur studies are very critical for CCC and long overdue ... effect of sulfur should be the top priority.... design of experiment technique should be considered to speed up the project

- **Relevance (100%):** addresses a key enabling issue with regards to low-temperature combustion engine technology ... low-temperature catalysts with high efficiencies and durability is a critical enabler for advanced engine technologies

- **Resources (33% Insufficient):** resources sufficient for HC/CO oxidation work, but likely not enough for SCR work ... much on HC remediation, unless more resources are added, the project will miss the NH₃ SCR goals

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**Responsive Actions**

1. **Sulfur exposure and hydrothermal aging being implemented**
2. **New ACEC protocols have been fully integrated into project**

1. **Effort on SCR last FY was literature review not experimental work**
2. **Will work to engage more suppliers, especially as promising technologies are identified for fully-formulated samples**
3. **Sulfur now studied on CCC**

1. **Added more partners; will engage more**
2. **...and catalyst suppliers**

1. **Aging studies being performed on CCC with sulfur**
2. **will introduce sulfur to adsorbers**
3. **will consider design of experiments**

1. **Partnering with several universities, and are aligning their fundamental studies to address challenges of low temperature catalysts**
2. **NH₃-SCR evaluation not currently planned**
Summary

• **Relevance:** These studies are targeted towards providing data and predictive tools to address gaps in information needed to enable increased use of biofuels

• **Approach:** Targeted, engine-based and flow-reactor studies with in-depth characterization of PM, HCs, and emissions control devices to better understand fuel and lubricant effects

• **Collaborations:** Wide-ranging collaboration with industry, academia, and national labs maximizes breadth of study and guides research from other funding sources

• **Technical Accomplishments:**
  – Identified new mixed metal oxide candidates (USC) that have improved HC activity
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• **Future Work:** expanding effort with new materials to increase active sites and understand interactions with sulfur; increased implementation of multi-component beds and Pt+Pd catalysts
Technical Backup Slides
Evaluating Mn, Ce and Sn with good durability and HC oxidation

• Collaboration with U. South Carolina (USC)
  – MC: $\text{MnO}_x\text{-CeO}_2$
  – SMC: $\text{SnO}_2\text{-MnO}_x\text{-CeO}_2$
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• Catalysts show good HC activity and durability
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- Evaluated at ORNL with LTC-D protocol
  - Conditions more challenging, but improved HC reactivity observed w/o Pd
  - Efforts for improvement continuing at USC

OC and HC Conversion (%)
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CCC as a component in a PGM-containing system lowers the HC light-off temperature

- Pt deposited on CCC shows less activity than Pt/Al₂O₃
  - But better than CCC
- CCC in front of Pt/Al₂O₃ improves C₃H₆ oxidation
- Mixing CCC with Pt/Al₂O₃ gives best C₃H₆ activity
- Still need additional improvements to get to lower light off temperatures

Pt/Al₂O₃ = 1% wt. (nominal) Pt/Al₂O₃
Pt/CCC = 0.5% wt Pt on CCC
CCC+PA = 50:50 physical mixture (wt)
CCC→PA = Split bed
Observed exotherm is highest with Pt/Al$_2$O$_3$ + CCC
Trapping for low temperature emissions control

- DOCs able to oxidize HCs and CO at ~ 275 °C;
- SCR: active at ~175°C for NO
- Ideal process:
  - Trap HC+NO during cold start and low temperature operation
  - At higher temperatures, desorb from the surface when catalysts are active

Zeolites can be effective traps that have variable material properties

- Understand zeolites in HC and NO adsorption and desorption study to help optimize processes
- Systematic variation of key zeolite properties:
  - **Cation type** (H⁺ vs. Ag⁺)
  - H₂O, CO₂, NO
  - **Acidity** (low vs. high SiO₂/Al₂O₃)
  - Metal loading

Ion-Exchanged Zeolites.

- **Retain** olefins and aromatics at low T.
- **Resistance** to water adsorption.

Loading: 0, 1, 5 wt.%
Calcination: 500-750°C (2 h)

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