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)

Diesel exhaust temperatures lower than gasoline over drive cycle

Higher efficiency of LTC (RCCI) lowers exhaust temperatures


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

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

- 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

**Cost-effective and thermally stable materials durable to multiple pollutants**

**Innovate**

**Challenge**

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

**Understand**
Systematic approach to evaluate novel catalysts and modifications to established technology

Strategy ultimately aims to achieve EPA Tier 3 compliance

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

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

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

• PGM-free catalyst study, Cu-Ce-Co

• Study of trapping materials
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/SiO₂ and Pt/Al₂O₃ show impact from NO and HCs

• CeO₂-ZrO₂ support lowers oxidation temperature

• CeO₂-ZrO₂ 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\(^\circ\)C
  - Pd/ZrO\(_2\)-SiO\(_2\): 257\(^\circ\)C

- **After aging at 800\(^\circ\)C, Pd/Zr shows excellent stability**
  - Increase in \(T_{90}\) observed on Pd/ZrO\(_2\)-SiO\(_2\)
  - Improved zirconia adherence necessary

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**Reaction Conditions**: 0.4% ppm CO / 0.05% ppm NO / 0.0-0.1% C\(_3\)H\(_6\) +10% O\(_2\) + 5% H\(_2\)O in Ar, W/F = 0.19 g·h mol\(^{-1}\), GHSV of Pd/ZrO\(_2\) = 150,000 hr\(^{-1}\)
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Intriguing non-precious metal catalyst

- Ternary mixed oxide with aqueous synthesis
- Durability not fully vetted...nor activity in presence of HC+NO
PGM-free CuO\textsubscript{x}-CoO\textsubscript{y}-CeO\textsubscript{2} catalyst oxidizes CO below 200°C in presence of HC

- Co-precipitated CuO\textsubscript{x}, CoO\textsubscript{y}, and CeO\textsubscript{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)
Technical areas of study

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• Study of trapping materials
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)

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>SiO₂/Al₂O₃ molar ratio</th>
<th>Nominal cation form</th>
<th>Surface area (m²/g)</th>
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<tr>
<td>Beta</td>
<td>25</td>
<td>H⁺</td>
<td>680</td>
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<td>ZSM-5</td>
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</tbody>
</table>

• Systematic variation of key zeolite properties
  — Pore structure (Beta vs. ZSM-5)
  — Acidity (low vs. high SiO₂/Al₂O₃)
  — Cation type (H⁺ vs. Ag⁺) 5 wt% Ag loading obtained for both zeolite types (low SiO₂/Al₂O₃ cases)

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

Large and medium pore structures allow easy HC transport

In progress
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% O₂, 5% H₂O, 5% CO₂

650 °C pretreatment  adsorption  desorption

80 °C

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

- **Support Study**: increase accessible area of the coated ZrO$_2$ layer on SiO$_2$ for durability and acidity; ceria-zirconia
- **PGM-Free Catalyst**: 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$_3$O$_4$-CeO$_2$ suggests separate active sites for CO and HC oxidation
- **Traps**: 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

Objective: Develop emission control technologies that perform at low temperatures (<150°C) 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:

• Relevant BES-based publications:
Objectives

Develop durable emission control technologies that perform at low temperatures (<150°C) 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

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

- 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$_3$H$_6$ oxidation due to acidity generated
  - Promising for sulfur tolerance
  - Characterized the accessible area of ZrO$_2$ layer on SiO$_2$ (critical for durability)

- 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

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

**General Starting Point:** CO oxidation

**Challenge with HCs and NOx (plus other real exhaust):**
- NOx OK, but HCs problematic

**Study durability at relevant exhaust temperatures:**
- ZrO$_2$-CeO$_2$ improves durability to 800°C

**Study durability to potential catalyst poisons:**
- Sulfur problematic

**Candidate for engine application:**
- Effort idle for now

**Au@Cu System:**

**Support Study:**
- Lower CO and HC oxidation
- ZrO$_2$-SiO$_2$ durability can be improved

**Next step: increase coverage of ZrO$_2$ on SiO$_2$:**

**Durability and resistance to poisons yet to be investigated**

**PGM-Free CCC Catalyst:**
- CO oxidation not inhibited by HCs, but HC oxidation poor

**Effort just beginning; lots of remaining work**

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

- Even with low weight loading high activity shown with unaged sample
  - \(W/F = 0.25 \text{ g*h/mol}\)
    - \(\text{SV} = \sim 95,000 \text{ h}^{-1}\)
  - \(T_{50\%} = 50^\circ\text{C}\)
  - \(T_{90\%} = 94^\circ\text{C}\)

- Activity drops after aging at 800°C, but is still very high
  - \(T_{50\%} = 103^\circ\text{C}\)
  - \(T_{90\%} = 182^\circ\text{C}\)