Cold-Start and Low-Temperature Emissions Challenges

Bob McCabe
Ford Motor Company

2014 CLEERS Symposium
EVOLUTION OF HYDROCARBON EMISSION STANDARDS

HC REDUCED BY 96%

99.9% REDUCTION OVERALL

0.01 g/mi
### FTP NMHC Emissions*

#### 2008 Ford SULEV Focus Test Vehicle

(1 test vehicle; not intended to represent fleet certification data)

<table>
<thead>
<tr>
<th>Non-methane hydrocarbon (NMHC)</th>
<th>Engine-out (g/mi)</th>
<th>Tailpipe (g/mi)</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bag 1 (cold bag)</td>
<td>1.3500</td>
<td>0.0326</td>
<td>97.6</td>
</tr>
<tr>
<td>Bag 2 (hot bag)</td>
<td>1.0130</td>
<td>0.0000</td>
<td>100</td>
</tr>
<tr>
<td>Weighted overall</td>
<td>1.2539</td>
<td>0.0069</td>
<td>99.45</td>
</tr>
</tbody>
</table>

*At full useful life aging (150,000 mi dynamometer equivalent)
Cold-start strategies

Tailpipe HC Emissions (FTP Bag 1)

Catalyst "Light-Off" Temperature
Boosted engines: the cold-start challenge

- The turbochargers used in downsized, boosted engines result in significant delay of the close-coupled catalyst warm-up
- Catalyst light-off may not be fast enough to meet the most stringent emission standards, especially for larger engines

Data provided by Joanne Temple

Exhaust T traces for turbo- and non-turbo engines in the FTP cycle at the Light-off and Underbody catalyst locations. Note delay in warm-up for the GTDI system relative to the GDI system.
Decreasing Cold-Start Emissions

• Engine-out emissions

• Catalyst warm-up strategies

• Aftertreatment (Sensors & Catalytic Converter)
  – At full useful life in a brutal aging environment

All 3 need to work in concert to achieve low tailpipe emissions
Decreasing Cold-Start Emissions

• **Engine-out emissions**

• Catalyst warm-up strategies

• **Aftertreatment (Sensors & Catalytic Converter)**
  - At full useful life in a brutal aging environment

*All 3 need to work in concert to achieve low tailpipe emissions*
Engine-out emissions reduction

• Base Engine Design:
  – Fuel injection (injector type & location, rail pressure, etc.)
  – Cam, throttle, valves, cylinder, bore, spark plug design/orientation, intake/exhaust manifolds, etc.

• Calibration/Strategy:
  – Painstaking, dyno-based process of mapping emissions as a function of numerous controllable parameters (injection & spark timing, throttle position, cam settings, etc.)
  – Must be done for all of the phases of cold start: engine start; neutral idle, neutral in drive, drive-away)
Decreasing Cold-Start Emissions

• Engine-out emissions

• catalyst warm-up strategies

• Aftertreatment (Sensors & Catalytic Converter)
  – At full useful life in a brutal aging environment

All 3 need to work in concert to achieve low tailpipe emissions
Catalyst warm-up strategies

• Gasoline:
  – Spark retard strategies; increased engine rpm; early exhaust valve opening

• Diesel:
  – Post-injection (with fuel deposition on the DOC); EGR; throttling, etc.

• Gasoline and Diesel:
  – Catalyst heating represents “lost fuel” from a fuel economy/CO₂ penalty standpoint
Decreasing Cold-Start Emissions

- Engine-out emissions
- Catalyst warm-up strategies
- Aftertreatment (Sensors & Catalytic Converter)

All 3 need to work in concert to achieve low tailpipe emissions
Aftertreatment

• Sensors:
  – Universal exhaust gas oxygen sensors (UEGOs)
  – Fore and aft sensors for primary and “trimming” control (and OBD)
  – Fast light-off sensors

• Catalyst actions:
  – Pd-based close-coupled TWCs (highly loaded)
  – High cell density, thin-wall (low thermal mass) monoliths (primarily ceramic) – reaction engineering!!
  – More durable washcoat components (i.e. stabilized aluminas and ceria-zirconia materials, etc.)

Note: More exotic approaches such as electrically heated catalysts, by-pass starter cats, HC traps, etc. have not yet seen widespread commercial application
Catalyst Light-off: Diesel

SAE 2009-01-1268 Katare & Laing

Ford lab reactor DOC data

FTP Bag 1 avg E.O. CO for (left to right): HD- & LD-diesel and gasoline vehicles

CO light-off in simulated diesel exhaust with 1000 & 5000 ppm CO in feed (solid=data; dash=model)
Pt-Pd DOCs

Data of Douglas Dobson (Ford)

HC Light-Off Conversion
2-Mode 100 hrs / 300 ppm S + 20 mgP/gal

- New urea-SCR catalysts decrease need for NO oxidation by DOC
- Main DOC need is HC oxidation
- Pd stabilizes Pt particles and improves HC oxidation
Particle size distributions by TEM (900°C-aged)

ALPS: Anomalously Large Particles

ALPs believed result from PtO₂ volatilization

Research Challenge: Making alloy particles

- Initially prepared (500°C calcined) 50/50 Pt:Pd/Al2O3 co-impregnated sample produces a bi-modal distribution of Pd-rich and Pt rich particles
- Aging at 900°C in O2 causes full alloying, but at the expense of particle growth

Ezekoye, et al., J. Catalysis 280 (2011) 125
Vehicle HC Light-off: Diesel vs Gasoline

- DOC is clearly lit off by 200°C; Gasoline warm-up is much quicker but complete light-off not observed until cat inlet temp is above 400°C.

- Diesel has the advantage of lower CO&HC engine-out emissions and leaner $\lambda$. Gasoline benefits from greater heat flux.

- The lower warmed-up temperatures of diesel exhaust also provide a catalyst durability benefit relative to gasoline.
What controls TWC light-off?

What can we do about it?
## Model Pd Catalysts

### Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Support Type</th>
<th>BET (m²/g)</th>
<th>Pd model catalyst</th>
<th>Pd dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃ (Sasol)</td>
<td>Al₂O₃</td>
<td>146</td>
<td>144</td>
<td>1.4</td>
</tr>
<tr>
<td>Pd/Stab-CZO (Rhodia)</td>
<td>Stab-CZO</td>
<td>82</td>
<td>79</td>
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</tbody>
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### Aging effect on Pd dispersion

<table>
<thead>
<tr>
<th>Aging T (°C)</th>
<th>Al₂O₃ Lean</th>
<th>Al₂O₃ Rich</th>
<th>Stab-CZO Lean</th>
<th>Stab-CZO Rich</th>
</tr>
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<tbody>
<tr>
<td>Fresh 500C cal in air</td>
<td>16.5</td>
<td>15.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>14.4</td>
<td>7.2</td>
<td>15.2</td>
<td>5.6</td>
</tr>
<tr>
<td>700</td>
<td>12.7</td>
<td>5.8</td>
<td>17.5</td>
<td>3.8</td>
</tr>
<tr>
<td>850</td>
<td>5.2</td>
<td>3.7</td>
<td>8.0</td>
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Model catalyst study done under Ford URP with U Michigan [Data by Xiaoyin Chen (UM) and Yisun Cheng (Ford)]

₉Obtained from H₂ chemisorption.
CO Light Off on Pd/Al₂O₃

Light-off Temp:
- Pd particle size: Small < Large
- Aging feed: Lean < Rich
- CO oxidation favored by pre-oxidation and leaner $\lambda$

CO Light Off, Lean vs. Rich Aging
Lambda = 1.01, Pre-oxidized

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<tr>
<th>Aging T (°C)</th>
<th>Disp. (%)</th>
<th>CO TOF (s⁻¹) @195 °C</th>
<th>$T_{50}$ CO (°C)</th>
<th>$T_{50}$ C₃H₆ (°C)</th>
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<tr>
<td>550</td>
<td>14.4</td>
<td>0.19</td>
<td>210</td>
<td>N/A</td>
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<tr>
<td>700</td>
<td>12.7</td>
<td>0.21</td>
<td>210</td>
<td>220</td>
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- Note roughly constant TOF despite aging from 550 to 1000 °C
- Implies structure insensitive reaction
- Intrinsic kinetic rate doesn’t change; only number of exposed Pd atoms
Nature of the CO Light-off

On $\text{Al}_2\text{O}_3$:

$\text{O}_2$ adsorption is rate limiting and prevents light-off until CO begins to desorb and opens sites for $\text{O}_2$ adsorption and dissociation.
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^g Obtained from H₂ chemisorption.
“Super” CO Light Off on Pd/Stab-CZO

CO Light Off

- Pd/Stab_CZO, 700C Lean Aged
  Light off before 90C
- Pd/Stab_CZO 1000C Lean Aged
- Pd/Al2O3 700C Lean Aged
- Pd/Al2O3 1000C Lean Aged

CO Conversion, %

Oven Temperature, °C

0 10 20 30 40 50 60 70 80 90 100

100 150 200 250
Nature of the Super CO Light-off

**On Al$_2$O$_3$:**
O$_2$ adsorption is rate limiting and prevents light-off until CO begins to desorb and opens sites for O$_2$ adsorption and dissociation.

**On CZO:**
CO surface-diffuses to CZO interface and reacts with O-atoms from the CZO. O-atoms are replenished by direct O$_2$ adsorption on CZO from the gas phase.
DRIFTS confirmation of CO reaction with O from Stab-CZO (under Ar purge)

- Spectra in flowing Ar
- Scans obtained after 32 minutes Ar purging
- CO desorption observed from Pd on both supports
- CO completely consumed by reaction with oxygen from Stab-CZO at 90°C
- Similar observations from TGA experiments

Data of Yisun Cheng
Why can’t super CO light-off be realized on a vehicle?
C₃H₆ Light Off: Pd/Stab-CZO vs Pd/Al₂O₃

C₃H₆ Light Off: Pre Oxidized @ Lambda=1.05

Conversion, %

Temperature, C
C$_3$H$_6$ adsorption on Pd(111)

- C$_3$H$_6$ adsorbs molecularly, but weakly on Pd.
- Adsorption at RT or above results in dehydrogenation leading to stable surface species as confirmed by reflection-absorption IR and TPD.
- These species may impede light-off by blocking sites for both C$_3$H$_6$ and O$_2$ adsorption. (i.e. not unlike CO)
- Intermediates may be much less mobile than CO.
CO and $\text{C}_3\text{H}_6$ Mixture Light Off: Pd/Stab-CZO vs Pd/Al$_2$O$_3$

**Pd/Al$_2$O$_3$**

- Mutual inhibition of both reactions
- Consistent with competitive adsorption of CO and $\text{C}_3\text{H}_6$ intermediates

**Pd/Stab-CZO**

- $\text{C}_3\text{H}_6$ completely shuts off the low-T CO oxidation mechanism
- Mutual inhibition and competitive adsorption as for Al$_2$O$_3$
Prospects for lowering C$_3$H$_6$ light-off temperature

Assuming 850°C rich-aging may emulate a “low-T combustion” TWC system

…if so, our data suggest:

1. Reducing pre-treatment is critical (favors C$_3$H$_6$ adsorption?)
2. Extremely lean $\lambda$ helps on pre-reduced catalyst (promotes O$_2$ adsorption and C$_x$H$_y$ reaction?)
Emission challenges for gasoline low-temperature combustion aftertreatment

- Still need high-temperature catalyst durability (rich and lean) – assume at least 850°C max catalyst temperatures for an advanced gasoline combustion system.
- Need a way to briefly produce very lean light-off conditions (and still manage NOx).
- Cannot back-track on engine-out emissions
- Need high heat flux to the catalyst during cold start.
- May need to pre-condition the catalyst surface.
- **We will still need to pursue a combined strategy of engine design, calibration/strategy, and aftertreatment system optimization to be successful**
Suggestions for low L.O. temp catalyst discovery

- Understand what is limiting light-off
- Don’t underestimate durability requirements
- Consider variations on proven catalyst formulations as well as novel materials
- Emulate engine conditions as much as possible (CLEERS protocol is a good start)
- Success is more than new materials & chemistry; reaction engineering is important
Researchers at Daihatsu claimed discovery of an intelligent catalyst based on Pd supported on perovskite materials. The catalyst’s intelligence was attributed to facile migration of the Pd into and out of the perovskite structure in response to rich and lean AF excursions:

- Pd (rich)  Pd (lean)

The catalyst may not work as originally suggested, but does have potential merit for stabilizing small Pd particles against sintering.

Self-regenerating Pd/LaFeO$_3$ catalyst concept based on UM study by Katz et al. (2011) 18090
Suggestions for low L.O. temp catalyst discovery

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- Don’t underestimate durability requirements
- Consider variations on proven catalyst formulations as well as novel materials
- Emulate engine conditions as much as possible (CLEERS protocol is a good start)
- Success is more than new materials & chemistry; reaction engineering is important
Don’t overlook reaction engineering


- Light-off occurs under conditions where the transition from kinetic control to mass transfer control occurs
- “Powder” studies may show large washcoat diffusion (WD) effects:
  - 10-20 micron thick monolith washcoat
  - **100-200** micron diameter powder particles
- CO oxidation kinetics couple with WD to give non-isothermal effectiveness factors and masked kinetic orders
Acknowledgments

• Douglas Dobson (Ford) – for help pulling together the diesel material
• Xiaoyin Chen (UM) and Yisun Cheng (Ford) for the model TWC data