EMISSION BENEFITS AND LIMITATIONS OF PASSIVE HYDROCARBON ADSORBER TECHNOLOGIES

Michelle H. Wiebenga, Se H. Oh and Gongshin Qi
General Motors Research and Development, Warren, MI 48092

CLEERS 2016 April 6\textsuperscript{th}, 2016
Contact: michelle.wiebenga@gm.com
OVERVIEW

• Background – Passive HC Adsorbers
• Methods – Establishing Testing Protocol
  • HC selection
  • Reactor design
  • Sample information
• Results & Discussion
  • Controlling various HCs
  • Aging effects
  • Space velocity and Pd loading
BACKGROUND - PASSIVE HC ADSORBER CATALYSTS

- Ability to store high concentrations of HCs during engine cold-start
- Ability to effectively convert (oxidize) stored HCs as they are released
- Good thermal durability

Three-way catalyst coating

Typical HC adsorber coating

Desired Characteristics:

- Ability to store high concentrations of HCs during engine cold-start
- Ability to effectively convert (oxidize) stored HCs as they are released
- Good thermal durability

Source: Nissan, SAE Paper 2001-01-0892
THREE WAY CATALYST HYDROCARBON LIGHT-OFF

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>HC Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>0</td>
</tr>
</tbody>
</table>

Inlet HC

HC Concentration

T-50 of TWC
50°C Inlet HC

Inlet HC Concentration

Store HC below TWC light-off Temp

Release HC above TWC light-off temp

IDEAL

Oxidize all stored HC
HC ADSORBER FUNCTION - REALITY

Temperature (°C)

HC Concentration (ppm)

Inlet HC

Partial storage of HC

Release HC below or near light-off temp

T-50 of TWC

HC Concentration

Oxidize some portion of stored HC
SIMULATED EXHAUST HYDROCARBON SELECTION

- Hydrocarbons common to gasoline exhaust:
  - Shorter chain olefins (C₂-C₆)
  - i-pentane is the major C₅ paraffin
  - i-octane is the major C₈ paraffin
  - Major aromatic components are C₇-C₉
- The concentration of normal paraffins is typically low
REACTOR SYSTEM

- Gaseous components fed via MFCs
- Liquid HC fed via Bronkhorst evaporator
- Feed was stabilized in bypass before switching over catalyst
- $T_{in}$ and $T_{out}$ measured in gas ~2mm from sample

[Diagram showing reactor system with reactant gas manifold, heated lines, core sample, and FTIR spectrometer]
HC ADSORBER SAMPLES AND AGING

Aging performed in lab reactor with L/R cycling - 5s 3% CO, 5s 3% O\textsubscript{2}; N\textsubscript{2} all other times; always with 10% H\textsubscript{2}O, 10% CO\textsubscript{2}

<table>
<thead>
<tr>
<th>HC Adsorber</th>
<th>Pd:Rh (g/ft\textsuperscript{3})</th>
<th>50h/800°C</th>
<th>50h/850°C</th>
<th>50h/900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-10</td>
<td>10:2</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-50</td>
<td>50:2</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>A-100</td>
<td>100:2</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-50</td>
<td>48:2</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-70</td>
<td>68:2</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>B-100</td>
<td>98:2</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X = Tested

Main focus of this study

- Two different passive HC adsorber technologies (each with varied PGM loadings)
- Three different aging temps: 800, 850, 900°C
EXAMPLE RUN – SAMPLE A-50, 800°C AGED

1. Pretreat 30 min/500°C with O\textsubscript{2} & H\textsubscript{2}O
2. Stabilize feed in BYPASS
3. Switch feed over catalyst at 75°C – ADSORPTION
4. Cut off HC flow after 1 minute
5. Immediately set inlet gas temp to 500°C and begin ramping (~40 °C/min) – DESORPTION & OXIDATION

<table>
<thead>
<tr>
<th></th>
<th>PRETREAT.</th>
<th>ADS.</th>
<th>DES. &amp; OX.</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-pentane</td>
<td>0</td>
<td>70 ppm</td>
<td>0</td>
</tr>
<tr>
<td>iso-octane</td>
<td>0</td>
<td>50 ppm</td>
<td>0</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0</td>
<td>100 ppm</td>
<td>0</td>
</tr>
<tr>
<td>propylene</td>
<td>0</td>
<td>250 ppm</td>
<td>0</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>500 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>10%</td>
<td>5610 ppm</td>
<td>5610 ppm</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
</tbody>
</table>

Note: No CO\textsubscript{2} in feed so that it could be used for carbon balance; 2300 ppm C1 HC during Ads.
### ADSORPTION PHASE

**TWC - 800°C Aged**

- **C₃H₆**
- **m-C₈H₁₀**
- **i-C₅H₁₂**
- **i-C₈H₁₈**

**HC Adsorber A-50 - 800°C Aged**

- **C₃H₆**
- **m-C₈H₁₀**
- **i-C₅H₁₂**
- **i-C₈H₁₈**

<table>
<thead>
<tr>
<th>% Storage Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₆</td>
</tr>
<tr>
<td>A-50 800°C</td>
</tr>
</tbody>
</table>

- TWC case comparable to empty reactor † no adsorption
- Adsorption of HC is real, not artifact of valve switching
- Case without adsorption integrated to determine total HC exposure
**DESORPTION AND OXIDATION PHASE**

**TWC - 800°C Aged**

**HC Adsorber A-50 - 800°C Aged**

- TWC stores no HC
- Order of release: i-pentane, i-octane, m-xylene (No propylene release)
- m-xylene is almost entirely oxidized here ‡ cannot determine true desorption temperature of m-xylene
PINPOINTING DESORPTION TEMP – TESTING IN ABSENCE OF O₂

- Peak desorption temperatures appear lower due to oxidation
- A significant portion of m-xylene and smaller portion of i-octane are oxidized on the 800°C aged adsorber
- i-pentane desorbs well before light-off

Both aged 50h/800°C/10%H₂O
EFFECT OF AGING ON DESORPTION TEMPERATURES – SAMPLE A-50

After 900°C aging all desorption peaks shift to lower temperature (10-30°C shift)

Desorption peak temperature of m-xylene is 30°C lower
**IMPACT OF AGING – SAMPLE A-50**

*Temperature Programmed Desorption/Oxidation*

<table>
<thead>
<tr>
<th>% Storage Efficiency</th>
<th>% Oxidation Efficiency of Stored HC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C3H6</td>
</tr>
<tr>
<td>A-50 800°C</td>
<td>38%</td>
</tr>
<tr>
<td>A-50 850°C</td>
<td>0%</td>
</tr>
<tr>
<td>A-50 900°C</td>
<td>0%</td>
</tr>
</tbody>
</table>

- Propylene storage deteriorates after aging at 850°C or higher
- i-octane and m-xylene storage are maintained with aging, but desorption shifts to lower temperature
- Less i-pentane stored with aging and desorption shifts to lower temperature
EFFECT OF AGING ON ADSORPTION CAPACITY AND LIGHT-OFF TEMPERATURE – SAMPLE A-50

1. PRETREAT 30 min with \( \text{O}_2 \) & \( \text{H}_2\text{O} \)
2. Cool RCTR to 75°C and stabilize feed in bypass
3. Switch feed over catalyst, 2h ADSORPTION at 75°C

Adsorption to Saturation – 800°C Aged

<table>
<thead>
<tr>
<th>Sample A-50</th>
<th>Quantity Adsorbed (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C Aged</td>
<td>15.8</td>
</tr>
<tr>
<td>900°C Aged</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Deactivation mechanisms at 900°C:
- Desorption peaks shift to lower temperature
- Oxidation (T-50) shifts to higher temperature
- Propylene storage capability is lost
- Total storage capacity is unaffected
OVERALL OXIDATION EFFICIENCY (% OF EXPOSED HC OXIDIZED) COMPARED TO ADSORBER B

* THC Oxidation Efficiency Calculated as Average of: (Exposed C1 HC - Released C1 HC), (CO+CO₂ Measured) / (Exposed C1 HC)

- ~45% of exposed HC are oxidized on A-50 aged at 800°C
- Adsorber B has significantly lower performance (30%)
- After 850°C both < 30%, after 900°C both < 10%
- For 800°C aged samples, significant differences in propylene and m-xylene performance (otherwise similar)
SPACE VELOCITY EFFECT – SAMPLE A-50

THC Oxidation Efficiency at 30k vs 60k h⁻¹

* THC Oxidation Efficiency Calculated as Average of:
  (Exposed C1 HC - Released C1 HC), \((\text{CO+CO}_2\text{ Measured})\)
  (Exposed C1 HC)

<table>
<thead>
<tr>
<th></th>
<th>C₃H₆</th>
<th>m-C₈H₁₀</th>
<th>i-C₈H₁₈</th>
<th>i-C₅H₁₂</th>
<th>% of Exposed HC Stored</th>
<th>% Oxidation Efficiency of Stored HC</th>
</tr>
</thead>
<tbody>
<tr>
<td>30,000 h⁻¹</td>
<td>38%</td>
<td>100%</td>
<td>100%</td>
<td>84%</td>
<td>100%</td>
<td>94%</td>
</tr>
<tr>
<td>60,000 h⁻¹</td>
<td>24%</td>
<td>92%</td>
<td>85%</td>
<td>57%</td>
<td>100%</td>
<td>67%</td>
</tr>
<tr>
<td>60,000 h⁻¹ (Blank in Front)</td>
<td>23%</td>
<td>92%</td>
<td>85%</td>
<td>56%</td>
<td>100%</td>
<td>76%</td>
</tr>
</tbody>
</table>

All aged 50h/800°C/10%H₂O

- At 30k h⁻¹ HC exposure is only 5% of the storage capacity (10% at 60k)
- Adsorption and oxidation rates are space velocity sensitive
- Longer sample may be able to re-adsorb HC downstream
**PALLADIUM LOADING EFFECT**

*THC Oxidation Efficiency (C1 Basis)*

- Increasing Pd loading of Sample A improves:
  - Propylene storage
  - M-xylene oxidation
- Effect of increased Pd is minor for Sample B

* THC Oxidation Efficiency Calculated as Average of:
  (Exposed C1 HC - Released C1 HC),   (CO+CO₂ Measured)
  (Exposed C1 HC)

**All aged 50h/800°C/10%H₂O**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd Loading (g/ft³)</th>
<th>% Storage Efficiency</th>
<th>% Oxidation Efficiency of Stored HC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₃H₆</td>
<td>m-C₈H₁₀</td>
</tr>
<tr>
<td>A-10</td>
<td>10</td>
<td>13%</td>
<td>100%</td>
</tr>
<tr>
<td>A-50</td>
<td>50</td>
<td>38%</td>
<td>100%</td>
</tr>
<tr>
<td>A-100</td>
<td>70</td>
<td>61%</td>
<td>100%</td>
</tr>
<tr>
<td>B-50</td>
<td>100</td>
<td>17%</td>
<td>100%</td>
</tr>
<tr>
<td>B-100</td>
<td>20</td>
<td>26%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Relatively high storage of propylene on adsorber A (always completely oxidized)
Propylene storage seems to be linked to Pd content
EFFECT OF NO - PROPYLENE VS. M-XYLENE

**THC Oxidation Efficiency (C1 Basis)**

<table>
<thead>
<tr>
<th>NO Concentration</th>
<th>% of Exposed HC Stored</th>
<th>% Oxidation Efficiency of Stored HC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C3H6</td>
<td>m-C8H10</td>
</tr>
<tr>
<td>0 ppm NO</td>
<td>69%</td>
<td>100%</td>
</tr>
<tr>
<td>200 ppm NO</td>
<td>57%</td>
<td>100%</td>
</tr>
<tr>
<td>500 ppm NO</td>
<td>38%</td>
<td>100%</td>
</tr>
</tbody>
</table>

- As NO concentration increases:
  - Less C₃H₆ stores
  - More m-xylene is oxidized
  - Overall % C1 HC oxidized is constant
- NO may inhibit adsorption of propylene
- Less propylene desorbing allows more m-xylene to be oxidized (similar T-50)

* THC Oxidation Efficiency Calculated as Average of:
  (Exposed C1 HC - Released C1 HC),  (CO+CO₂ Measured)
  (Exposed C1 HC)                     (Exposed C1 HC)

* All aged 50h/800°C/10%H₂O
CONCLUSIONS

- Hydrocarbon make-up critical to overall HC adsorber performance
- Olefins and aromatics ‡ controlled to some degree
- Alkanes ‡ difficult to control
  - i-octane stores but releases before T-50
  - i-pentane stores <70% and releases well before T-50
- 900°C aging destroys performance of all adsorbers tested, but zeolite does not collapse
  - Total storage capacity is unaffected
  - Oxidation (T-50) shifts to higher temperature
  - Desorption peaks shift to lower temperatures
- Propylene storage appears to be linked to Pd sites

Controllable

Improvement Needed

Durability
≥ 850°C
THANK YOU FOR YOUR ATTENTION!

Questions?