The impacts of Pd in BEA zeolite on decreasing cold start HC emission of an E85 vehicle

Lifeng Xu*, Jason Lupescu, Jeffery Hepburn, Giovanni Cavataio, Kevin Guo, Paul Laing, Hungwen Jen & Rachael Harrington

Research and Innovation Center
Ford Motor Company

*Contact information: Lxu1@ford.com
Outline

• Introduction
• Experimental
• Results & discussions
• Summary
Introduction

• More stringent emission regulations LEV III
  – In 2025, 100% light-duty vehicle meet NMOG+NOx emissions standards of 30 mg/mile (about a 76% decrease from LEV II (125mg/mile))

• Cold-start & cold-start NMOG emissions
  – Cold-start NMOG emission counts for 80~90% of total NMOG emission of vehicles in FTP 75 test cycles
  – Cold-start NMOG emission nearly double when E85 fuel is used in a flex fuel vehicle (95% of total NMOG emission)
  – Reducing cold start NMOG emission, especially from E85 fuel is critical for a flex fuel vehicle to meeting LEV III standards
Introduction (continued)

A 2012MY 2.0L gasoline direct injection (GDI) naturally aspirated Ford Focus with E85 fuel

- The left chart shows the compositions of NMOG slipping out of close-coupled TWC during cold start (from 0 to 50 seconds measured by FTIR), which counts for 95% of the total NMOG emission over FTP75 as shown in right figure.
Introduction (continued)

• Solution - cold start catalyst
  – It adsorbs NMOG at cold start and releases out at high T when TWC lights off
  – It’s composed of two key elements, cold start emission adsorbents (aluminosilicate zeolites) and TWC catalyst

• Zeolites
  – A crystalline material of tetrahedral silica (SiO$_4$) with alumina (AlO$_4^-$) bonded in a network of rings (as pores) that traps HC molecules of smaller sizes
  – A Brønsted acid site can attract or protonate stored HC species
  – Ion-exchange of the cation, like Ag$^+$, Pd$^{2+}$ or Cu$^{2+}$ achieves a stronger adsorption (chemisorption) by sharing electrons with C=C bonds
Introduction (continued)

• Challenges
  – Zeolites of existing HC trap NMOG release out temperature is too low (<200°C) compared to the TWC light off temperature (~300°C) to have a high cold start NMOG conversion efficiency

• Our approaches
  – Modify zeolites by adding Pd & other metals to increase cold-start adsorption, improve the cold-start NMOG release temperature and conversion
  – Pd in BEA zeolite improves the ethanol release temperature, chemically alter the reactions and products in favor of overall ethanol conversions
  – Pd added to zeolite may also serve as a catalyst for reactions
  – Vehicle test results confirmed improvement in reducing cold start NMOG emissions by Pd-zeolite based HC trap
Experimental

• BEA 25 powder catalyst
  – Pd was added to BEA 25 zeolite through incipient wetness impregnation of Pd(NO$_3$)$_2$ solution;
  – Calcination at 650°C for 2 hours in oven with air;
  – Powder size: 80 to 40 meshes (0.250 to 0.425mm in diameter);

• Sample aging conditions – lab 4-mode at 750°C 25cycles
  – Stoichiometry 41 min: 2%CO2+5%H2O
  – Rich 6 min: 1% (severe) or 1500ppm CO/H2 (mild)+2.0%CO2+5%H2O
  – Stoichiometry 5 min: 2%CO2+5%H2O
  – Lean 8 min: 2%O2+2%CO2+5%H2O
Experimental

Typical laboratory test includes adsorption and desorption

Adsorption: room temperature for 30 seconds, N₂+10%H₂O & adsorption gases;
Desorption: heating rate 60°C/min in N₂+10%H₂O or selected desorption gases
Vehicle cold-start NMOG emissions & temperature profile over FTP 75 cycles

A 2012MY 2.0L gasoline direct injection (GDI) naturally aspirated Ford Focus over FTP 75 cycles

- Most of the inlet emissions were stored over the first 30s, then less than half of the stored emissions were released unconverted through 250s
- The HC trap temperature profile produced a weighted effective temperature (Teff) of 1400°F or 760°C for a 25h aging cycle for the HC trap
Results and discussions

• Cold-start ethanol trapping and TPD
  – BEA25 fresh & aged
  – BEA25+Pd fresh & aged
  – BEA25 and Pd-BEA25 powder mixture with TWC
  – Ethanol reaction mechanisms during the releases

• Vehicle cold start ethanol and NMOG results
Fresh BEA 25 pre-lean treated Ads: 450ppm ethanol+10%H2O
ethanol trapping efficiency: 98.1%
Des: 10%H2O+N2
ethanol release: 42.2%, ethylene: 46.1%

Lab mild age BEA 25 pre-lean treated Ads: 450ppm ethanol+10%H2O
ethanol trapping efficiency: 97.3%
Des: 10%H2O+N2
ethanol release: 96.7%, ethylene: 3.6%

\[ \text{CH}_3\text{-CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

- After aging, BEA 25 releases out most of the stored ethanol at low T
- Ethanol dehydration reaction mechanism is minimized after aging
Adding Pd to BEA25 reduces ethanol slip and significantly decreases ethylene generation.

After aging, Pd-BEA 25 retains low ethanol slip compared with BEA 25 only results.
• Adding Pd to BEA 25 significantly decreases the ethanol slip.
• Increase Pd loading beyond 0.2wt% doesn’t show significantly more benefits
Lab simple mixture of particles, severe age 0.5g BEA25+0.25gTWC, pre-lean treated Ads: 450ppm ethanol+10%H2O ethanol trapping efficiency: 95.4% Des: 10%H2O+N2 Stored ethanol release ethanol: 49.3%, acetaldehyde: 9.2% CH4: 7.3%, CO: 0.4%, CO2: 33.7%

Lab simple mixture of particles, severe age 0.5g BEA25+0.2%Pd+0.25gTWC, pre-lean treated Ads: 450ppm ethanol+10%H2O ethanol trapping efficiency: 94.7% Des: 10%H2O+N2 Stored ethanol release ethanol: 30.7%, acetaldehyde: 17.6% CH4: 16.1%, CO: 3.0%, CO2: 32.7%

- After severe aging, Pd-BEA 25 ethanol slip increases
- TWC enhances ethanol oxidation and generates CO2 at high T
• Pd in BEA 25 significantly decreases the ethanol slip (> 30%)
Ethanol reaction mechanisms over Pd-BEA25 during TPD

Lab aged BEA 25+0.2%Pd, pre-lean treated Ads: 450ppm ethanol+10%H2O ethanol trapping efficiency: 96.6% Des: 10%H2O+N2 ethanol release: 28.3% (peak: 53.7 ppm) acetaldehyde: 20.89 % (peak 71.0ppm); CH4: 19.1%

Lab aged BEA 25+0.2%Pd, pre-lean treated Ads: 450ppm ethanol+10%H2O ethanol trapping efficiency: 93.5% Des: 10%H2O+N2+300ppm CO ethanol release: 39.8% (peak: 93.0 ppm), acetaldehyde: 37.1% (peak: 92.3 ppm); CH4: 6.3%

CH$_3$-CH$_2$OH $\rightarrow$ CO + CH$_4$+H$_2$ \hspace{1cm} (1)
CH$_3$-CH$_2$OH $\rightarrow$ CH$_3$-CHO + H$_2$ \hspace{1cm} (2)
CH$_3$-CHO $\rightarrow$ CO + CH$_4$ \hspace{1cm} (3)

• Stored ethanol reaction in Pd-BEA25 starts with (2) & (3) at low T; and then Reaction (1) when T increases
Reference


Vehicle test results (FTP 75) – cold-start NMOG

A 2012MY 2.0L gasoline direct injection (GDI) naturally aspirated Ford Focus over FTP 75 cycles

<table>
<thead>
<tr>
<th></th>
<th>NMOG (0-250s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η_A [%]</td>
</tr>
<tr>
<td>No Pd in zeolite</td>
<td>74%</td>
</tr>
<tr>
<td>+ TWC 25g/ft³</td>
<td></td>
</tr>
<tr>
<td>Pd in zeolite+TWC</td>
<td></td>
</tr>
<tr>
<td>Total 15g/ft³</td>
<td>78%</td>
</tr>
</tbody>
</table>

Overall Efficiency, η_O [%] = η_A [%] * η_X [%]

- Pd-zeolite based HC trap demonstrates significantly decreased ethanol slip and higher cold-start NMOG conversion
Summary*

- After laboratory 4-mode aging at 750°C, BEA 25 releases out most stored ethanol as ethanol at low temperature and the ethanol dehydration reaction becomes insignificant.
- Adding Pd to BEA25 significantly decreases ethanol slip and alters ethanol release reactions. However, when a Pd loading higher than 0.2wt%, further improvement in reducing ethanol slip becomes less significant.
- With Pd in BAЕ 25, the release of stored ethanol reaction starts with ethanol dehydrogenation & acetaldehyde decomposition reactions, followed by ethanol decomposition reaction with temperature increasing.
- Pd-zeolite based HC trap greatly reduces cold start NMOG emissions of a flex fuel vehicle running E85 fuel.

* Pd in zeolite is not thermally stable and sinters easily under high temperature rich conditions; A metal stabilizer “M” helps to keep Pd dispersed in zeolite and Pd-BEA25 retain activities after aging. Due to time constraints, this part of the work will not be presented.
Backup slides
• Ethanol reaction mechanisms at zeolite
  – Ethanol dehydration at bronsted acid sites of zeolites to Ethylene is the very well known ethanol reaction mechanism

\[ \text{CH}_3\text{-CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

  – However, after aged at 750°C, most bronsted acid sites of BEA zeolite disappear
  – In our work, when Pd is added to the zeolite, ethanol dehydration is no longer a significant release (reaction) mechanism
Ethanol Reaction Mechanisms from literatures*

• Ethanol decomposition
  \[ \text{CH}_3\text{-CH}_2\text{OH} \rightarrow \text{CO} + \text{CH}_4 + \text{H}_2 \]  
  (1)

• Ethanol dehydrogenation & acetaldehyde decomposition
  \[ \text{CH}_3\text{-CH}_2\text{OH} \rightarrow \text{CH}_3\text{-CHO} + \text{H}_2 \]  
  (2)
  \[ \text{CH}_3\text{-CHO} \rightarrow \text{CO} + \text{CH}_4 \]  
  (3)

• Water gas shift & methane steam reforming
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  
  (4)
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  
  (5)

* Ethanol dehydrogenation & acetaldehyde decomposition is very well accepted ethanol reaction mechanisms over Pd-based catalyst in fuel industry
0.5g BERA25+0.2wt%Pd mild aged pre lean
Ads: 0ppm ethanol+10%H2O 30s 2L
des: 10%H2O+300ppmCO; heat up from 30C to 600C at 60c/min