Zeolite Supported Pd Catalysts for Low Temperature NOx and HC storage

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Outline

- Challenges in controlling NOx and HC emissions at low temperatures
- Development of zeolite supported Pd catalysts for low temperature NO/HC storage and conversion
- Characterization of the active sites in zeolite supported Pd catalysts
- Fully formulated catalysts with zeolite supported Pd catalysts
- System demonstration on vehicles
- Modelling study
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Federal Tier 3 and CA LEV III emission standards call for significant reduction of criteria pollutants

**Federal Tier 3 standards**

<table>
<thead>
<tr>
<th>Bin</th>
<th>NMOG+NOx</th>
<th>PM*</th>
<th>CO</th>
<th>HCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bin 160</td>
<td>160</td>
<td>3</td>
<td>4.2</td>
<td>4</td>
</tr>
<tr>
<td>Bin 125</td>
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<td>3</td>
<td>2.1</td>
<td>4</td>
</tr>
<tr>
<td>Bin 70</td>
<td>70</td>
<td>3</td>
<td>1.7</td>
<td>4</td>
</tr>
<tr>
<td>Bin 50</td>
<td>50</td>
<td>3</td>
<td>1.7</td>
<td>4</td>
</tr>
<tr>
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<td><strong>30</strong></td>
<td><strong>3</strong></td>
<td><strong>1.0</strong></td>
<td><strong>4</strong></td>
</tr>
<tr>
<td>Bin 20</td>
<td>20</td>
<td>3</td>
<td>1.0</td>
<td>4</td>
</tr>
<tr>
<td>Bin 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**California LEV III standards**

Figure 1. LEV III Fleet Average NMOG+NOx Standards

LDT1: 0–3750 lbs LVW. LDT2: 3751–8500 lbs LVW.

www.dieselnet.com
Fuel economy and Green House Gases (GHG) are also part of the future emission legislations.

**Additional GHG limits:**
- $N_2O$: 0.010 g/mile
- $CH_4$: 0.030 g/mile

www.theicct.org
Advanced engines can improve the fuel efficiency, but result in lower exhaust temperatures

- Advanced combustion, downsizing of engine, turbocharging, all result in lower exhaust temperatures

- Diesel CO₂ reduction leads to even lower exhaust temperatures
Control of cold-start emissions is crucial to meet the future emission regulations

- e.g. SULEV30 (HC + NOx = 30 mg/mile)
  - Current TWC, DOC, SCR, NAC catalysts function at >~200°C
  - ~100-200s for these components to reach the operating temp
  - Engine-out HC/NOx emissions exceed SULEV30 during the cold start period
Zeolite based HC traps can store HC’s at low temperatures, but release them too early.

HC storage at 80°C
1500ppm HC inlet

HC release
Temp ramping rate 40°C/min

Zeolite
Zeolite/M1
Zeolite/M2
Conventional NACs store NO at LT but with low trapping efficiency, oxidation of NO to NO\textsubscript{2} is kinetically limited at LT.
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• Modelling study
Laboratory evaluation protocol

- NO/HC storage, release, and conversion testing

![Graph showing temperature changes over time with labeled time periods: Preconditioning, NOx, CO, HC on, Storage, 100 s (storage), TPR 100°C/min.]

- 
  - Preconditioning: 10% O₂ / 5% H₂O / 5% CO₂
  - Storage: 200 ppm NO/200 ppm CO/500 ppm (C₁)(C₁₀H₂₂)/10% O₂ / 6% H₂O / 6% CO₂
  - TPR: 100°C/min

- S.V.: 30,000 hr⁻¹
  - (Flow rate = 21.2 L / min)

- Hydro-thermally aged 750°C/5% H₂O/16h
Zeolite supported Pd catalysts exhibit high NO storage capacity with nearly 100% trapping efficiency.
Zeolite structures have a strong influence on the temperature profiles of the NOx storage capacity.
Zeolite structures also affect the NOx release profiles
Zeolite structures affect the HC storage and release profiles – the larger the pores, the higher HC storage capacity
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Pd is located at the exchange sites of the zeolite supports.

IR spectra of 1%Pd/Zeolite (red) and bare zeolite (black) samples after dehydration at 400 °C under 6%O₂/Helium for 2 hours; (A) BEA, (B) MFI; (C) CHA.
CO adsorption experiments confirm that Pd is at the exchange sites.
Pd at the exchange sites adsorbs NO directly, other non-zeolite supported Pd catalysts need formation of nitrates

Transmission IR spectra of NO adsorption on 1%Pd/CHA (red) and 1%Pd/Alumina (black) [samples were dehydrated at 400 °C under 6%O₂/Helium for 2 hours; spectra recorded after 15 min exposure to 500ppm NO/Helium at 100°C]
The presence of H$_2$O has little impact on NO adsorption on Pd sites

DRIFTS spectra recorded at 100 °C for Pd-CHA after exposure to (NO + O$_2$) with or without H$_2$O in the gas mixtures
Zeolite structures affect the NO bonding strength

Transmission spectra of NO adsorption on Pd/Zeolites
Pd/zeolite shows good sulfur tolerance and can be desulfated at >600°C under lean conditions.
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dCSC™ technology utilizes Pd/zeolite providing combined functions of NOx trap, HC trap, and DOC

- **NOx Trap**
  - Store NOx during cold start
  - Thermal release of NOx
  - Low temperature NOx conversion activity
  - $N_2$ selectivity

- **HC Trap**
  - Improved HC storage capacity
  - Additional HC conversion activity

- **DOC**
  - Improved CO/HC light-off activity
  - Comparable NO to NO$_2$ activity

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dCSC™ technology
dCSC™ catalysts exhibit high NOx storage capacity/efficiency, NOx thermally release at ~200-350°C

H.-Y. Chen, et al., SAE 2013-01-0535
dCSC™ catalysts also show improved HC/CO conversion, less N₂O formation, and similar NO oxidation activity.

H.-Y. Chen, et al., SAE 2013-01-0535
dCSC™ catalysts can be regenerated at ~350°C

(750°C/5%H₂O/16h aged, SV=30K, NO, CO=200ppm, C10=500 ppm, 10% O₂)

H.-Y. Chen, et al., SAE 2013-01-0535
Long-term sulfur tolerance and desulfation properties of the dCSC™ catalyst were evaluated by SOx/DeSOx cycle test.

- **Sulfation**
  - Perframnce test (100 s store+TPR)

- **Desulfation**
  - Perframnce test (100 s store+TPR)

- **SOx/DeSOx**
  - Repeat 4 times

- **Perframnce test (100 s store+TPR)**
  - Repeat 10 times

Population:
- 10% O$_2$ / 5% H$_2$O / 5% CO$_2$
- 200 ppm NO/200 ppm CO/500 ppm (C$_1$)$_3$H$_6$ /10% O$_2$ / 5% H$_2$O / 5% CO$_2$
- 200 ppm NO/200 ppm CO/1% (C$_1$)$_3$H$_6$ /10% O$_2$ / 5% H$_2$O / 5% CO$_2$
- 10 ppm SO$_2$ /200 ppm NO/200 ppm CO/500 ppm (C$_1$)$_3$H$_6$ /10% O$_2$ / 5% H$_2$O / 5% CO$_2$

- **SO$_2$**
  - = 10 ppm @ 350C for 70 min (0.5 g S/L cat)

- **S.V.**
  - : 30,000 hr$^{-1}$ (Flow rate = 21.2 L / min)
The dCSC™ catalyst has good sulfur tolerance is stable after long-term sulfation/desulfation testing.

Sulfation was carried at 350°C with an exposure level of 0.5g sulfur /L catalyst

Desulfation was carried at 650°C gas inlet (~720°C catalyst bed) temperature under lean conditions for 15 minutes
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dCSC™ catalyst vehicle testing on EU LDD

- Eu6 3.0L engine

  - DOC
    PGM loading: 115g/ft³ 4:1(Pt:Pd), total volume: 2.0 L
  - dCSC™
    PGM loading: 152g/ft³ 8:13(Pt:Pd), total volume: 2.0 L

- Aging
  DOC/dCSC™ – hydrothermal 800°C for 16 hours
  SCRF® - hydrothermal 800°C for 16 hours
dCSC™ catalyst show excellent NOx storage and release properties
**dCSC™ catalyst engine testing on a 8.9L engine HDD FTP transient test cycles**

![Diagram of Urea Dosing](image)

<table>
<thead>
<tr>
<th>System</th>
<th>Fresh/Aged</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Start Concept catalyst</td>
<td>Aged at 650°C/100 hrs</td>
<td>10.5x6”</td>
</tr>
<tr>
<td>SCR-DPF</td>
<td>Aged at 650°C/100hrs</td>
<td>10.5x12”</td>
</tr>
<tr>
<td>SCR</td>
<td>Aged at 650°C/100hrs</td>
<td>HP substrate, 600 cpsi, 10.5x6”</td>
</tr>
</tbody>
</table>

M. Naseri, et al., SAE 2015-01-0992
Systems with dCSC™ catalyst + SCRF show promise for HDD low temperature NOx emission control

M. Naseri, et al., SAE 2015-01-0992
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Modeling study has been carried out to compare various system configurations

- Different system configurations (simulated)
  - **System 1**
    - DOC
    - CSF
    - SCR
    - ASC
    - PGM1
      - 10.5”x4.5”
    - 12”x12”
    - 10.5”x10”
    - 10.5”x3”
  - **System 2**
    - DOC
    - SCR-DPF
    - SCR
    - ASC
    - PGM2
      - 12”x6”
    - 12”x12”
    - 12”x10”
    - 12”x3”
  - **System 3**
    - dCSC™ Technology
    - SCR-DPF
    - SCR
    - ASC
    - PGM2
      - 12”x6”
    - 12”x12”
    - 12”x10”
    - 12”x3”

- **Focus:**
  - NOx reduction
  - NH₃ slip
  - N₂O formation (limited systems)

- **Design flow:**
  - DOC
  - SCR-DPF/CSF
  - SCR
  - ASC

Max SV: 150k/hr 75k/hr 90k/hr 300k/hr

B. Sukumar, et al., 2014 CLEERS
HD-FTP data used for simulation purpose

Engine out data

![Graph showing temperature and NOx concentration over time]

- Average Temp: 219°C
- NOx: 8.78 g/kwhr

B. Sukumar, et al., 2014 CLEERS
The system with the dCSC™ technology clearly shows advantages, mainly due to low temperature NOx reduction.

**System1:**
DOC+CSF+SCR+ASC

**System2:**
DOC+SCR-DPF +SCR+ASC

**System3:**
dCSC™ +SCR-DPF +SCR+ASC

<table>
<thead>
<tr>
<th></th>
<th>NOx (g/kwhr)</th>
<th>N₂O (g/kwhr)</th>
<th>NOx Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>System1</td>
<td>0.91</td>
<td>0.26</td>
<td>89.6%</td>
</tr>
<tr>
<td>System2</td>
<td>0.81</td>
<td>0.34</td>
<td>90.8%</td>
</tr>
<tr>
<td>System3</td>
<td>0.40</td>
<td>Not modeled</td>
<td>95.4%</td>
</tr>
</tbody>
</table>

Very low NOx levels

B. Sukumar, et al., 2014 CLEERS
Summary

- Low temperature emission control is a major challenge
  - Control of cold-start emissions is crucial to meet the future stringent emission regulations
  - Fuel economy and GHG legislation lead to lower exhaust temperatures

- Zeolite supported Pd catalysts exhibit high NOx/HC storage capacity with high trapping efficiency at low temperatures
  - Pd at the exchange sites can adsorb NO directly
  - Zeolite structures affect both the NO storage and release profiles
  - Catalysts show good tolerance to sulfur poisoning

- Fully formulated catalysts show promising results on vehicle testing

- Modeling study is instrumental in system design