Dual Layer Coated High Porous SiC for SCR Integration into DPF

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18th ETH Conference on Combustion Generated Nanoparticles
Outline

- Motivation for this development
- The high porous SiC substrate
- The first coating layer for improvement of mechanical strength
- The second functional layer: SCR catalyst
- Analysis of coated lab samples
- SCR efficiency in lab scale test
- Engine bench test data
- Summary
Need for future diesel exhaust emission systems: Euro VI/Tier 4 final and beyond

Reduction of space and costs

**CO₂ reduction via the exhaust system**

- Weight
- Back pressure
- Regeneration strategy – efficient control of temperature – optimal use of fuel – lower fuel consumption

Integration of DeNOₓ (SCR) functionality into DPF

**Literature:**

- SAE 2011-01-1312 → reduced packaging by SCR-DPF / SCR
- SAE 2011-01-1140 → Cu zeolite on Cordierite DPF
- SAE 2013-01-0840 → high porous SiC
Design of a high porous DPF substrate for SCR integration

- High porosity level (> 60%)
- High spec. Surface area
- Good mechanical strength
- Reasonable soot load limit (> 5g/l)
- Specific weight high enough
  → sufficient heat capacity
- High filtration efficiency

High wash coat loading for high NO\textsubscript{X} conversion
Robustness and protection of catalyst
PN efficiency requirements

SiC with 65% porosity
The high porous SiC substrate

SAE 2010-01-0539

WO 2013/076045A1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE (RT – 800°C), 1/K</td>
<td>4.7</td>
</tr>
<tr>
<td>Therm. heat cond. 400°C, W/mK</td>
<td>2.2</td>
</tr>
<tr>
<td>Spec. heat capacity 400°C, J/gK</td>
<td>1.032</td>
</tr>
<tr>
<td>Bending strength, MPa</td>
<td>2.8</td>
</tr>
<tr>
<td>Maximum operating temperature, °C</td>
<td>1400</td>
</tr>
</tbody>
</table>
Performance of blank filters due to filtration and back pressure

<table>
<thead>
<tr>
<th>PN efficiency</th>
<th>Back pressure @ 200kg/h, 450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 cpsi – 5.66”x8”</td>
<td>fresh</td>
</tr>
<tr>
<td>58% 15-18µm 400µm</td>
<td>&gt;98%</td>
</tr>
<tr>
<td>60% 15-18µm 400µm</td>
<td>&gt;93%</td>
</tr>
<tr>
<td>65% 20-22µm 400µm</td>
<td>&gt;80%</td>
</tr>
</tbody>
</table>

| 300 cpsi – 5.66”x8” | fresh | 3 ESC | fresh | 5g/l |
| 58% 14-16µm 300µm | >92% | >99.9% | 3.7kPa | 8.8kPa |
| 60% 14-16µm 300µm | >92% | >98% | 3.5kPa | 8.2kPa |
First coating layer for improvement of mechanical strength
Second coating layer for SCR functionality
SCR catalyst candidates

<table>
<thead>
<tr>
<th>Function of every single compound</th>
<th>Vanadia-based $(V_2O_5/WO_3-TiO_2)$</th>
<th>Cu-Zeolite (Cu-ZSM-5)</th>
<th>Fe-Zeolite (Fe-β)</th>
<th>Mixed metal oxide (CeO$_2$-ZrO$_2$ based)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Function of every single compound</strong></td>
<td>$V_2O_5$: SCR active center</td>
<td>Cu: NO oxidation to NO$_2$</td>
<td>Fe: NO oxidation to NO$_2$</td>
<td>CeO$_2$: SCR active center, O$_2$ storage</td>
</tr>
<tr>
<td></td>
<td>WO$_3$: promoter</td>
<td>ZSM-5: host, SCR reaction, NH$_3$ storage</td>
<td>Beta: host, SCR reaction, NH$_3$ storage</td>
<td>ZrO$_2$: thermal stabilizer, NH$_3$ storage</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$: support</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SCR activity</strong></td>
<td>High (dependent on $V_2O_5$ content, best: $\sim$ 3 wt%)</td>
<td>High at low temperatures steadily decreasing beyond 350°C</td>
<td>High (at high temperatures up to 600°C, above NH$_3$ over-consumption) Low (&lt; 300°C)</td>
<td>High (variable temperature window dependent on Ce/Zr ratio, dopants, surface area + water content)</td>
</tr>
<tr>
<td><strong>SCR temperature interval</strong></td>
<td>$T_{50}$: 200°C</td>
<td>$T_{50}$: 180°C</td>
<td>$T_{50}$: 300°C</td>
<td>$T_{50}$: $\sim$ 250°C or lower</td>
</tr>
<tr>
<td></td>
<td>$\geq$ 90%: 300°C – 500°C</td>
<td>$\geq$ 90%: 250°C – 400°C</td>
<td>$\geq$ 90%: 400°C – 650°C</td>
<td>$\geq$ 90%: $\sim$300°C – 500/550°C</td>
</tr>
<tr>
<td><strong>NH$_3$ storage</strong></td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td><strong>$N_2O$ formation</strong></td>
<td>Increasing formation at $&gt;400°C$ (at 10 ppm NH$_3$ slip)</td>
<td>High formation tendency even at low temperatures</td>
<td>No formation Reduces $N_2O$ to $N_2$ above 400°C</td>
<td>Low formation tendency</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>$V_2O_5$ volatility ($&gt;690°C$)</td>
<td>Concerns due to CuSO$_4$ creation</td>
<td>No</td>
<td>No/low</td>
</tr>
</tbody>
</table>
## Lab sample specifications

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>First layer</th>
<th>Second layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>#FeZ01</td>
<td>—</td>
<td>Fe-β-zeolite, 120g/l</td>
</tr>
<tr>
<td>#FeZ02</td>
<td>—</td>
<td>Fe-β-zeolite, 60g/l</td>
</tr>
<tr>
<td>#FeZ03</td>
<td>SiO₂, 60g/l</td>
<td>Fe-β-zeolite, 65g/l</td>
</tr>
<tr>
<td>#CeZr01</td>
<td>CeO₂/ZrO₂/Nb₂O₅ nano slurry, 160g/l</td>
<td>—</td>
</tr>
<tr>
<td>#CeZr02</td>
<td>CeO₂/ZrO₂/Nb₂O₅, 130g/l</td>
<td>—</td>
</tr>
<tr>
<td>#CeZrFeZ01</td>
<td>—</td>
<td>CeO₂/ZrO₂/Nb₂O₅, 50g/l + Fe-β-zeolite, 50g/l</td>
</tr>
<tr>
<td>#CeZrFeZ02</td>
<td>SiO₂, 60g/l</td>
<td>CeO₂/ZrO₂/Nb₂O₅, 50g/l + Fe-β-zeolite, 40g/l</td>
</tr>
<tr>
<td>#CeZrFeZ03</td>
<td>CeO₂/ZrO₂/Nd₂O₃/Pr₆O₁₁ nano slurry, 55g/l</td>
<td>Fe-β-zeolite, 55g/l</td>
</tr>
</tbody>
</table>
Test of lab samples

- Main gas flow: pressurized air
- NO concentration: 250/500 ppm
- NO\textsubscript{2} concentration: 250/0 ppm
- NH\textsubscript{3} concentration: 500 ppm
- Water content: 10 %
- Space velocity: 31,000/h (normalized 20°C, 1013 hPa)
  - (50,000/h @ 200 °C – 75,000/h @ 450 °C)
- Temperature range: 200 – 450 °C
Fe-β zeolite

#FeZ01

65% / 20µm → 56% / 18µm

#FeZ03

65% / 20µm → 55% / 18µm

NO$_2$/NO$_x$ ratio was adjusted to 50%
CeO$_2$-ZrO$_2$ based mixed metal oxides

#CeZr01

65% / 20µm → 60% / 18µm

#CeZr02

65% / 20µm → 61% / 19µm

NO$_2$/NO$_x$ ratio was adjusted to 50%
The combinations Fe-\(\beta\)-zeolite with CeO\(_2\)-ZrO\(_2\) mixed metal oxides

\[
\begin{align*}
#CeZrFe01 & \quad 65\% / 20\mu m \rightarrow 47\% / 17\mu m \\
#CeZrFe03 & \quad 65\% / 20\mu m \rightarrow 50\% / 18\mu m
\end{align*}
\]

NO\(_2\)/NO\(_X\) ratio was adjusted to 50%
NO\textsubscript{X} conversion under standard SCR conditions compared to fast SCR
Engine bench test setup

- OM 904 engine, 4.25L – 4 Cyl. - 129 kW
- Dynamometer: Horiba T250
- Gas analyzer: Horiba MEXA6000-FT
- AdBlue dosing: Emitec Airless urea doser
- An uncoated DPF was mounted upstream to take the soot out of exhaust mass flow
Filters with SCR coatings for engine bench tests

<table>
<thead>
<tr>
<th></th>
<th>#FeZ01-DPF</th>
<th>#FeZ03-DPF</th>
<th>#CeZrFeZ01-DPF</th>
<th>#CeZrFeZ03-DPF - layered</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PN efficiency, fresh</strong></td>
<td>&gt;99.8%</td>
<td>&gt;99.8%</td>
<td>&gt;99.8%</td>
<td>&gt;99.8%</td>
</tr>
<tr>
<td><strong>Back pressure cold flow @ 600m³/h</strong></td>
<td>6.8kPa</td>
<td>6.9kPa</td>
<td>6.2kPa</td>
<td>6.0kPa</td>
</tr>
<tr>
<td><strong>Back pressure @ 140kg/h 480°C</strong></td>
<td>3.4kPa</td>
<td>3.5kPa</td>
<td>3.3kPa</td>
<td>3.1kPa</td>
</tr>
</tbody>
</table>

60g/l SiO₂
60g/l Fe-β-Z

60g/l CeO₂/ZrO₂/Nb₂O₅
60g/l Fe-β-Z
SCR efficiency for all the test filters
Performance of CeZrFeZ03-DPF_layered during ESC

- SCR performance over cycle: 70.0 %
- Filtration performance over cycle: 99.6 %
Performance of CeZrFeZ03-DPF_layered during ETC

- SCR performance over cycle: 76.3 %
- Filtration performance over cycle: 99.7 %
Summary and conclusions

- A high porous SiC with a dual layer coating was presented
  - Enhancing mechanical strength
  - High SCR performance at low catalyst loadings

- Catalyst solutions based on a Fe-β-zeolite and mixed metal oxides (doped ceria/zirconia) have been developed

- Lab scale and engine bench test show a high SCR efficiency between 80 % and 95 % for the zeolite and zeolite/mixed metal oxide solutions

- High porosity of 65 % combined with the initial layer is the optimum substrate for the used catalysts

- The developed SCR coated DPF is a very promising candidate for future Euro VI systems with reduced packaging size
Thank You for your Attention!

For more details see: SAE2014-01-1484