Progress on Acidic Zirconia Mixed Oxides for Efficient NH$_3$-SCR Catalysis

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DeNOx SCR for EU6 is the preferred technology to target the NOx regulation limits and low CO₂ emissions

Worldwide emission regulations push the need for DeNOx catalysts

NOₓ regulations + pressure on CO₂ emissions = need for NH₃-SCR

Source: W. Mattes (BMW), Minnox 2008

Source: T. Seguelong, IAA 2009
SCR/DPF concepts for EU6

**SCR catalyst downstream of filter:**
- SCR catalyst more isothermal due to heat capacity of DPF
- NO$_2$ formation in filter improves SCR performance
- Bad NO$_x$ light-off
- Erroneous DPF regeneration may damage SCR catalyst

**SCR catalyst upstream of filter:**
- Good NO$_x$ light-off
- SCR catalyst cannot be damaged by DPF regeneration
- SCR catalyst exposed to larger temperature gradients
- Initiation of DPF regeneration by temperature increase through the SCR catalyst

**SCR catalyst on filter:**
- DPF regeneration may damage SCR catalyst
1) Rhodia lab tests on *powder model catalysts* as preliminary screening of Ac Zr materials

2) Paul Scherrer Institute (Switzerland) lab tests on *coated catalysts* as first indicator for real-world performance

3) Engine Bench Test on *Full size model catalysts* as proof of concept
Three investigation levels

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Focus on the progress and testing of Acidic Zirconia (Ac Zr)

<table>
<thead>
<tr>
<th>Label</th>
<th>Surface area fresh (m²/g)</th>
<th>Surface area hydrothermally aged at 750 °C for 16 h (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acidic Mixed Oxide REV1</strong></td>
<td>85</td>
<td>63</td>
</tr>
<tr>
<td>Acidic Zr sample with low CeO₂ loading</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Acidic Mixed Oxide REV3</strong></td>
<td>60</td>
<td>44</td>
</tr>
<tr>
<td>New Process Acidic Zirconia sample</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Introduced at SAE 2008
- Last generation of Ac Zr successfully up-scaled to the pilot level
Ammonia storage capacity of Ac Zr materials

Fresh

<table>
<thead>
<tr>
<th></th>
<th>REV 1</th>
<th>REV 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>0.236 mol / kg</td>
<td>0.252 mol / kg</td>
</tr>
</tbody>
</table>

Hydrothermal aged 750°C/16 h

<table>
<thead>
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<th>REV 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>0.170 mol / kg</td>
<td>0.180 mol / kg</td>
</tr>
</tbody>
</table>

REV 3 shows a rather flat temperature NH₃-TPD profile

NH₃-TPD profiles of fresh powder samples

Rev1 & Rev2 samples show very similar NH₃-TPD profile. Rev3 sample shows a flat profile even after ageing.

<table>
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<th>Sample</th>
<th>Amount/mol/kg</th>
</tr>
</thead>
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<tr>
<td>REV 1</td>
<td>0.236</td>
</tr>
<tr>
<td>REV 3</td>
<td>0.252</td>
</tr>
</tbody>
</table>

REV 1 0.170 mol / kg
REV 3 0.180 mol / kg

(*) Ageing: 750 °C / 16 h
10% H₂O, 10% O₂, balance N₂

NH₃-TPD profiles of aged (*) powder samples
Three investigation levels

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PSI laboratory test apparatus

Testing conditions:
• Ac Zr powders coated on cordierite substrates of 400 cpsi, 7.5 cm³
• T = 200 - 650 °C
• GHSV = 30000 - 52000 h⁻¹
• Gas composition NO-SCR: 10% O₂, 5% H₂O, 1000 ppm NO, 0 - 1500 ppm NH₃, balance N₂
• Gas composition NO/NO₂-SCR: 10% O₂, 5% H₂O, 500 ppm NO, 500 ppm NO₂, 0 - 1500 ppm NH₃, balance N₂

1. Water reservoir
2. Liquid MFC’s
3. MFC’s
4. Water evaporator
5. Reactor
6. Catalyst sample
7. Filter
8. Flow meter
9. Diaphragm pump
10. Gas cell
NO-only SCR: M-zeolite and V-TiO$_2$

1000 ppm NO, 10 % O$_2$, and 5 % H$_2$O in N$_2$, NH$_3$ variable.

- Cu-ZSM-5 very active at T $\leq$ 300 °C.
- Fe-ZSM-5 very active at T $>$ 400 °C.
- V$_2$O$_5$/WO$_3$-TiO$_2$ active at intermediate temperatures.
NO-only SCR: AcZr REV3

1000 ppm NO, 10 % O₂, and 5 % H₂O in N₂, NH₃ variable.

NEW Fresh Ac. Zr based catalyst - WC loading = 225 g/l

NO only -SCR; GHSV = 30'000 h⁻¹

DeNOx [%]

max. DeNOx
DeNOx at 10 ppm NH3 slip
N₂O at 10 ppm NH3 slip; [ppm]

Temperature [°C]
N₂O selectivity of V-cat., Fe-ZSM-5, Cu-ZSM-5 and Ac Zr REV3

N₂O formation at 10 ppm NH₃ slip
1000 ppm NO, 10 % O₂, and 5 % H₂O in N₂, NH₃ variable

• Only small amounts of N₂O produced over Ac Zr REV3.
Effect of hydrothermal aging

NEW Ac. Zr based catalyst - WC loading = 225 g/l

FRESH vs AGED - Max DeNOx

NO only conditions -SCR; GHSV = 30’000 h⁻¹

750 °C/16h
10% steam

No effect under “Max deNOx” conditions
Effect of hydrothermal aging

NEW Ac. Zr based catalyst - WC loading = 225 g/l

FRESH vs AGED - DeNOx at 10 ppm NH3 slip
NO only conditions -SCR; GHSV = 30'000 h-1

Decrease in deNOx activity due to limited amount of NH₃ storage
Fast-SCR over fresh AcZr REV3

500 ppm NO, 500 ppm NO₂, 10 % O₂, and 5% H₂O in N₂, NH₃ variable

> 95% NOx conversion @ T>200 oC under fast-SCR conditions.
NEW Ac. Zr based Catalyst - WC loading = 225 g/l
*aged: 16 h 750°C air + 10% H₂O*
Fast SCR conditions  NO/NO₂-SCR; GHSV = 30'000 h⁻¹

No effect of hydrothermal aging under fast SCR conditions
NO\textsubscript{x} conversion at different NO/NO\textsubscript{2} ratios

NO/NO\textsubscript{2}-SCR; GHSV = 30'000 h\textsuperscript{-1}

\begin{center}
\begin{tikzpicture}
\begin{axis}[
    width=\textwidth,
    height=\textwidth,
    xlabel=Temperature [°C],
    ylabel=DeNO\textsubscript{x} at 10 ppm NH\textsubscript{3} slip [%],
    xmin=100, xmax=400,
    ymin=0, ymax=100,
    xtick={100,150,200,250,300,350,400},
    ytick={0,10,20,30,40,50,60,70,80,90,100},
    legend style={at={(0.5,0.1)},anchor=north},
    nodes near coords={\%NO\textsubscript{2}/NO\textsubscript{x}},
    ]
    \addplot[color=black,mark=square] coordinates {
    (100,0) (150,0) (200,0) (250,0) (300,0) (350,0) (400,0)
    (100,10) (150,10) (200,10) (250,10) (300,10) (350,10) (400,10)
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    (100,70) (150,70) (200,70) (250,70) (300,70) (350,70) (400,70)
    (100,80) (150,80) (200,80) (250,80) (300,80) (350,80) (400,80)
    (100,90) (150,90) (200,90) (250,90) (300,90) (350,90) (400,90)
    (100,100) (150,100) (200,100) (250,100) (300,100) (350,100) (400,100)
    };
    \addlegendentry{DeNO\textsubscript{x} at 10 ppm NH\textsubscript{3} slip; measurement}
    \addplot[color=black,mark=triangle] coordinates {
    (100,100) (150,100) (200,100) (250,100) (300,100) (350,100) (400,100)
    (100,90) (150,90) (200,90) (250,90) (300,90) (350,90) (400,90)
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    };
    \addlegendentry{DeNO\textsubscript{x} at 10 ppm NH\textsubscript{3} slip; calculation}
\end{axis}
\end{tikzpicture}
\end{center}
Three investigation levels

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3) *Full size model catalysts as proof of concept*
Engine bench test / Testing procedure

• **SCR prototype**
  • SCR catalyst based on Acidic Zirconia
  • SCR catalyst stabilised: 4 h at 570°C then aged for 25 h at 800°C
  • Washcoat loading: ~120 g/L
  • Cordierite substrate (400 cpsi)
    • $\varnothing$ 5.66 in, length 7.00 in
      $V = 2.9 \, \text{L}$

• **DOC**
  • 400 cpsi
    $\varnothing$ 5.66 in, length 3.80 in
    $V = 1.6 \, \text{L}$

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**Engine test conditions:**

• Engine speed: 1300 - 3500 min$^{-1}$
• $T = 175 - 450^\circ\text{C}$
• $\text{NO}_x$ measurement upstream and downstream of SCR catalyst
• $\alpha = \text{NH}_3,\text{in}/\text{NO}_x,\text{in} = 0.9$
AcZr SCR catalyst shows good light-off at the engine test bench even after aging.
Conclusions / Perspectives

• Zirconia-based mixed metal oxide SCR catalysts show:
  • Good thermal stability
  • High NOx conversion
  • Good light-off
  • Low N$_2$O emissions
  • Low but constant NH$_3$ storage

• Catalyst compositions need to be optimized for improved light-off and ammonia storage
Thank you for your attention