Sulfur Effect and Performance Recovery of a DOC + CSF + Cu-Zeolite SCR System

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Outline

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    - Performance
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- Reactor experiments to simulate transient behavior
  - Accelerated low temperature sulfation behavior
  - Sulfation effects and mechanism
  - Desulfation methods
- Summary
Recent developments have led to Cu-zeolite SCR catalysts with remarkably improved low temperature activity and high thermal stability.

On the other hand, Cu-zeolite SCR also provides benefit over V/Ti SCR for applications with “cold” exhaust that never see high temperatures.
Zeolite SCR sulfation issue: literature

- Several recent presentations have highlighted effects of sulfur compounds on zeolite-based SCR performance

- Past experience from Euro IV applications has shown V/Ti SCR to be insensitive to sulfation, although overall NOx conversion may be lower than zeolite-based SCR
Background and motivation

- **Background:**
  - Systems with active regeneration used in low sulfur environments have shown stable, sustained performance to end-of-useful life*
  - Some systems running under high sulfur conditions and/or extended low temperature operation have shown performance loss

- **Motivation:**
  - Better understanding of degradation mechanism
  - Generate system-level performance features with realistic SCR-inlet $\text{SO}_2/\text{SO}_3$ and $\text{NO}_2/\text{NO}_x$ in a DOC + CSF + Cu-SCR system
  - Determination of conditions for system performance recovery

Laboratory study of sulfation effect at system level

- **Diesel System Simulator (DSS)**
  - System level study
  - Capable of simulating various transient cycles
    - By matching temperature, space velocity and compositions from engine experiments

- **Catalyst size**
  - DOC: 1.5"x3"
  - CSF: 1.5"x6"
  - SCR: 1.5"x6"
Engine HDFTP data “derated” to simulate cold engine operation

Temperatures in the first 4 FTP cycles of D3C3S6_061209_3 sulfation runs

Transient temperature and space velocity profiles in the first four cycles
(200-300°C SCR inlet
~55,000 h⁻¹ peak SCR SV)

High SO₂ in feed to simulate extended sulfur exposure on engine:
• ~1.0 g/L sulfur exposure = 100 h on engine
  (using ULSD fuel)
• ~12.5 g/L sulfur exposure on reactor ≈ 1250 h
  on engine (~35 PPM SO₂ for 12 h in reactor)
System deactivation after accelerated sulfur exposure at low temperature

System response to 12h continuous derated HDFTP cycles under 35 ppm SO₂ in feed conditions

Conversion (%) or NO₂/NOx (x100%)

Approx. 1300 h on engine

Multiple derated FTP runs
(200-300 °C SCR in, NSR=1, 35ppm SO₂ in feed)

Cycle deNOx

CSF/O NO₂/NOx

Sulfur (SO₂) breakthrough after different components

Loss after DOC
Loss after CSF
Loss after SCR

SO₂ overall consumption (%)
After sulfur exposure, Cu-zeolite SCR became sensitive to NO$_2$/NOx ratio, especially for $T < 250$ $\degree$C.
Sulfur concentration gradients in Cu-SCR after 13 g/L_SCR sulfur exposure

Washcoat surface to substrate

Front to rear

Washcoat sulfur profile via EPMA

Sulfate content via ICP wet analysis
TGA/DTA-MS of sulfated sample shows two major sulfation modes

- **Low-T** sulfate
- **High-T** sulfate

Absence of NH$_3$ during sulfation

**CuSO$_4$**

**CuSO$_4$**

**Sulfated Cu-SCR (w/o NH$_3$)**

Sulfur release and weight loss
NOx conversion recovery is incremental with temperature

- Parametric study for desulfation effectiveness
  - NSR (NH₃/NOx) = 0.0, 1.0, 1.5
  - Durations = 0.5, 1.0 hr
  - Temperature = 375, 400, 450, 500, 600 °C (SCR in)

NOx conversion (Baseline: ~95%, all evaluated at NSR=1.0)
Full performance recovered at 500 °C deSOx … and does not further degrade during multiple sulfation-desulfation cycles.
DOC/CSF generated fairly repeatable HDFTP NO$_2$/NOx profile in post-deSOx evaluations

After 1$^{st}$ Sulfation-deSOx

After 3$^{rd}$ Sulfation-deSOx
SCR-out NOx slip values were very similar after 500 °C deSOx
Zeolite-based SCRs provide high thermal stability and durability in active regeneration systems with periodic high temperature exposures.

Literature reveals all zeolite-based SCRs are susceptible to sulfation under low temperature SO$_3$ exposure.

This study has shown that Cu-Zeolite SCR degrades after severe sulfur exposure under extended low temperature conditions.

- Two major sulfation modes are most likely involved:
  - Formation of (NH$_4$)$_2$SO$_4$ or (NH$_4$)HSO$_4$
  - Formation of CuSO$_4$

System performance can be recovered:

- Temperature is the most important factor determining desulfation efficiency.
- The system recovered most but not all of its performance after 450 °C desulfation.
- Upon 500 °C desulfation, NOx conversion efficiency was fully restored and sustained in multiple sulfation-desulfation experiments.
Thank You!