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

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Outline

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    - Performance
    - Sulfation issue: literature
- 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

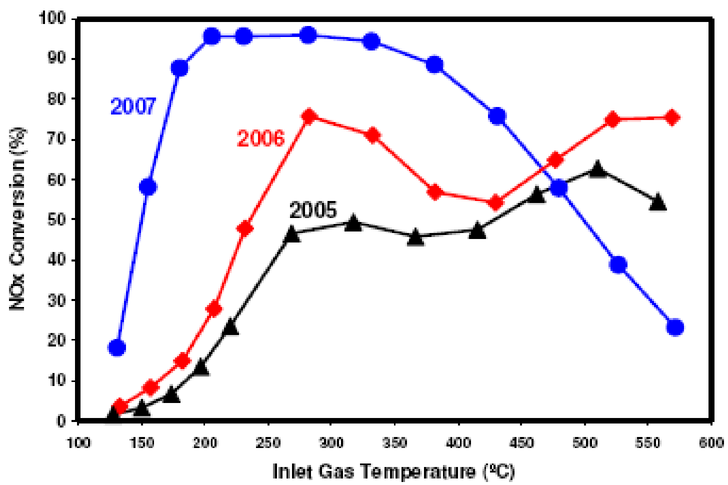


FIGURE 7. NOx conversion of best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 1 hour at 900°C.

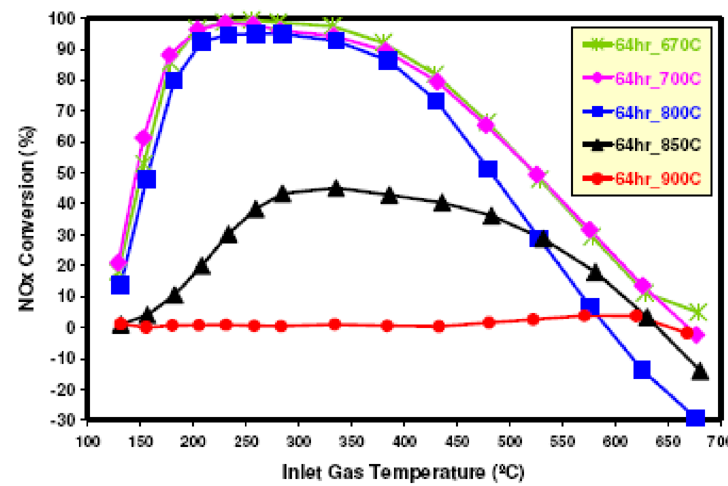
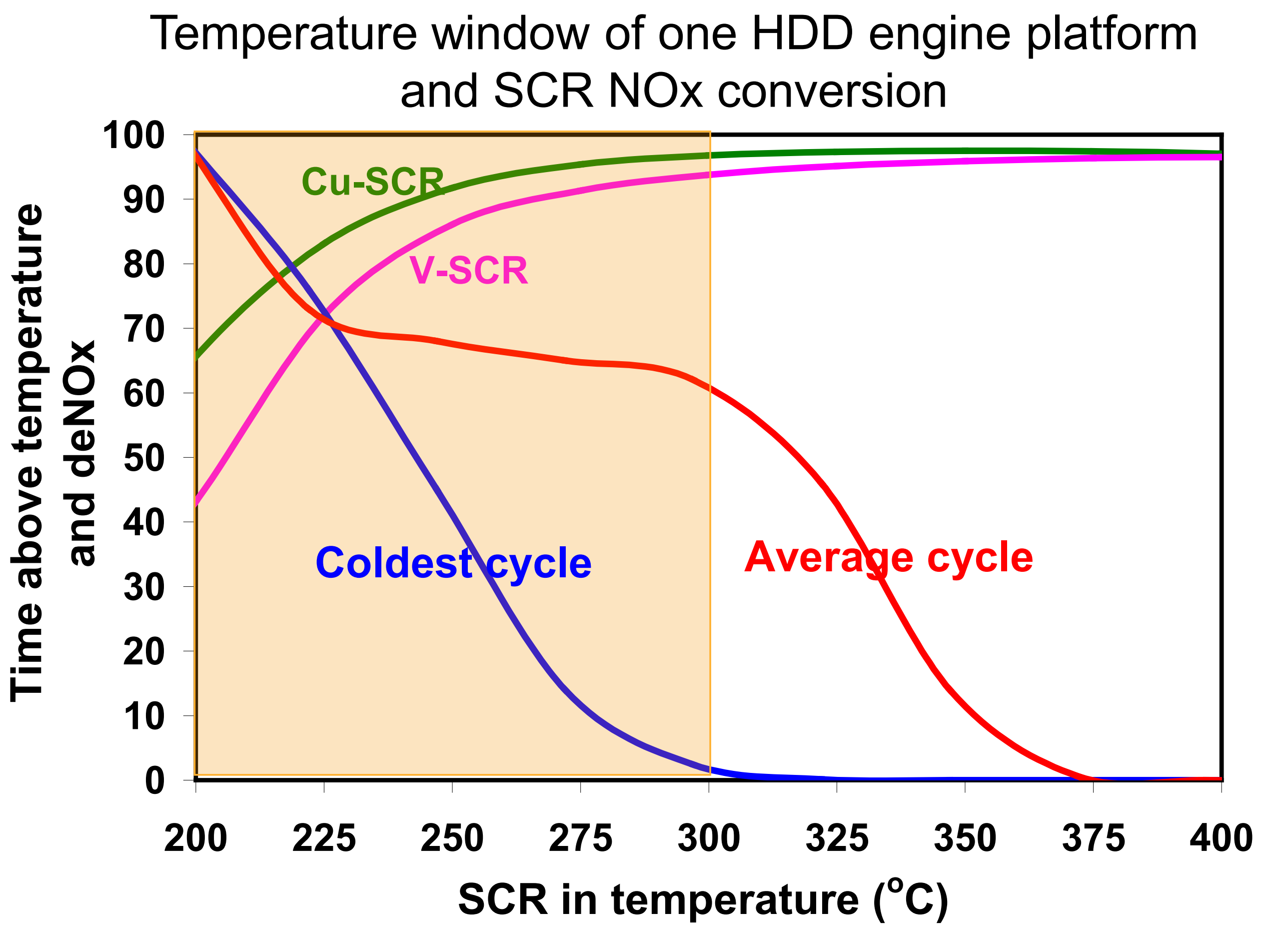


FIGURE 13. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at <u>64 hours</u> from 670°C – 900°C.

SAE 2008-01-1025: Enhanced Durability of a Cu/Zeolite Based SCR Catalyst. Giovanni Cavataio, et al

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

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- Several recent presentations have highlighted effects of sulfur compounds on zeolite-based SCR performance
  - "The Effects of SO_2 and SO_3 Poisoning on Cu/Zeolite SCR Catalysts". Christine Lambert, et al: SAE 2009-01-0898
  - "Investigation of Sulfur Deactivation on Cu/Zeolite SCR Catalysts in Diesel Application". Yisun Cheng, et al: 2009 DEER Conference
  - "The Effects of Sulfur Poisoning and Desulfation Temperature on the NOx Conversion of LNT+SCR Systems for Diesel Applications". Joe Theis, et al: SAE 2010-01-0300
- 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

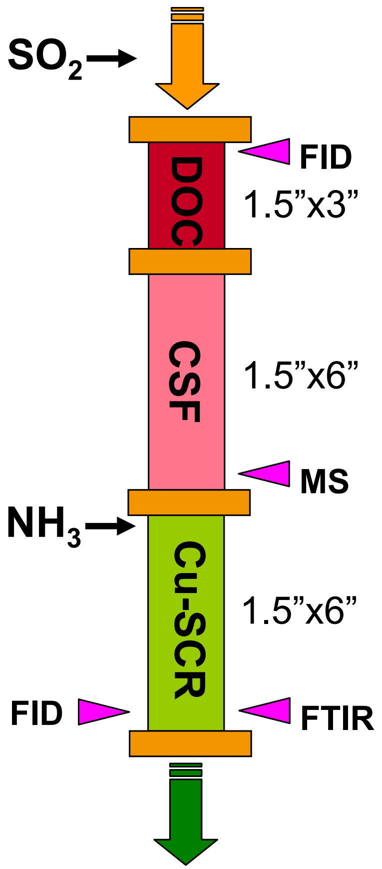
- Background:
  - Systems with active regeneration used in low sulfur environments have shown stable, sustained performance to end-of-useful life*
  - Some systems running under high sulfur conditions and/or extended low temperature operation have shown performance loss
- Motivation:
  - Better understanding of degradation mechanism
  - Generate system-level performance features with realistic SCR-inlet SO_2/SO_3 and NO_2/NO_x in a DOC + CSF + Cu-SCR system
  - Determination of conditions for system performance recovery

* The New Challenge -Heavy Duty Diesel Engine Emission Control. Sanath V Kumar; SIAT 2011 Keynote Presentation

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"

DSS setup



Engine HDFTP data “derated” to simulate cold engine operation

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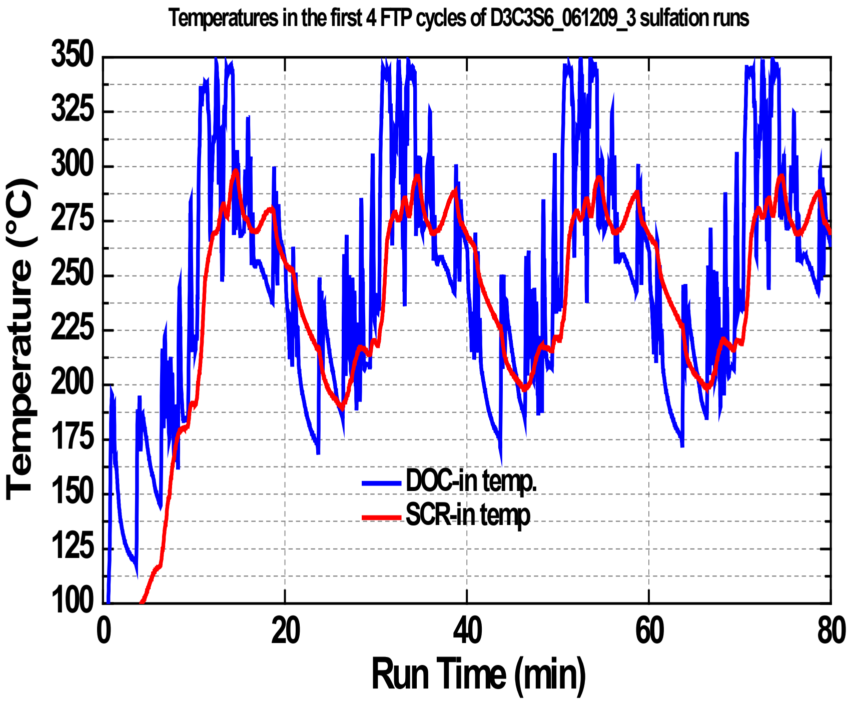
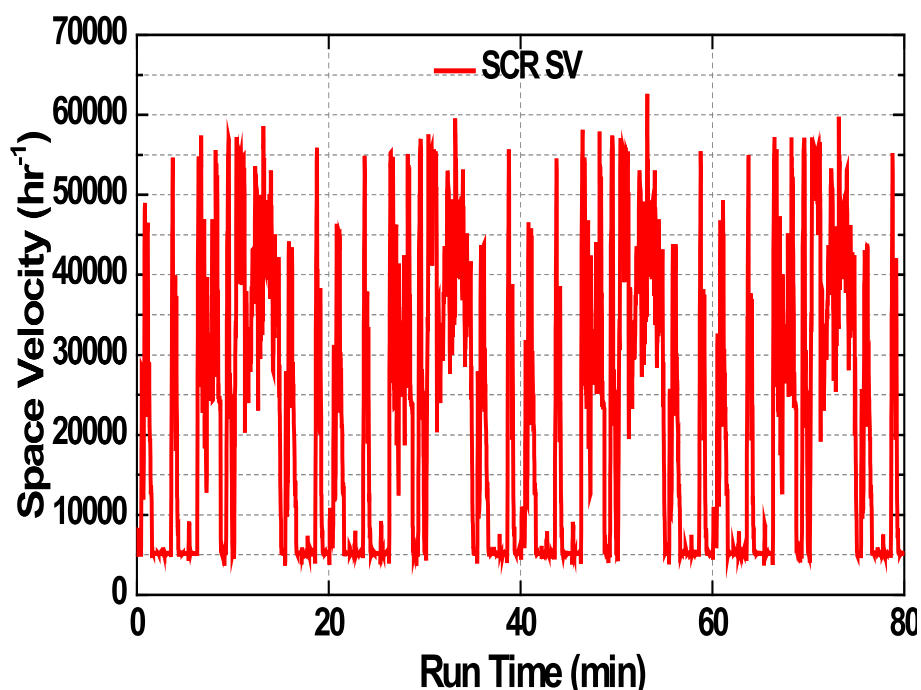


Transient temperature and space velocity profiles in the first four cycles

(200-300 C SCR inlet
~55,000 h^{-1} peak SCR SV)



High SO_2 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 SO_2 for 12 h in reactor)

System deactivation after accelerated sulfur exposure at low temperature

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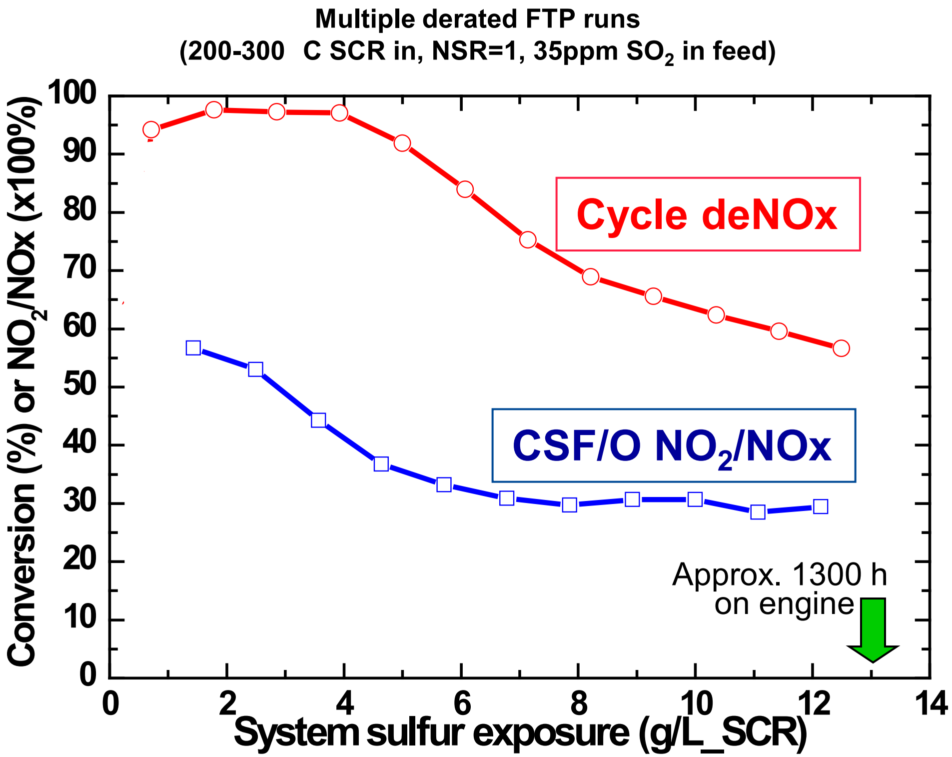
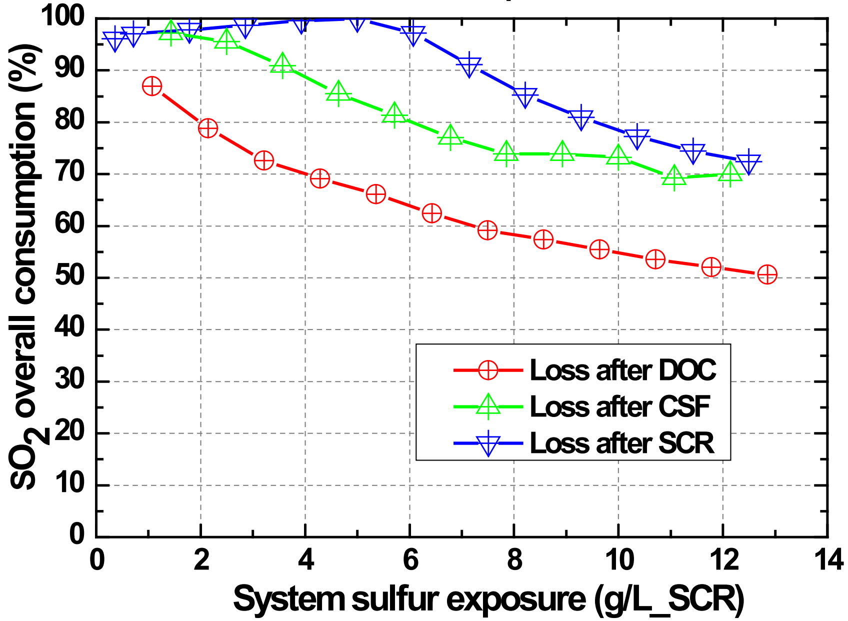
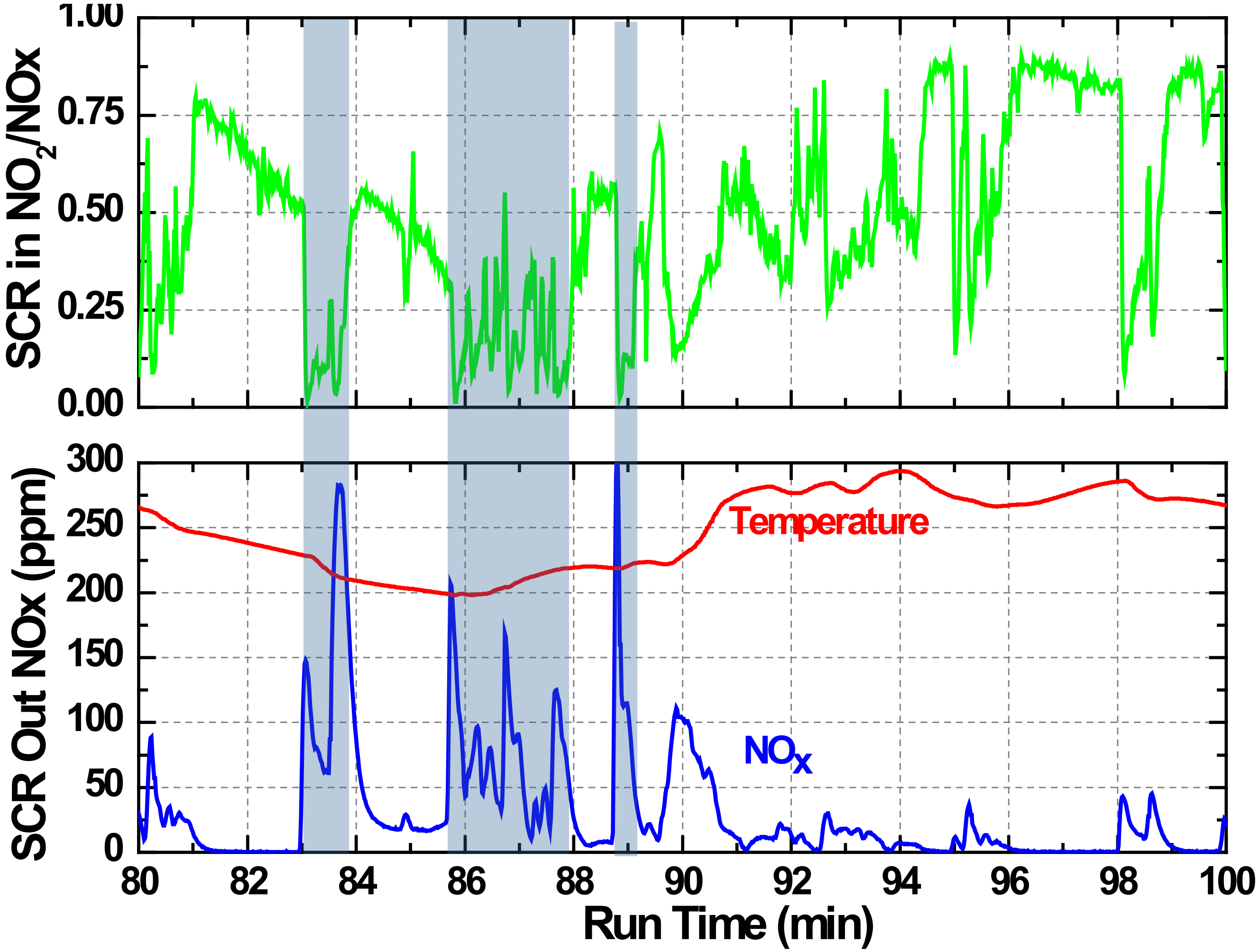
System response to 12h continuous derated HDFTP cycles under 35 ppm SO_2 in feed conditions



Sulfur (SO_2) breakthrough after different components



After sulfur exposure, Cu-zeolite SCR became sensitive to NO_2/NOx ratio, especially for T < 250 C



Sulfur concentration gradients in Cu-SCR after 13 g/L_SCR sulfur exposure

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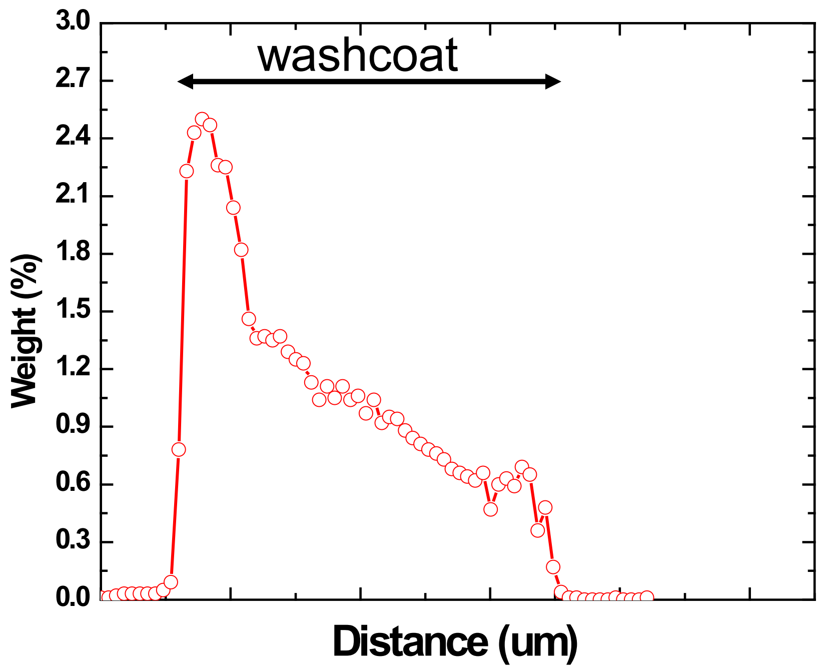
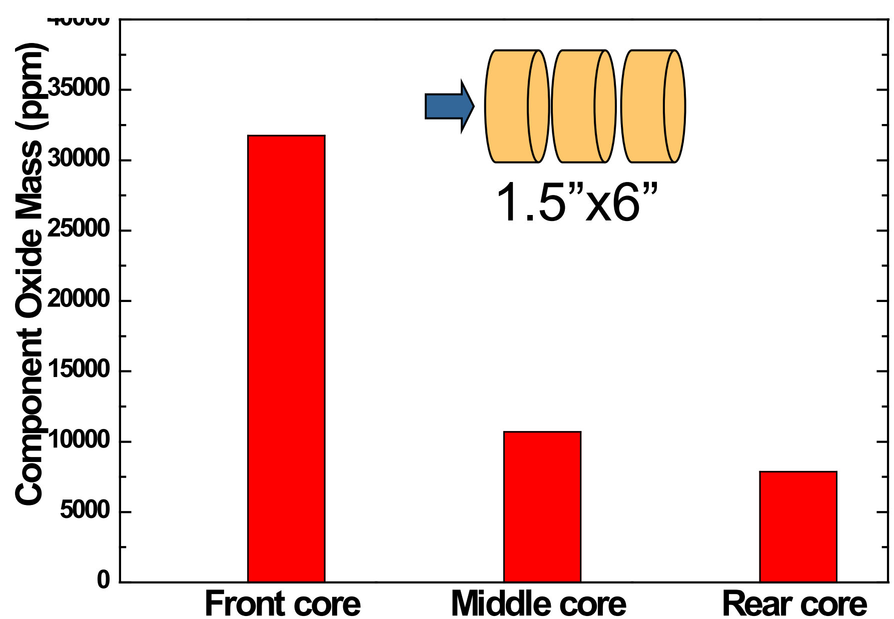
Washcoat surface to substrate



Washcoat sulfur profile via EPMA

Front to rear



Sulfate content via ICP wet analysis

TGA/DTA-MS of sulfated sample shows two major sulfation modes

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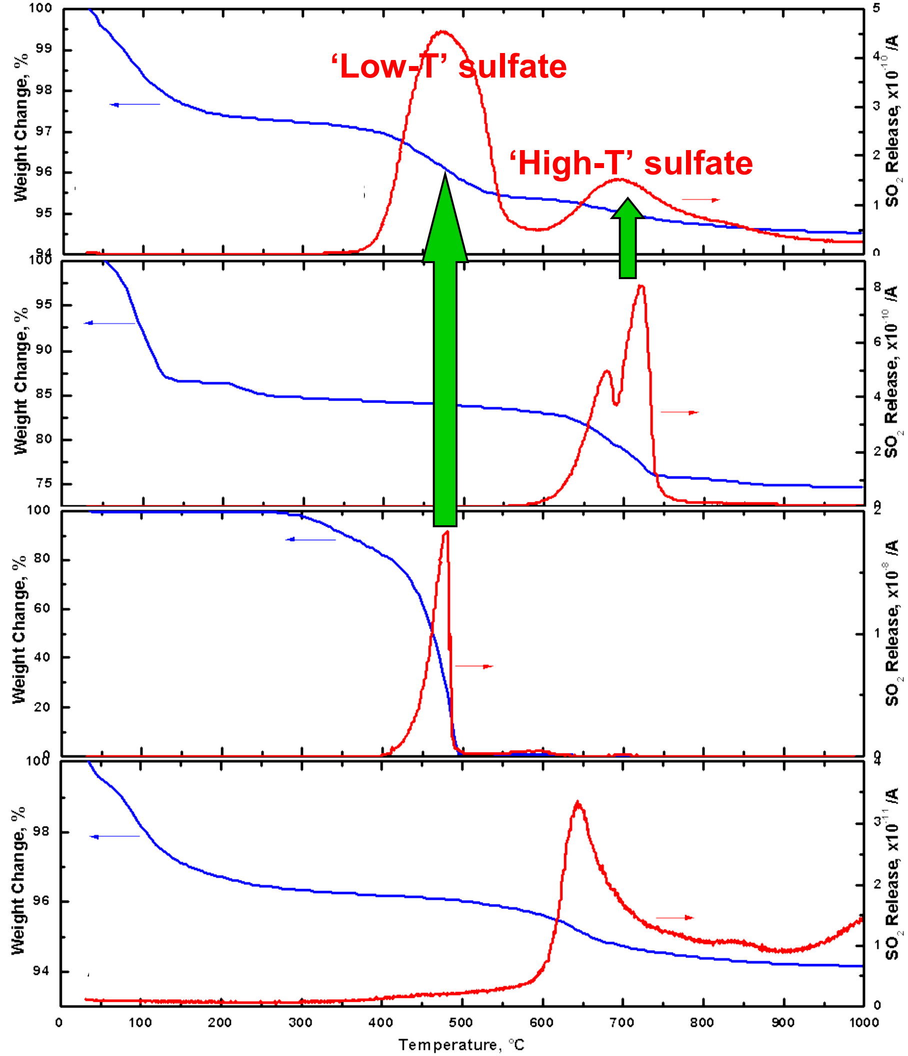
(a) Sulfated Cu-SCR

(b) $CuSO_4$

(c) $(NH_4)_2SO_4$

(d) Sulfated Cu-SCR (w/o NH_3)



Sulfur release and weight loss

NOx conversion recovery is incremental with temperature

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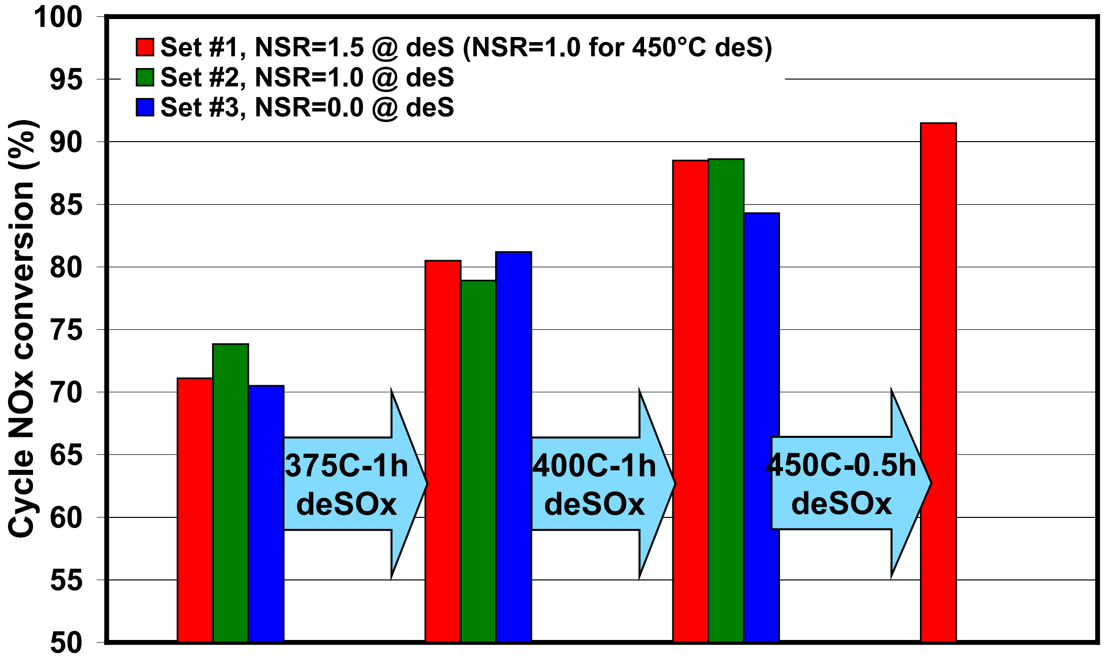
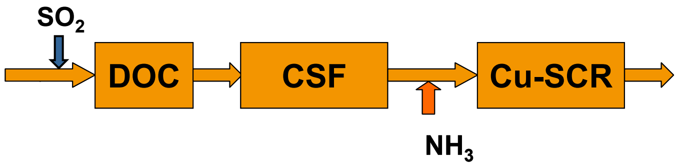
- Parametric study for desulfation effectiveness
  - NSR (NH_3/NOx) = 0.0, 1.0, 1.5
  - Durations = 0.5, 1.0 hr
  - Temperature = 375, 400, 450, 500, 600 C (SCR in)

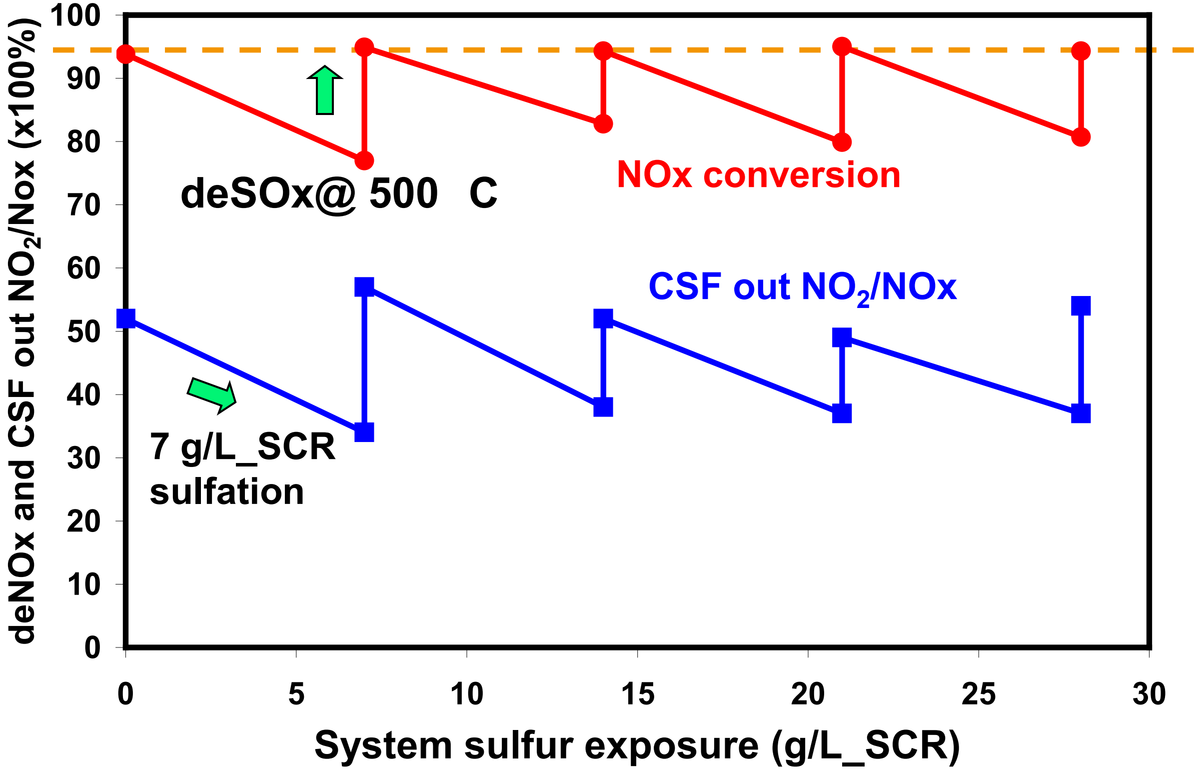
NOx conversion (Baseline: ~95%, all evaluated at NSR=1.0)



Full performance recovered at 500 C deSOx … and does not further degrade during multiple sulfation-desulfation cycles



NO_2/NOx ratio and NOx conversion after sulfation and desulfation



DOC/CSF generated fairly repeatable HDFTP NO_2/NOx profile in post-deSOx evaluations

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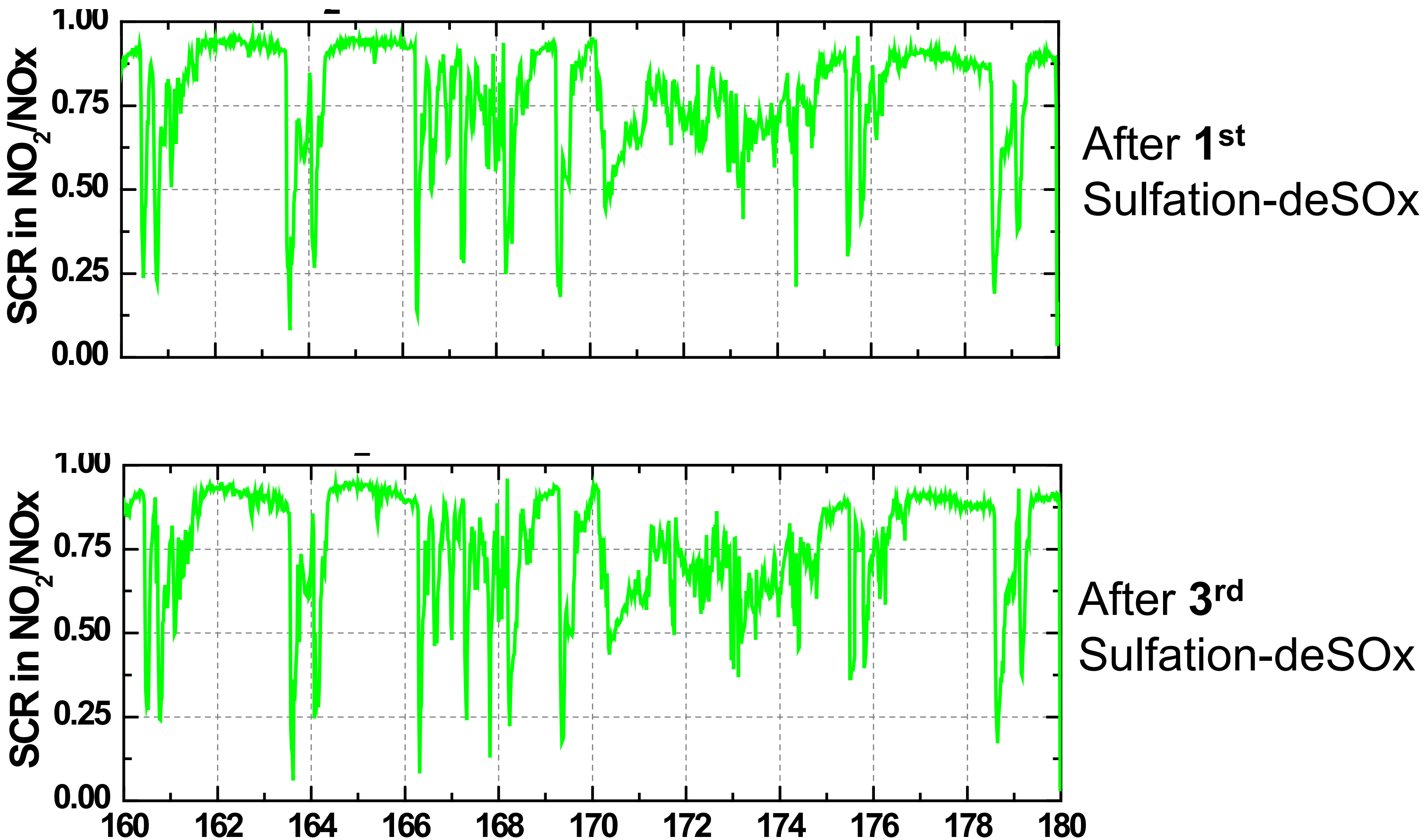

SCR-out NOx slip values were very similar after 500 C deSOx

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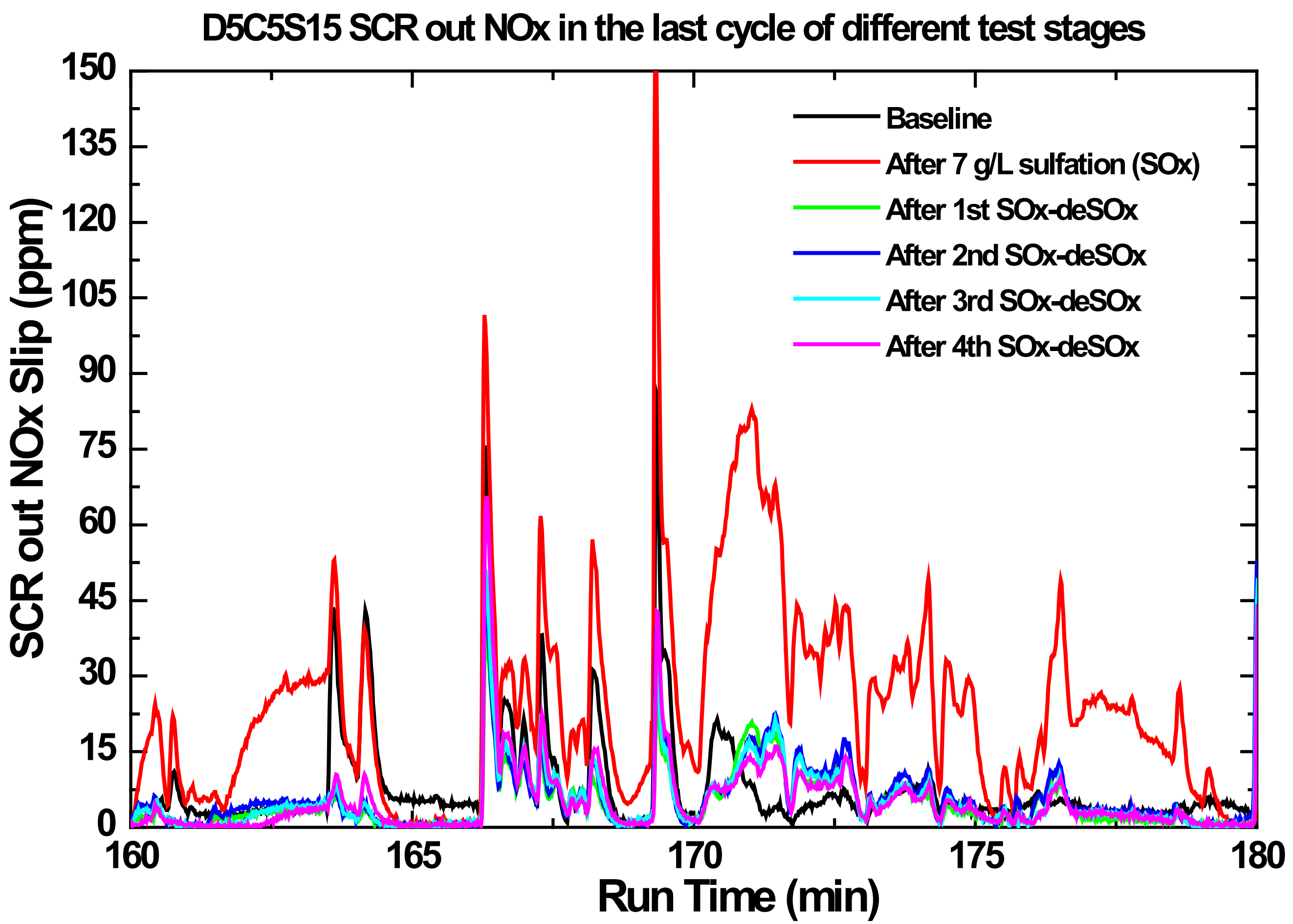

Summary

- 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 $(NH_4)_2SO_4$ 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!