Diesel Aftertreatment
Accelerated Aging Cycle Development
(DAAAC)

Aging of Zeolite Based SCR Systems

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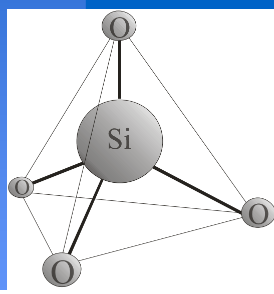
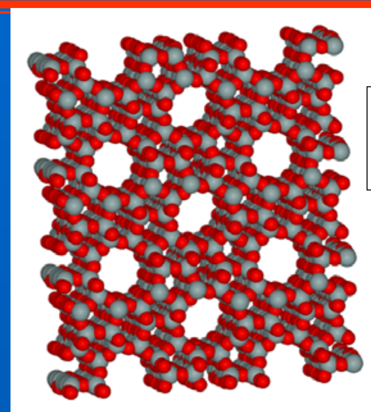
Aging of Zeolite SCR Catalysts

- Zeolite structure
- Steps in SCR reaction
  - Structure, SCR steps, aging
- Potential aging modes
- Recent studies from Ford Research Lab

Zeolite Structure



tetrahedral building block (T-unit); sometimes Si replaced by Al



gray: Si or Al
red: O
ZSM-5

T-units are assembled into larger structures w/ regular pores

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Zeolite characteristics

- Silicon/aluminum and oxygen + cation
  - Al atom: NH_3 storage site
  - Additional cations (Fe etc): acid site
- Uniform crystal structure
  - regular pore size: “molecular sieve”
  - many different types
- Stores/adsorbs species
  - NH_3, water, polar molecules, etc

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Zeolite Pore Sizes

Class	T-units per pore	Pore Size (nm)	Example
Small	8	0.35-0.45	Linde A
Mid	10	0.45-0.60	ZSM-5
Large	12	0.60-0.80	Faujasite (Zeolite Y)

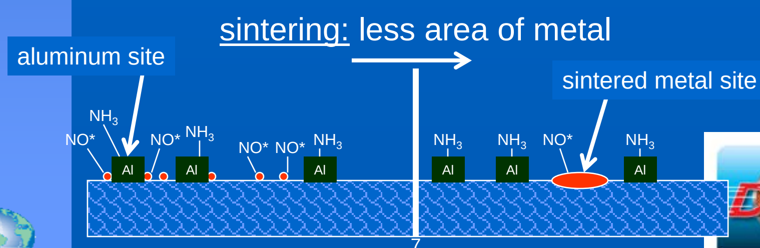
Note: molecular diameters of water and ammonia are 0.35 and 0.30 nm, respectively

Main SCR Steps

Step	Zeolite Feature	Deactivation Mechanism
NH_3 storage	Al atom	Hydrothermal de-alumination
NO → NO* activation	Metal oxide, acid sites	Metal sintering, poisoning
Diffusion in/out of crystal	Pores	Blockage

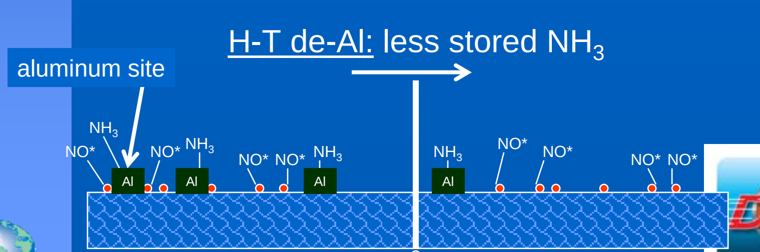
Sintering

- high temp leads to metal sintering
  - loss of active metal surface area
- Less activation of NO to NO*
- SCR slows down
  - stored NH_3 not consumed by NO_x → transient NH_3 slip



Hydrothermal De-Alumination

- High temperature water causes de-Al
  - for example, engine exhaust
- Loss of Al sites → less NH_3 storage → less SCR
  - SS NH_3 slip



Rate of de-Alumination and Rapid Aging

T. Sano et al., "Estimation of dealumination rate of ZSM-5 zeolite by adsorption of water vapor". *Zeolites*, 16:258.264, 1996.

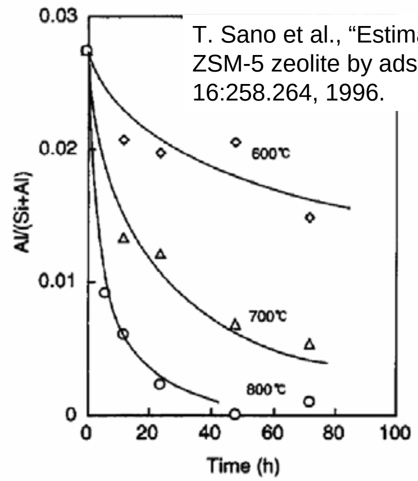


Figure 9 Time dependence of amount of framework aluminums (Al(Si + Al)) of HZSM-5 zeolites during thermal treatment.

$$\frac{dA}{dt} = -kA^2$$

A: aluminum content
k: Arrhenius term

Poisoning and Clogging

- Reversible
  - coke, HC's, N compounds
  - removable in hot (~600°C) conditions
  - loss of conversion until "burned-off"
- Irreversible
  - Ca, P, Zn: lubricating oil

van Kooten, W.E.J et al. "Deactivation of zeolite catalysts used for NO removal," Applied Catalysis B: Environmental. 25 (2000) 125-135.

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Relative Importance of Aging Modes

- H-T de-Al clearly important
  - exhaust contains steam
- Others not clear
- Does one dominate?
- Experimental data required
- Note: DEER conference requested more experimental aging data

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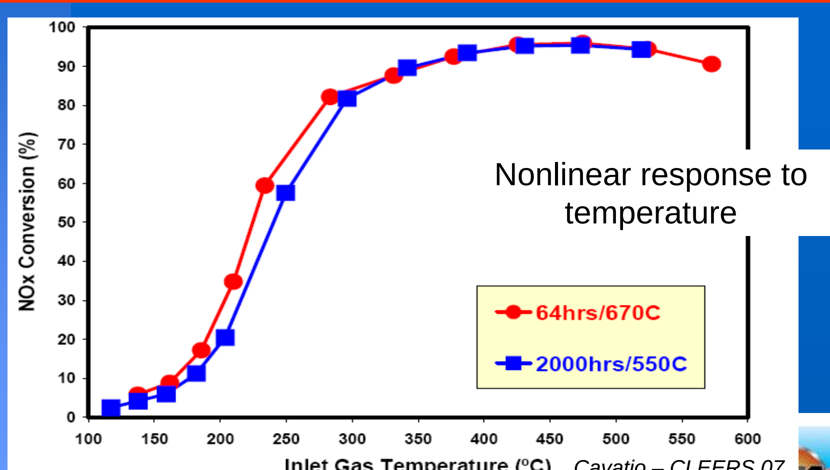
Zeolite SCR Durability
Cu-Zeolite and Temperature



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H-T Stability of Fe-Zeolite

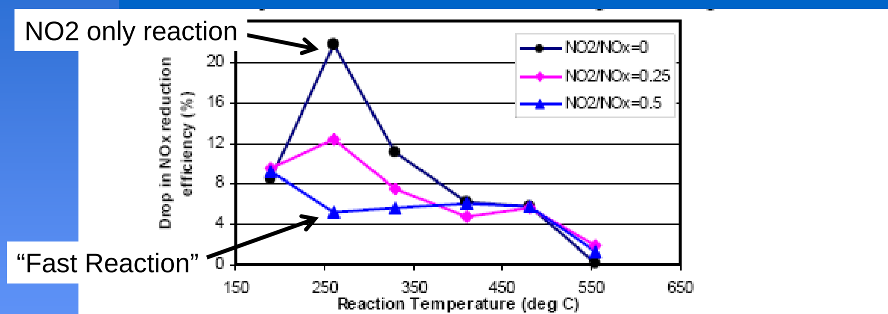
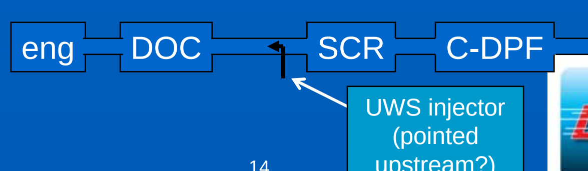


Figure 1. Drop in NOx reduction efficiency due to hydrothermal aging at 700 ^{0}C for 50 hrs.

North American Catalyst Society, 2007 Meeting, Z. Liu et al, "Hydrothermal Stability of Fe/Zeolite SCR Catalysts for NOx Reduction of Diesel Engine Exhaust Gas."

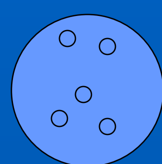
120k Dynamometer Aging Study

- Ford Research and Innovation Center
  - Cu-zeolite
- SAE 2007-01-1579
  - "Laboratory Postmortem Analysis of 120k mi Engine Aged Urea SCR Catalyst"
- Aging included ~650 DPF regenerations @ ~650°C

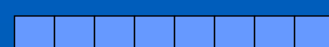


Samples

- SCR substrate: 8”dia x 8” long
- Axial and radial aging studied
  - 5 core samples, 1” dia x 8” long



5 core samples were taken; 1 inch dia each



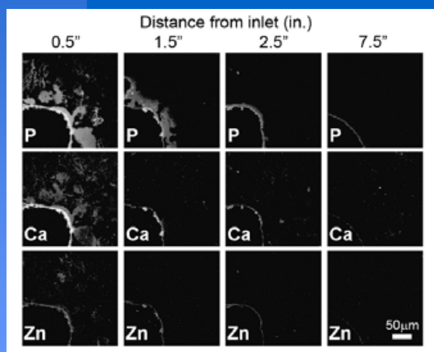
each core cut into 8 pieces, each 1 inch long

Key Findings

- Cu sintering found
  - size of Cu fresh: < 5um
  - size of Cu 120k: up to 30 um
  - loss of catalytic activity
  - particles much larger than zeolite pores
- Likely some urea related residue
  - found a N-C-N bond
  - not identified absolutely
  - urea deposits are potential concern

data from Y. Cheng et al, “Laboratory Postmortem Analysis of 120k Engine Aged Urea SCR Catalyst,” SAE 2007-01-1579

Chemical Poisoning



- P, Ca, and Zn all present
  - mostly at inlet, less at outlet
- BET surface area very low at inlet

data from Y. Cheng et al, "Laboratory Postmortem Analysis of 120k Engine Aged Urea SCR Catalyst," SAE 2007-01-1579

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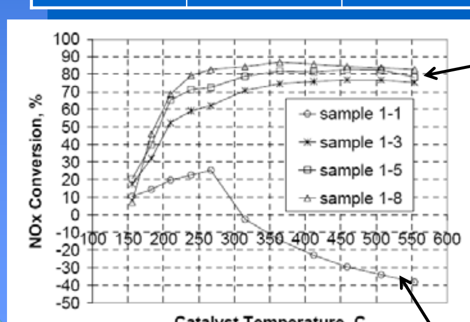
Key Findings, cont

Sample	1st inch	3rd inch	5th inch	8th inch
BET area	23.4	71.6	101.7	112.4



mid to back

front section

data from Y. Cheng et al, "Laboratory Postmortem Analysis of 120k Engine Aged Urea SCR Catalyst," SAE 2007-01-1579

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Key Findings, cont

- H-T de-Al caused by hot steam
  - temperature, water fairly uniform axially
  - DPF regen could cause hot front face
- Loss of BET in front suggests another aging mode
  - Chemical poisoning (pore clogging)
  - Sintering due to regen of DPF

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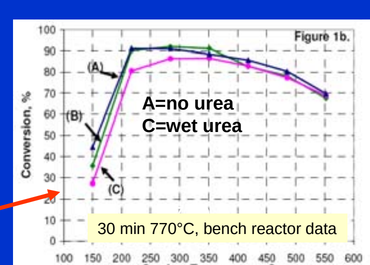
Zeolite SCR Catalyst Durability Summary

- Mechanisms understood, more engine data needed
- System interaction important
  - NO/NO_2 ratio from oxidation catalyst
- More focus needed on
  - temporary deactivation / pore blocking
  - chemical poisoning
- Most aging results are without urea dosing BUT…



Cheng et al – NACS NAM20 2007

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