Function Specific Analysis of the Thermal Durability of Cu-Zeolite SCR Catalyst

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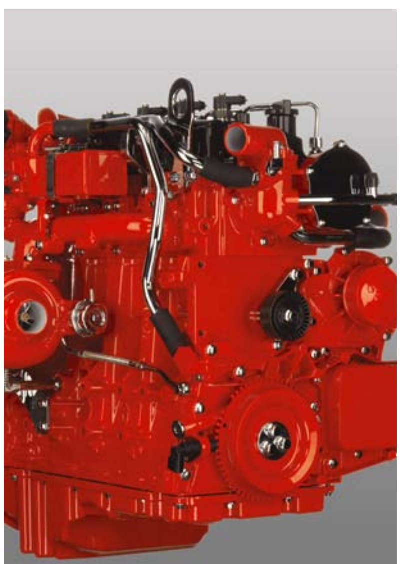
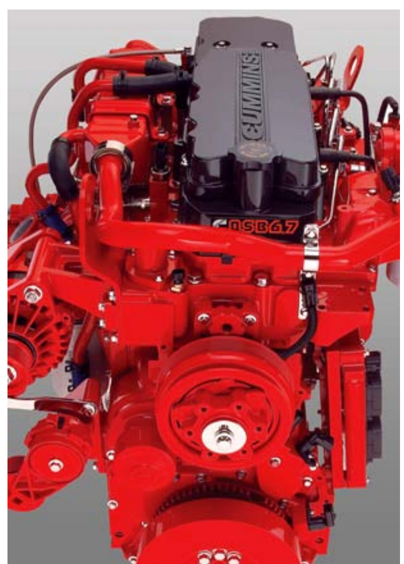
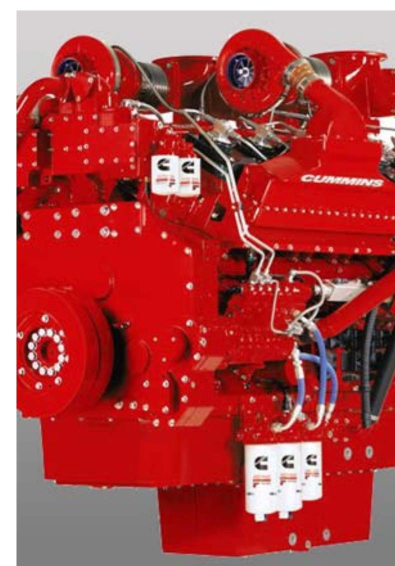
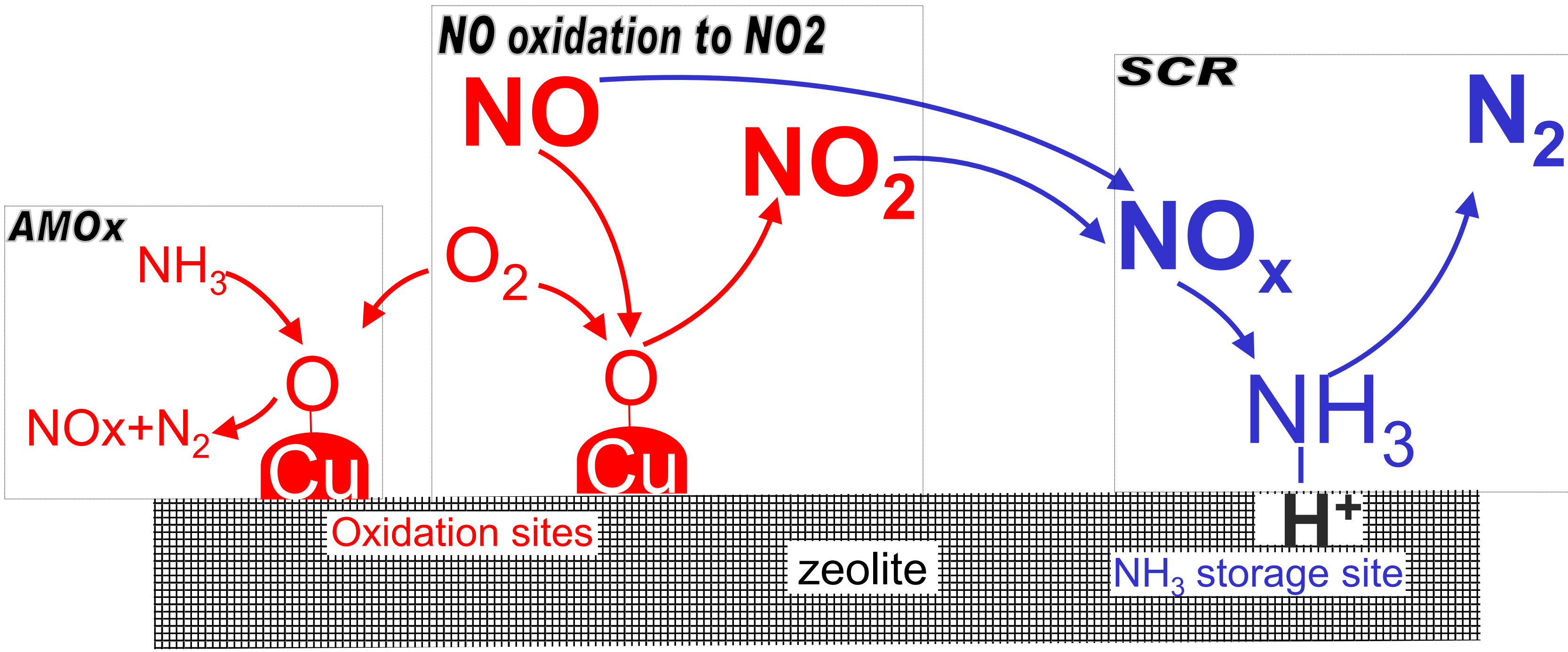





Cu-Zeolite Catalyst Functions



Oxidation (Cu) sites

- **Oxidizes NO+O_2 to NO_2**: *NO_2 increases NOx conversion, when "NO" only is used for SCR*
- **Oxidizes NOx to nitrites/nitrates**: *Actual reactants on the catalyst surface*
- **Oxidizes NH_3 with O_2**: *Decreases effective ANR and therefore NOx conversion*

NH_3 storage sites

- **NH_3 is stored on "acid site" in the zeolite structure:** *NOx (nitrites and nitrates) reacts with stored NH_3 to N_2*

New Generation of Hydrothermally Stable Cu-Zeolite

Cavatio et al. SAE 2008-01-1025

- Discussed new generation Cu-Zeolite with unparalleled hydrothermally stability at temperatures up to 950C for 1hr
- Quantified the NOx conversion performance of new generation Cu-Zeolite as a function of aging time and temperature

Fedeyko et al. SAE 2009-01-0899

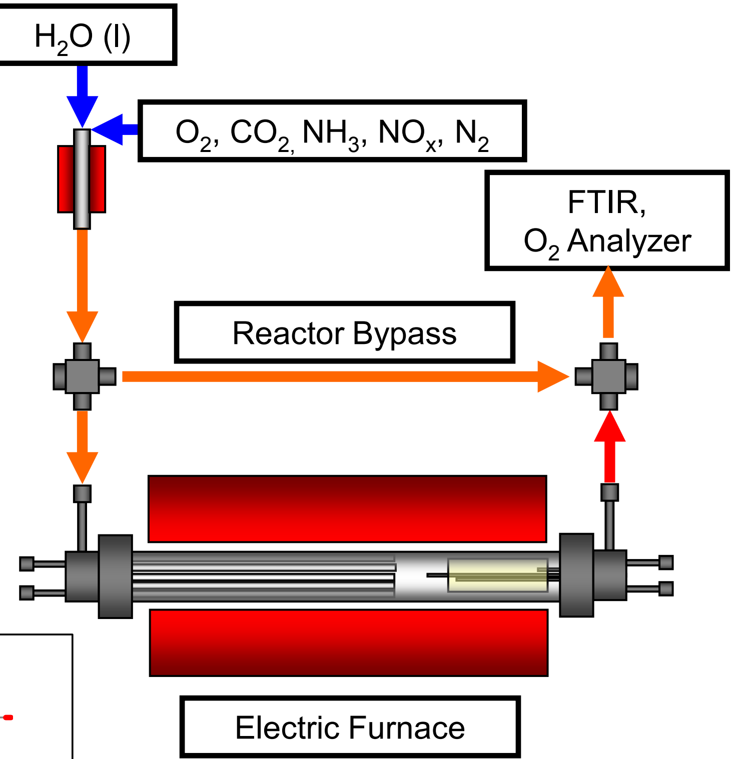
- Improved stability of acid sites on new generation Cu-Zeolite was shown to improve NOx conversion efficiency after aging when compared to previous generation catalyst

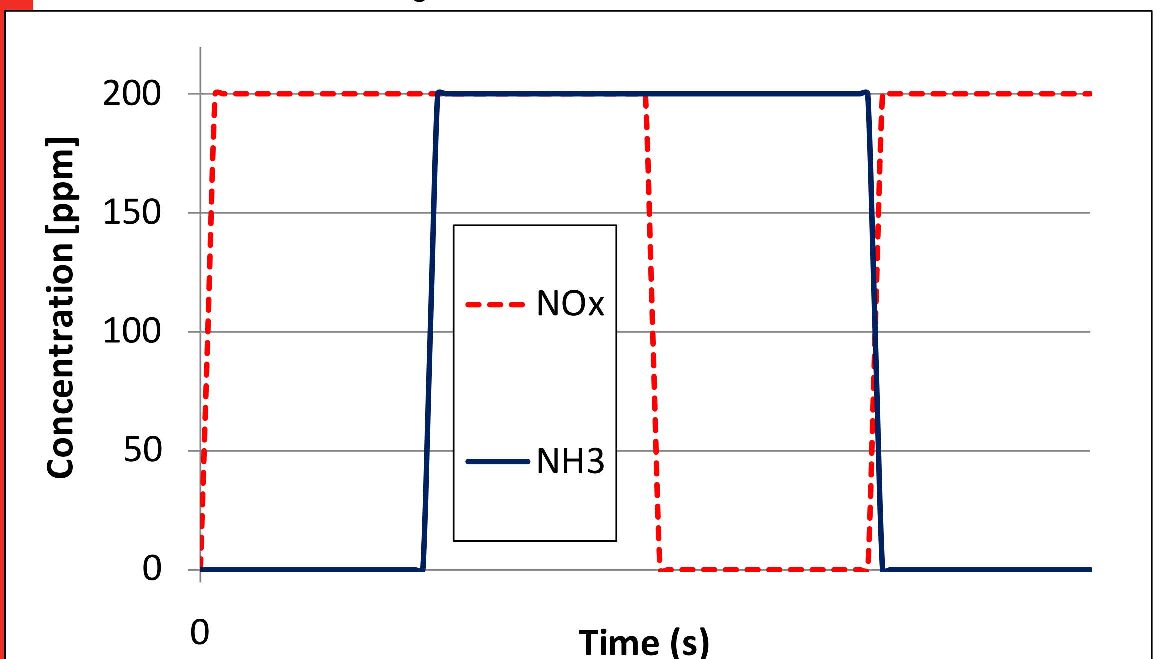
Objective

- Quantify the effect of hydrothermal aging on the specific catalyst functions
    - Overal NOx conversion performance is a complex additive structure based on the specific individual functions of the catalyst
    - Understanding the individual aging mechanisms will allow for improved controls strategies and OBD
- Multiple aging protocols completed
    - End of useful life 700C-100hrs
    - Accelerated aging 900C-10hrs
    - Long term aging 700C-1000hrs

Experimental Apparatus and Test Protocol

- 4 step protocol allows for steady state and transient function specific analysis of NH_3-SCR catalyst performance
  - As described by Kamasamudram et al. Catalyst Today 151 (2010) 212-222
- Specific functions probed include: NO_x conversion performance, NH_3 storage, and NO & NH_3 oxidation





Expected Hydrothermal Aging Effects on Cu/zeolite Functions

NH_3 storage function degradation (irreversible)

- Aging reduces acidity of the support material through processes such as dealumination and collapse of framework structure
- NH_3 storage capacity is a good indicator of the number of acid sites
- NH_3 storage will be quantified as a function of aging time and temperature

Oxidation function (of Cu) degradation

- Hydrothermal aging may have an effect on the oxidation capacity of the catalyst due to degradation of the Cu oxidation sites
- Both the oxidation of NO and NH_3 will be quantified as a function of aging time and temperature

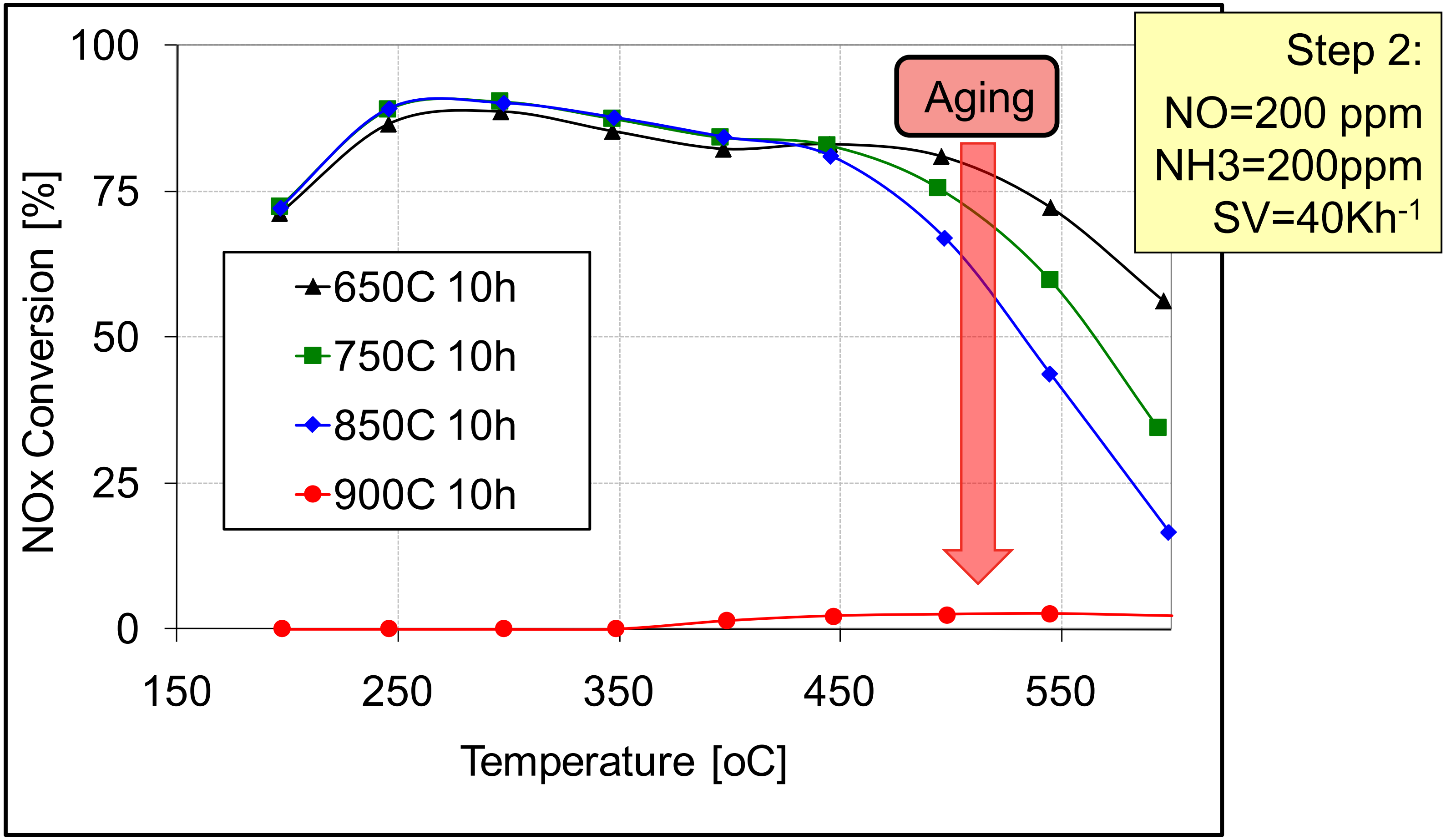
Structure collapse due to extreme aging (irreversible)

- The catalyst will be exposed to gas temperatures as high as 900C for 10hr in order to determine the point at which the catalyst loses all function performance

Experimental

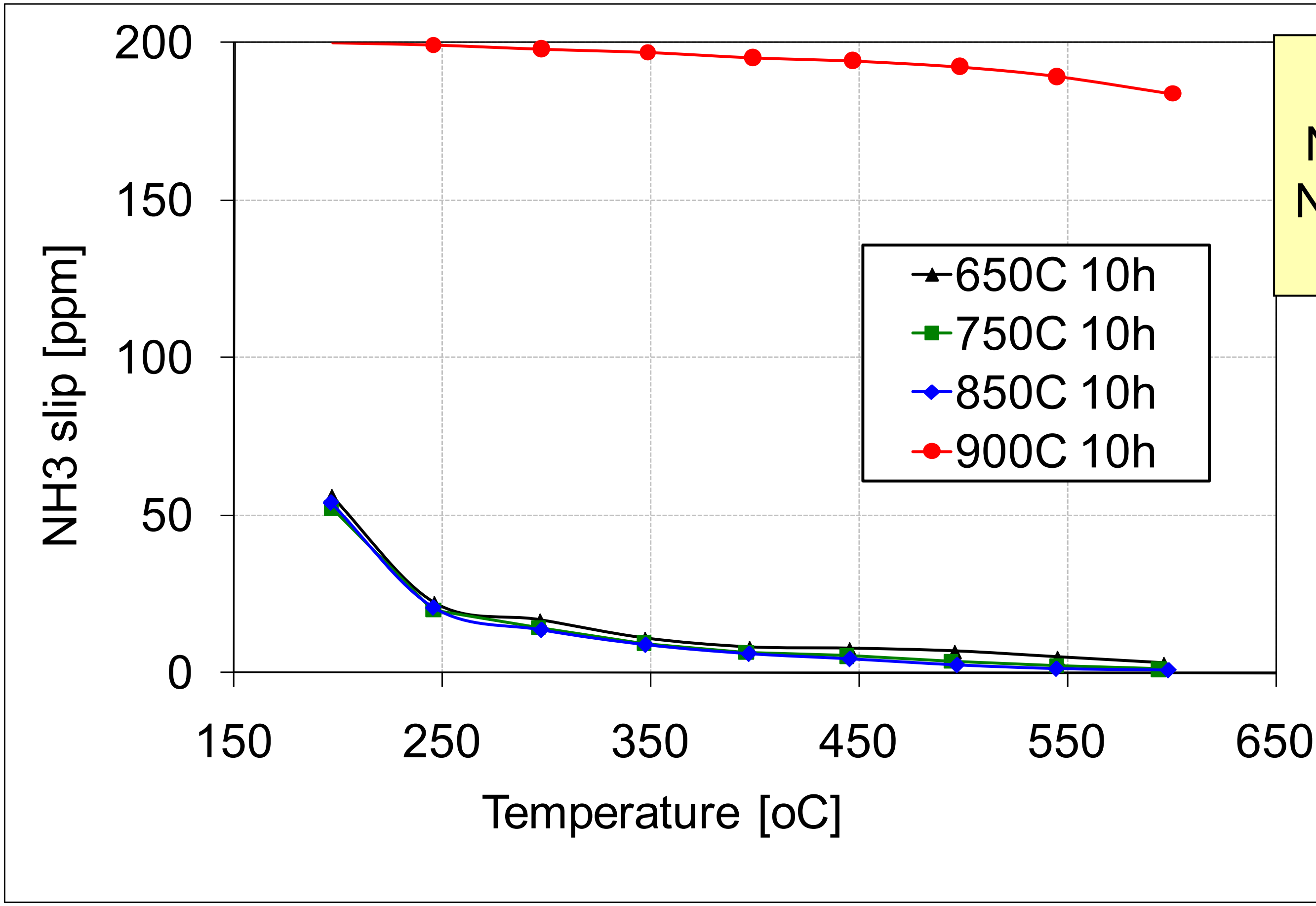
Sample	State of the Art Cu-Zeolite
Core sizes	0.25"D x 1"L
Progressive Hydrothermal Aging	650C/10hr → 750C/10hr → 850C/10hr → 900C/10hr
Lean Gas Composition	O_2=10%, H_2O=8%, CO_2=7%, Balance N_2, SV=40Kh^{-1}
SCR Composition	NO=200 ppm, NO_2/NOx=0, ANR=1, SV=40Kh^{-1}
NH_3 oxidation	NH_3=200 ppm, SV=40 Kh^{-1}
NO oxidation	NO=200 ppm, SV=40Kh^{-1}

Effect of accelerated hydrothermal aging on NOx conversion



- Progressive aging of Cu-Zeolite up to 850 C for 10h lead to
  - *-very limited increase in NOx conversion below 400 C*
  - *-significant decrease in NOx conversion above 450 C*
- Further 900 C 10h aging resulted in substantial loss of NOx conversion
  - *Potentially the catalyst structure is collapsing*

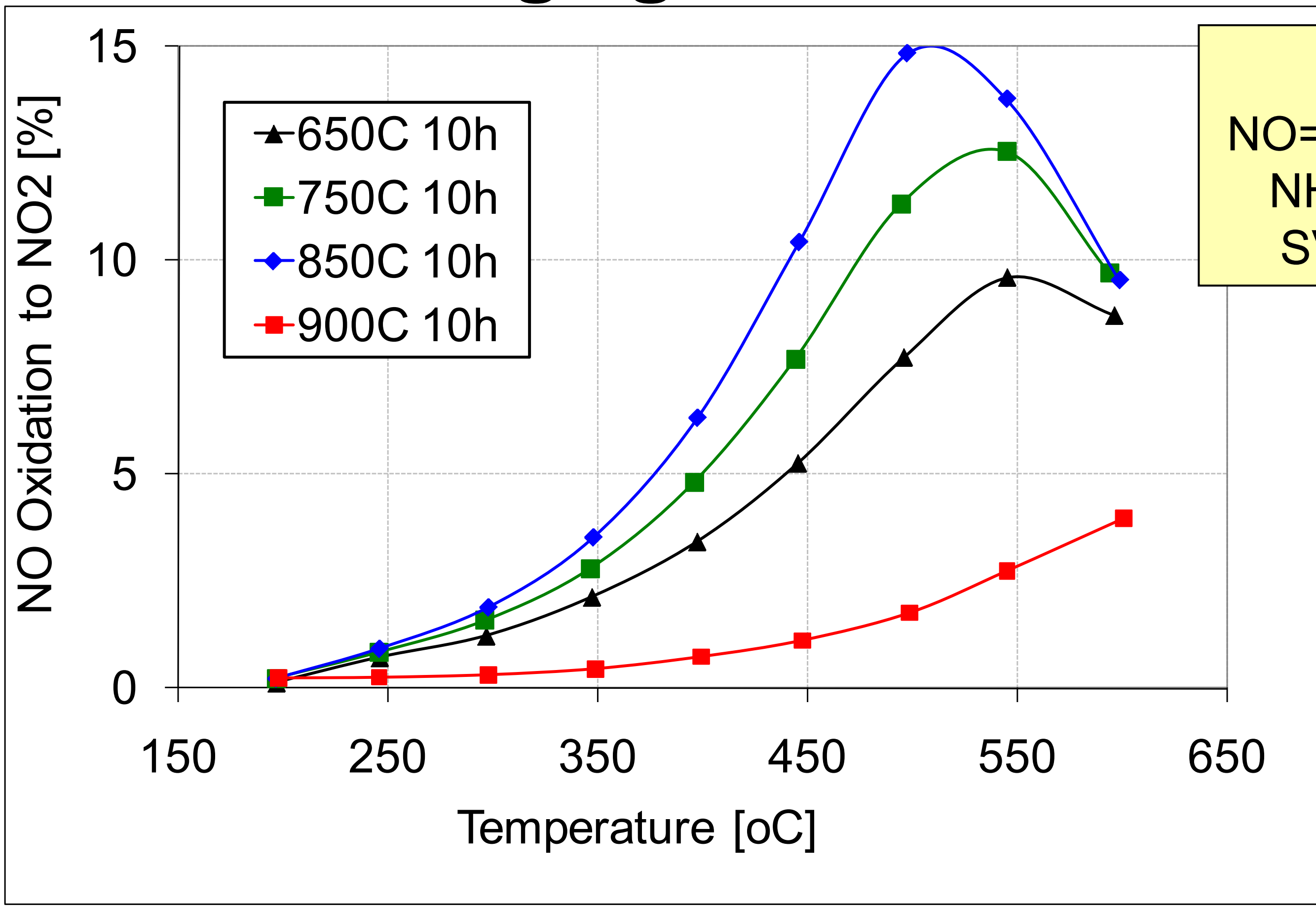
Effect of accelerated hydrothermal aging on NH_3 slip



Step 2:
NO=200 ppm
NH3=200ppm
SV=40Kh^{-1}

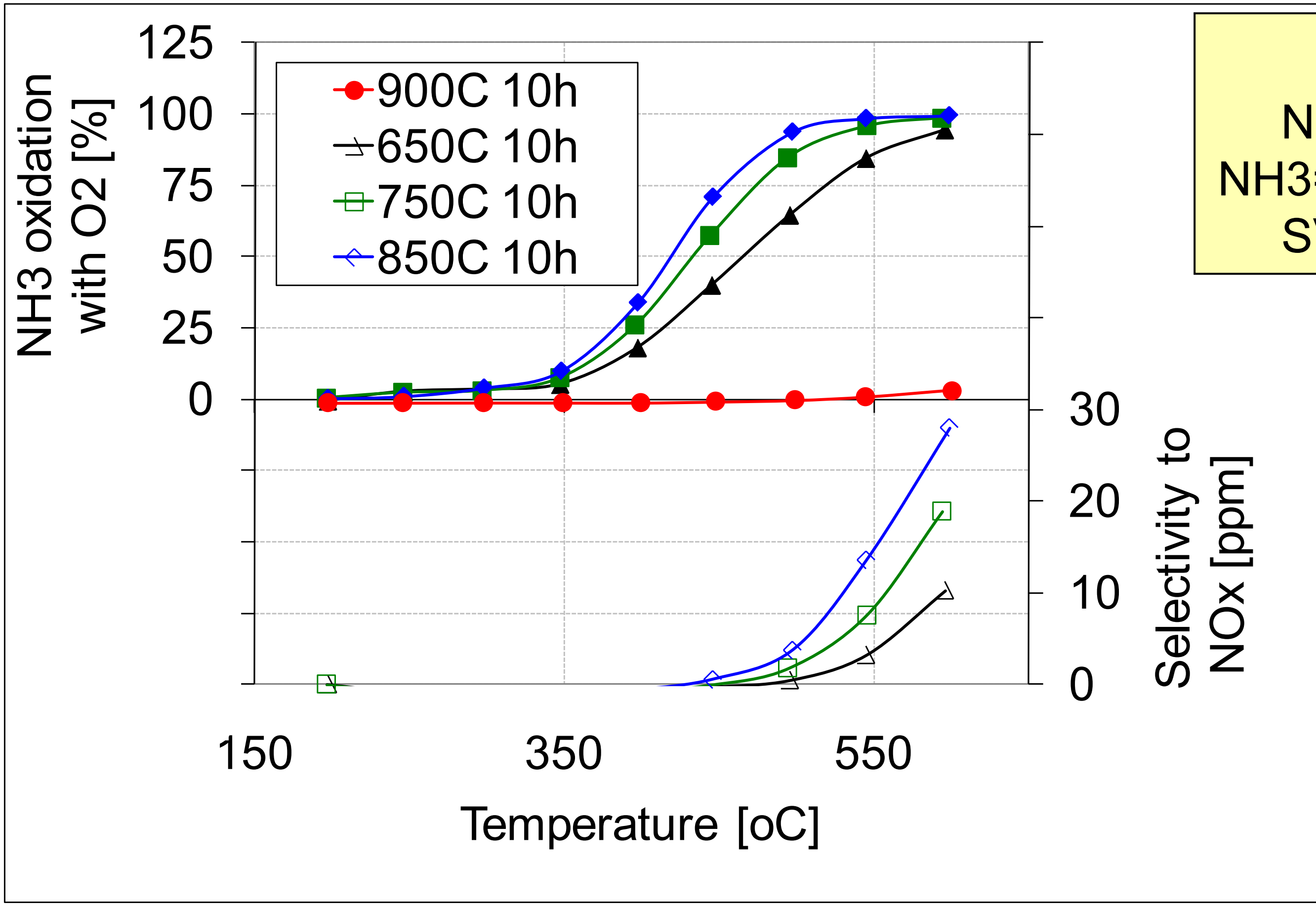
- Due to high NOx conversions (previous slide), changes in NH_3 slip trends were not obvious, on catalysts aged below 850 C
- 900 C 10 h aging resulted in high NH_3 slips, since NOx conversions were low

Effect of accelerated hydrothermal aging on NO oxidation to NO_2



- With progressive aging up to 850 C for 10h, NO oxidation to NO_2 increased throughout the reaction temperature range
- Further aging at 900 C for 10 h resulted in substantial degradation of NO conversion
    - *Under challenging SCR conditions, when NO only is present, the increase of NO oxidation to NO_2 increases NOx conversion*

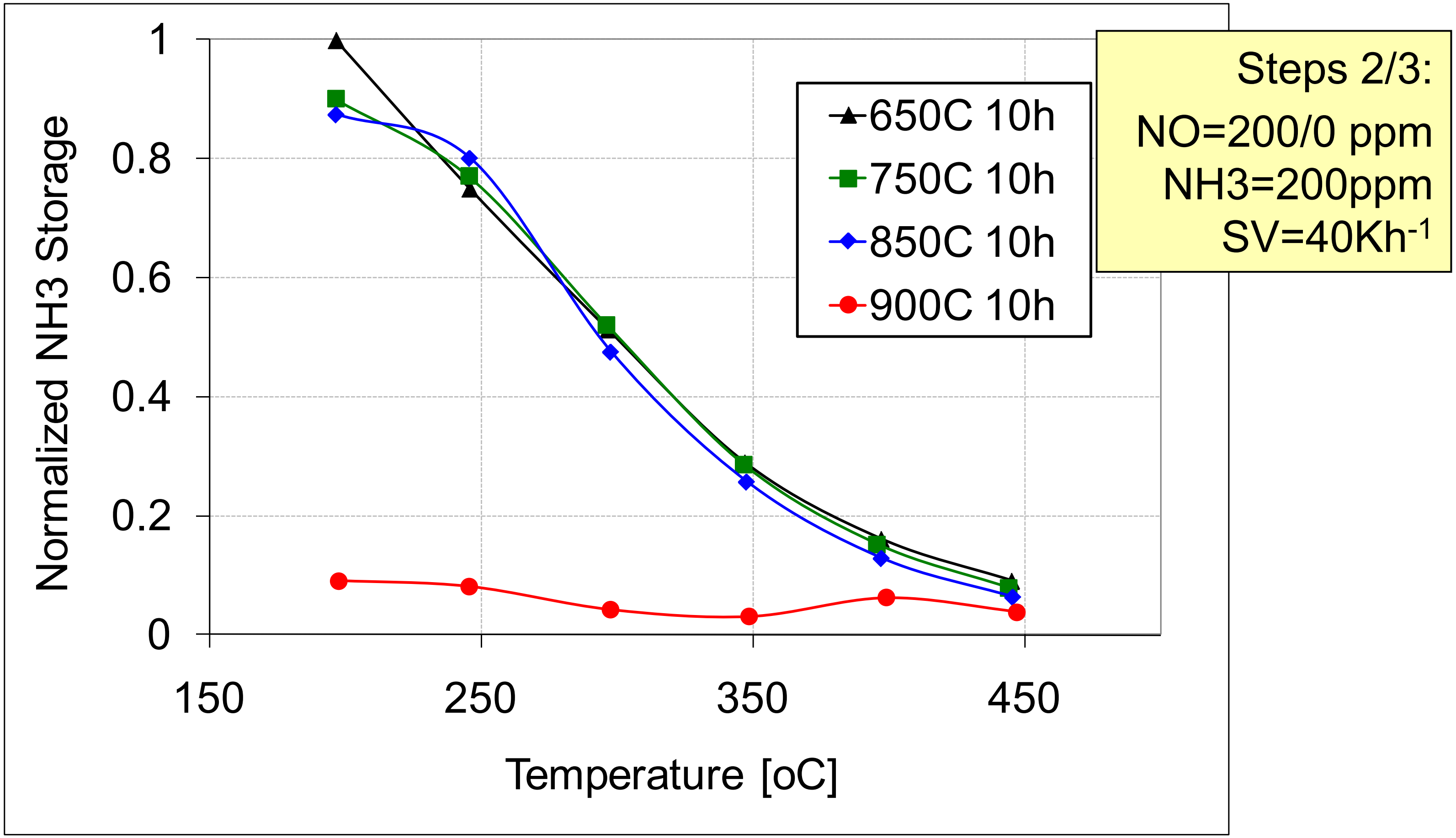
Effect of accelerated hydrothermal aging on NH_3 oxidation



Step 3:
NO=0 ppm
NH3=200ppm
SV=40Kh^{-1}

- Progressive aging of Cu-Zeolite, up to 850 C, increased NH_3 oxidation and selectivity to NOx
- 900 C for 10 h aging lead to substantial degradation in NH_3 oxidation
  - *Parasitic NH_3 oxidation and its selectivity to NOx, under SCR conditions above 450 C leads to a decrease in effective ANR, which reduces the overall NOx conversion*

Effect of accelerated hydrothermal aging on NH_3 storage



- Negligible change in NH_3 storage capacity for hydrothermal aging up to 850C for 10 hrs
- 900 C 10 h aging resulted in substantial degradation of NH_3 storage capacity

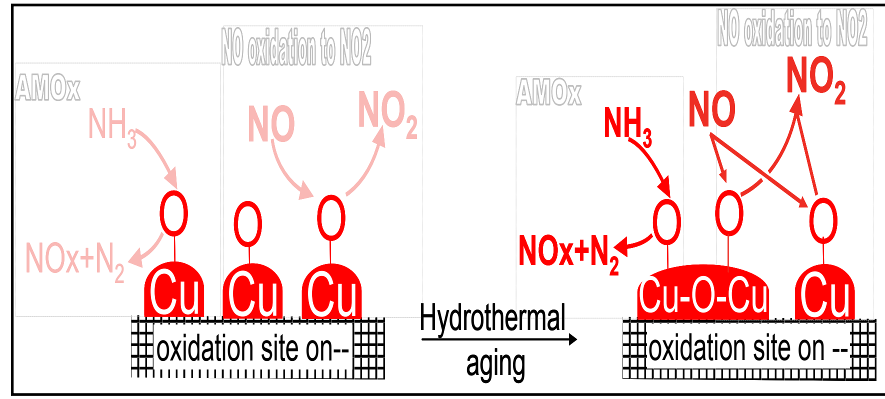
Simplified SCR Catalyst Degradation Mechanism

Oxidation function (Cu)

- Oxidation ability is increasing with hydrothermal aging

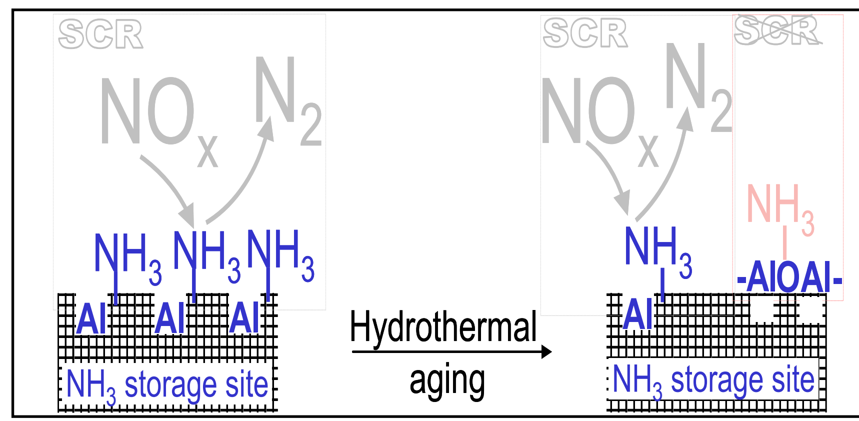
Net impact

- NOx performance loss due to increase in parasitic NH_3 oxidation at high temperatures
- Improvement of low temperature performance, when NO only is used as in reactor tests



NH_3 storage function

- Anticipated decrease in NH_3 storage, but decrease was not substantial, even under severe aging conditions (below 850 C for10h)



Extreme catalyst aging (>850 C)

- Expected catalyst structure collapse
- severe degradation of oxidation and storage functions

Net impact

- Extensive degradation of NOx conversion

Summary

- The unparalleled hydrothermal stability of the new generation Cu-Zeolite SCR catalyst has been confirmed at exceedingly aggressive aging conditions
  - Consistent with Cavatio et al. SAE 2008-01-1025 and Fedeyko et al. SAE 2009-01-0899)
- Long-term hydrothermal exposure at 700 C for 1000hrs confirmed the validity of aging trends observed with accelerated aging up to 850 C.
- Nascent changes in the catalyst material and its functions, brought about by the aggressive aging, differ from the conventional wisdom expectations for zeolite-based catalysts
  - No measurable impact on NH_3 storage; increased activity/reduced selectivity of oxidation functions
  - Direct implications for catalyst control and diagnostics