Performance Characterization of Cu/Zeolite and Fe/Zeolite Catalysts for the SCR of NOx

Giovanni Cavataio

James Girard, Joseph Eli Patterson Clifford Montreuil,

Yisun Cheng, and Christine K. Lambert

Ford Motor Company
Research and Innovation Center

10th DOE Crosscut Workshop on Lean Emissions Reduction Simulation
May 1st – 3rd, 2007
University of Michigan – Dearborn

Motivation

The durability requirements and diverse operating conditions of light-duty compared to heavy-duty vehicles make it necessary to understand the differences between SCR formulations.

Parameters studied include:

- **Durability to active DPF regenerations.**
- **Robustness to occasional over-temperature.**
- **Impact of NO_2/NOx, O_2 level, SV, and NH_3 storage.**
- **Influence due to sulfur and hydrocarbon poisoning.**

Laboratory Characterization of Cu/zeolite and Fe/zeolite SCR Formulations

OUTLINE:

1. SCR Catalyst Description
2. Durability/Robustness
3. Factors Affecting SCR Activity

SCR Catalyst Description

1) **Cu/Zeolite**
   - 400/6.5 CPSI
   - 2006 state of the art supplier formulation
   - Optimized zeolite formulation for stabilizing Cu

2) **Fe/Zeolite**
   - 400/6.5 CPSI
   - 2006 state of the art supplier formulation
   - Optimized zeolite formulation for stabilizing Fe

NOTE: Cu and Fe SCR formulated with the same zeolite-type.

3) **Vanadium Based**
   - Commercially available
   - V_2O_5-WO_3 on corrugated TiO_2 carrier

Laboratory Characterization of Cu/zeolite and Fe/zeolite SCR Formulations

OUTLINE:

1. SCR Catalyst Description
2. **Durability/Robustness**
3. Factors Affecting SCR Activity

Standard Hydrothermal Aging (HTA)

Purpose: Develop hydrothermal aging (HTA) representative of time at temperature conditions typical during active DPF regeneration events.

Hydrothermal Aging

14% O_2

4.5% H_2O

5% CO_2

0 ppm SO_2

balance N_2

Flowrate = 6.44L/min

Sample Size = 1.0" D x 1.0"L

Space Velocity = 30,000/hr

Temperature = 670°C

Time = 64 hrs

Standard aging unless otherwise noted

Standard SCR Baseline Evaluation

Purpose: Determine activity window for NOx conversion versus temperature for the worst case NO only evaluation (0% NO_2/NOx ratio).

Steady State Evaluation

350 ppm NO

350 ppm NH_3

14% O_2

4.5% H_2O

5% CO_2

0 ppm SO_2

bal N_2

S.V. = 30,000 hr^{-1}

T = 150 - 600°C

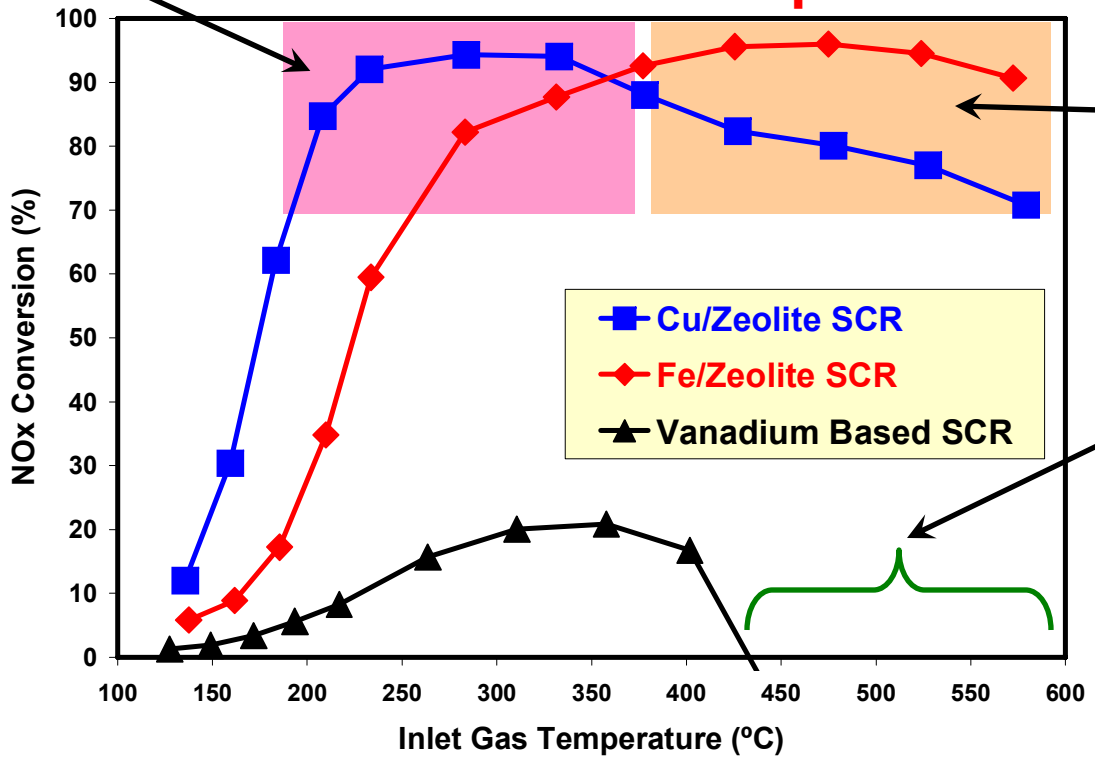
ANR = 1.0 (NH_3/NOx)

Standard evaluation unless otherwise noted

SCR Technology Selection

(HTA 64h/670°C)

Light-Duty
Chassis
Certification



Heavy-Duty
Engine Dyno
Certification

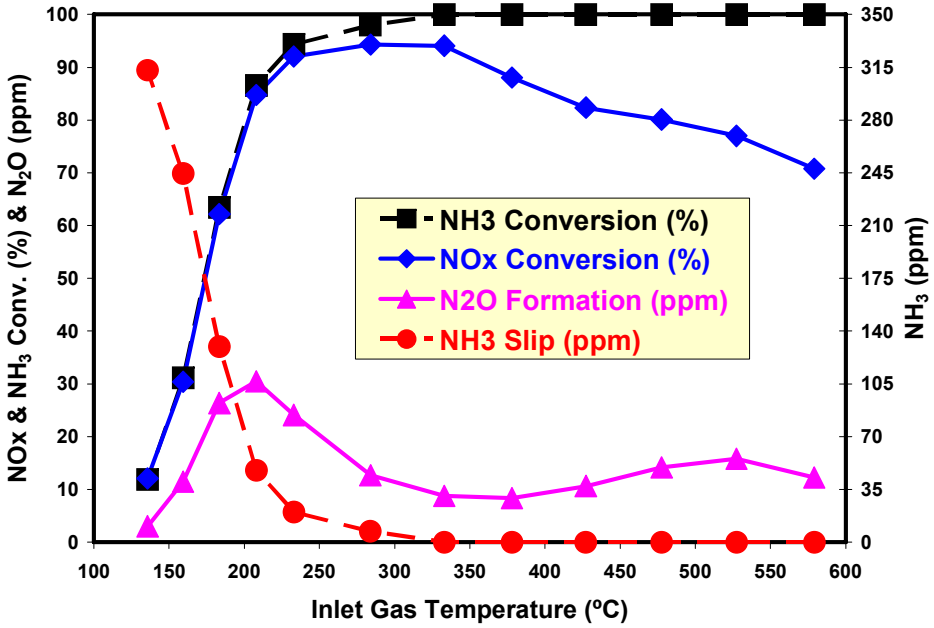
NOx remake from NH_3 oxidation

- **Base metal/zeolite SCR formulations were found to be more thermally stable than a vanadium-based formulation at temperatures typical of diesel applications.**

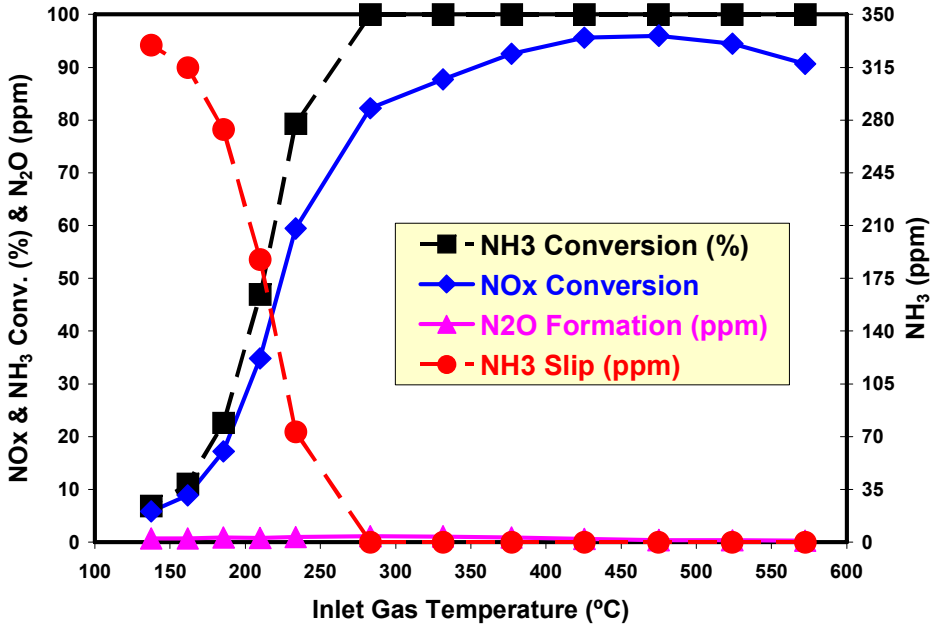
SCR Reaction Activity Profile

NOx and NH_3 Conversion, N_2O Formation, and NH_3 Slip

Cu/zeolite



Fe/zeolite



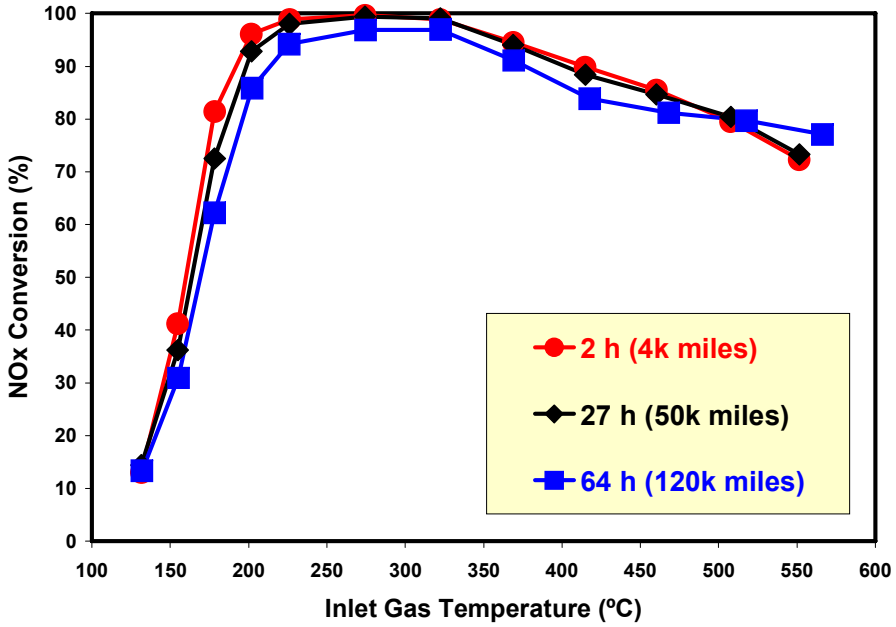
- Cu/zeolite is more activity below 350°C and generates high levels of N_2O.
- Fe/zeolite is more activity above 350°C and generates very low N_2O.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad \text{"Standard" Reaction}$$

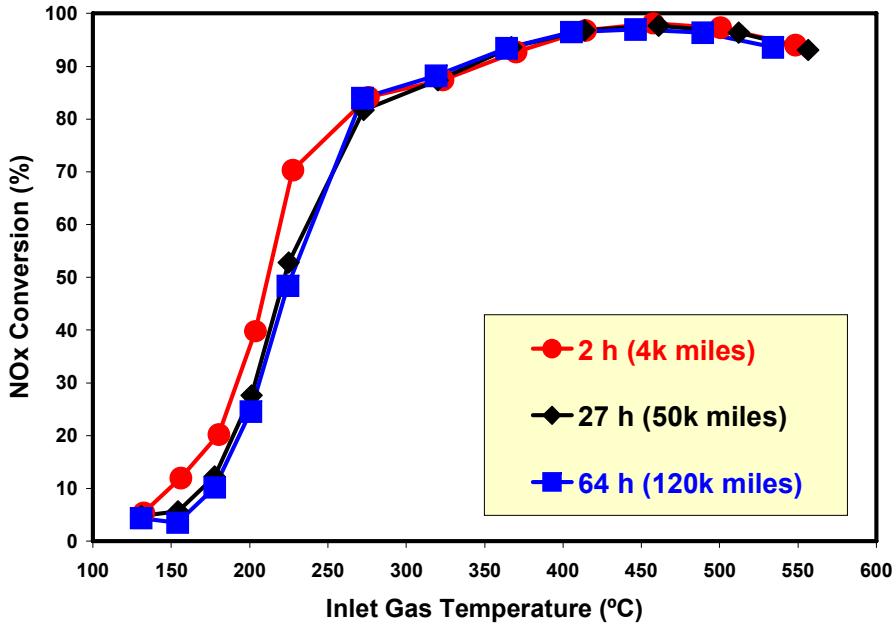
Thermal Durability as a Function of Mileage

Effect of thermal aging at 670°C

Cu/zeolite



Fe/zeolite

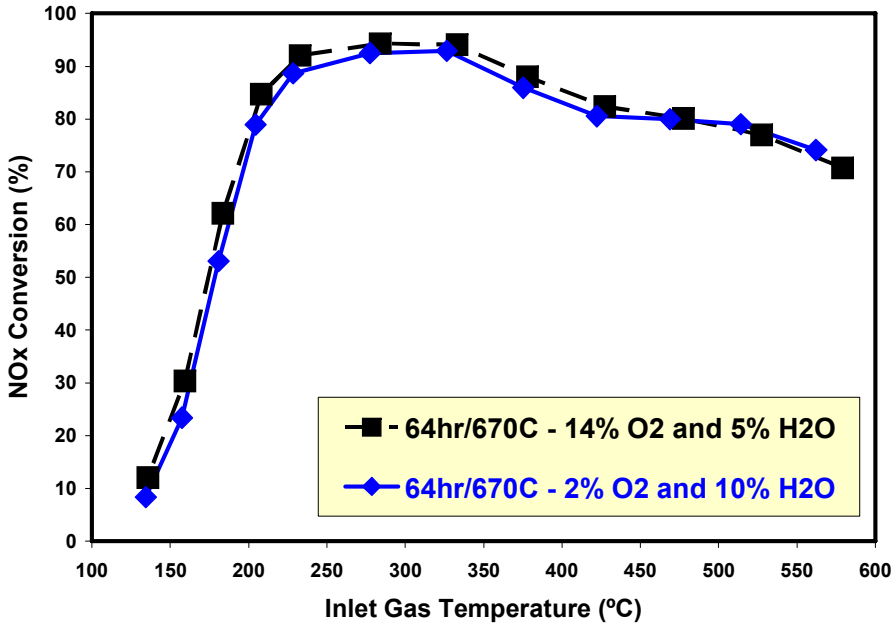


- Cu/zeolite deactivates from 80% to 60% NOx conversion at 175°C.
- Fe/zeolite deactivates from 70% to 50% NOx conversion at 225°C.

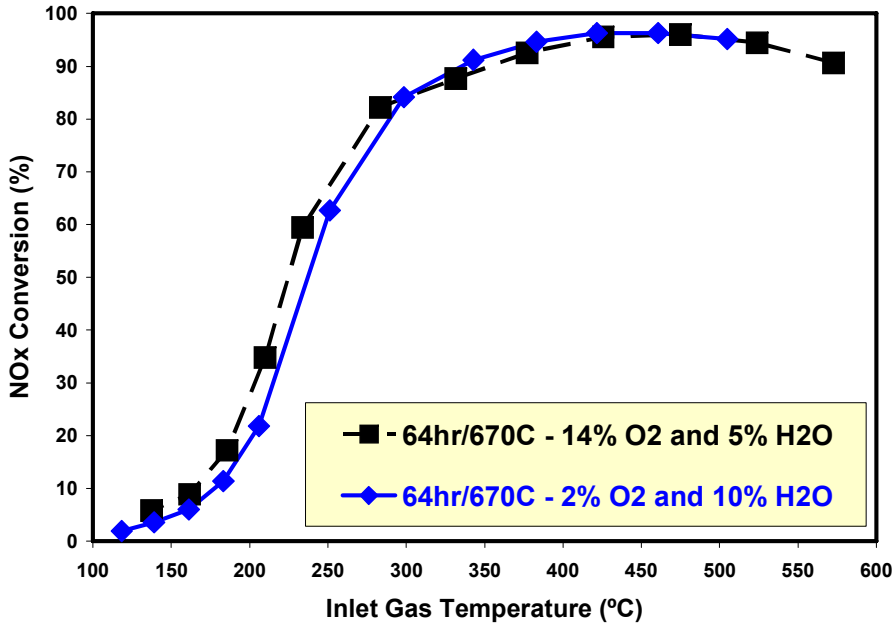
Impact of O_2 and H_2O Levels During Aging

HTA 64hr/670°C: 2% O_2/10% H_2O vs. 14% O_2/5% H_2O

Cu/zeolite



Fe/zeolite

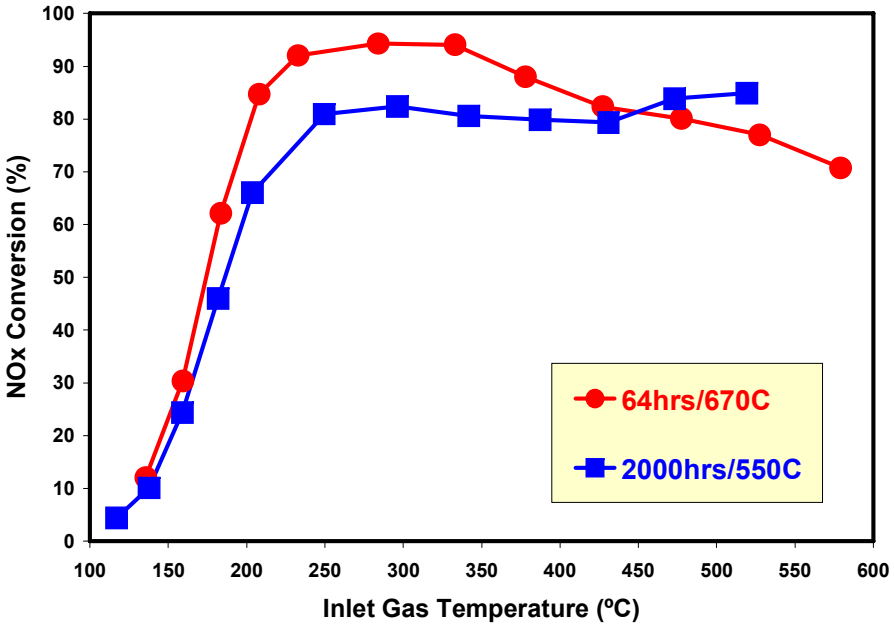


- Vehicle high load and cDPF events can cause low O_2 and high H_2O levels.
- Both Cu and Fe/zeolite show mild deactivation with 2% O_2 & 10% H_2O.

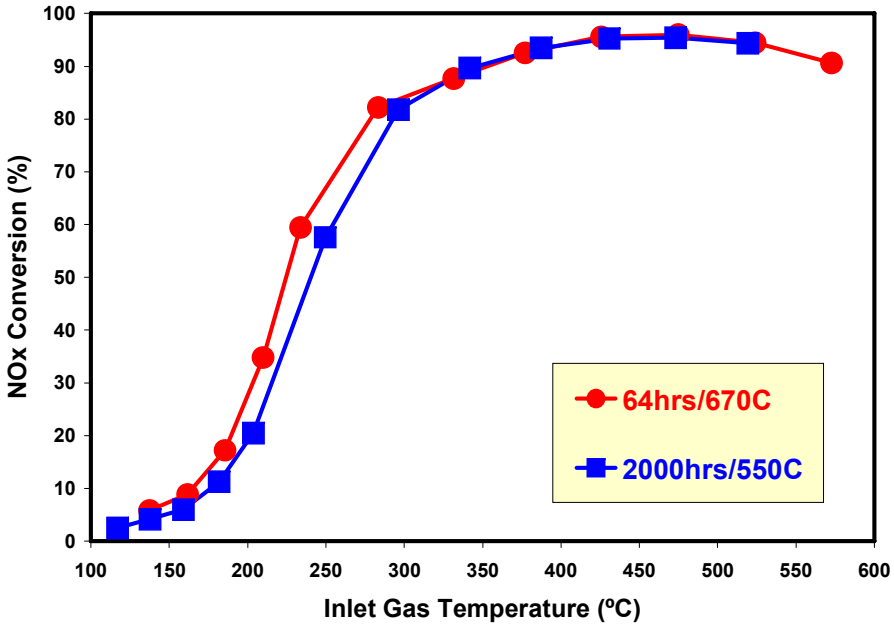
HTA with Longer Time & Lower Temp.

64hrs/670°C vs. 2000hrs/550°C

Cu/zeolite



Fe/zeolite



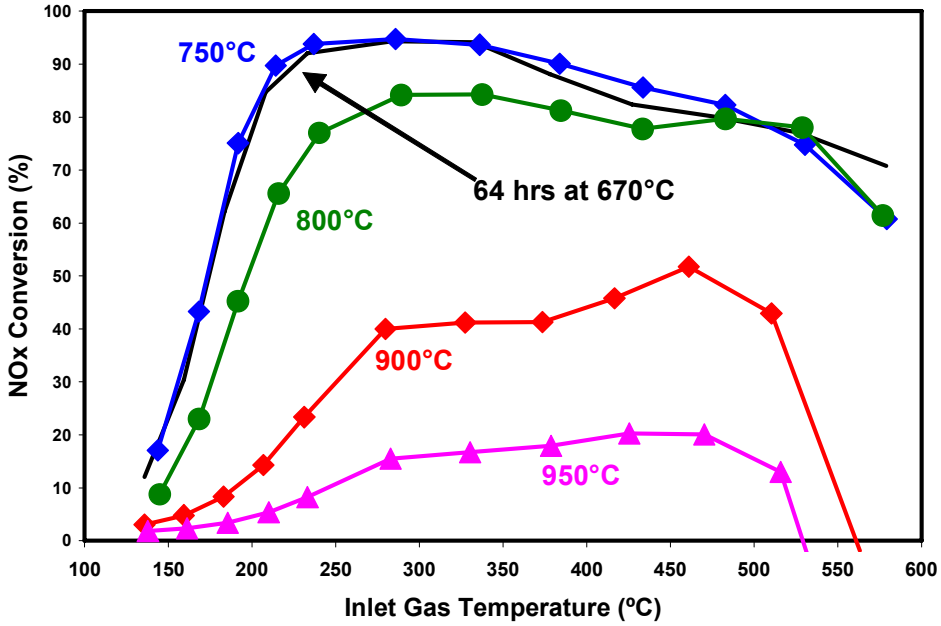
- Cu/zeolite deactivates significantly at low T and improves at high T.
- Fe/zeolite deactivates slightly at low temp. and remains stable at high T.

HTA with Shorter Time & Higher Temp.

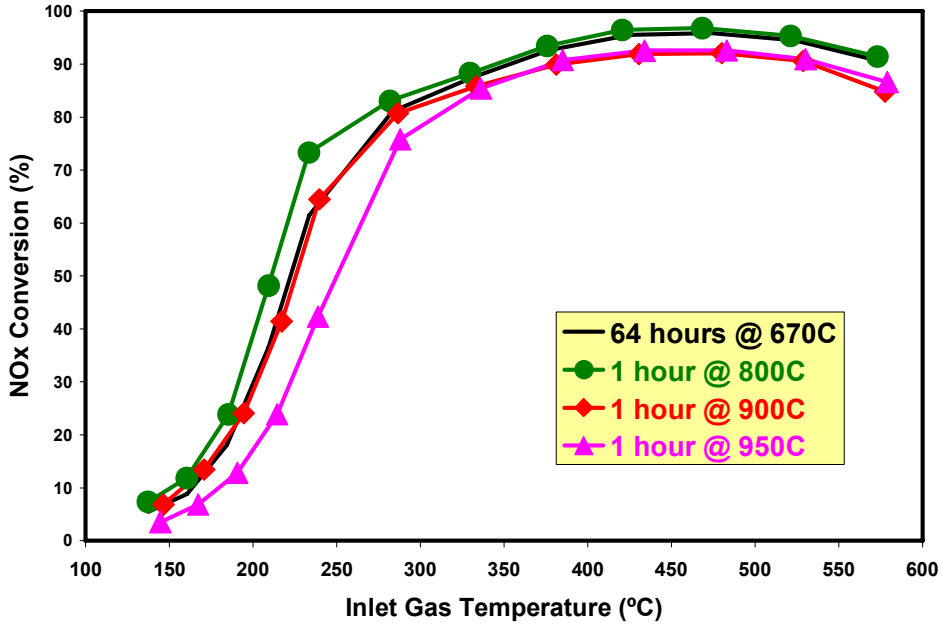
(Robustness to Occasional DPF Over-Temperature)

Determination of Never-To-Exceed (NTE) Temperature

Cu/zeolite



Fe/zeolite



- Cu/zeolite deactivates rapidly with increasing temperature, NTE = 775°C.
- Fe/zeolite is much more stable, NTE = 925°C.

Laboratory Characterization of Cu/zeolite and Fe/zeolite SCR Formulations

OUTLINE:

1. SCR Catalyst Description
2. Durability/Robustness
3. **Factors Affecting SCR Activity**

Standard Aging and Evaluation Conditions

Purpose: Determine SCR temperature activity window

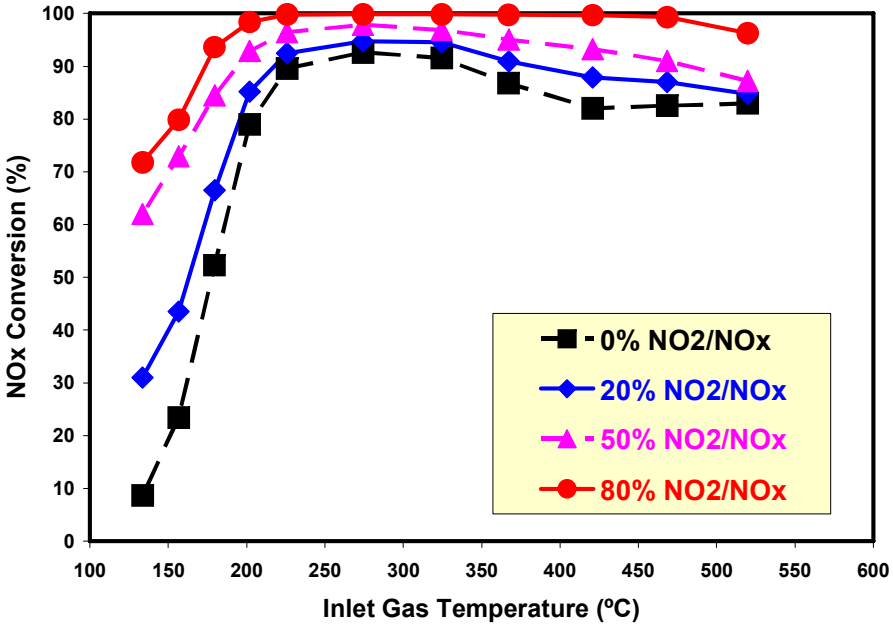
Hydrothermal Aging	**Steady State Evaluation**
14% O_2	350 ppm NO
4.5% H_2O	**(NO_2/NOx = 0%)**
5% CO_2	350 ppm NH_3
0 ppm SO_2	14% O_2
bal N_2	4.5% H_2O
S.V. = 30,000 hr^{-1}	5% CO_2
T=670°C	0 ppm SO_2
64 hrs	bal N_2
	S.V. = 30,000 hr^{-1}
	T = 150 - 600°C
	ANR = 1.0 (NH_3/NOx ratio)

Aging and evaluation conditions unless otherwise noted.

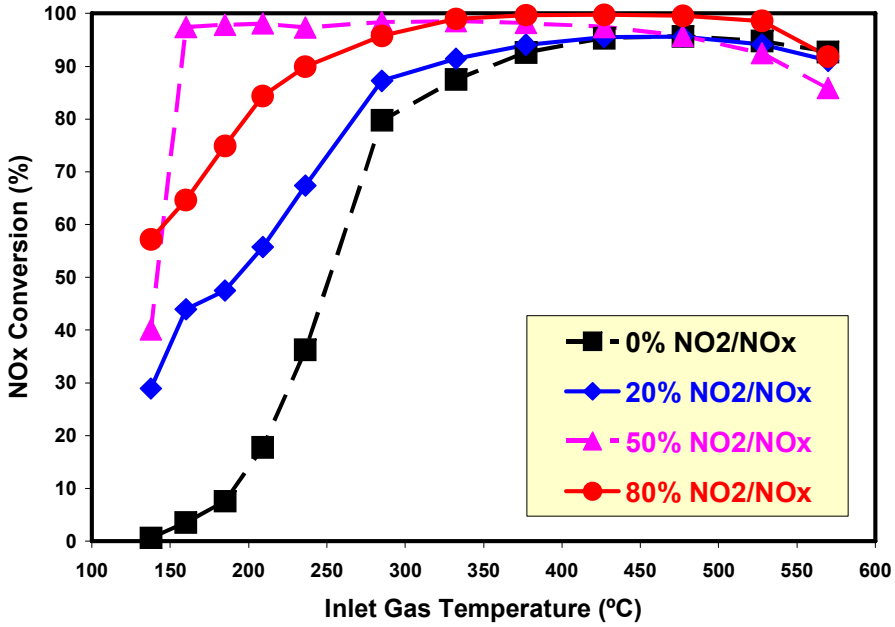
Effect of NO_2/NOx Ratio on Activity

NOx Conversion vs. Temperature

Cu/zeolite



Fe/zeolite

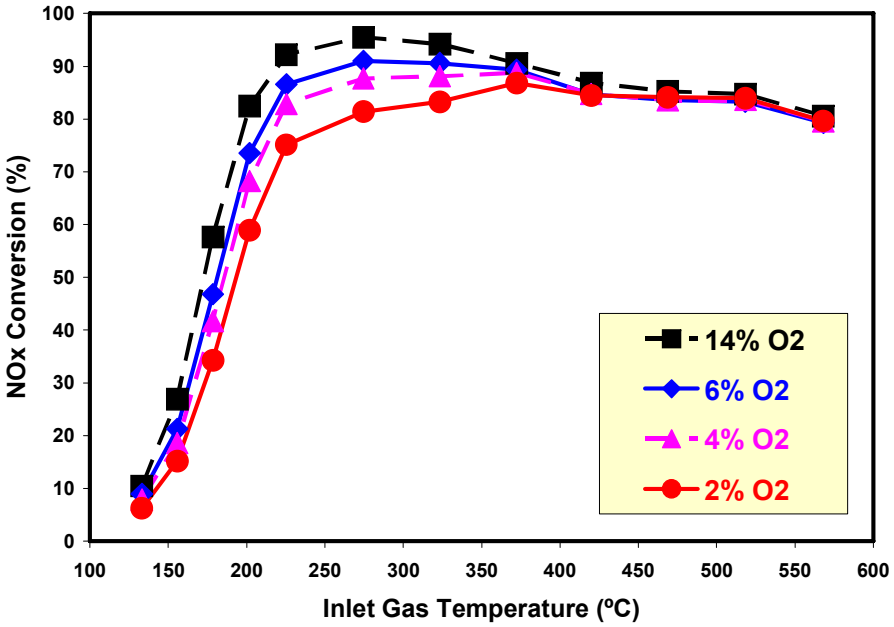


- NOx performance is significantly improved for both Cu and Fe SCRs.
- At low T, Fe/zeolite is more sensitive to the NO_2/NOx ratio than Cu.

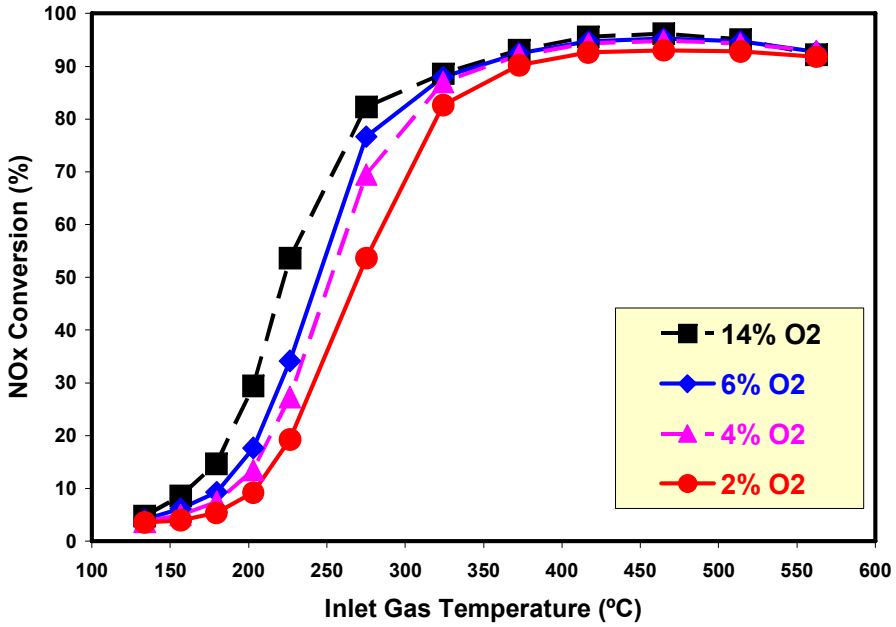
Effect of O_2 Concentration (2-14% O_2)

NOx Conversion vs. Temperature

Cu/zeolite



Fe/zeolite



- **Both Cu and Fe light-off NOx activity NOx drops as the [O_2] decreases.**

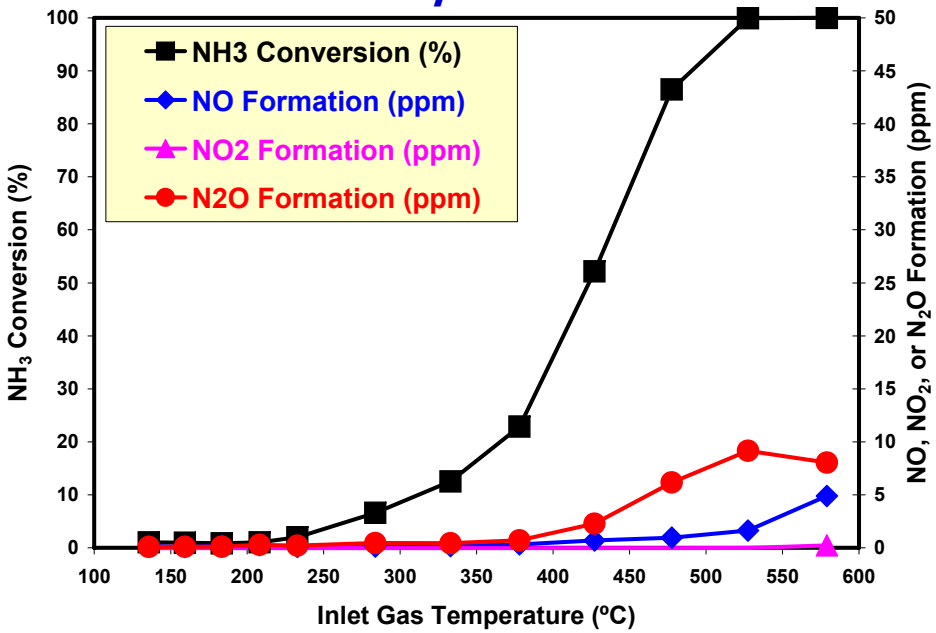
  Recall: $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ "Standard" Reaction

- **High T NOx conversion is not affected in O_2 range tested (2-14%)**

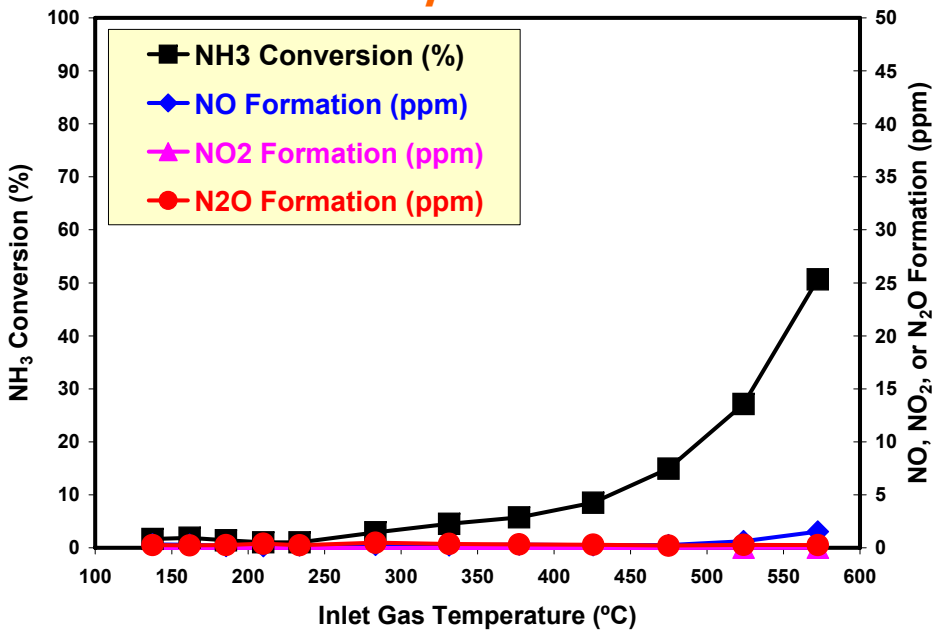
NH_3 Oxidation in the Absence of NOx

NH_3 Oxidation and By-product Formation vs. Temperature

Cu/zeolite



Fe/zeolite

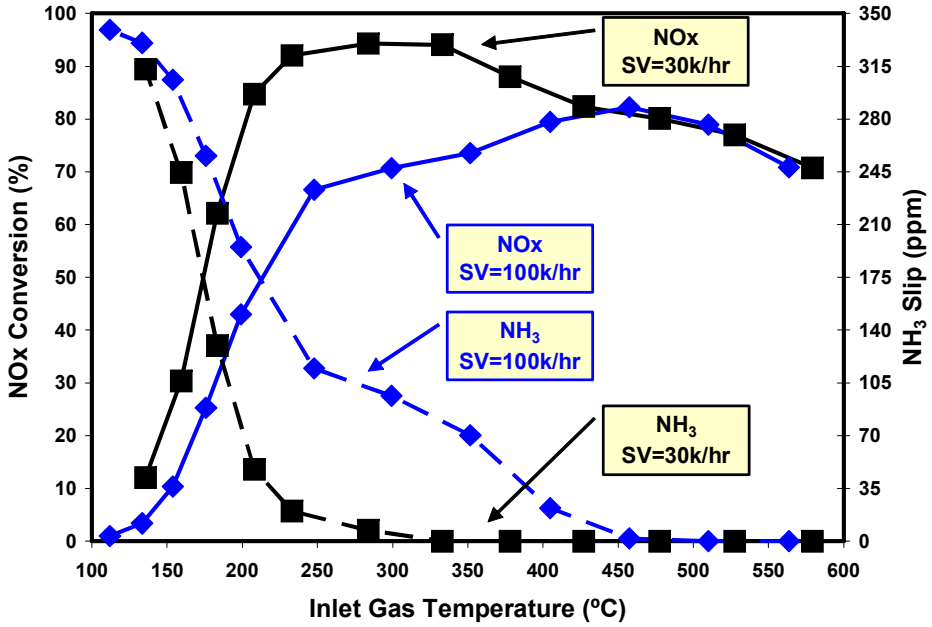


- **Cu/zeolite is active for NH_3 oxidation above 300°C (95% selectivity to N_2).**
- **Fe/zeolite demonstrates similar behavior but much less active.**

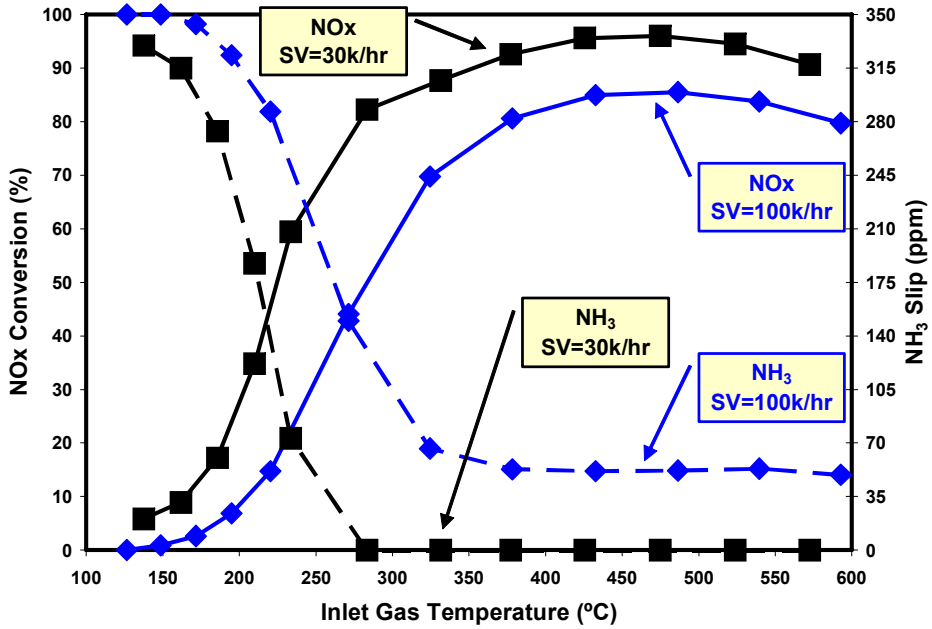
Effect of Increasing Space Velocity

NOx Conversion and NH_3 Slip vs. Temperature

Cu/zeolite



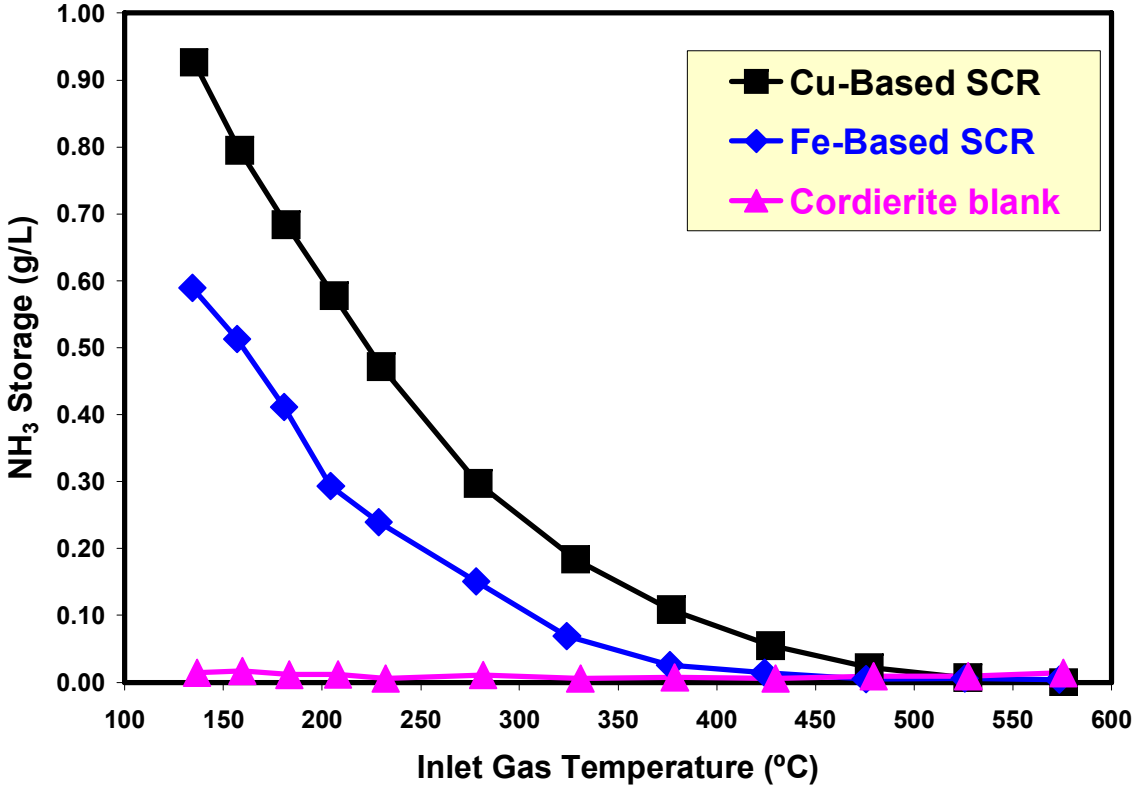
Fe/zeolite



- **Cu/zeolite NOx activity is reduced at low T but unaffected above 425°C. In addition, no NH_3 slip is observed above 450°C**
- **Fe/zeolite NOx activity is reduced for the entire temperature range while NH_3 slip becomes more of an issue.**

NH_3 Storage Capacity

NH_3 Storage Capacity vs. Temperature

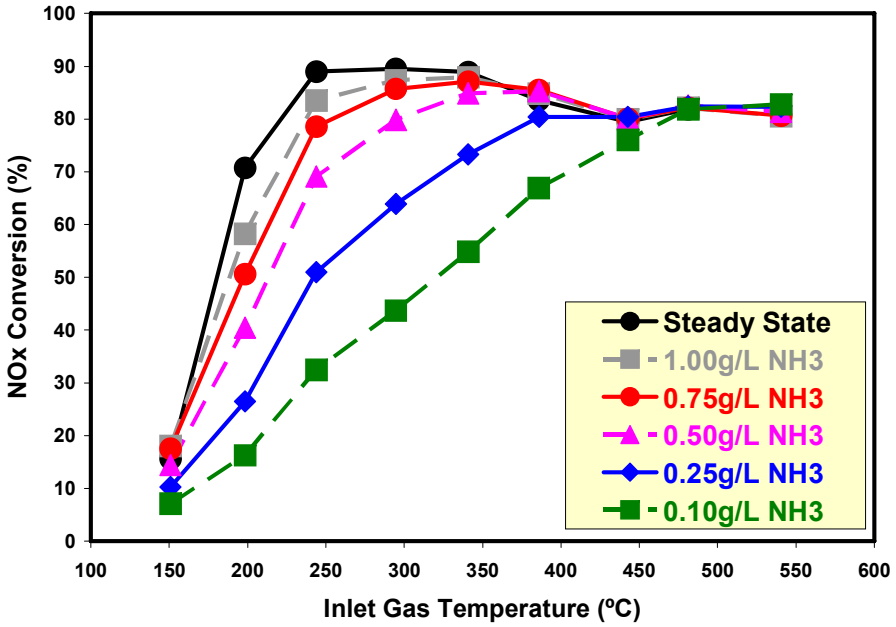


- Base-metal/zeolites store high levels of NH_3 at low T and less as a f (T).
- Cu/zeolite stores up 2x more NH_3 than the Fe/zeolite formulation.

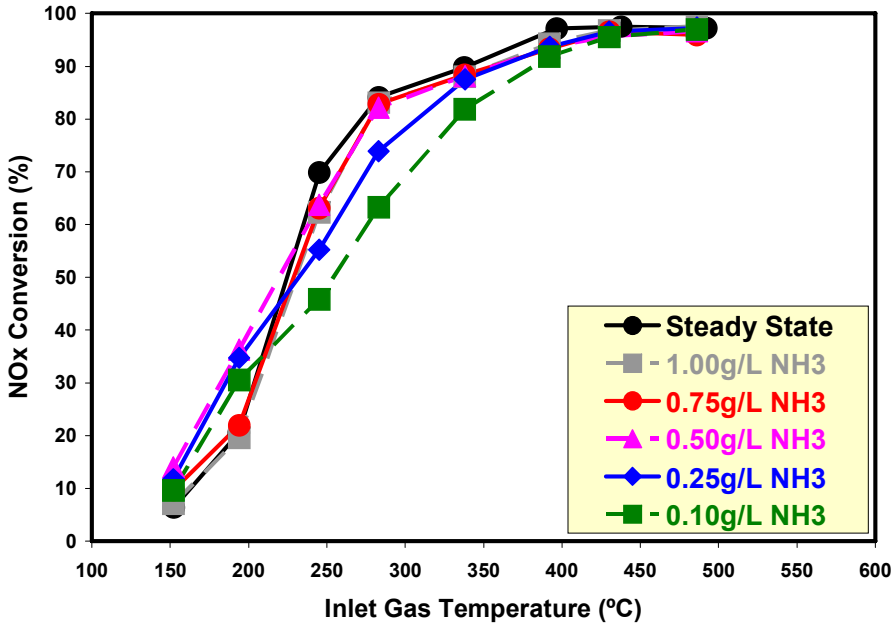
Impact of NH_3 Exposure Level

NOx Conversion vs. Temperature

Cu/zeolite



Fe/zeolite

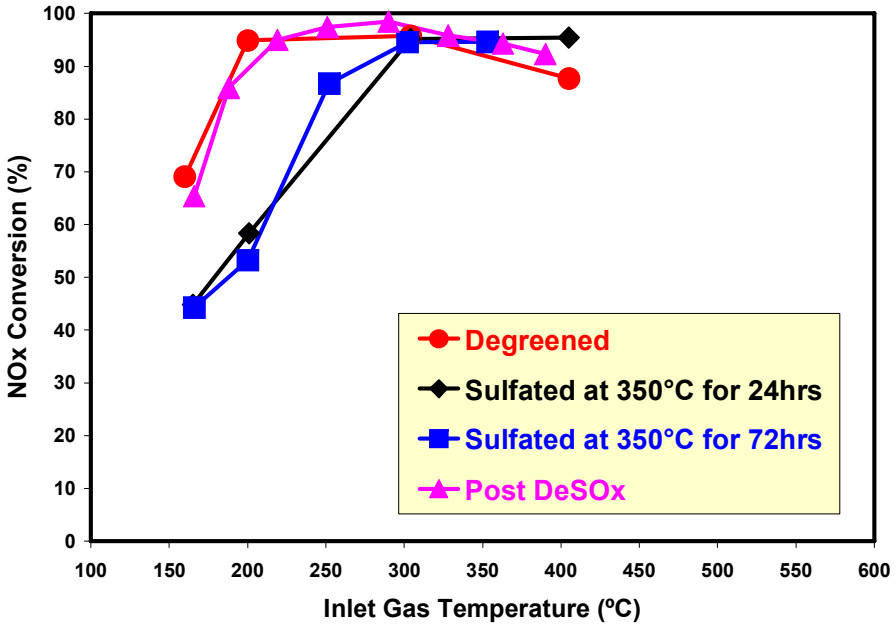


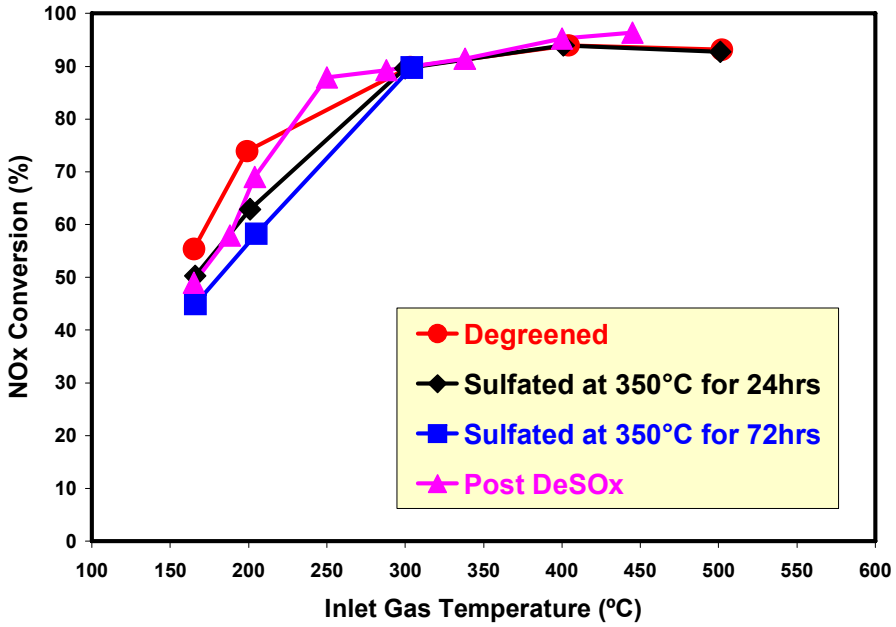
- **Exposing SCR catalysts to less than the saturated value of NH_3 results in a loss of NOx performance.**
- **Cu/zeolite is more sensitive to NH_3 storage than Fe/zeolite.**

Sulfur Poisoning and Regeneration

NOx Conversion vs. Temperature

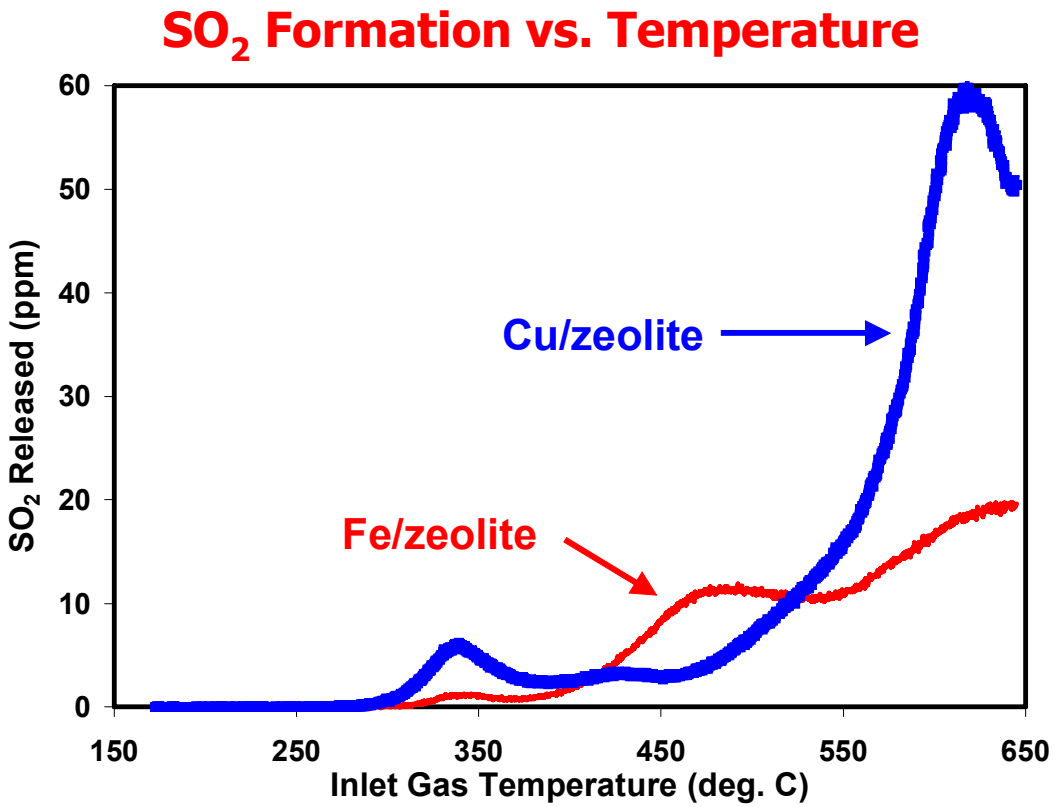
Cu/zeolite | **20% NO_2/NOx** | **Fe/zeolite**





- **29g S/L exposure (24hrs ~ 120k miles) was more significant on the Cu/zeolite than Fe/zeolite.**
- **NOx performance recovered after short 650°C lean exposure.**

Sulfur Poisoning and Regeneration

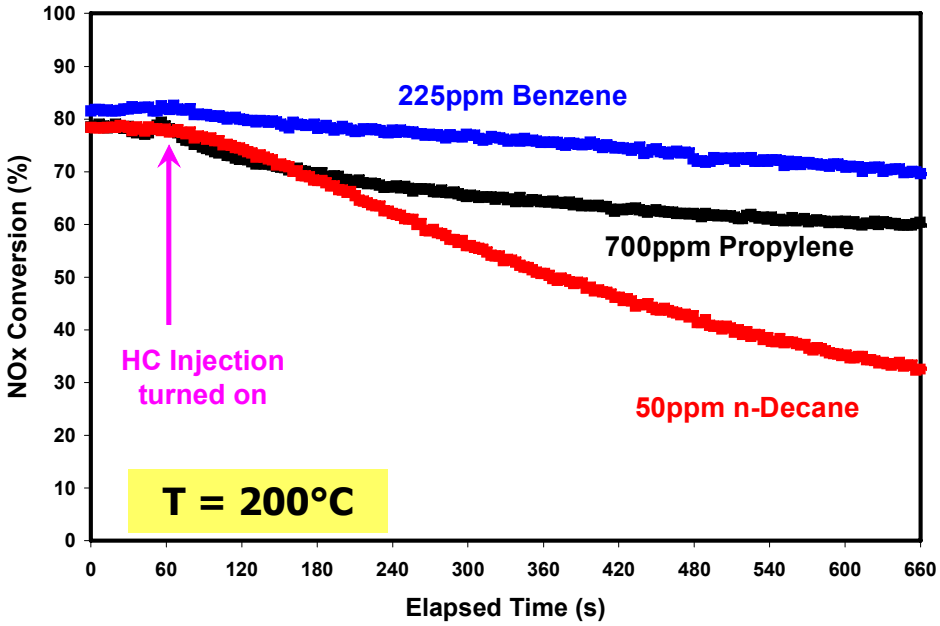


- **DeSOx was achieved by temperature programmed desorption in the presence of oxygen.**
- **Consistent with active DPF regenerations, Cu/zeolite requires 650°C to remove most of the sulfur.**

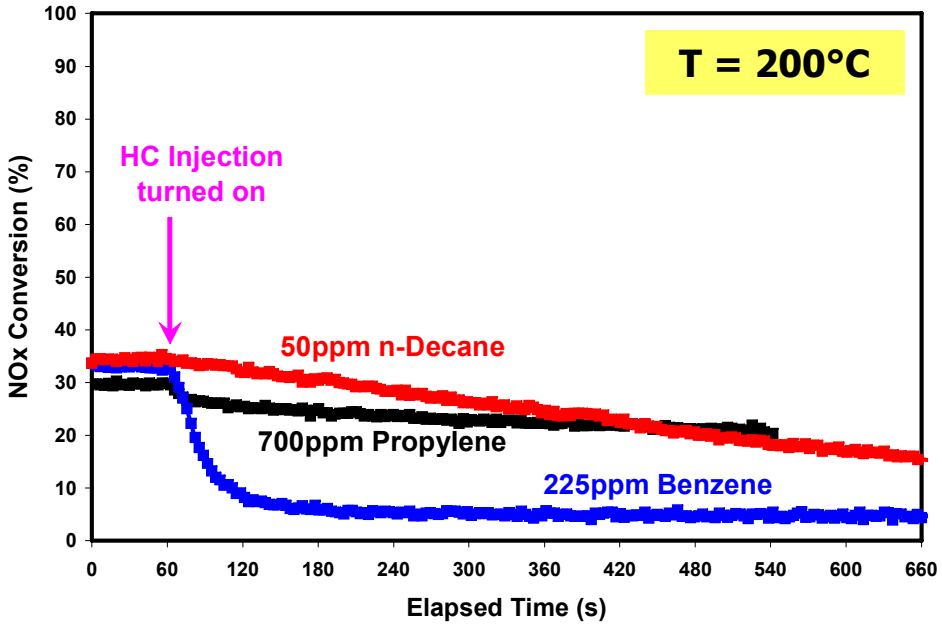
Hydrocarbon Poisoning at 200°C

NOx Conversion vs. Elapsed Time

Cu/zeolite



Fe/zeolite

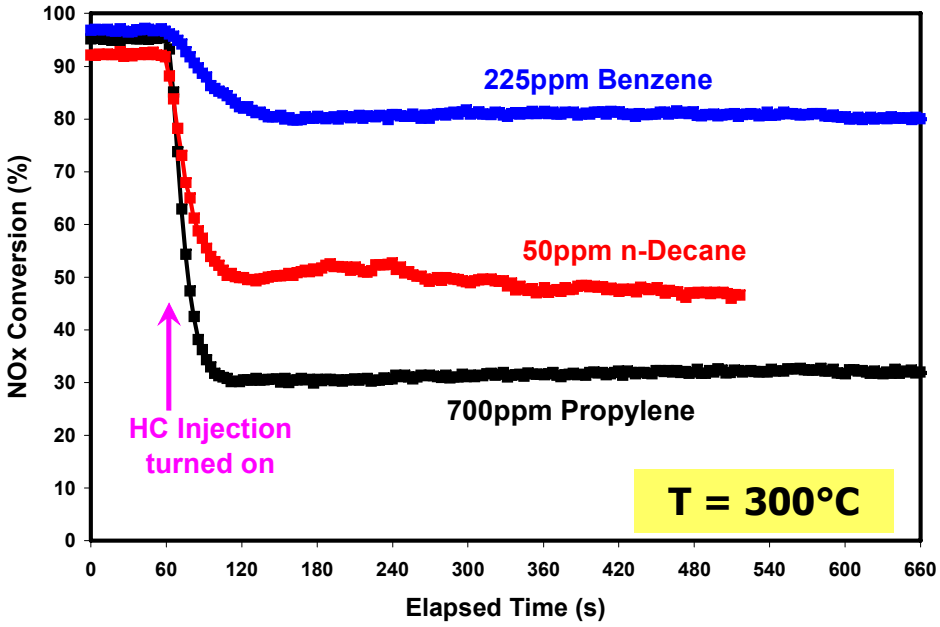


- HC exposure significantly impacts NOx conversion for both Cu and Fe.
- n-Decane is most severe for Cu while benzene is most severe for Fe.

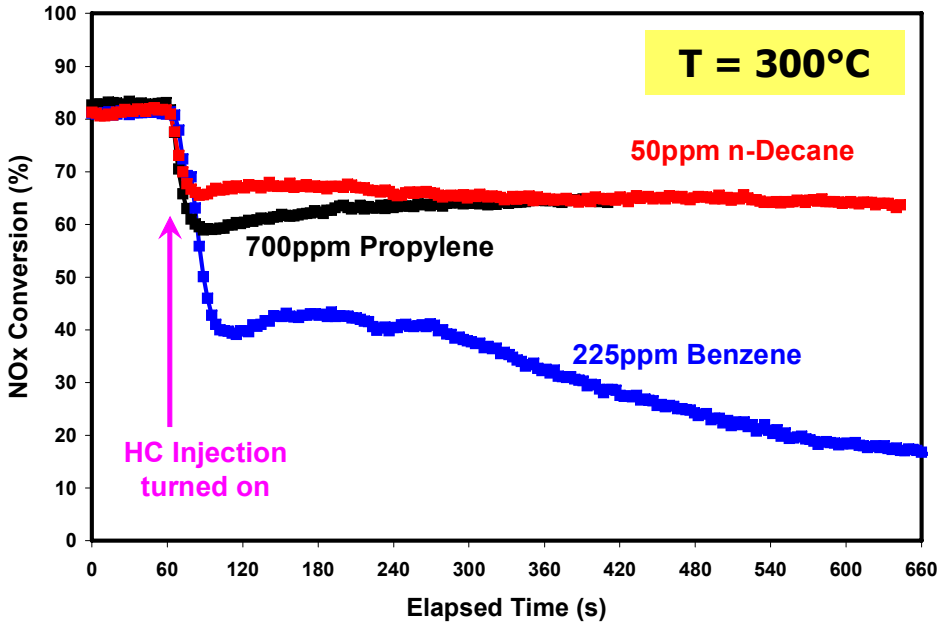
Hydrocarbon Poisoning at 300°C

NOx Conversion vs. Elapsed Time

Cu/zeolite



Fe/zeolite



- HC exposure results in an instant inhibition of the NO + NH_3 SCR reaction.
- Propylene is most severe for Cu while benzene is most severe for Fe.

Summary

- Both Cu and Fe formulations are durable under typical DPF generations conditions (<670°C).
- Cu rapidly deactivation above 750°C while Fe rapidly deactivates above 900°C.
- Cu is more active at low temperature whereas Fe is more active at high T.
- Cu is least sensitive to NO_2 to achieve high NOx conversion.
- Both Cu and Fe oxidize NH_3 with high selectivity to N_2.
- At high SV, Fe slips excess NH_3 while Cu does not.
- Cu requires a larger amount of pre-stored NH_3 to achieve high NOx conversion at low temperature.
- Cu and Fe are adversely impacted by sulfur and HC. However, poisoning is reversible with frequent active DPF regenerations.

Thank you for your attention!

QUESTIONS?

Giovanni Cavataio, Ph.D.
Technical Expert, Diesel Aftertreatment
Ford Research and Innovation Center
jcavatai@ford.com