Understanding the Deactivation Mechanisms of Cu/Zeolite SCR Catalysts in Diesel Application

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August 5, 2008

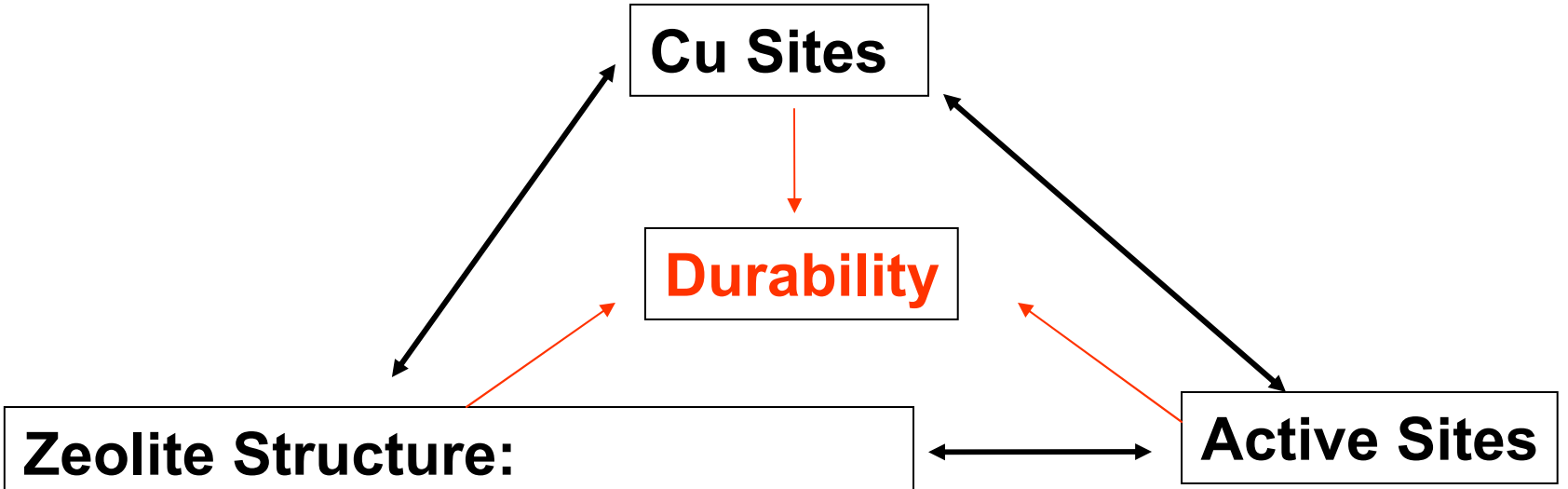
2008 DEER Conference

Pacific Northwest
NATIONAL LABORATORY

Introduction

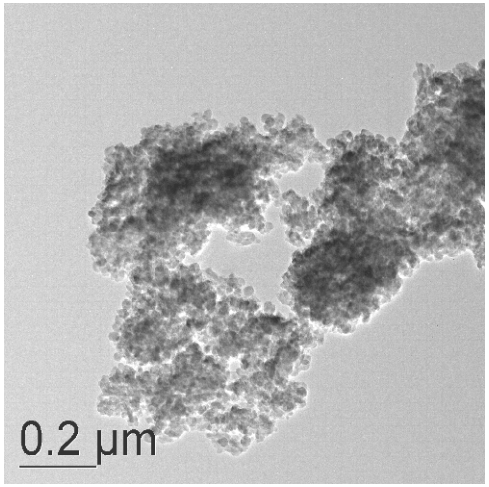
- The effects of engine and lab aging on Cu/zeolite SCR catalysts reactivity and material properties were assessed by performance tests and multiple characterization techniques that included ^{27}Al NMR, XRD, and TEM.
- The impacts of zeolite structure, Cu sites, and active sites on SCR catalyst durability are discussed.
- The results aid the development of the understanding of Cu/zeolite SCR catalyst deactivation mechanisms in diesel application.

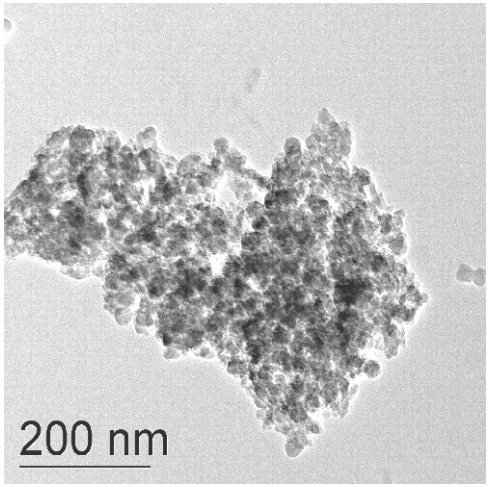
The Durability of Cu/Zeolite SCR Catalysts

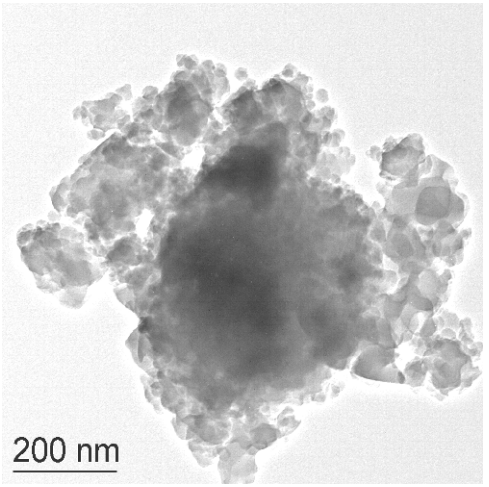


Zeolite Structure:
Increasing the collapsing temp to maintain zeolite structure during thermal aging is the key for Cu/zeolite SCR Catalysts in Diesel Application.

Zeolite Stability – Thermal Deactivation

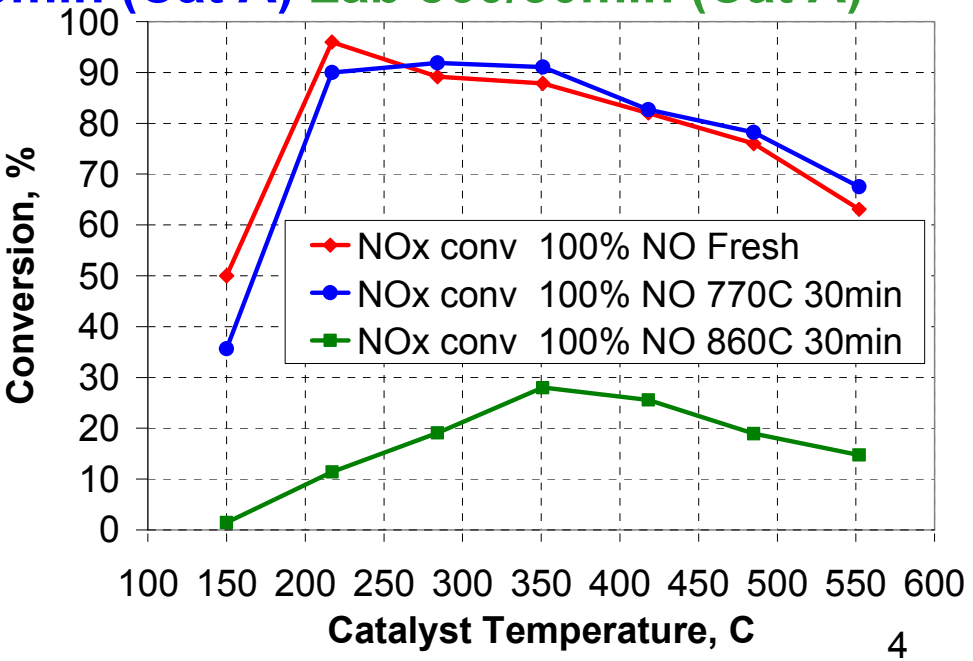




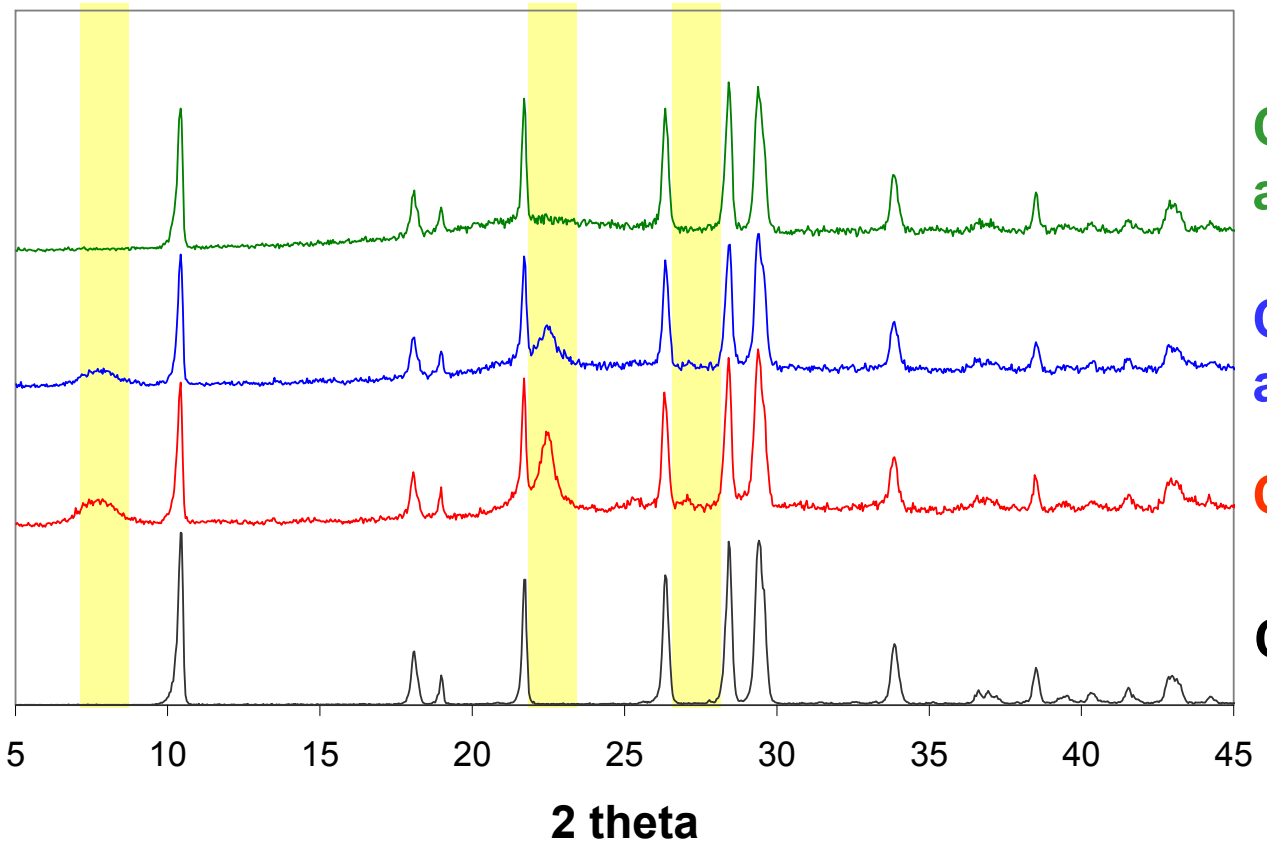


Fresh (Cat A) **Lab 770C/30min (Cat A)** **Lab 860/30min (Cat A)**

- **770C/30min: Zeolite crystal structure maintained**
- **860/30min: Zeolite structure collapsed. Large particles of amorphous alumino-silicate are formed (XRD)**
- **No evidence for Cu sintering**



SCR Deactivation Mechanism – Zeolite Durability



Cat A – 860 °C 30 min aged

Cat A – 770 °C 30 min aged

Cat A – fresh

Cordierite (honey comb)

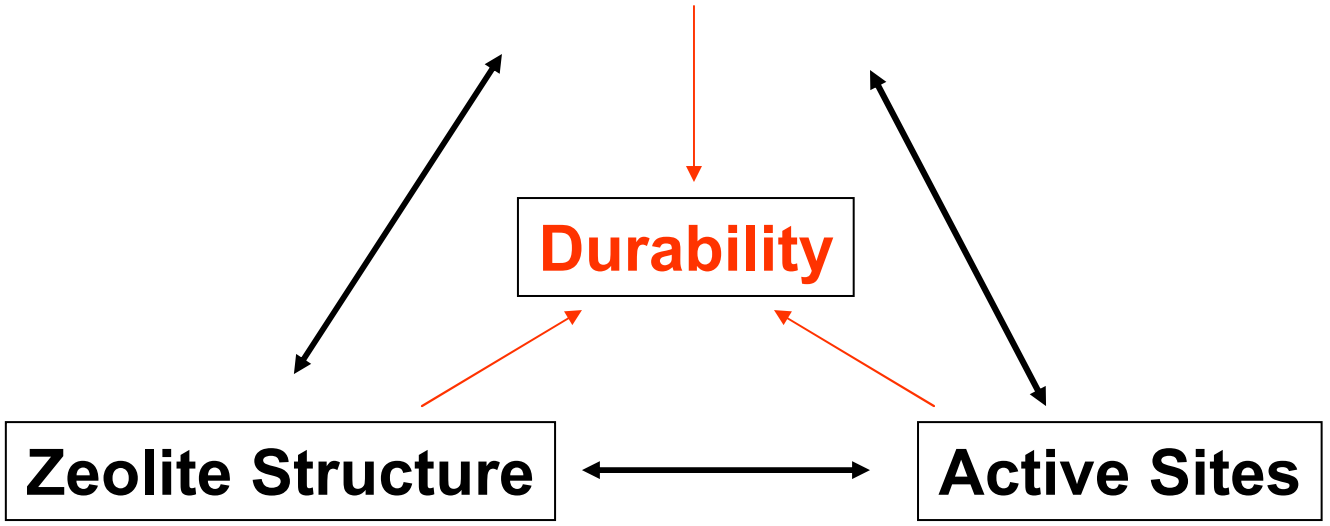
XRD (Cat A)

- Zeolite structure mostly stable after 770 °C treatments
- Only amorphous phase remained after 860 °C 30 min aged
  - ☞ **Zeolite structure collapsed for 860 °C treatment**

SCR Deactivation Mechanism Understanding

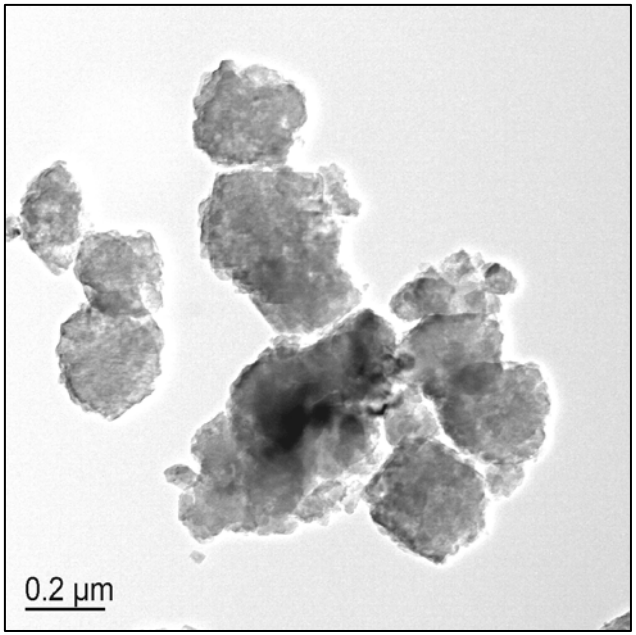
Cu Sites:

- Found Cu sintering on engine aged samples, especially the gas inlet section.
- Cu sintering seems to be controlled by gas phase chemistry rather than the aging temp.

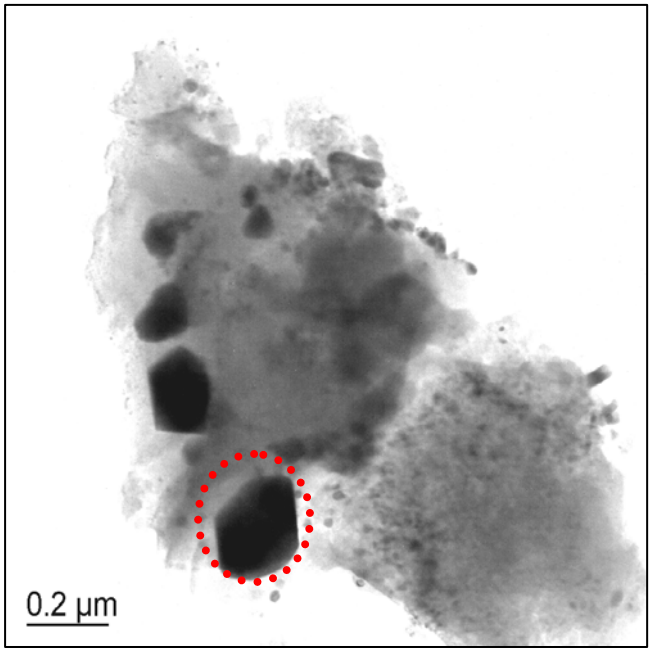


SCR Deactivation Mechanism – Cu Sites

Fresh Cat B →



Engine 120K 1st inch Cat B →

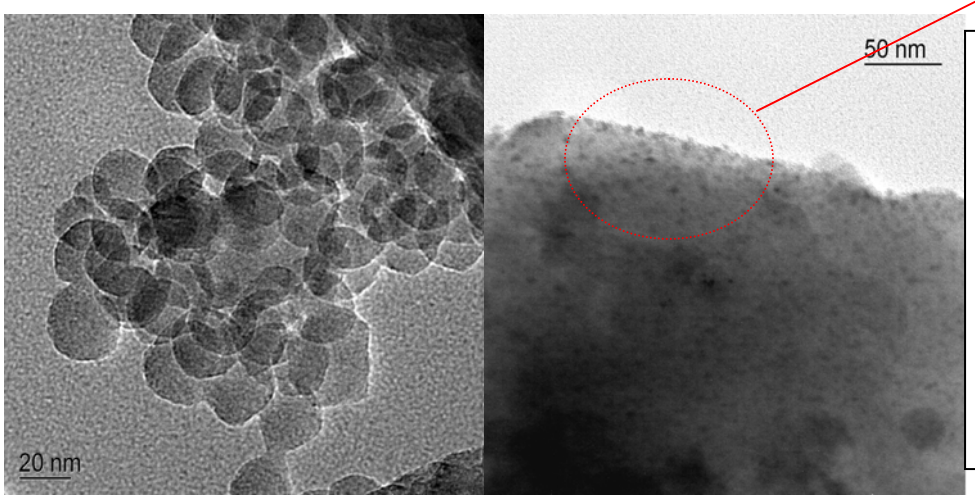


- Basically same morphology as the fresh material
- Very (!!) significant Cu sintering behavior evident (consistent with XRD and EPMA)

SCR Deactivation Mechanism – Cu Sites

Cu sintering behavior

120K
1st inch
Cat C

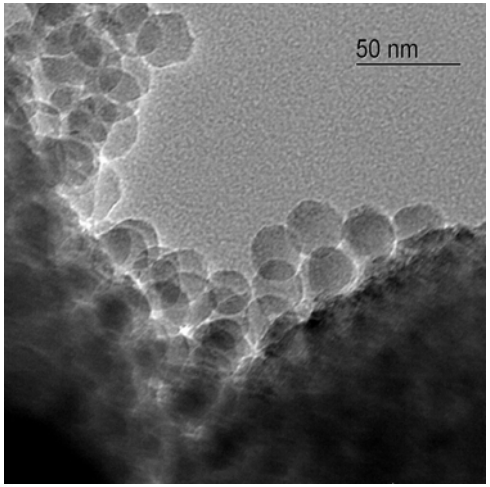


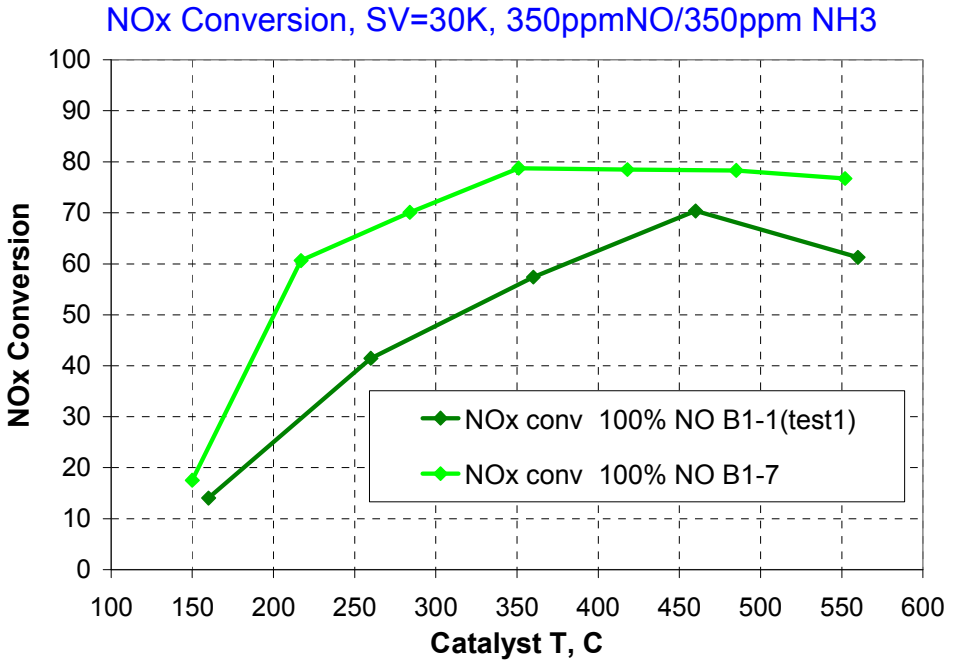
Basically same morphology.

No evidence of Cu sintering on the 7th.

Some minor portion shows Cu sintering behavior on the 1st.

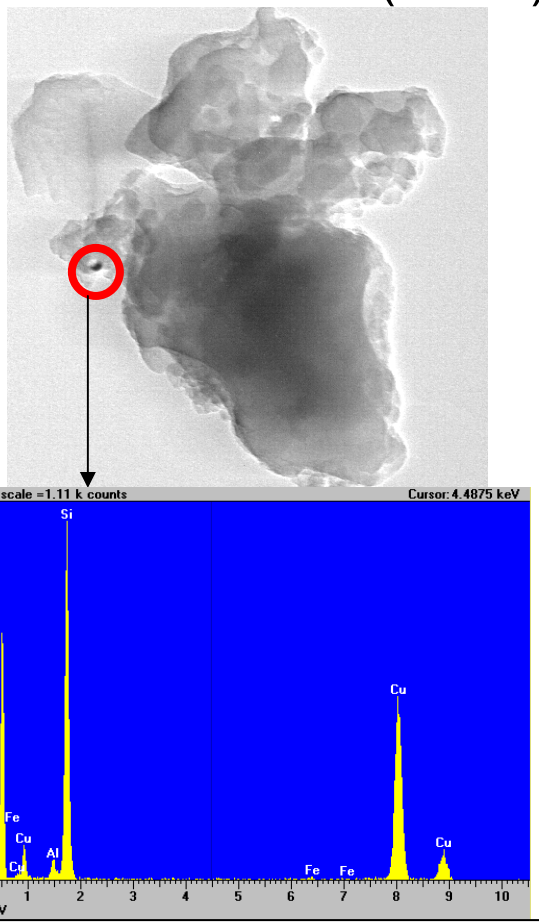
120K
7th inch
Cat C





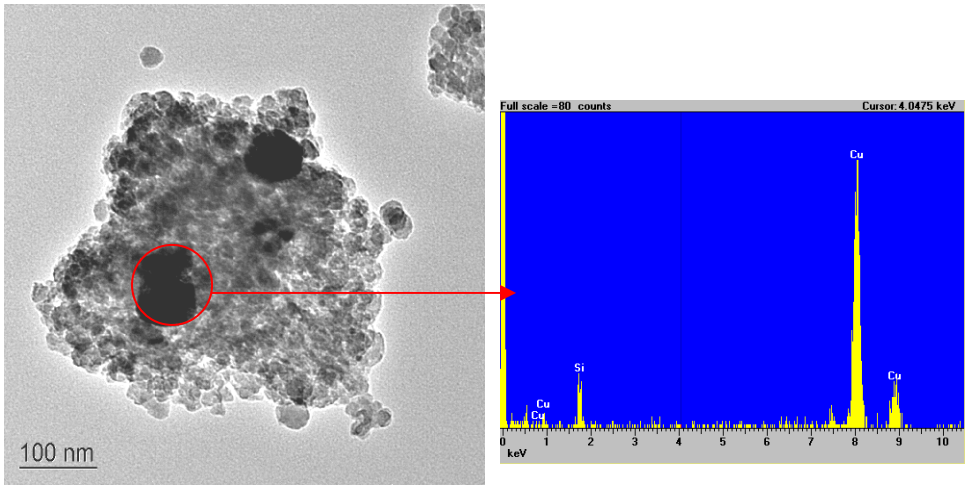
SCR Deactivation Mechanism – Cu Sites

Lab 860/30min (Cat A)



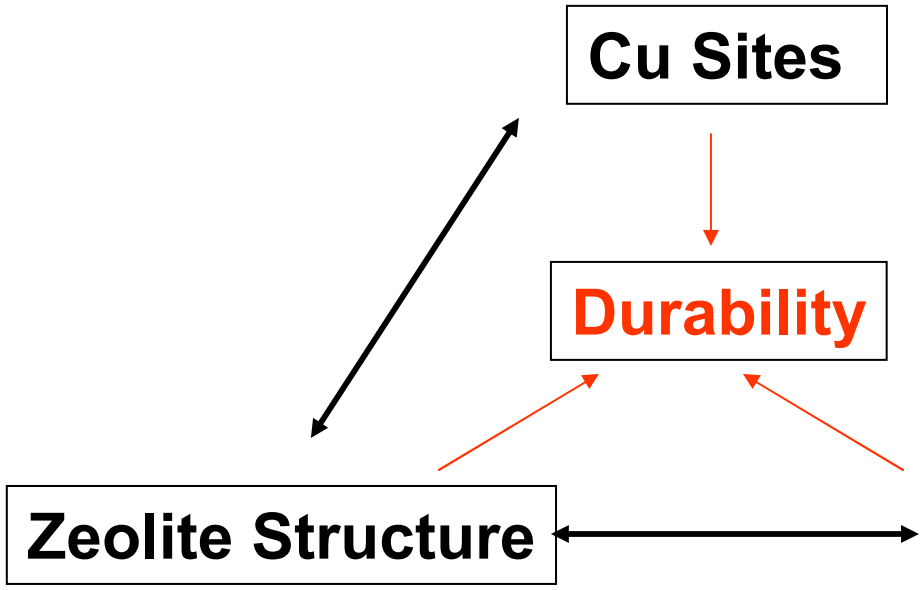
Cu still located inside – not sintered on the external surface of the oxide particle

Fresh after NH3 TPD (Cat A)



- Serious Cu sintering after the NH_3 TPD.
- Aging at 700°C under O_2 atmosphere – no serious sintering.
- Reduction with H_2 flow – sintering started <300°C.

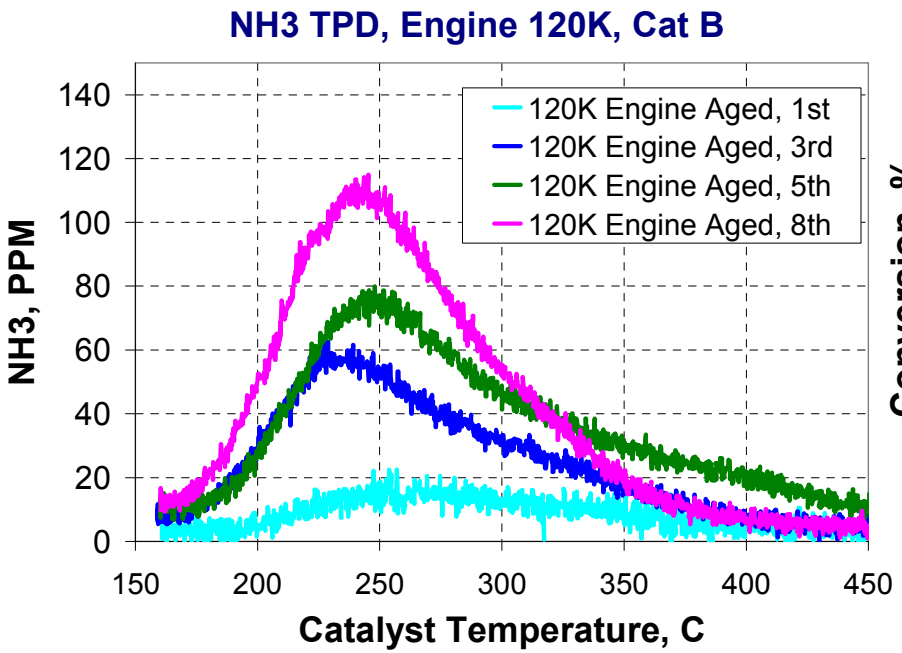
SCR Deactivation Mechanism Understanding

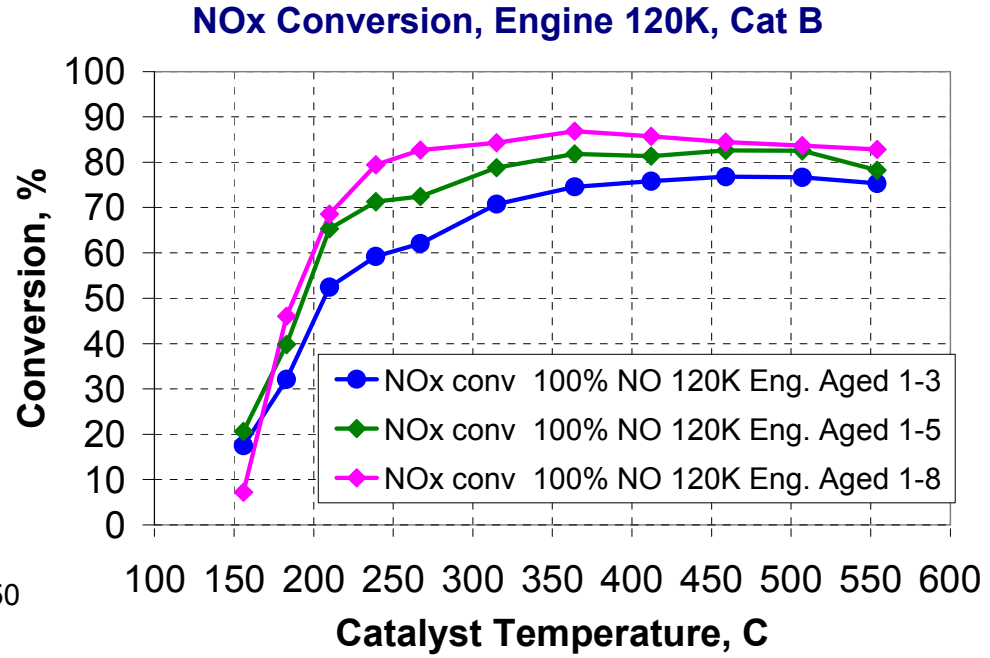


Active Sites:

- The overall activity is not high if the Al is not stable in the framework structure of zeolite (dealumination).
- Acidity of SCR catalysts reflects the status of active sites.
- Not only the thermal factor, but also “chemical” factors, such as reductants and urea, impact the stability of active sites.

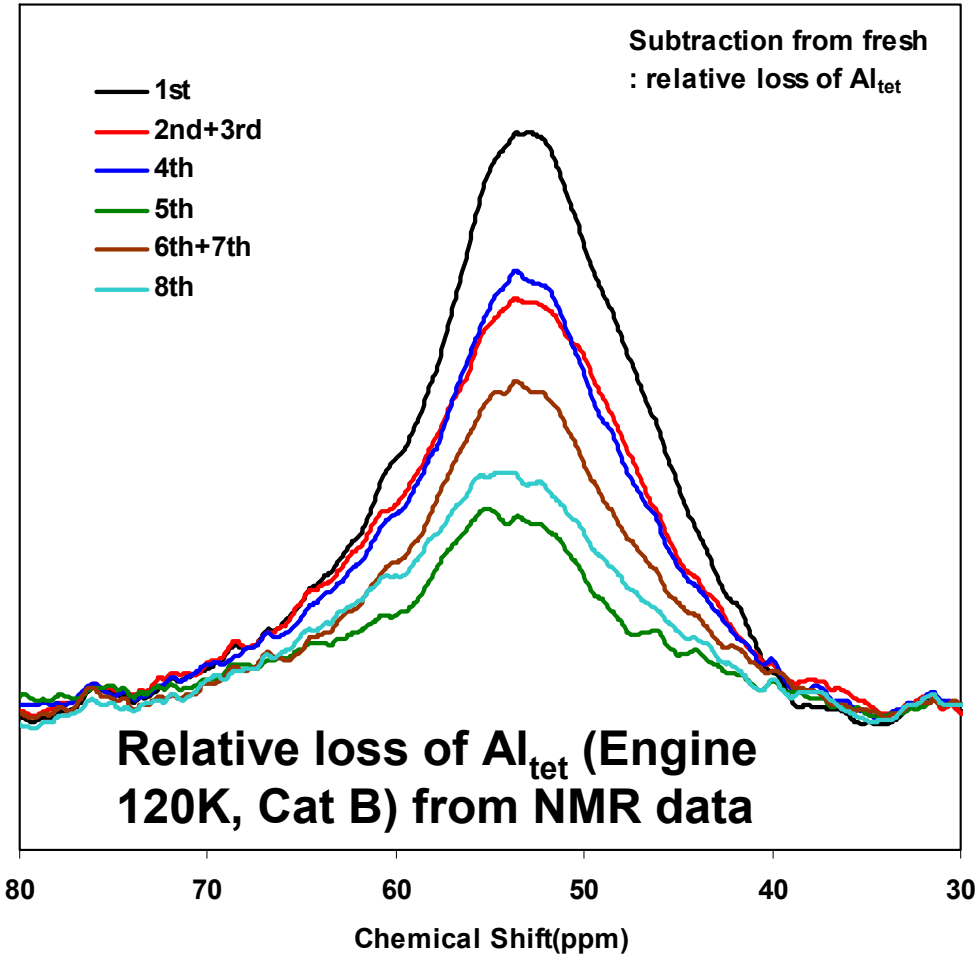
SCR Deactivation Mechanism – Active Sites

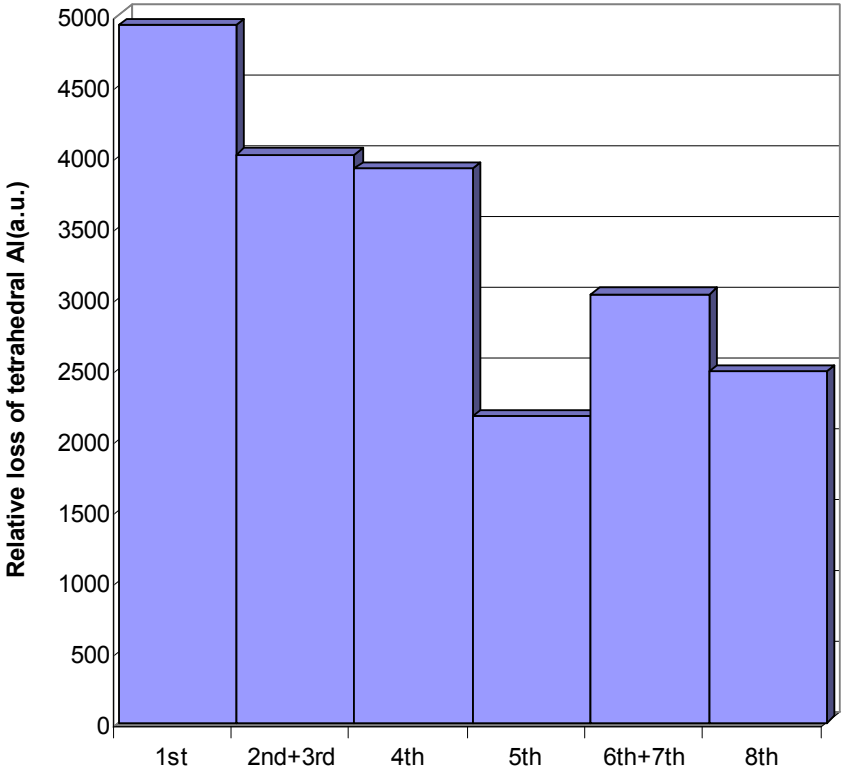




- It is known that surface acidity is important for ammonia SCR reaction.
- Characterize the acidity through measuring adsorbed NH3 that associated to the acid sites on the catalysts. But, can not measure the types (Bronsted or Lewis) of acid sites.
- The overall acidity of SCR reflects its activity.

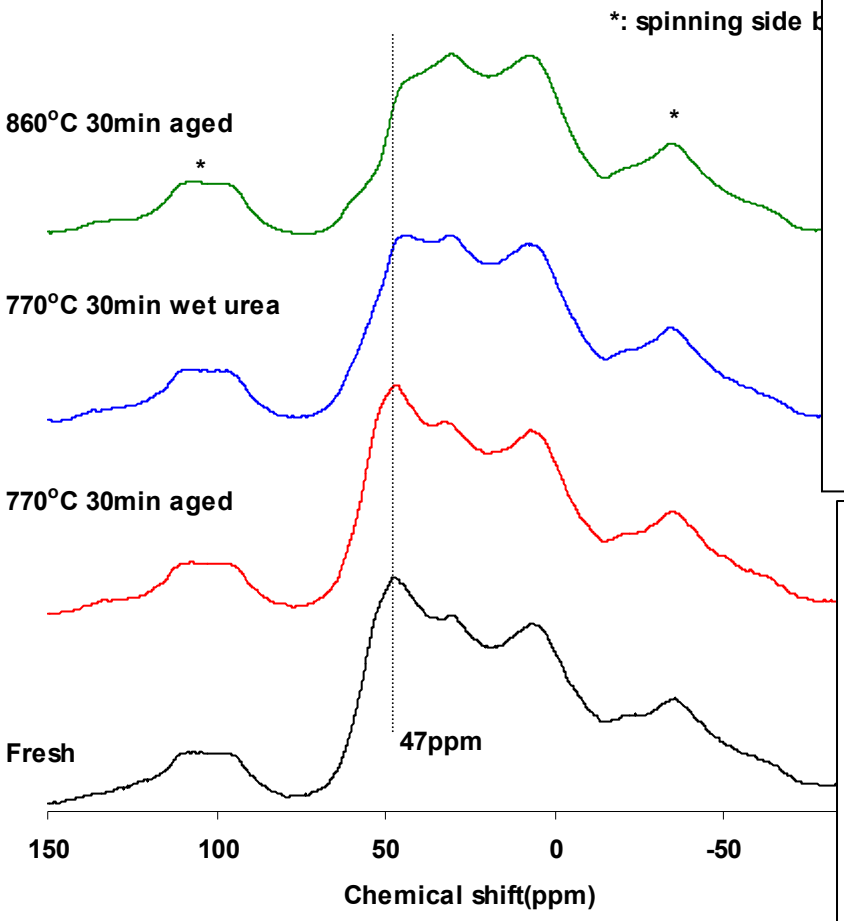
SCR Deactivation Mechanism – Active Sites





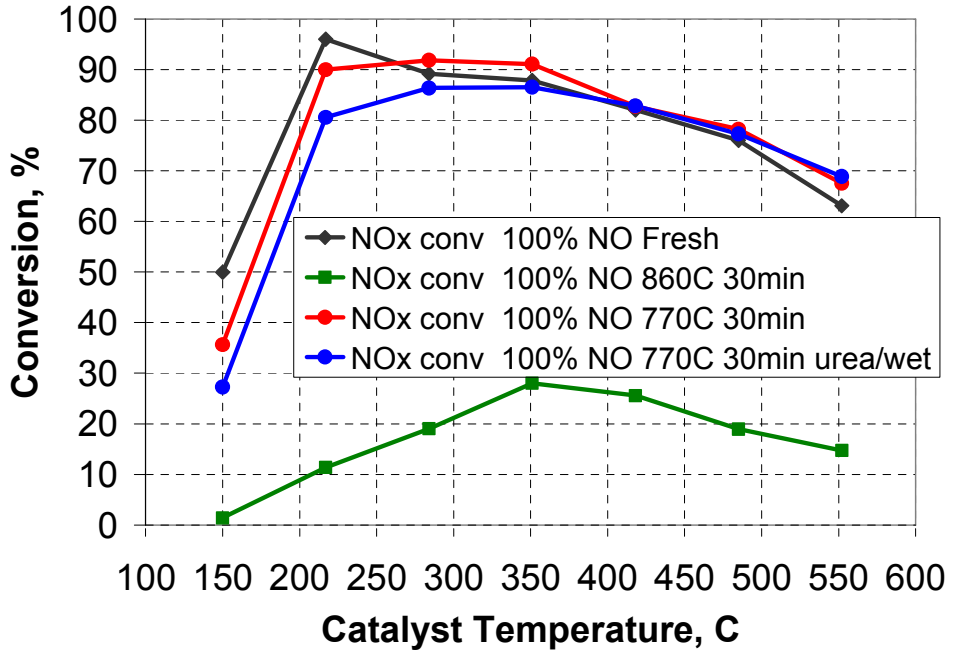
The decreasing of acidity is not the only factor that causes the decreasing of SCR activity.

SCR Deactivation Mechanism – Active Sites

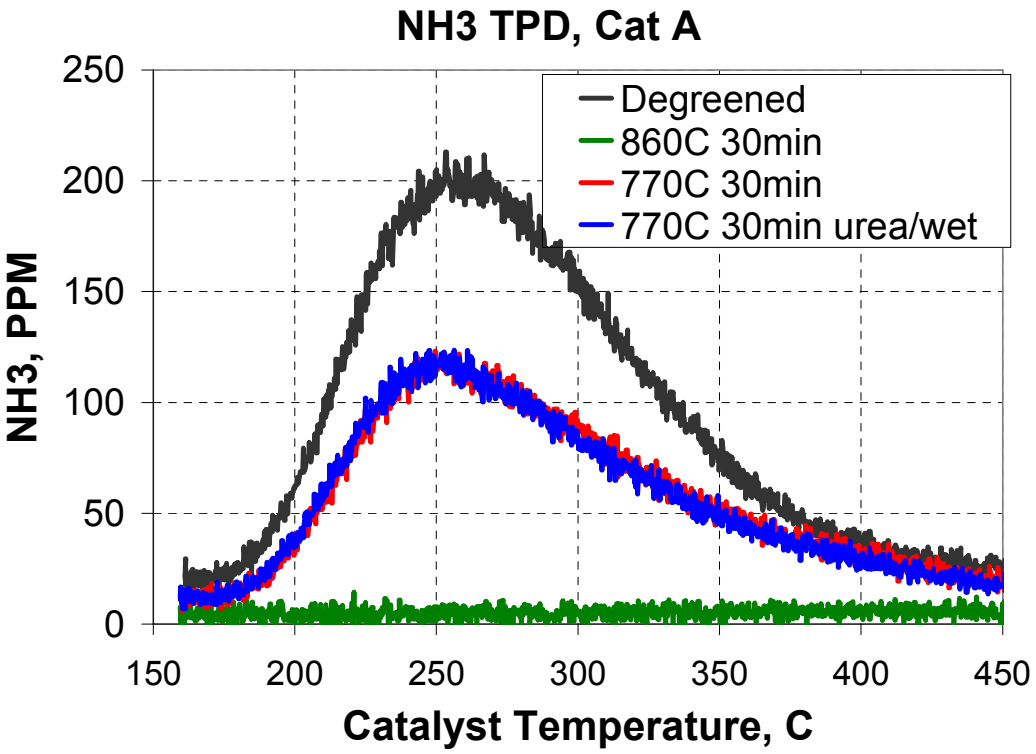


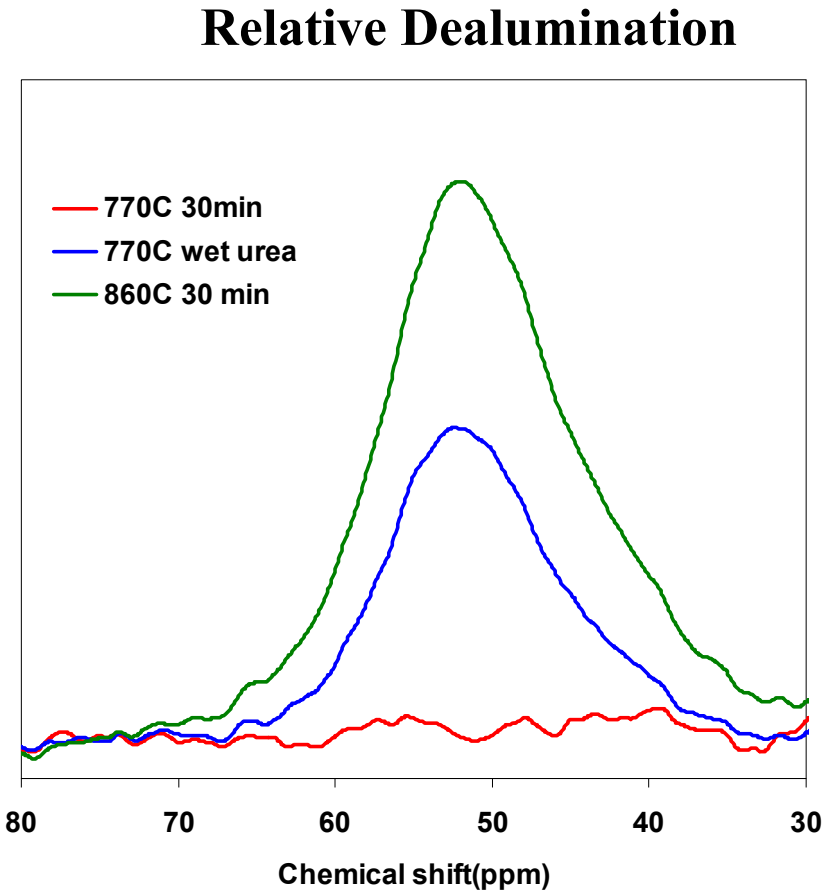
Solid state ^{27}Al-NMR

- 860 °C 30 min aged sample: no evidence for tetrahedral aluminum which means decompose of zeolite structure.
- 770 °C 30 min aged: no significant change from fresh sample.
- 770 °C 30 min wet urea: less amount of tetrahedral aluminum which indicate some dealumination.



Active Sites – Acidity and Relative Dealumination





Aging factors impact SCR acidity differently.

SUMMARY

- The stability of zeolite structure, Cu sites, and active sites all contribute to the durability of SCR catalysts. They are correlated with each other and equally important.
- Dealumination, zeolite structure damage, base metal sintering are the root causes of SCR deactivation.
- Some aging conditions impact all three features, but some might just impact one or two or them.
- There are lots of unknowns that need to be investigated
  - Zeolite structure, Cu sites, and active sites each contribute to the SCR catalyst durability.
  - Control of the aging factors to minimize the impact on Cu/zeolite SCR catalysts in diesel applications.

ACKNOWLEDGEMENTS

- Financial support for studies performed at Pacific Northwest National Laboratory (PNNL) was provided by the U.S. Department of Energy (DOE), Office of FreedomCar and Vehicle Technologies.

- Portions of the work were performed in the Environmental Molecular Sciences Laboratory (EMSL) at the PNNL. The EMSL is a national scientific user facility and supported by the U.S. DOE Office of Biological and Environmental Research.