Deactivation Mechanisms of Base Metal/Zeolite Urea Selective Catalytic Reduction Materials

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Project ID: ace_25_peden

Project Overview

Timeline

- Start – February 2007
- Finish – January 2010
- 38% Complete at the end of this fiscal year

Budget

- Total project funding
  - DOE – $800K
  - Ford – $525K
- DOE funding received:
  - FY07 – $100K
  - FY08 – $100K
  - FY09 – $100K

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- Ford Motor Company

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Barriers

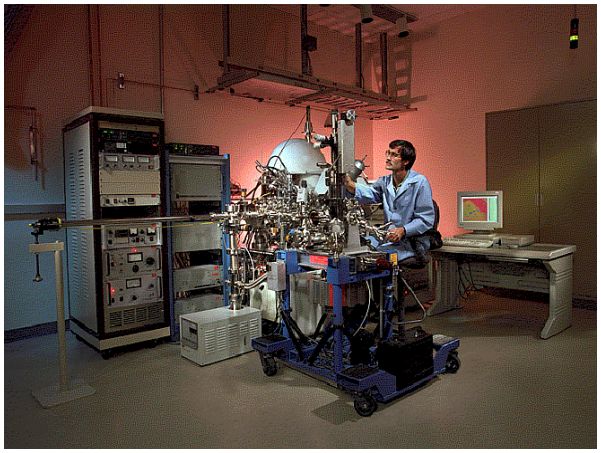
- Lean-NOx emission control technologies, including urea selective catalytic reduction (SCR) are needed to enable wider use of fuel-efficient diesel engines.
- Regulations impose challenging requirements for catalyst activity and durability, with durability especially difficult due to a relative lack of experience with this new technology.
- As such, there is a critical need to develop realistic laboratory aging protocols that effectively simulate engine aging induced catalyst deactivation. For this, a fundamental understanding of the deactivation mechanisms is essential.

Purpose of the Work

- Develop an understanding of various aging factors that impact the long-term performance of urea selective catalytic reduction (SCR) materials in diesel vehicle applications.
- Improve the correlation between laboratory and engine aging.
- (Ford activity): Use this fundamental understanding to develop realistic laboratory aging protocols, saving experimental time and cost.

Approach

- **Ford tasks:**
  - Preparation of fresh and laboratory-aged samples.
  - Laboratory and engine performance testing.
  - Provide engine-aged urea SCR catalysts for PNNL characterization.
  - Develop refined laboratory aging protocols.



- **PNNL tasks:**
  - Use PNNL/IIC's state-of-the-art tools to characterize sets of laboratory- and engine-aged samples provided by Ford.
  - Correlate urea SCR catalyst materials characterization results with catalytic performance data (provided by Ford), and with changes in catalyst surface chemical properties as a function of wide array of laboratory and engine aging conditions.
  - Use this information for determining important mechanisms for performance degradation of urea SCR catalysts.

FY 2008 Objectives/Activities

Three primary areas of focus to date:

1. Characterize the nature and thermo-chemical properties of deposits observed on engine-aged urea SCR catalysts.
2. Characterize laboratory- and engine-aged catalysts and correlate the results with Ford performance measurements:
   - An initial aging protocol was developed and applied by Ford to monolith-wash coated zeolite-based urea SCR catalysts.
   - Unexpected effects of urea during laboratory aging observed in early Ford studies.
   - Some of the results obtained in this part of the work contain proprietary information regarding catalyst composition and structure.

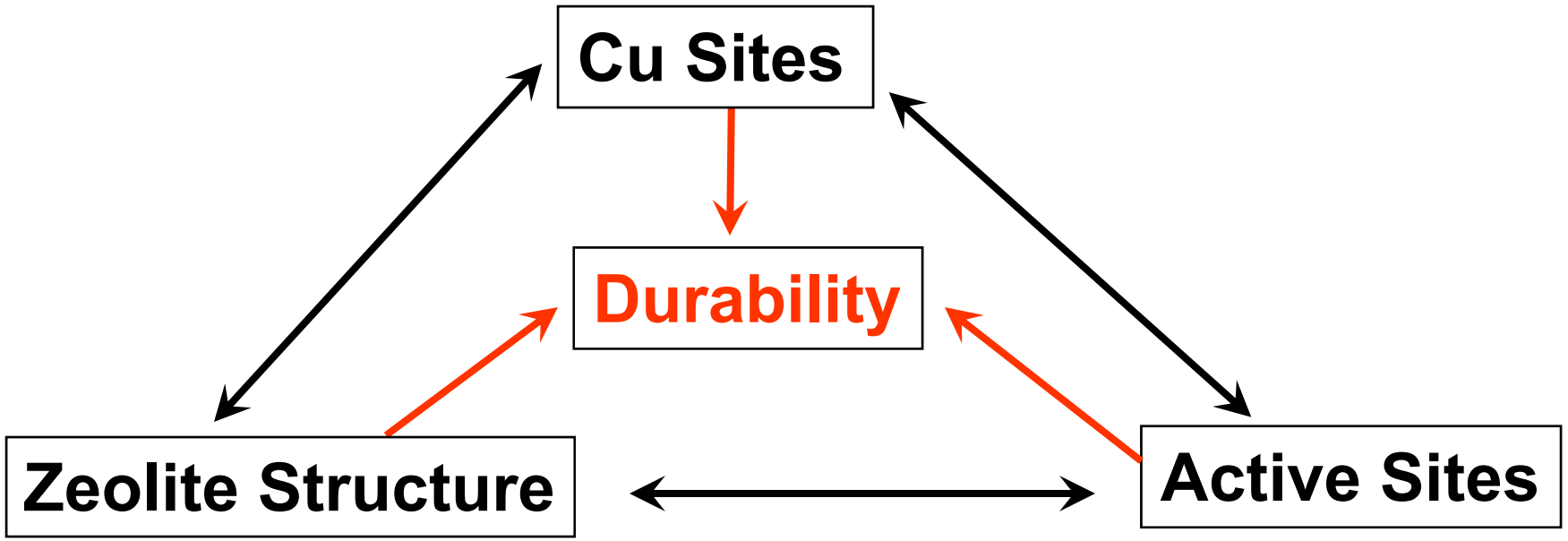
FY 2008 Objectives/Activities

Three primary areas of focus to date:

3. Sulfur poisoning of urea SCR catalysts that follow a diesel oxidation catalyst (DOC):
   - Studies of sulfur poisoning of urea SCR catalysts look at effects of SO_2 since this is the primary S-species in the exhaust.
   - However, DOC's (which typically contain Pt) will oxidize SO_2 to SO_3.
   - Recent Ford work has shown significantly greater poisoning by SO_3 than with SO_2.
   - PNNL is now performing detailed studies to develop an understanding of the differing effects of these two sulfur species, and to identify mechanisms of poisoning.

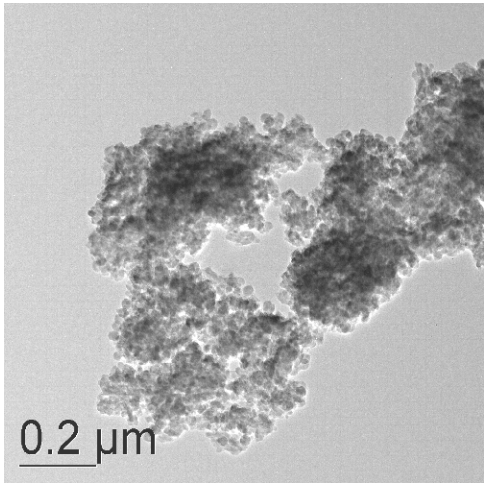
Will present some highlights from the second and third areas in the following.

Factors Effecting The Durability of Cu/Zeolite SCR Catalysts

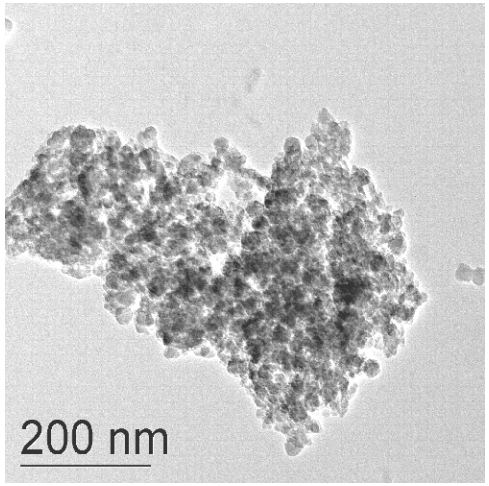


Studies are aimed at determining the relative importance of these factors for laboratory and field-aged catalysts.

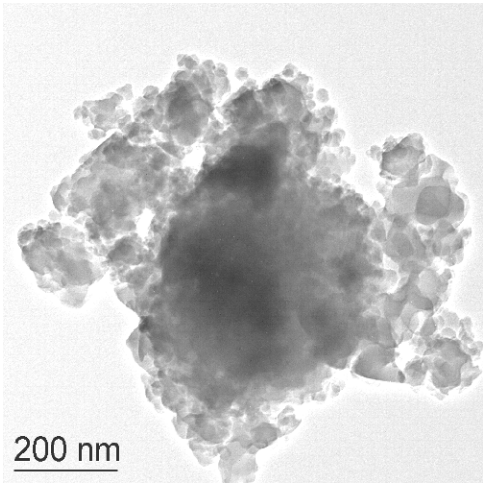
Technical Accomplishments/ Progress/Results – LAB AGING



Fresh (Cat A)

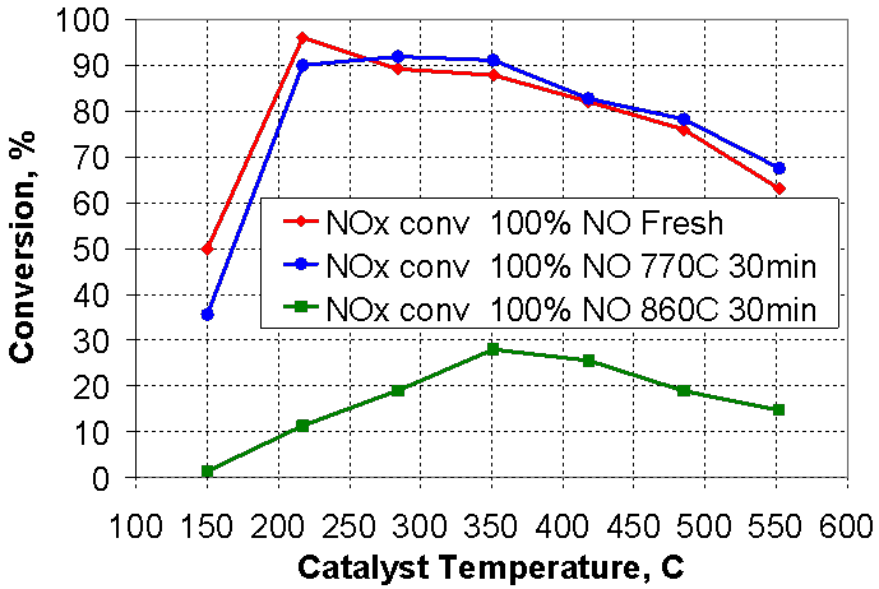


Lab 770°C/30min



Lab 860°/30min

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



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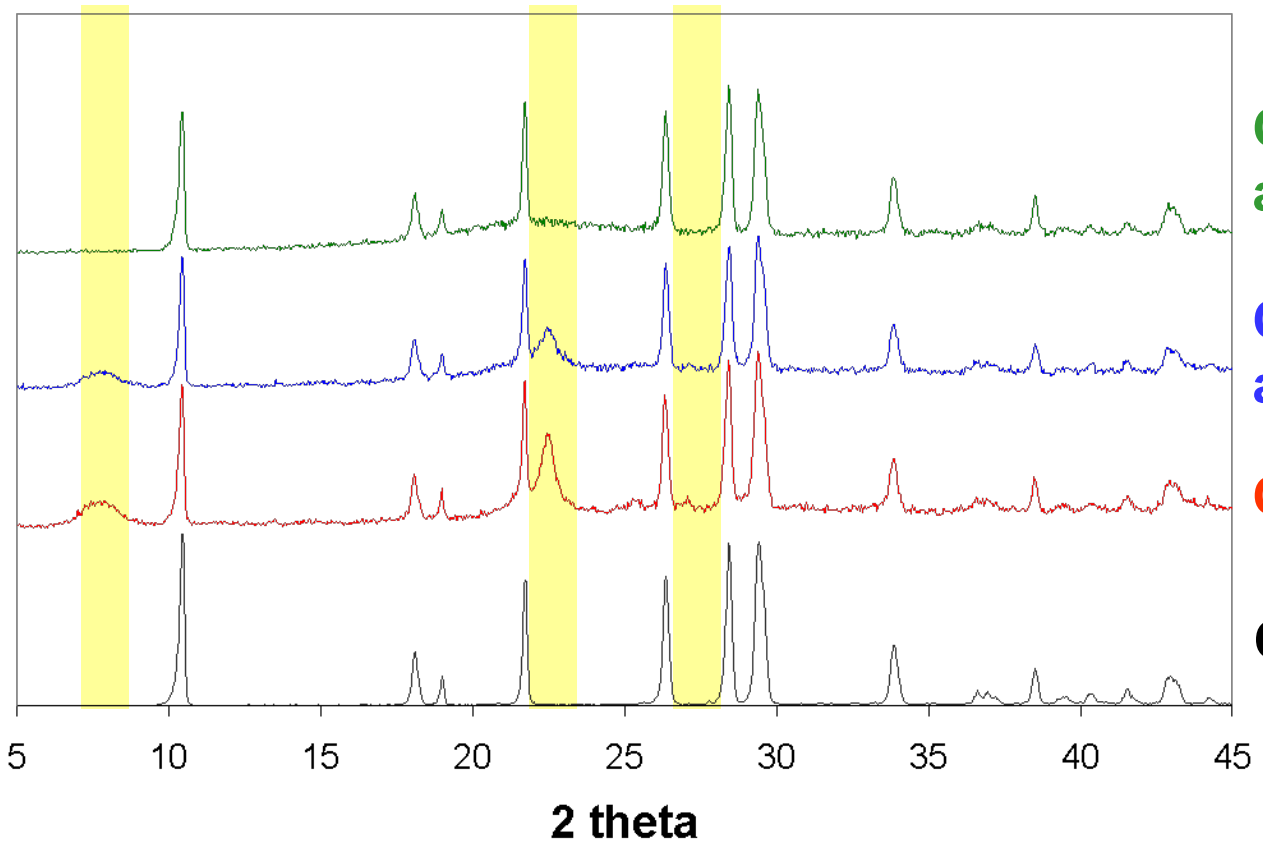
Technical Accomplishments/ Progress/Results – LAB AGING



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**

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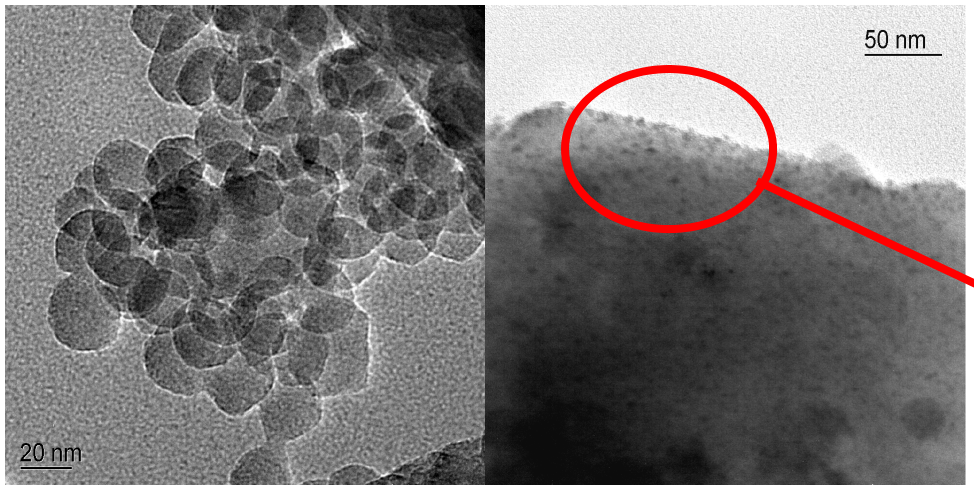
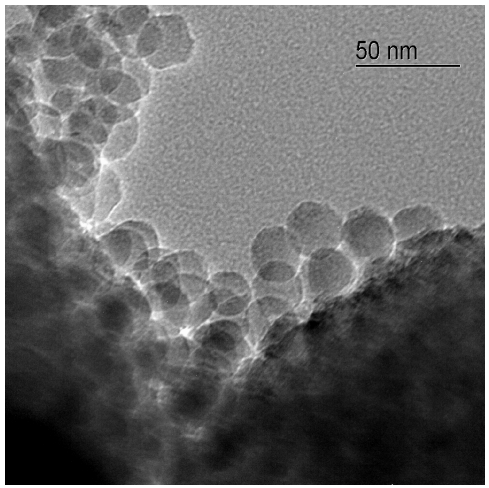
Technical Accomplishments/ Progress/Results – VEHICLE AGING

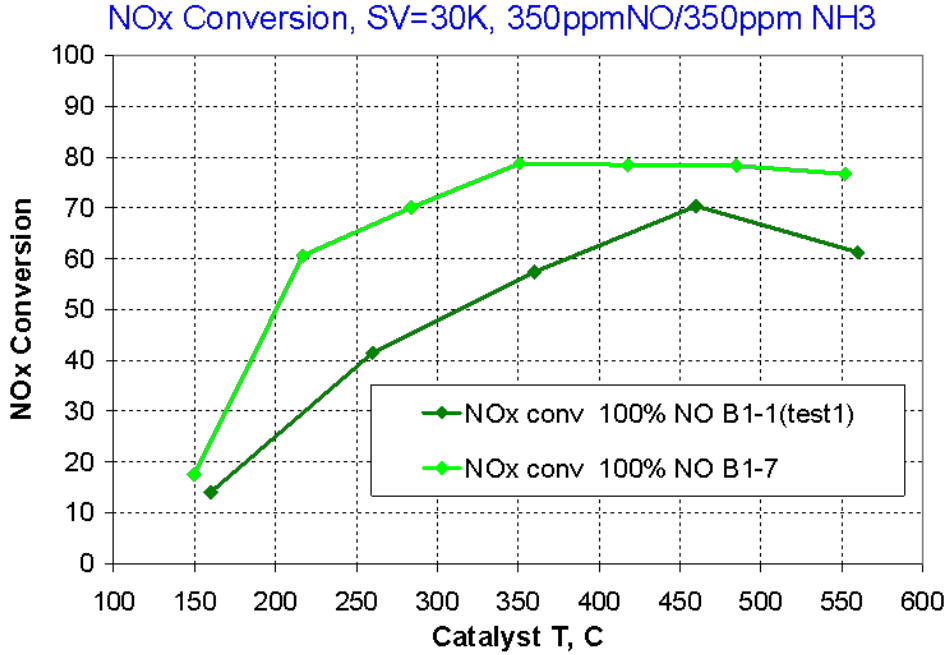
120K
1st inch
Cat C



Basically same morphology.
No evidence of Cu sintering on the 7th catalyst section.
Some Cu sintering behavior observed on the 1st section.

120K
7th inch
Cat C





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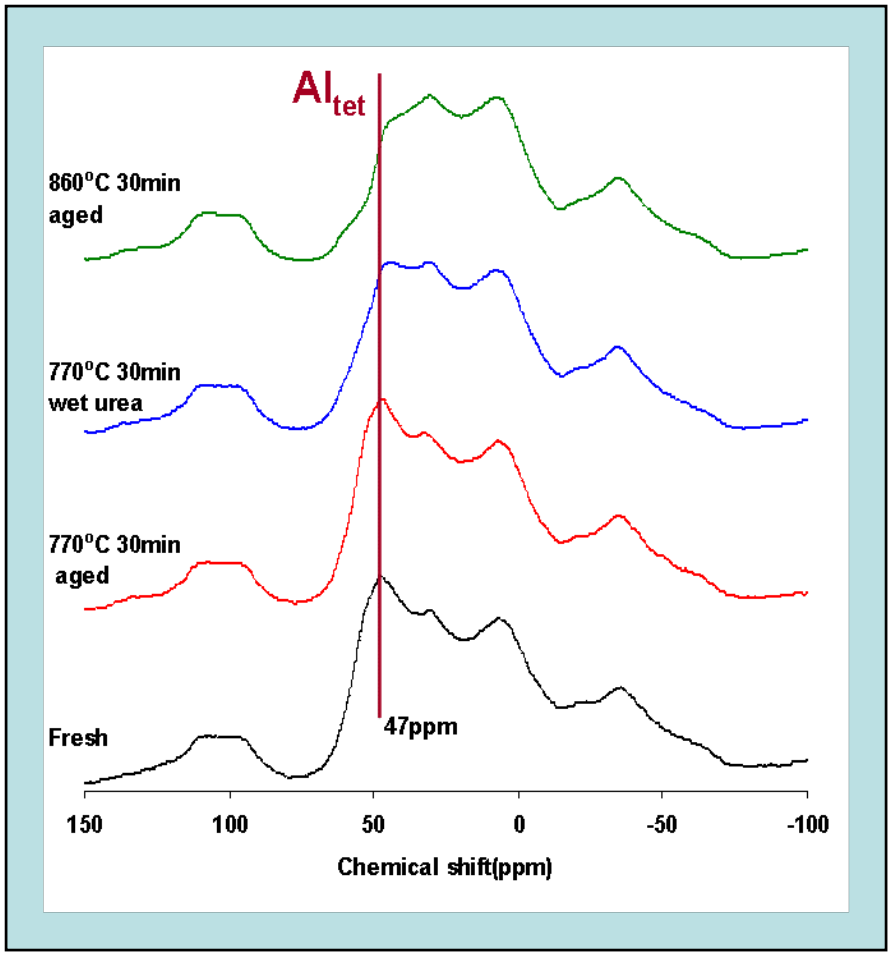
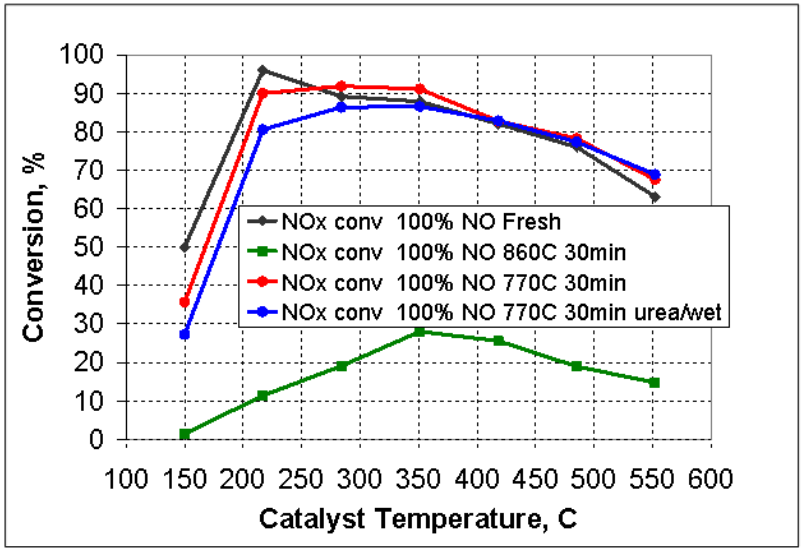
Technical Accomplishments/ Progress/Results – LAB AGING

For laboratory-aged model catalyst, the extent of zeolite dealumination correlates well with reactivity data.



- 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.



Technical Accomplishments/ Progress/Results

Experimental: The deactivation difference between SO_2 and SO_3 aging

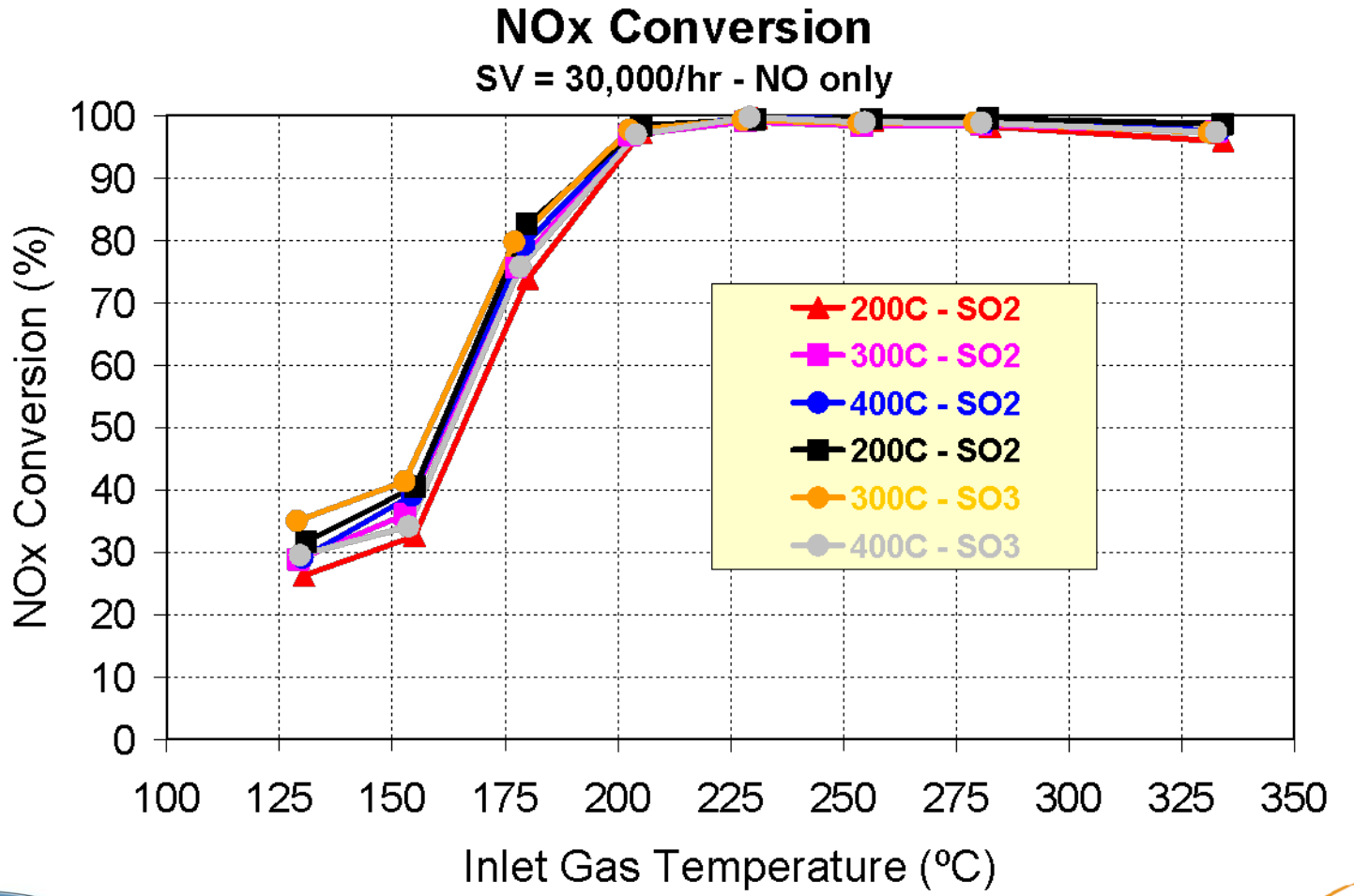
- Catalysts: 6 1x1 Cu/Zeolite samples

Procedure:

- Hydrothermal aging at 670°C for 20hr (37.5K)
- S poisoning:
  - 1.5hr w/40ppm SO_2 or SO_3 (S exposures equivalent to 500 miles with 350ppm sulfur fuel)
  - 200°C, 300°C, 400°C
  - DeSOx: 150°C to 760°C at 5°C/min
- SCR activity measurements (up to 340°C)
  - Test 1 (T1): after hydrothermal aging
  - Test 2 (T2): after S poisoning
  - Test 3 (T3): after DeSOx

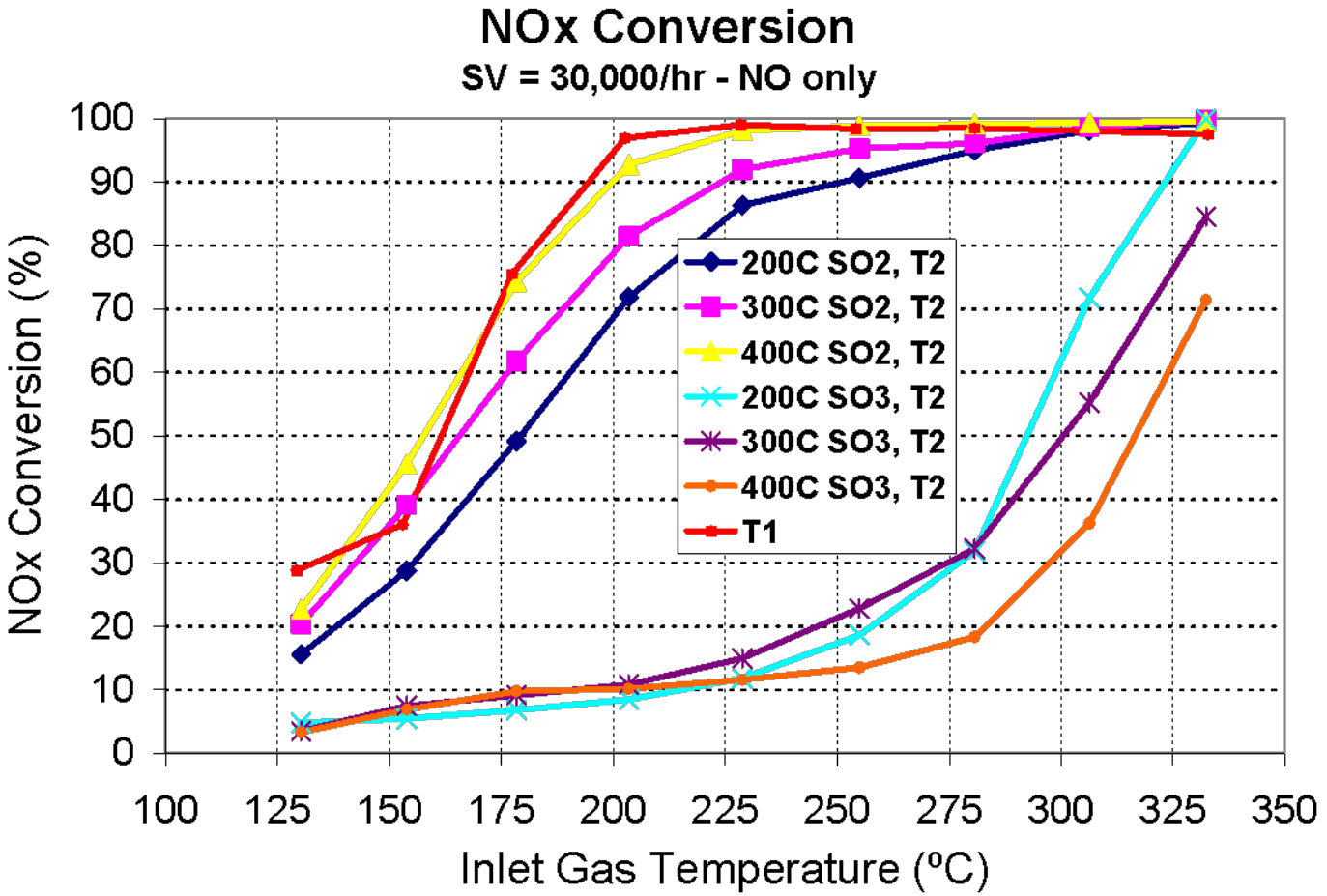
Technical Accomplishments/ Progress/Results

All catalysts display highly similar activity profiles after hydrothermal aging.



Technical Accomplishments/ Progress/Results

SCR activity was significantly reduced for samples poisoned by SO_3 versus those poisoned by SO_2.

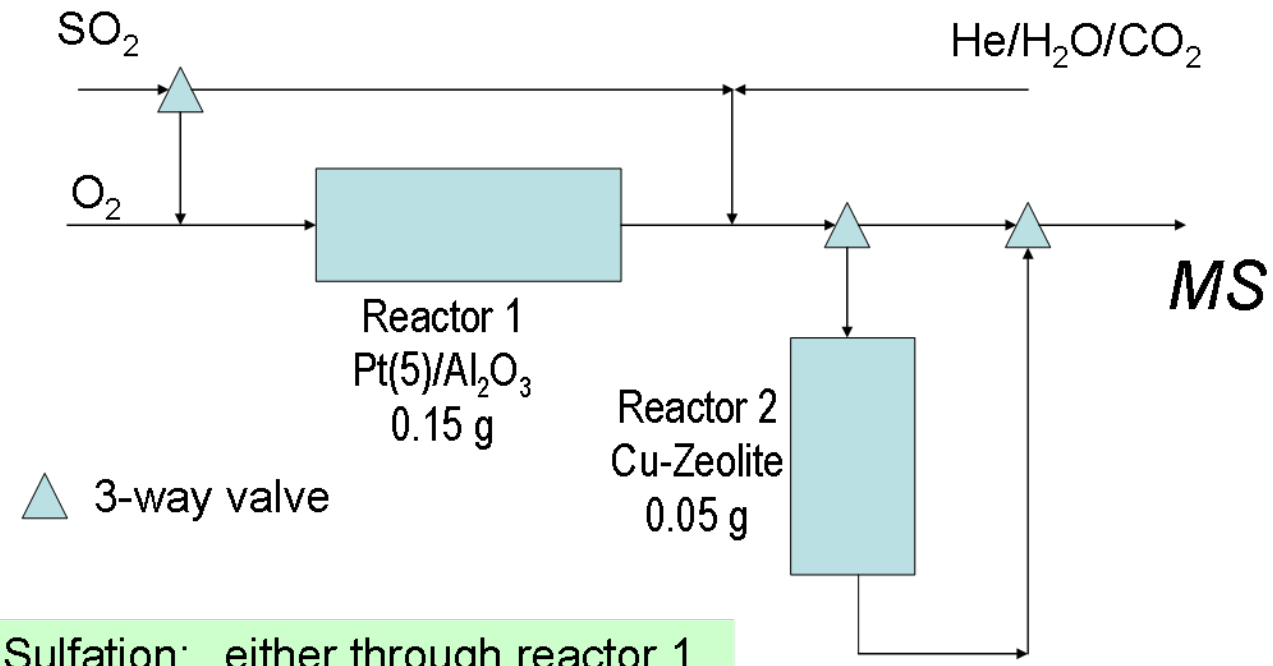


These results raise an important sulfur poisoning concern for systems with DOCs in front of zeolite-based SCR catalysts.

Technical Accomplishments/ Progress/Results

Post-sulfation TPD and XPS performed to determine sulfur levels and speciation.

Reaction system



Sulfation: either through reactor 1 (SO_3) or bypass (SO_2)

No sulfur species observed with SO_2 exposures.

Technical Accomplishments/ Progress/Results

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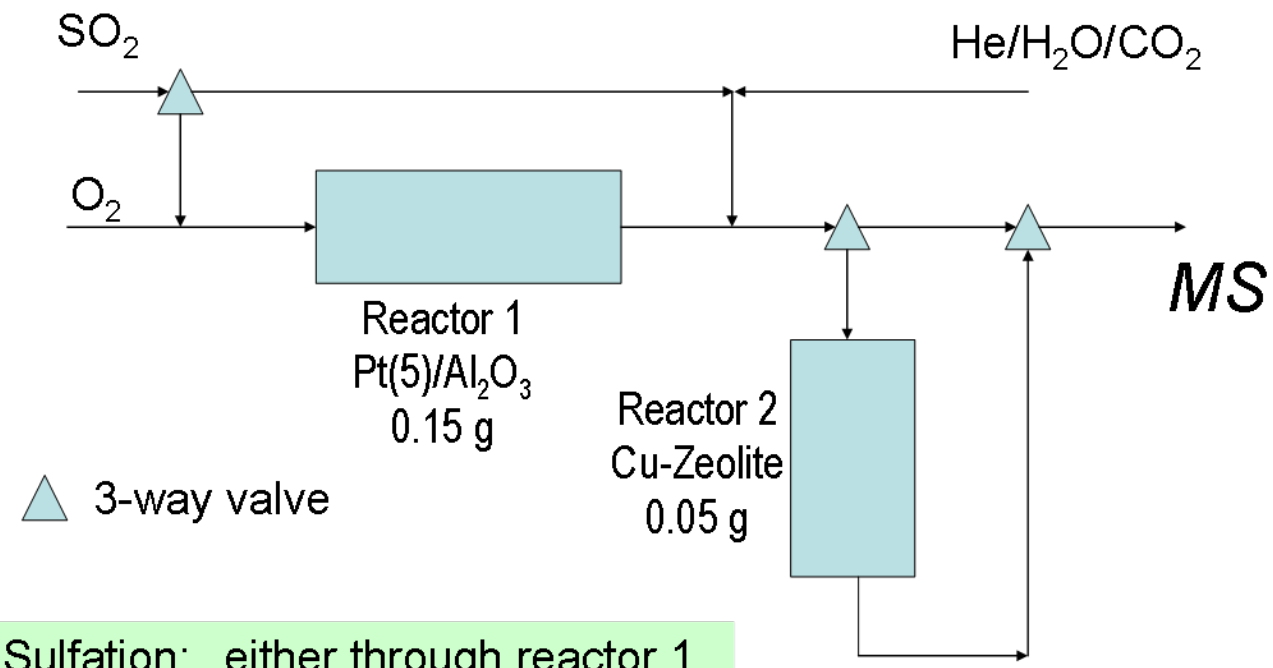

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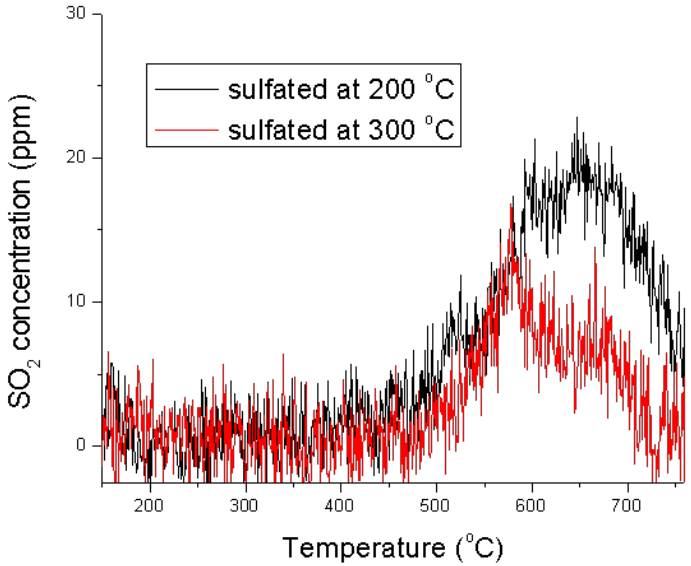
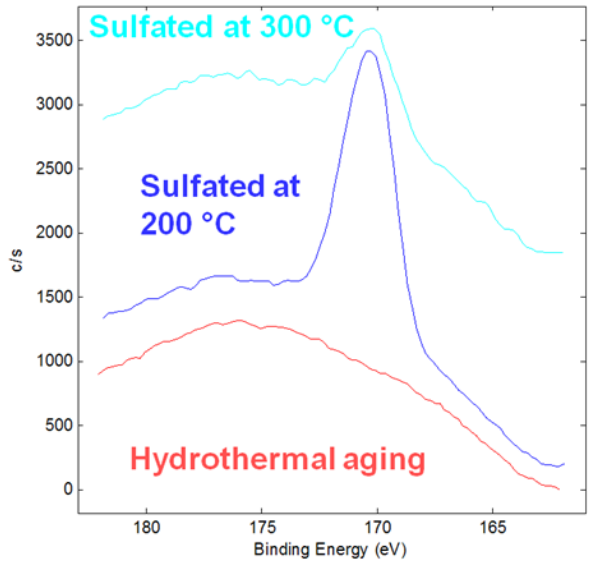
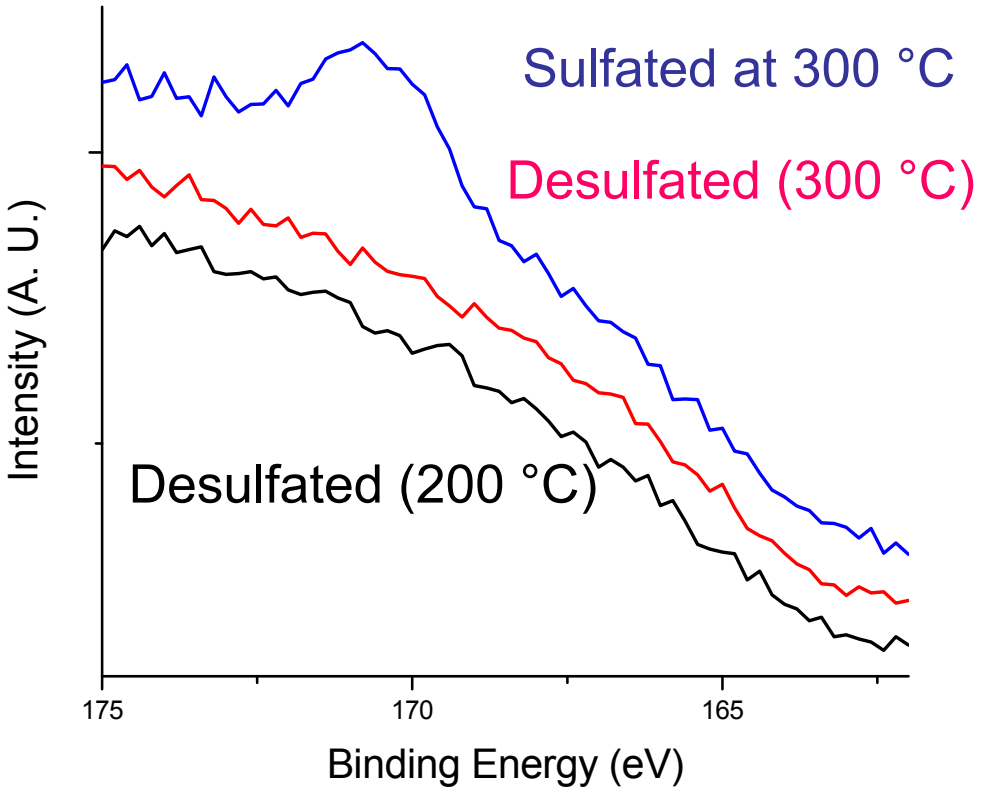
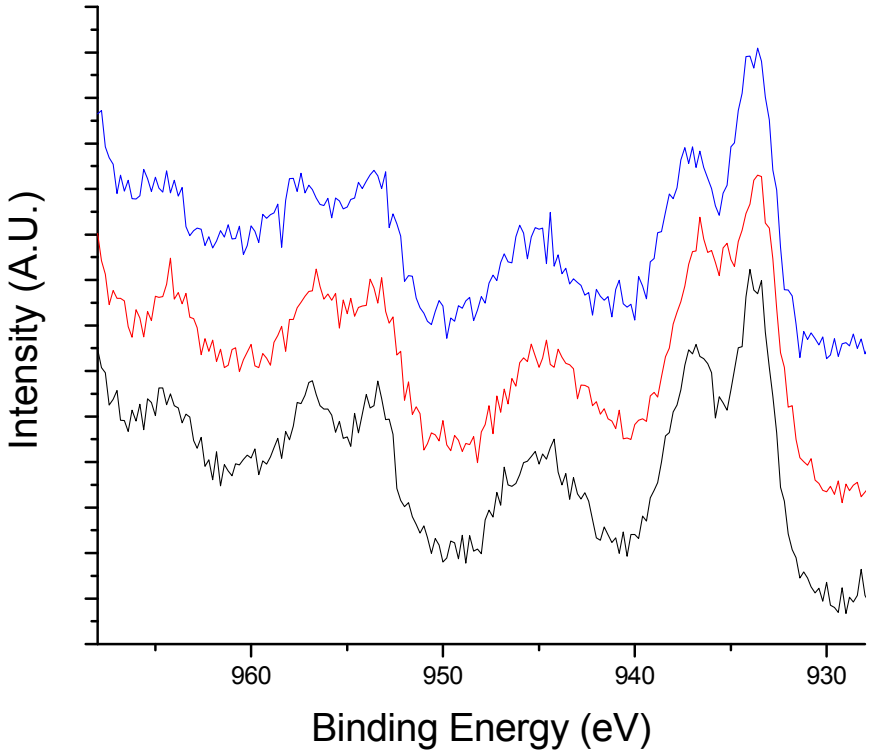




No sulfur species observed with SO_2 exposures.

After desulfation: S 2p and Cu 2p XPS

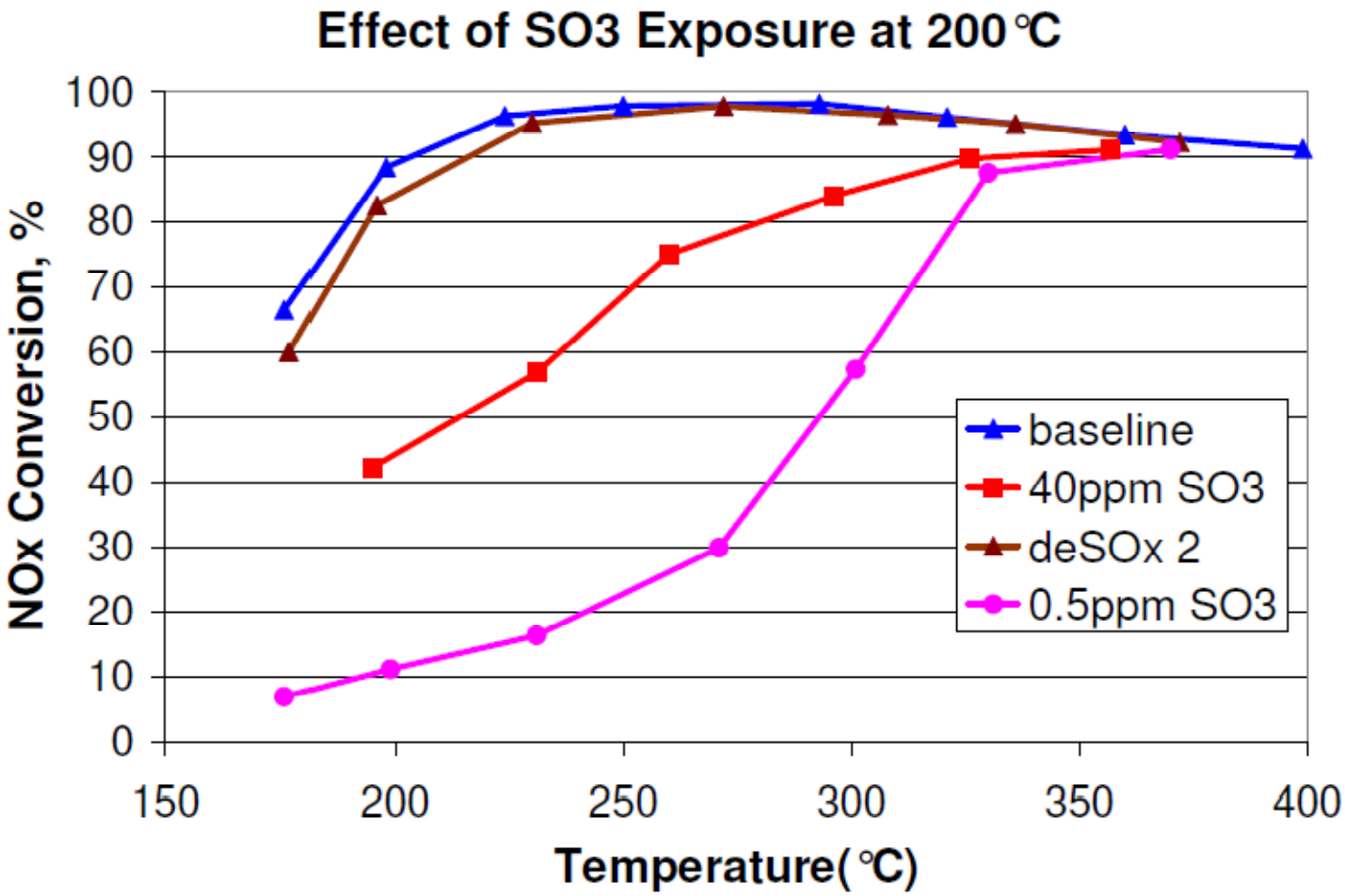




- Not much difference in Cu region before and after desulfation.
- Sulfur is completely removed after desulfation for both samples.

FreedomCAR & Fuel Partnership

Full NOx Conversion Activity Recovered After a DeSOx.



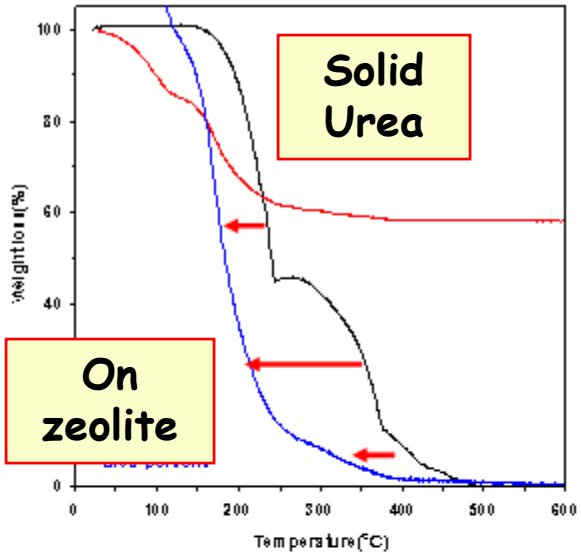
FreedomCAR & Fuel Partnership

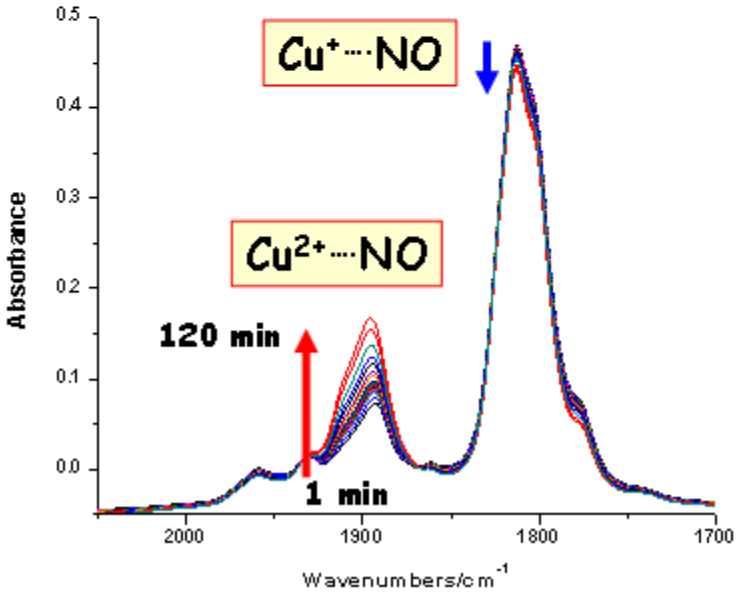
Principal conclusions of these studies to date:

- 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.
- SCR activity was significantly reduced for samples poisoned by SO_3 versus those poisoned by SO_2.
- XPS and TPD shows only SO_3 exposure leads to measurable sulfate formation.
- The sulfate is readily thermally desorbed above 500 °C explaining the complete recovery of performance after a 'deSOx'.

Activities for Next Fiscal Year

- Complete mechanistic studies of catalytic urea decomposition in the presence of water and CO_2.
- Identify nature of Cu^{+2} species and its relationship to observed dealumination and deactivation.
- Initiate FTIR and NH_3 TPD studies of chemical effects of aging with urea (e.g., reaction with HNCO).
- Determine the speciation and location of sulfur poisons as a function of the nature of the gas-phase sulfur species.





Summary

- PNNL has been carrying out a CRADA program with Ford Motor Company to study deactivation mechanisms in zeolite-based urea SCR catalysts. A specific goal of this work is to use this fundamental information to develop realistic laboratory aging protocols.
- Technical progress to date has included correlation of catalyst characterization with performance of laboratory- and field-aged samples, and initial studies of the variable effects of SO_2 versus SO_3 poisoning.
- Future work will be studying possible catalyst materials effects of urea with FTIR, and mechanistic studies of sulfur species adsorption and removal processes.