Effects of hydrothermal aging on the properties and performance of a commercial small pore copper zeolite SCR catalyst

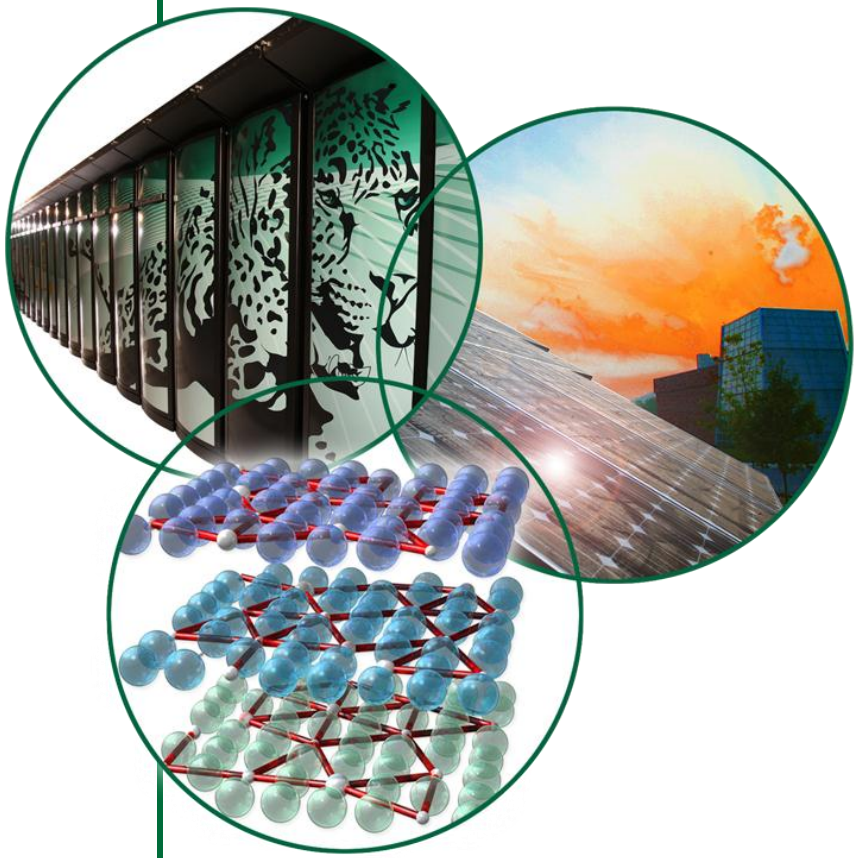
Josh Pihl, Stuart Daw

Fuels, Engines, and Emissions Research Center
Oak Ridge National Laboratory

Presentation to:

2012 CLEERS Workshop

Dearborn, MI
April 30, 2012



U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Acknowledgements

Funded by DOE EERE Vehicle Technologies Program:
- Ken Howden
- Gurpreet Singh

Conducted in collaboration with PNNL:
- Maruthi Devarakonda
- John Lee
- George Muntean

Supported by ORNL team:
- Jim Parks
- Todd Toops
- Bill Partridge
- Jae-Soon Choi
- Vitaly Prikhodko
- Zhiming Gao

Motivation

- Emission compliance is a critical barrier to adoption of high efficiency vehicle technologies
  - aftertreatment systems add cost and complexity
  - high efficiency operating regimes create new emissions challenges
    - advanced combustion modes: low exhaust temperatures, high CO and HCs
    - waste heat recovery: low exhaust temperatures
    - high efficiency diesel operating points: high NOx
    - lean gasoline: high NOx, high temperatures
    - electrification: start/stop operation
  - regulated emissions levels continue to decrease
- DOE's aftertreatment R&D enables high efficiency vehicle architectures that provide a path to reduced petroleum consumption
- High fidelity simulation tools are essential for designing and evaluating high performance multi-component aftertreatment systems and associated operating strategies
  - better models = higher performance, lower cost systems

Approach: Support development of better aftertreatment component models

- ORNL supports model developers by
  - performing specialized experiments to measure critical catalyst parameters
  - developing reaction mechanisms
  - identifying modeling strategies
- We coordinate our efforts with partner institutions
  - for SCR systems: Maruthi Devarakonda and George Muntean at PNNL
  - ORNL provides experimental data and insights
  - PNNL develops global SCR model (see next presentation)
- Current focus:
  - identify how aging impacts critical catalyst properties and model parameters over an SCR catalyst's useful life
  - develop mechanistic description of SCR reaction pathways and associated active sites
    - what are the key reactions
    - where are they occurring

Experimental investigations of commercially available Cu zeolite SCR catalyst

- PNNL provided Cu exchanged small pore zeolite SCR monolith
- Cut cores (2 cm diameter, 5 cm length)
- Aged in laboratory furnace under flowing 10% H_2O in Air

core	T(°C)	time (hr)	description
1	N/A	N/A	fresh
2	700	4	degreened
3	800	6	aged 1
4	800	16	aged 2

note: aging conditions suggested by PNNL based on work with GM

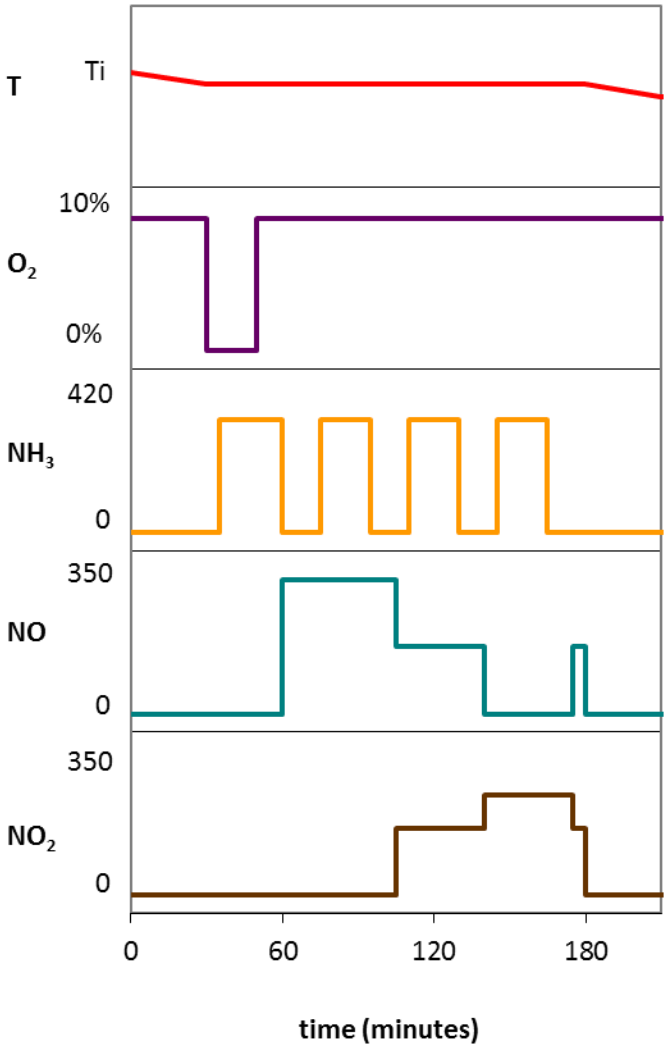
*800 °C 16 hr ≈ 135000 miles**

- Conducted CLEERS transient SCR laboratory evaluation protocol on each core in automated flow reactor
  - 550-150°C @ 50°C
  - 60000 hr^{-1} GHSV
  - 350 ppm NOx
  - MKS Multigas 2030HS FTIR for gas analysis

*Schmieg et al., Catal. Today (2011), doi:10.1016/j.cattod.2011.10.034

CLEERS transient SCR laboratory evaluation protocol

- Designed to generate data for model calibration/validation and performance evaluation with minimal operating time
- Revised since last CLEERS workshop
  - create better-defined starting points for transient steps
  - add NO_2 SCR
- Measures:
  - SCR conversion & selectivity:
    - NO_2/NOx = 0.0, 0.5, 1.0
    - NH_3/NOx = 1.0 (others by repeating protocol)
  - NO oxidation and NO_2 decomposition
  - NH_3 oxidation by O_2
  - NH_3 storage
    - saturation capacity (with and without O_2)
    - SCR inventories
  - NH_3 stability: adsorption/desorption/TPD



note: all steps include 5% H_2O, 5% CO_2

General insights into catalyst function from experiments on degreened core sample

NO_2/NOx controls kinetics and performance by changing reaction pathways

- Three global pathways to N_2:

1. **NO SCR:**

   $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$

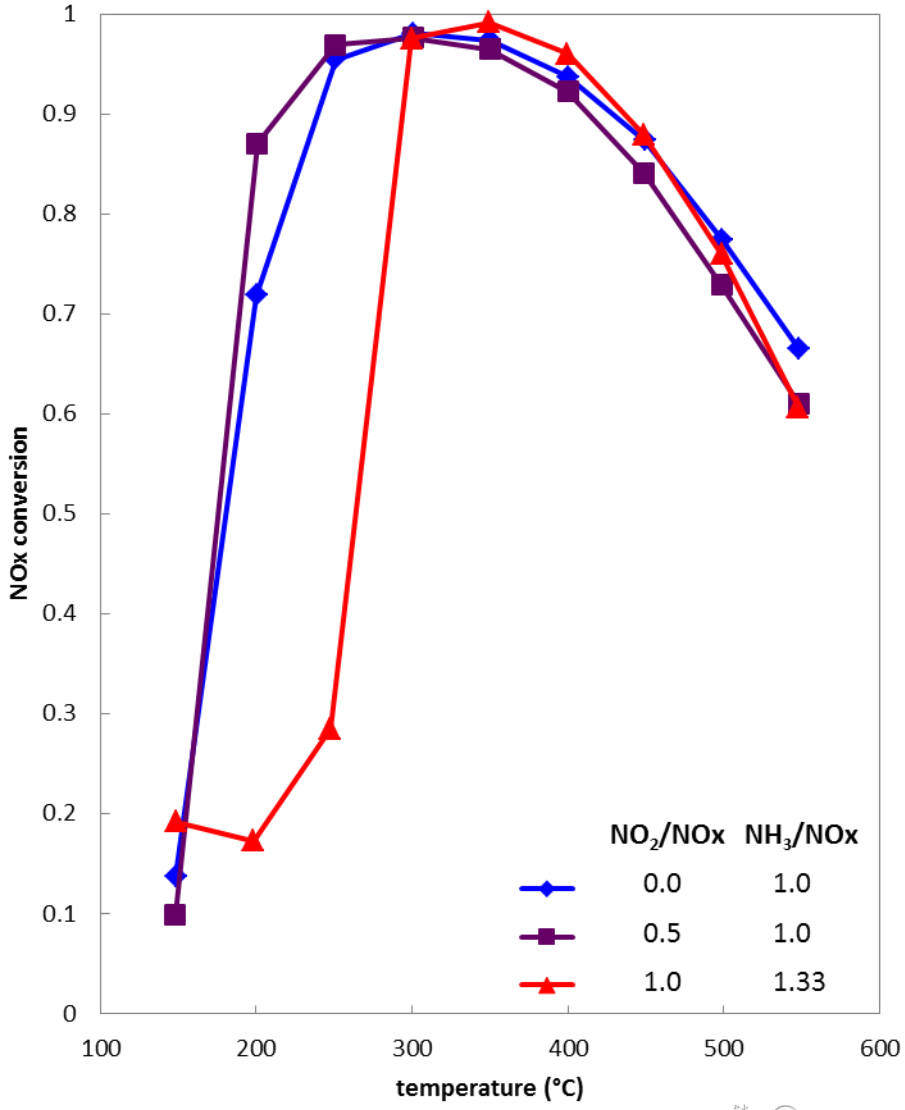
2. **NO+NO_2 SCR:**

   $4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$

3. **NO_2 SCR:**

   $4NH_3 + 3NO_2 \rightarrow 7/2N_2 + 6H_2O$

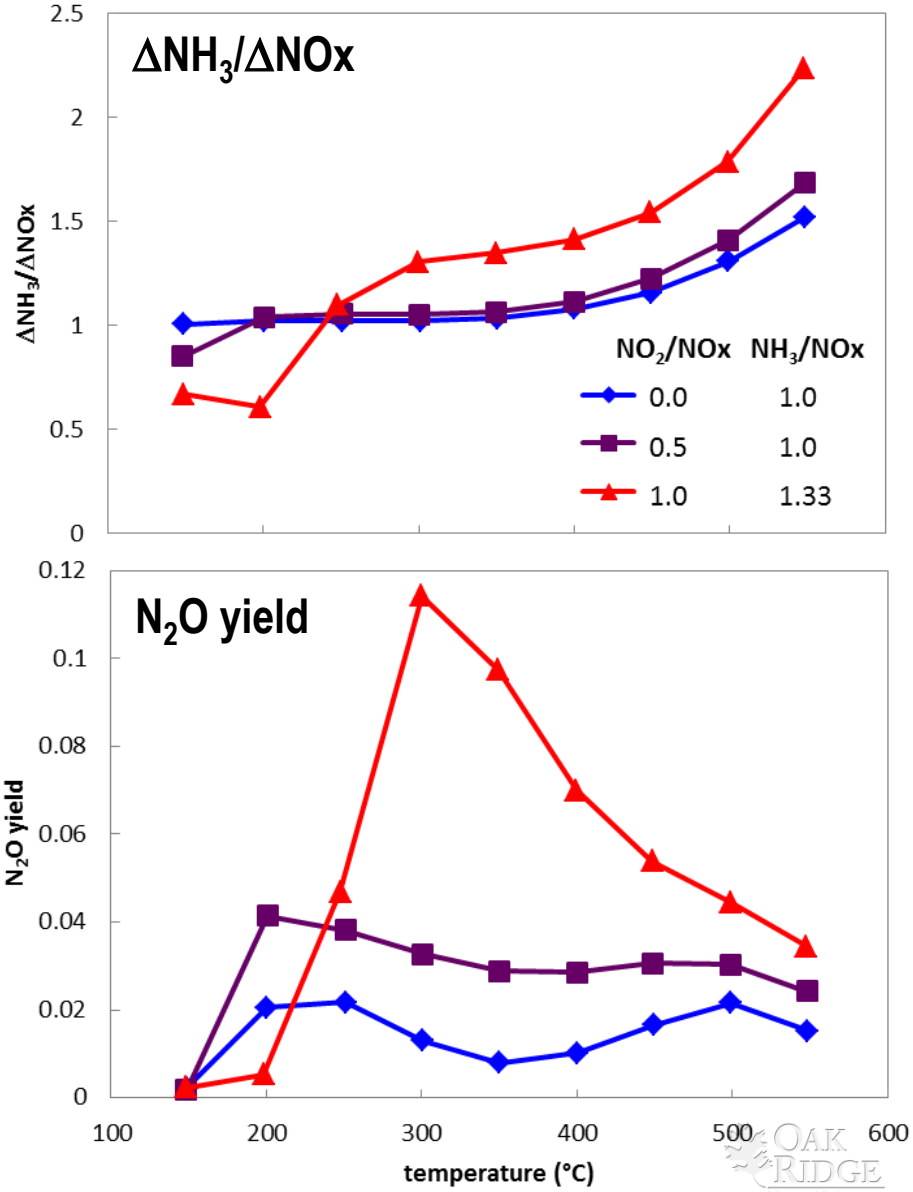
- Assumption: NO+NO_2 > NO > NO_2
  - holds at low T
  - not necessarily true at high T
- May need to consider contribution of NO_2 SCR even when NO_2/NOx ≤ 0.5



NO_2 SCR reaction involvement impacts NH_3 consumption, N_2O selectivity

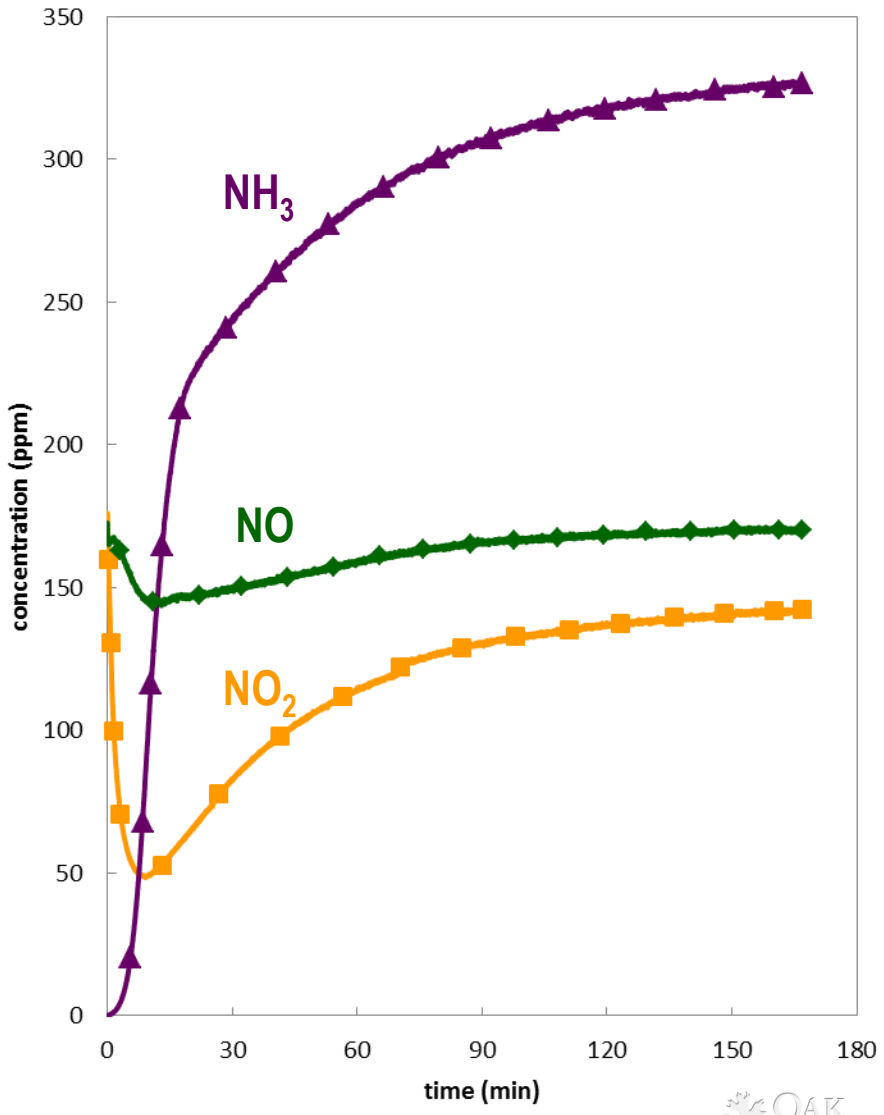
- 4:3 stoichiometry of NO_2 SCR reaction consumes more NH_3
  - particularly important under NH_3 limited conditions found at high T
  - requires increased dosing to compensate
  - potential explanation for drop in conversion between NO and NO+NO_2 SCR at high T

- N_2O selectivity significantly higher for NO_2 SCR reaction
  - N_2O included in proposed greenhouse gas emissions standards

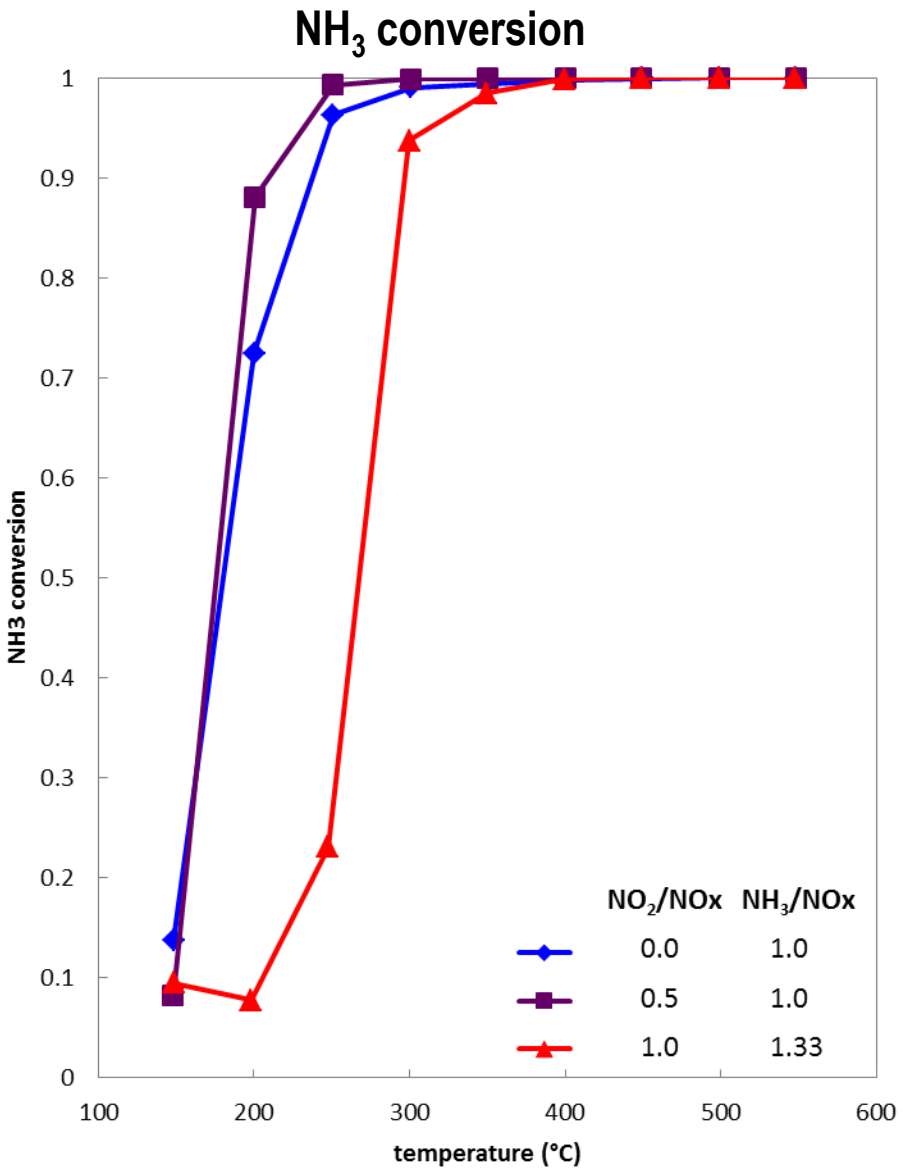


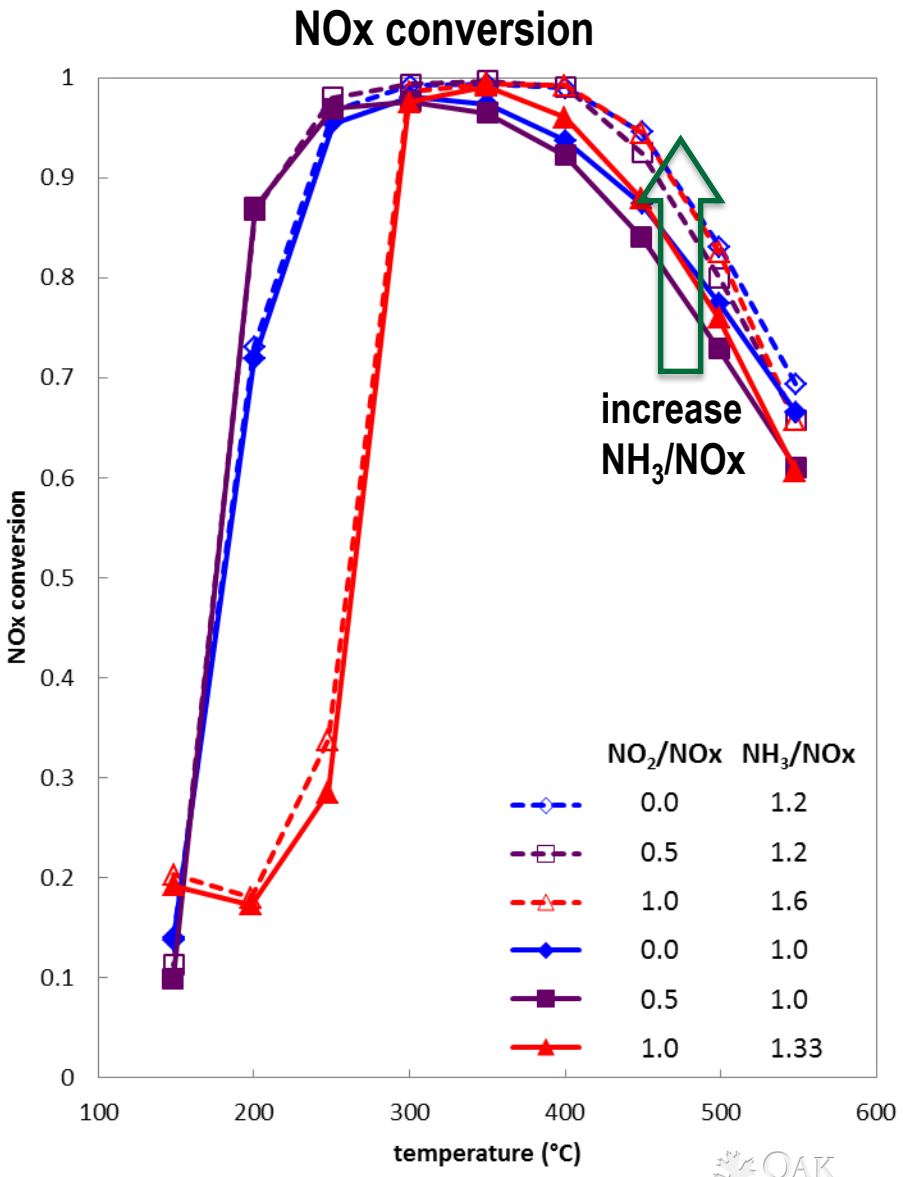
NO_2 reactions also play a critical role at low T

- Transient concentration profiles for $NO+NO_2$ SCR reaction: 150 °C
  - 175 ppm NO, 175 ppm NO_2
  - start 350 ppm NH_3 at time = 0
- Initial consumption of NH_3 due to storage, reaction with NO_2
  - very little NO consumed
- NH_3 + NO_2 reaction generates intermediates that build up on catalyst surface (such as NH_4NO_3)
  - eventually block active sites
  - inhibit further reaction
- Low T performance limitations due to:
  - slow reaction kinetics
  - inhibition by intermediate species



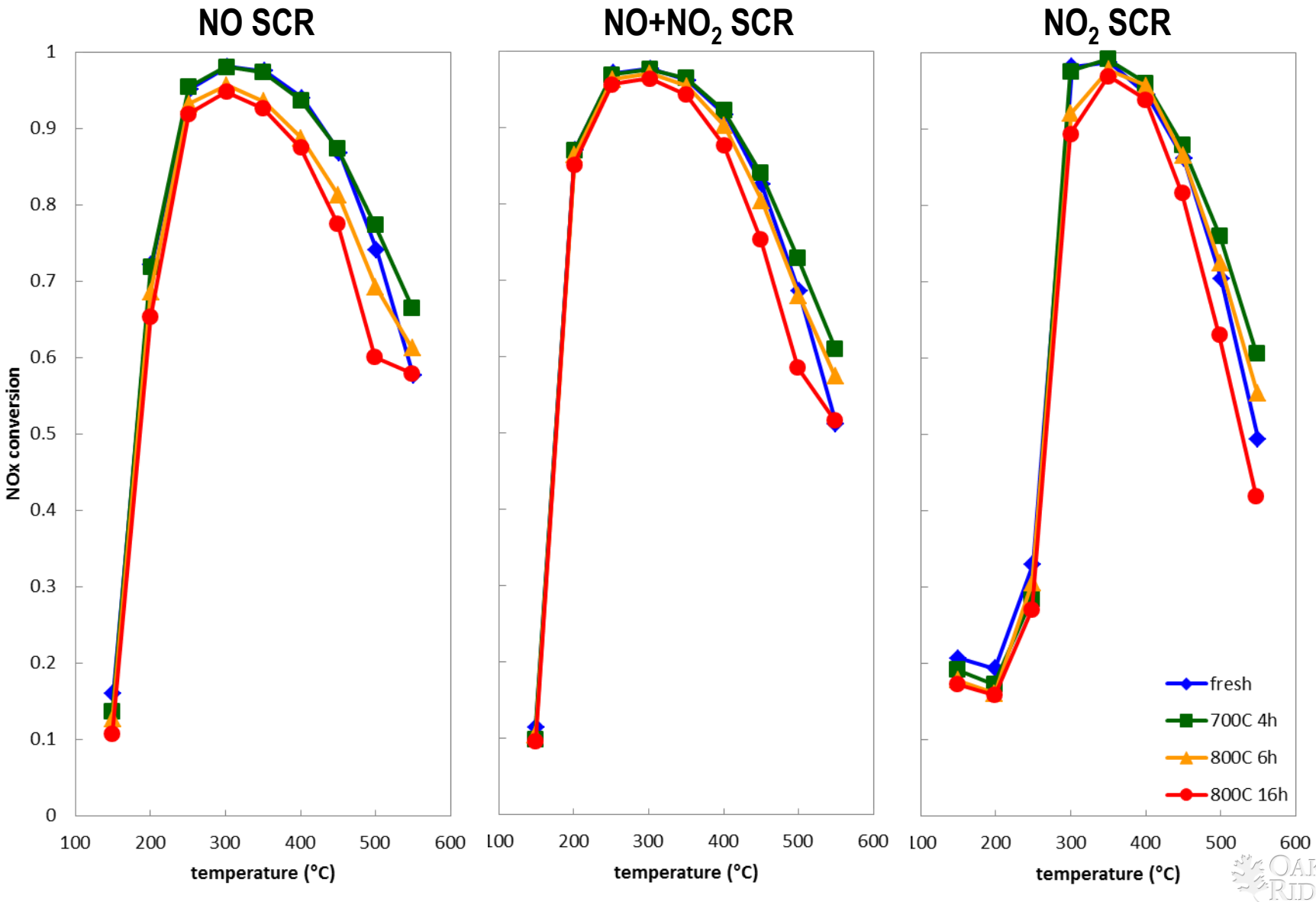
High T NOx conversion limited by NH_3 oxidation





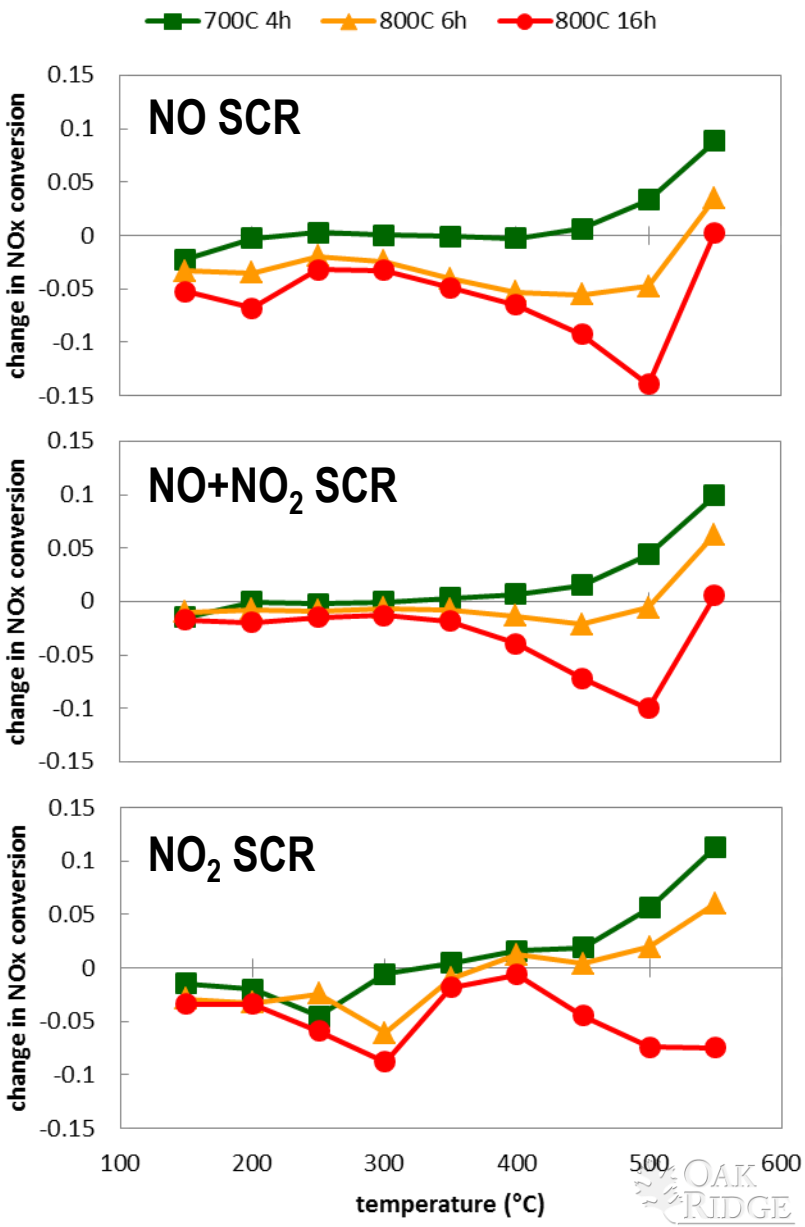
Effects of hydrothermal aging on catalyst properties

Summary of hydrothermal aging impacts on SCR NOx conversion

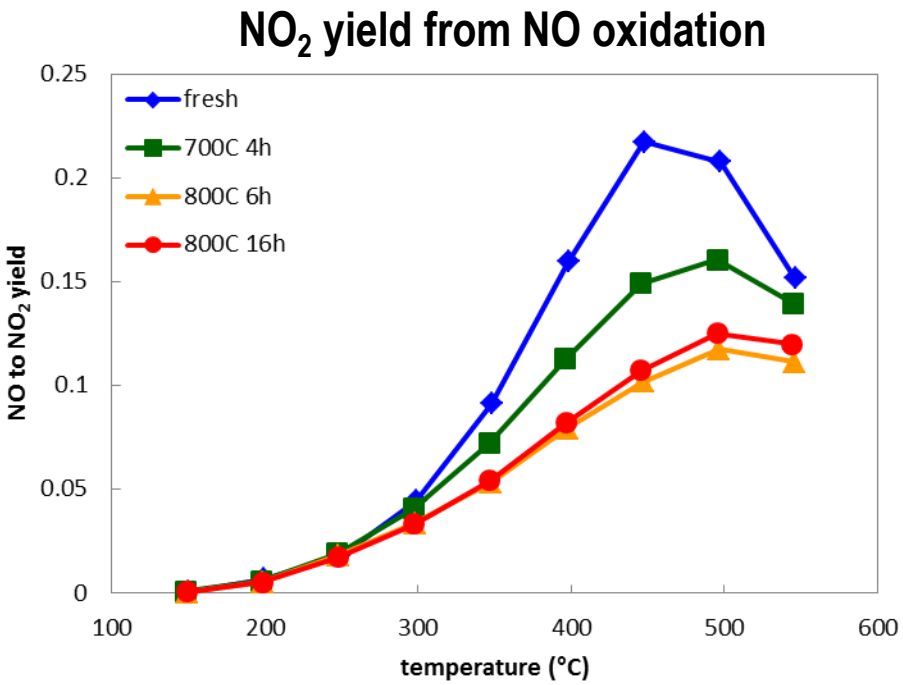


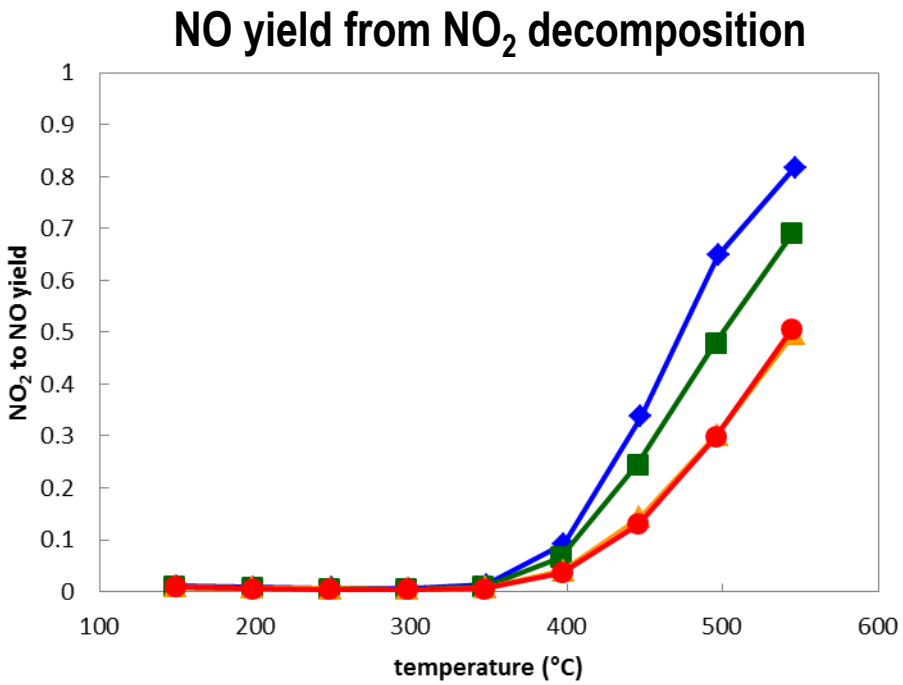
Aging sensitivity varies with operating temperature and reaction pathway

- Calculated change in NOx conversion relative to fresh catalyst
- Catalyst durable under aging conditions used here: maximum drop in NOx conversion ~15%
- Magnitude of aging impact strongly depends on operating temperature
  - biggest changes at high T and near SCR light-off
  - relevance to models will depend on expected operating regimes
- Aging impact also changes with SCR pathway
  - NO+NO_2 different from others: minimal aging impact at low T
  - implies different active sites involved in reactions



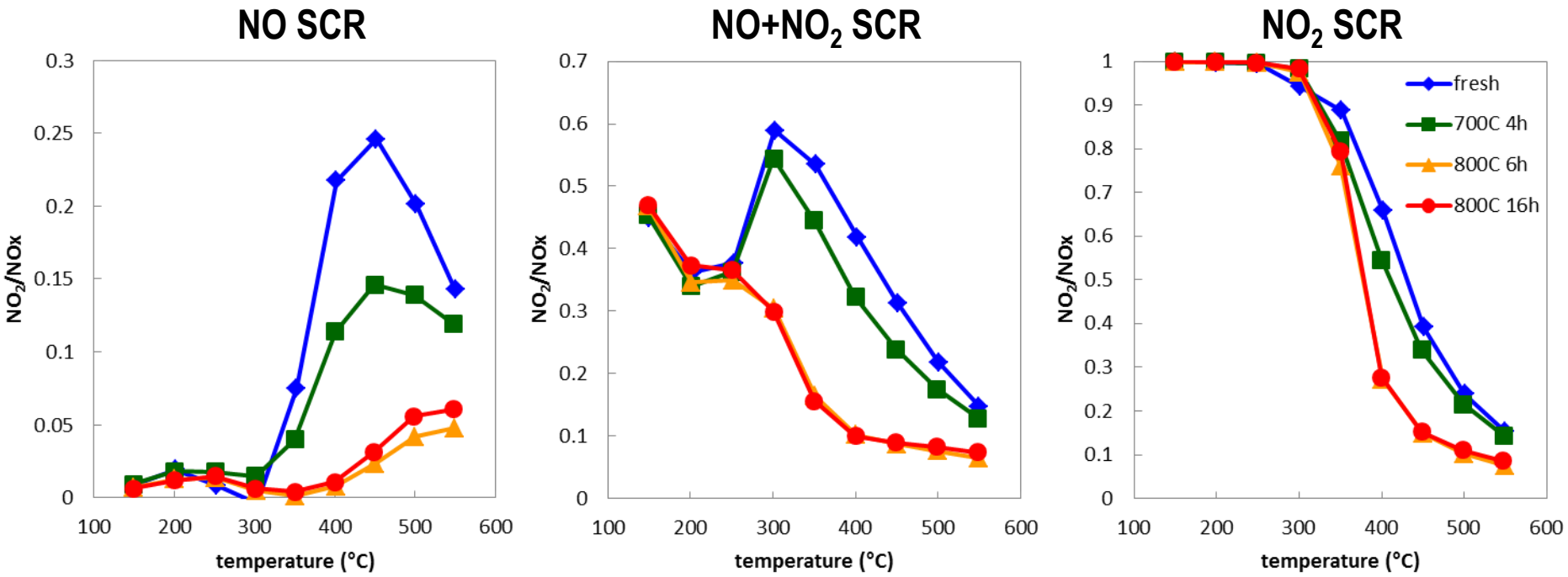
Rates of NO oxidation and NO_2 decomposition decrease with aging





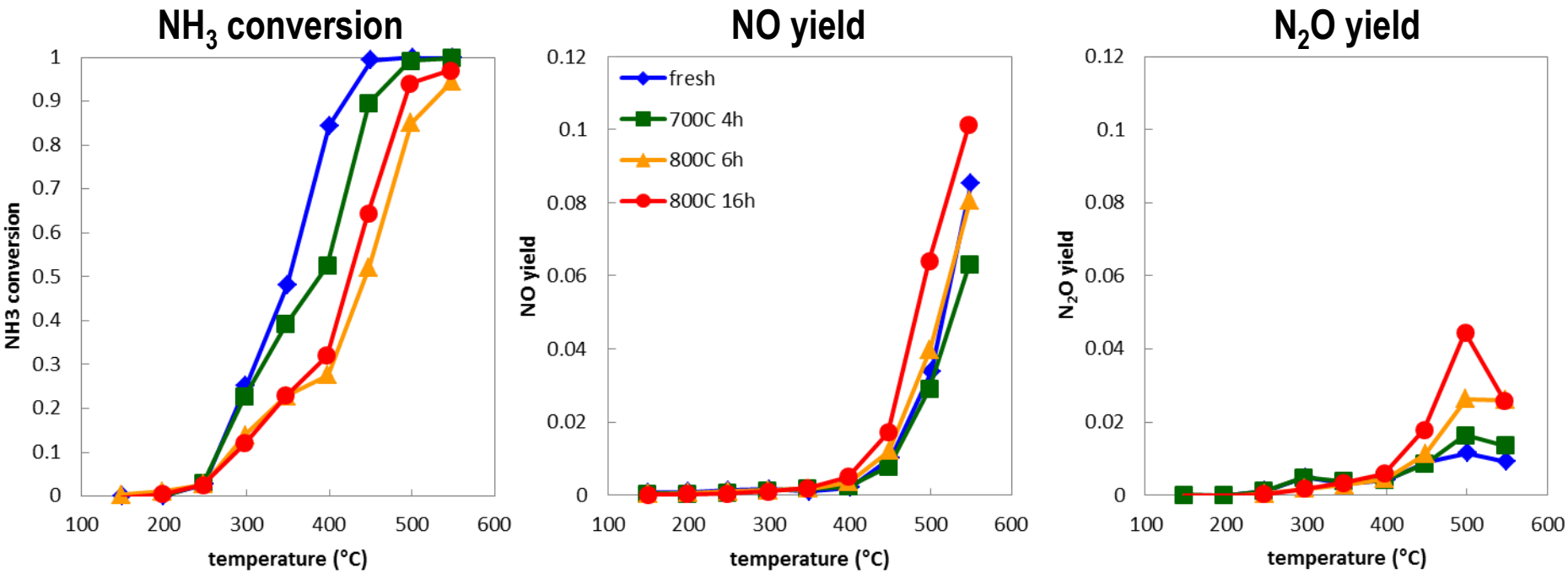
- Clear evidence for hydrothermal aging impact on active sites with oxidation/reduction functionality
- Consistent with loss of activity near light-off for NO and NO_2 SCR pathways

Outlet NO_2/NOx under SCR conditions could provide a sensitive aging diagnostic



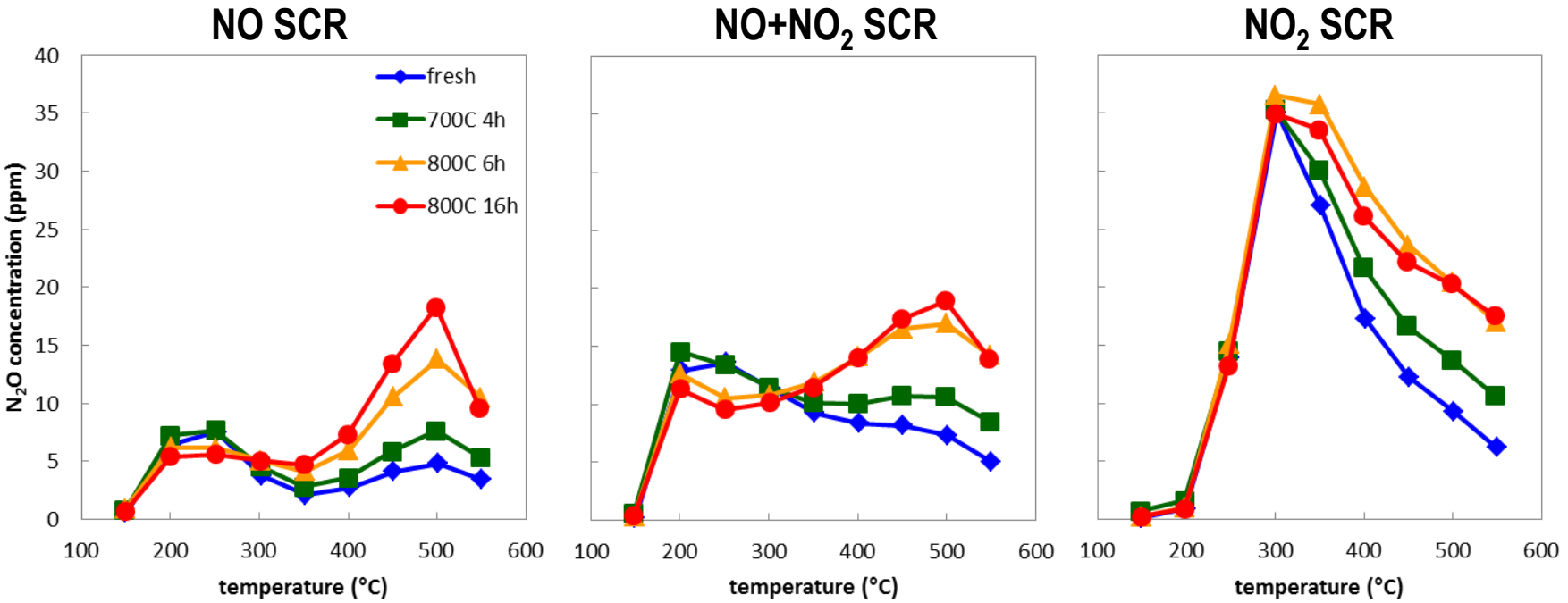
- Changes in NO oxidation and NO_2 decomposition with aging shift NO_2/NOx under SCR operating conditions
- Reliable method for quantifying NO_2/NOx would allow measurement of catalyst state
  - enable adaptive control

Aging impacts rate and selectivity of NH_3 oxidation



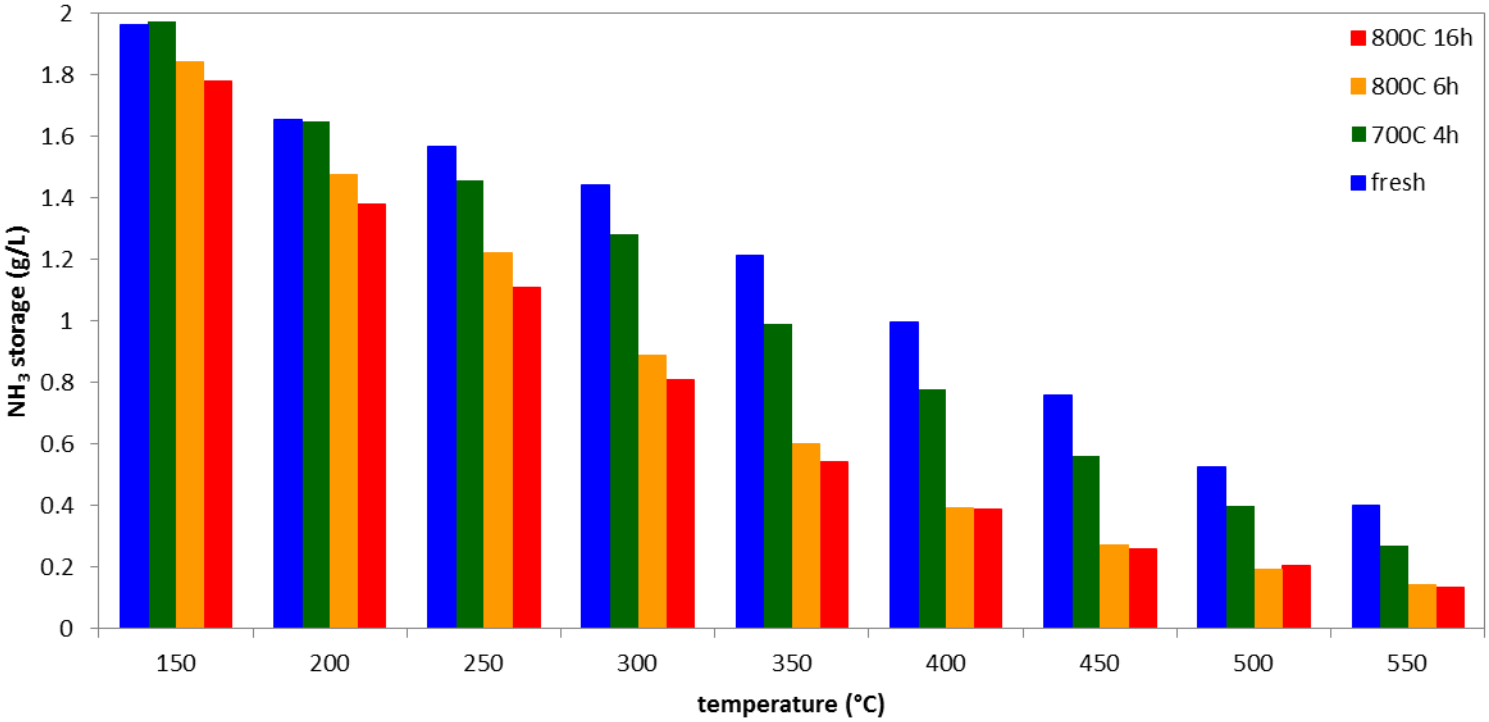
- Further evidence for loss of sites with oxidative function due to aging
  - increased NH_3 oxidation *not* main cause of drop in high T SCR conversion after aging
  - note trend reversal after additional exposure at 800 °C
- Aging increases selectivity of NH_3 oxidation to NO formation (double whammy)
  - N_2O selectivity also increased at high T
- Could provide another sensitive indicator for catalyst state
  - for example: overdose and monitor NH_3 conversion at 450 °C

Aging increases SCR N_2O selectivity



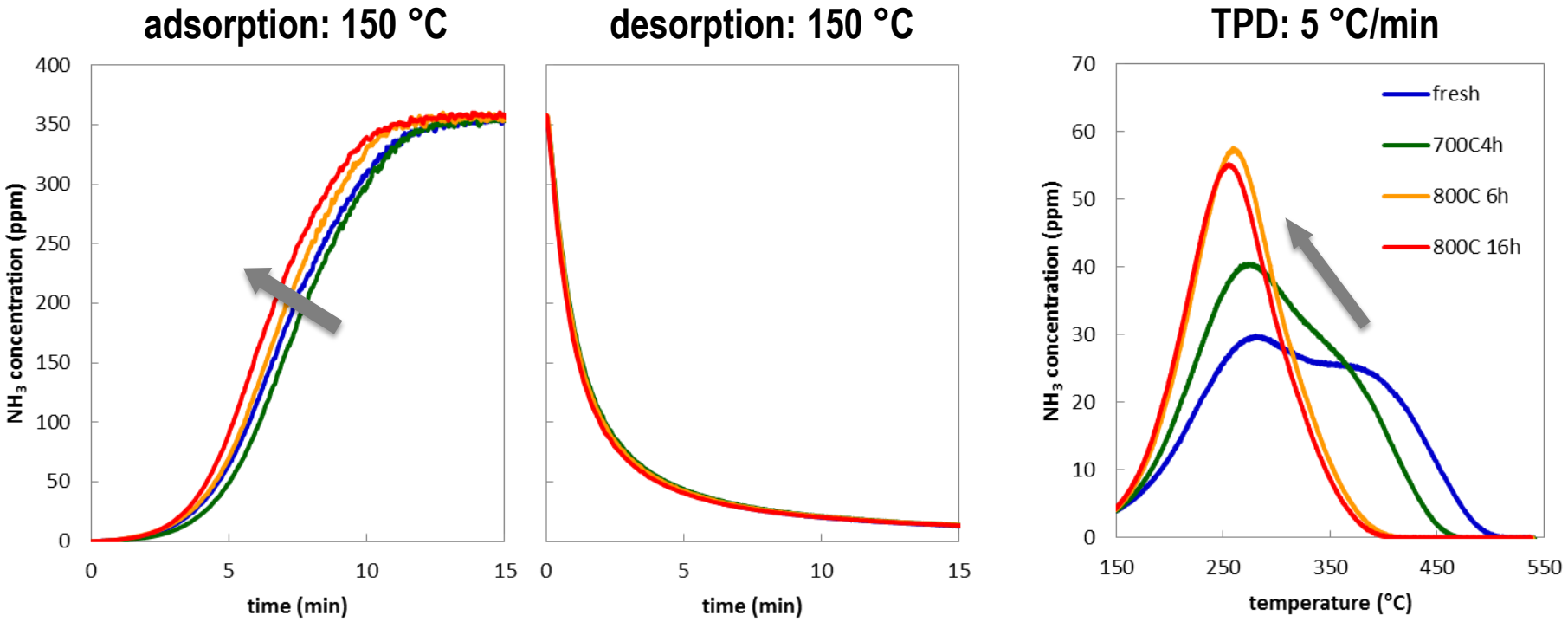
- N_2O in proposed greenhouse gas emissions standards
  - model predictions important for design of compliant systems
- Increases in N_2O at high temperatures
  - partly due to increased N_2O selectivity of NH_3 oxidation?

Aging reduces NH_3 storage capacity



- NH_3 storage measured in the absence of O_2 or NOx
  - avoids confounding effects of NH_3 oxidation or SCR reactions
- Storage drops a bit at low temperatures, significantly at high temperatures
- Perhaps the biggest observed impact of hydrothermal aging on a catalyst property with direct model relevance

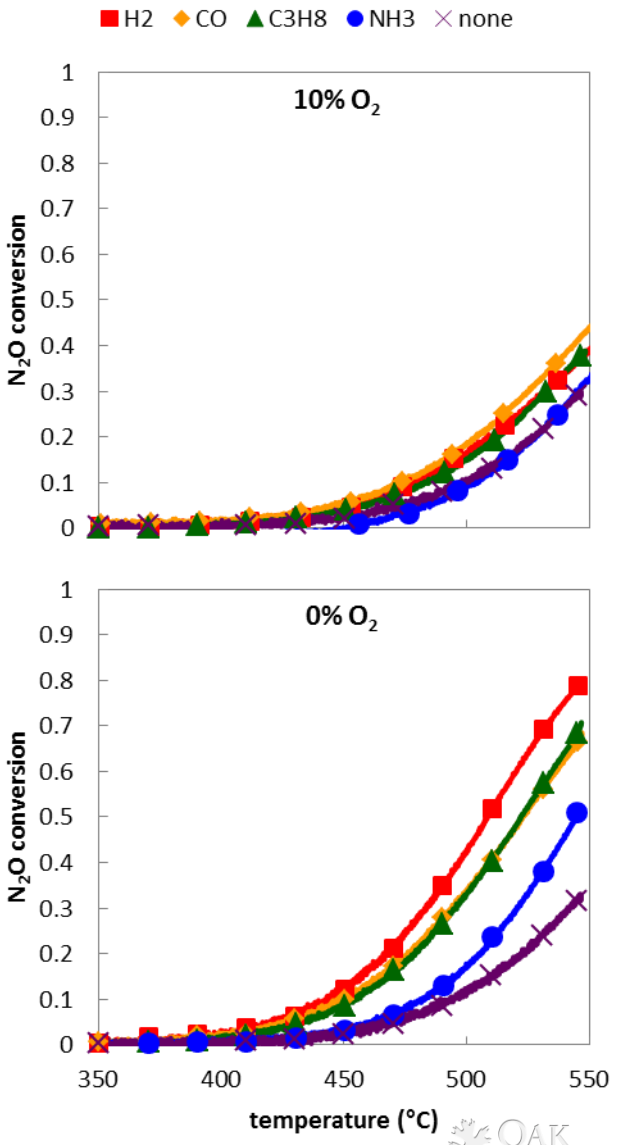
Loss of high T NH_3 storage due to shift in stability



- Uptake profiles very similar for all four aging states
  - slight loss in capacity results in earlier breakthrough
- Isothermal desorption profiles identical: no aging impact on release of "weakly bound" NH_3
- Two desorption features in TPDs, likely corresponding to two distinct storage sites
  - hydrothermal aging converts higher stability sites into lower stability sites
  - potential mechanism for modeling impact of aging on storage capacity

Small pore copper zeolite SCR catalyst decomposes N_2O at high temperatures

- Experiment conditions:
  - 30000 hr^{-1}: 200 ppm N_2O, 5% H_2O, 0 or 10% O_2
  - reductant: 1000 ppm H_2, 1000 ppm CO, 100 ppm C_3H_8, 667 ppm NH_3, or none
- N_2O decomposes at T > 450 °C
  - same rate with or without O_2
  - could explain drop in SCR N_2O selectivity at high T
- No evidence of NH_3 + N_2O SCR
- Other reductants slightly increase decomposition rate in O_2
- N_2O decomposition increases significantly under net reducing conditions
  - H_2 > CO = C_3H_8 > NH_3 > none
  - Implications for N_2O control in LNT/SCR or TWC/SCR systems



Conclusions

- NO_2 SCR may play a more important role than is typically assumed
- Hydrothermal aging impacted several SCR catalyst properties:
  - decreased SCR NOx conversion
    - at high temperatures
    - near light-off for NO and NO_2 SCR (but not NO+NO_2 SCR)
  - degraded oxidation/reduction functionality
    - reduced rates of NO oxidation, NO_2 decomposition, NH_3 oxidation
  - shifted selectivity
    - higher NO yield for NH_3 oxidation
    - higher N_2O formation for NH_3 oxidation, all SCR reactions
  - decreased NH_3 storage capacity
    - converted more stable NH_3 storage sites into less stable sites
- SCR catalyst decomposes N_2O at high T even in presence of O_2
  - net reducing conditions increase rate of decomposition

pihlja@ornl.gov