Development and Implementation of Experimental Protocol for Steady-State and Transient SCR Kinetics

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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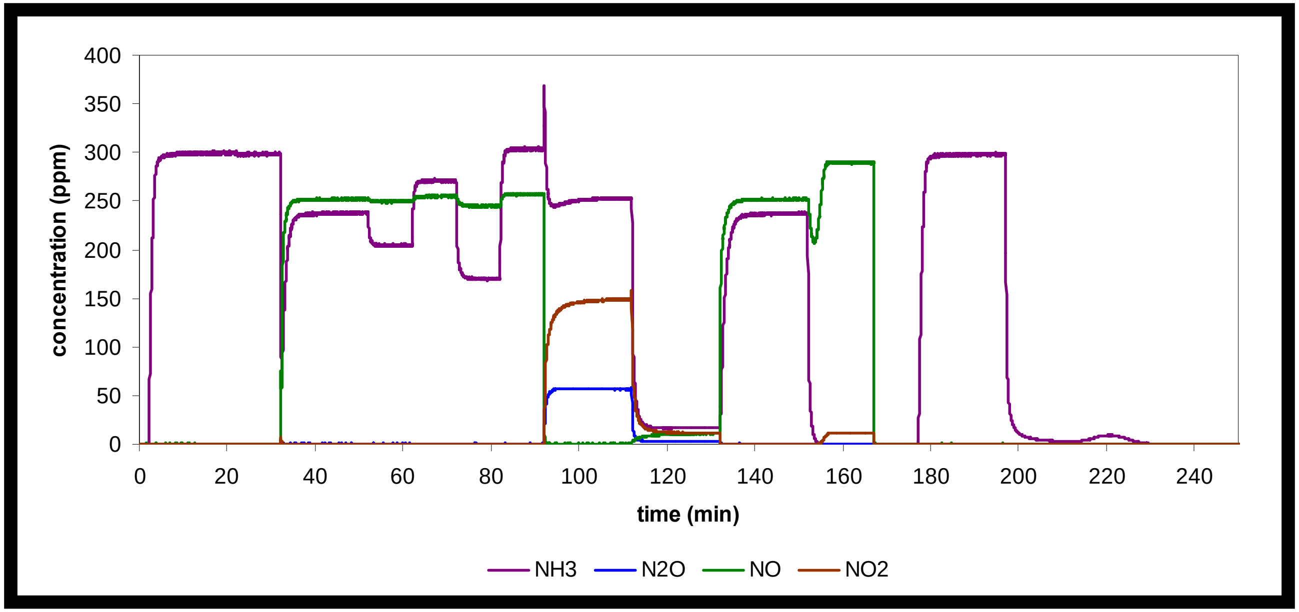
Objectives

- Develop experimental protocol for SCR catalysts to determine specific rate parameters for control strategies
  - Include steady-state and transient behavior

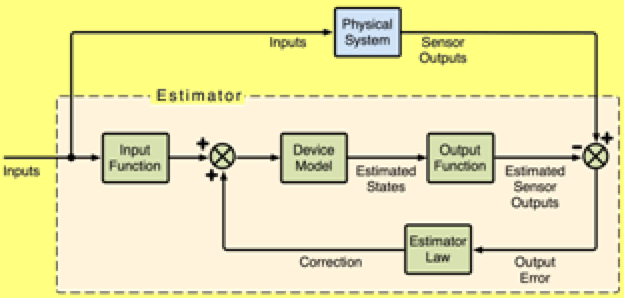
- Obtain accurate temperature dependent data under steady-state and transient operation
  - Covering typical operating range
  - Includes activity of stored NH_3



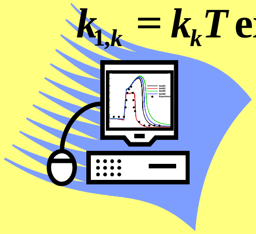
Approach to Protocol and Model Development

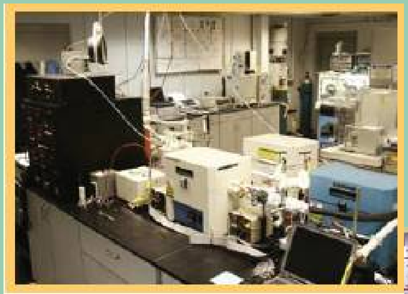
Catalyst Supplier

- ORNL provides unique capabilities and expertise not available at Navistar
- Michigan Tech models results with input from ORNL
- Navistar implements control model for device operation



$$k_{1,k} = k_k T \exp\left[-\frac{E_k}{RT}\right]$$



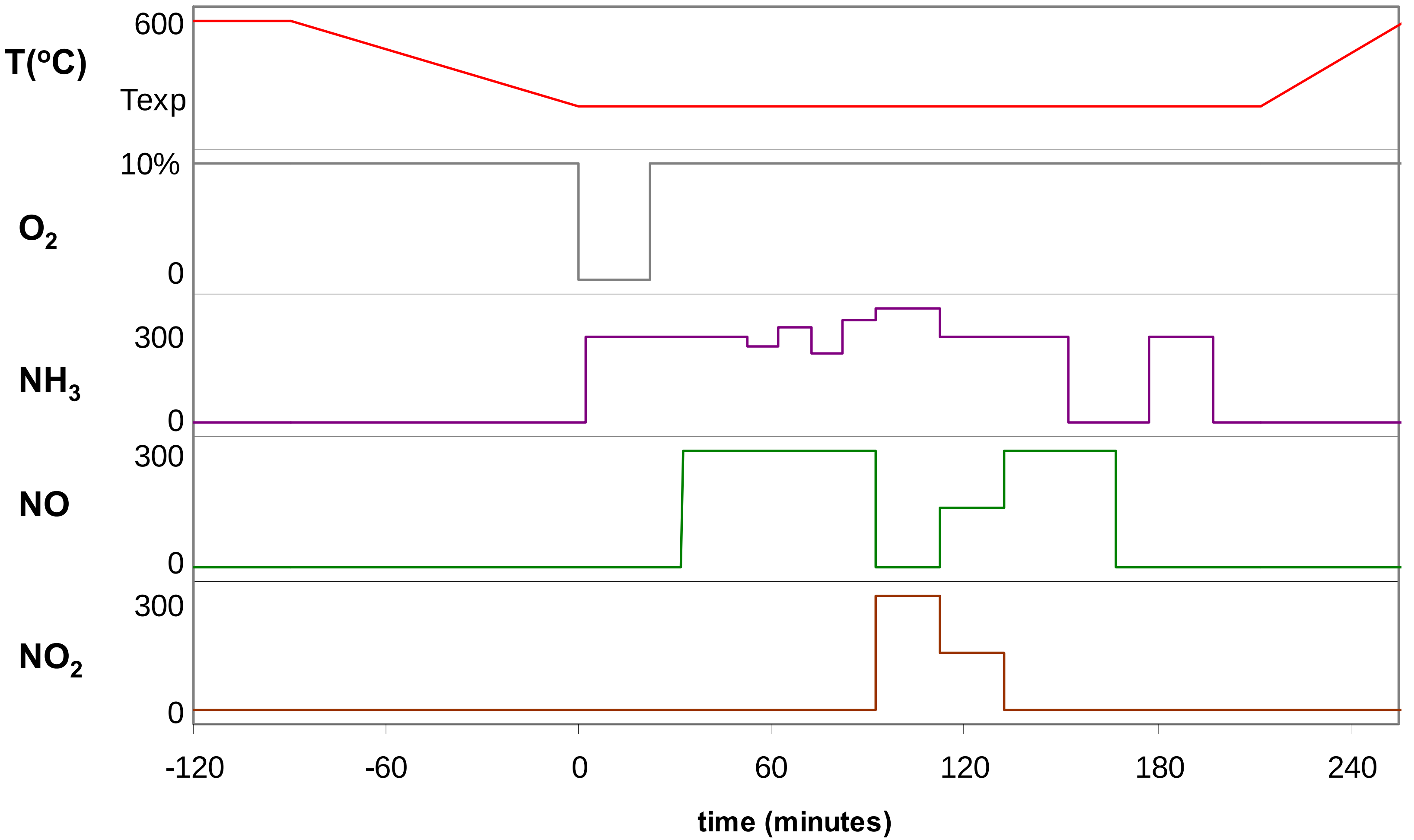


Automated bench reactor used to evaluate core samples

- Protocol programmed into system that enables automated switching of gases and furnace control
  - Solenoid valves
  - HPLC pump for H_2O introduction
- Gas Analysis: MKS FTIR
- Zeolite-based SCR catalyst
  - Evaluated at 150-600°C
    - 25°C steps for 150-250°C
    - 50°C steps for 250-600°C
  - GHSV: 60,000 - 120,000 h^{-1}

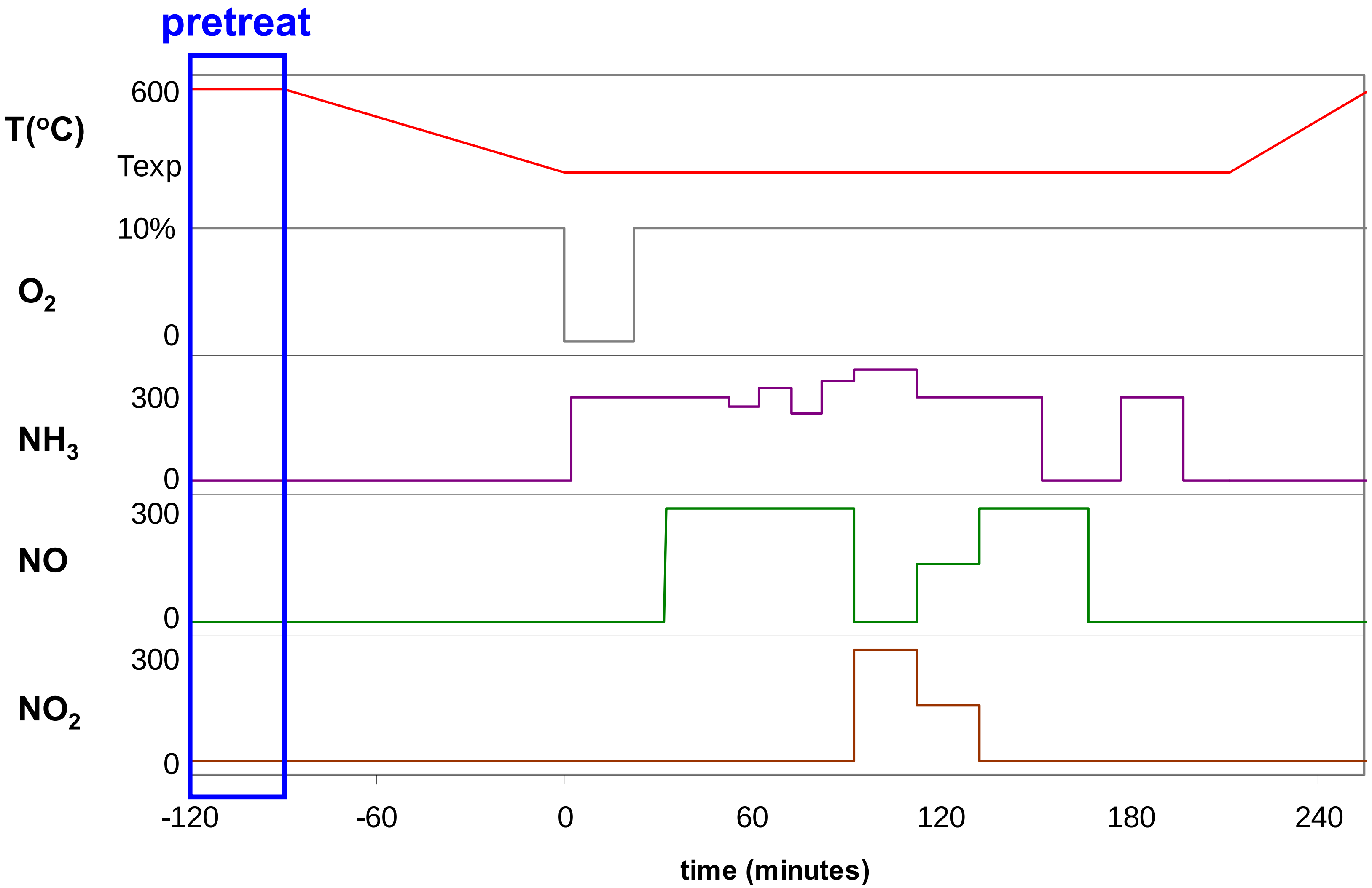
Evaluation Protocol Developed for SCR

- CLEERS SCR focus-group has posted a steady-state SCR protocol
- Accurate models also require transient data; especially for system control
- Proposed protocol provides both transient & steady-state model parameters



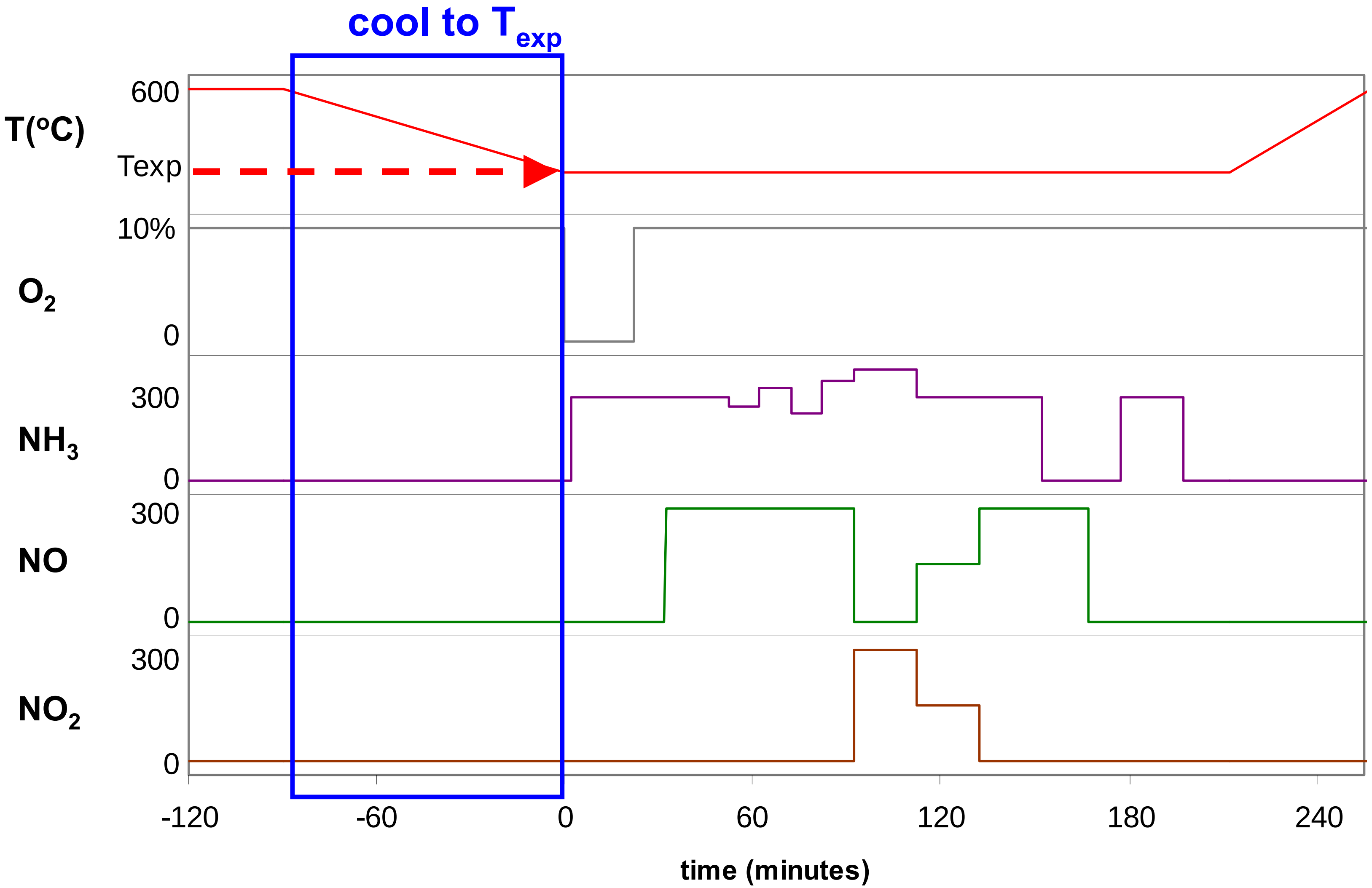
Evaluation Protocol Developed for SCR

- Pretreatment establishes consistent starting point for before making measurements
  - 30 minutes at 600°C in 10% O_2 and 5% H_2O/CO_2



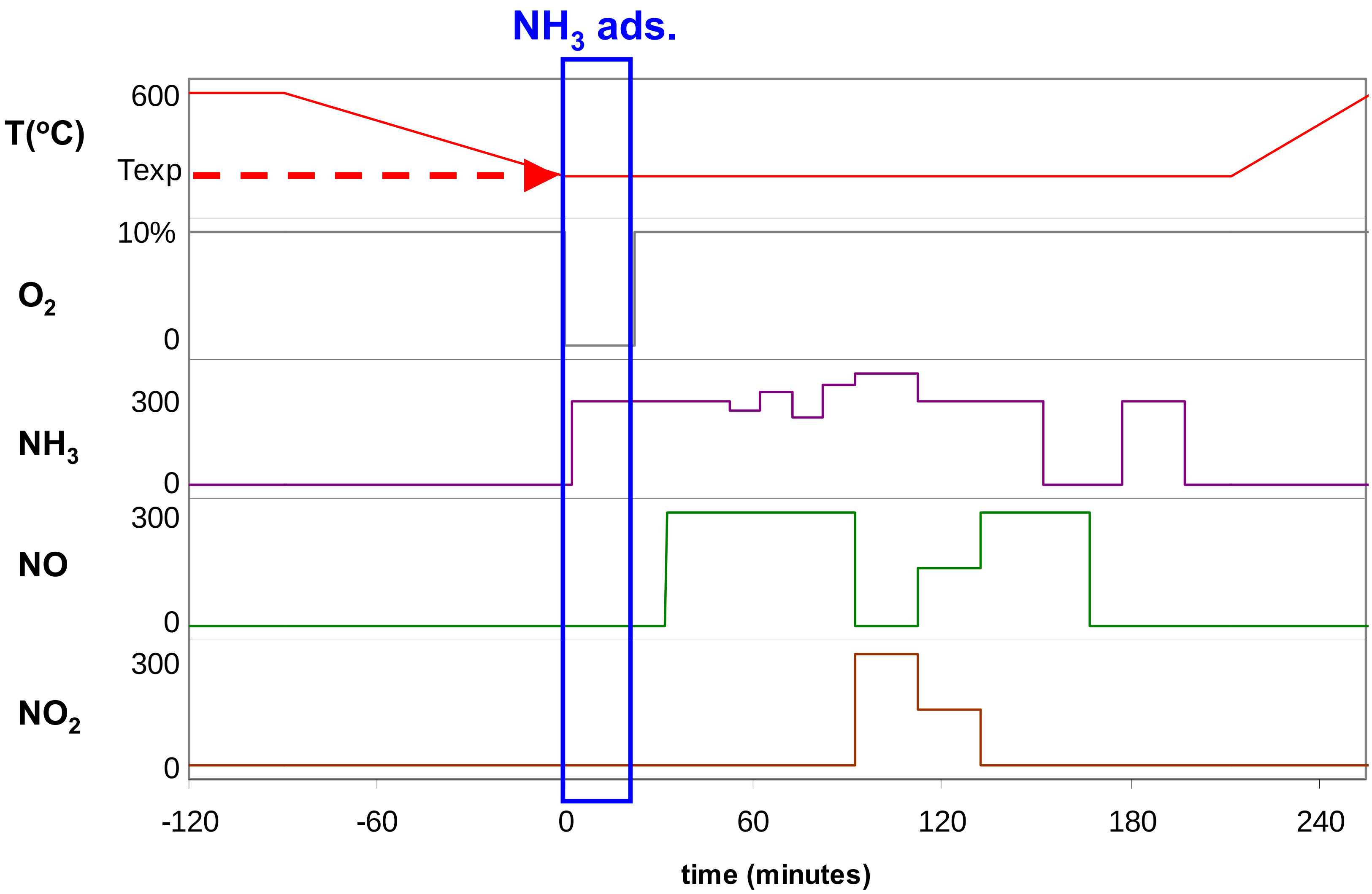
Evaluation Protocol Developed for SCR

- Cool to temperature of interest
  - Maintain flows in 10% O_2 and 5% H_2O/CO_2



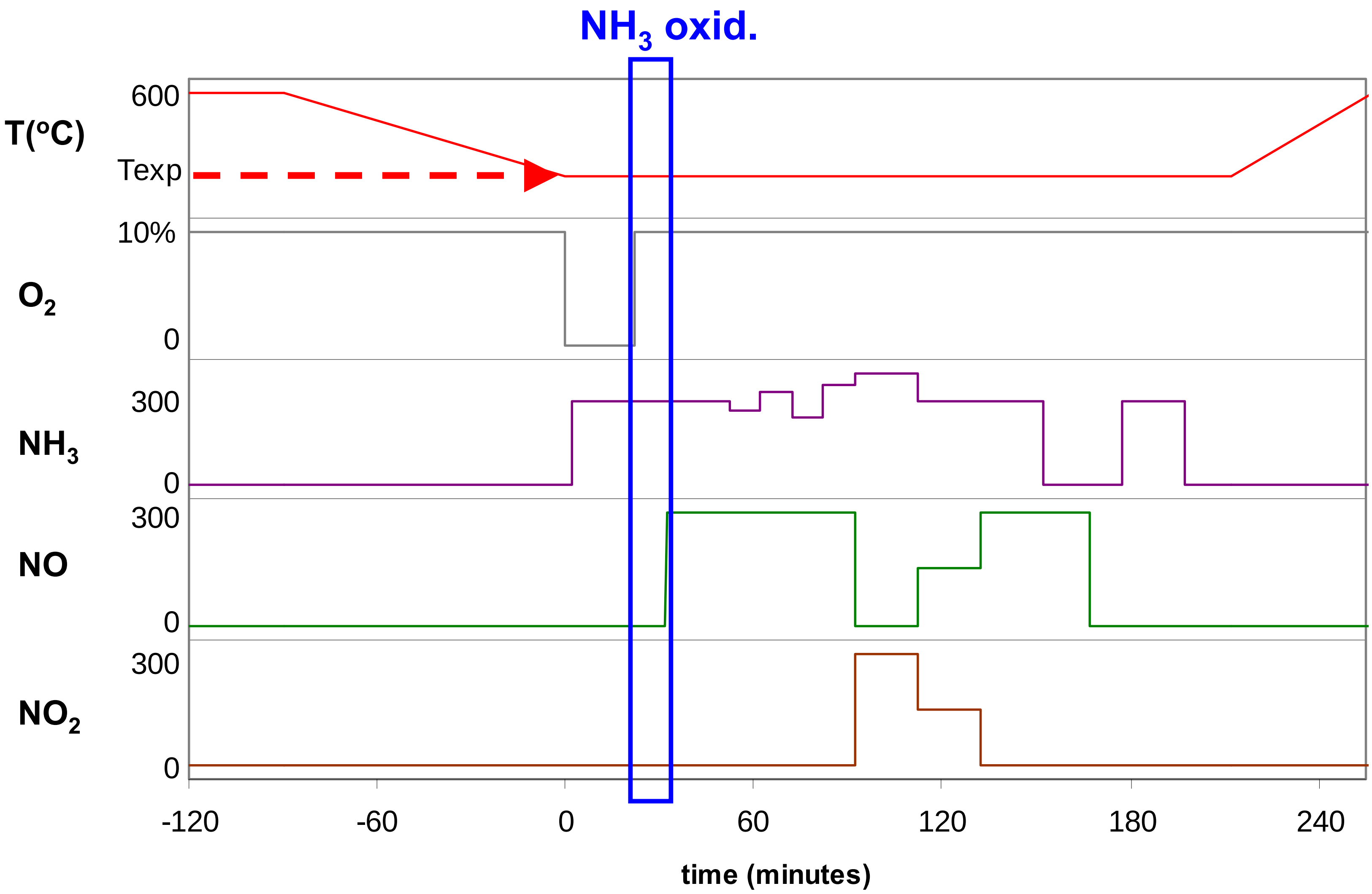
Evaluation Protocol Developed for SCR

- Measure NH_3 storage capacity under rich conditions
  - Remove O_2 from flow; Introduce 300 ppm NH_3 with 5% H_2O/CO_2



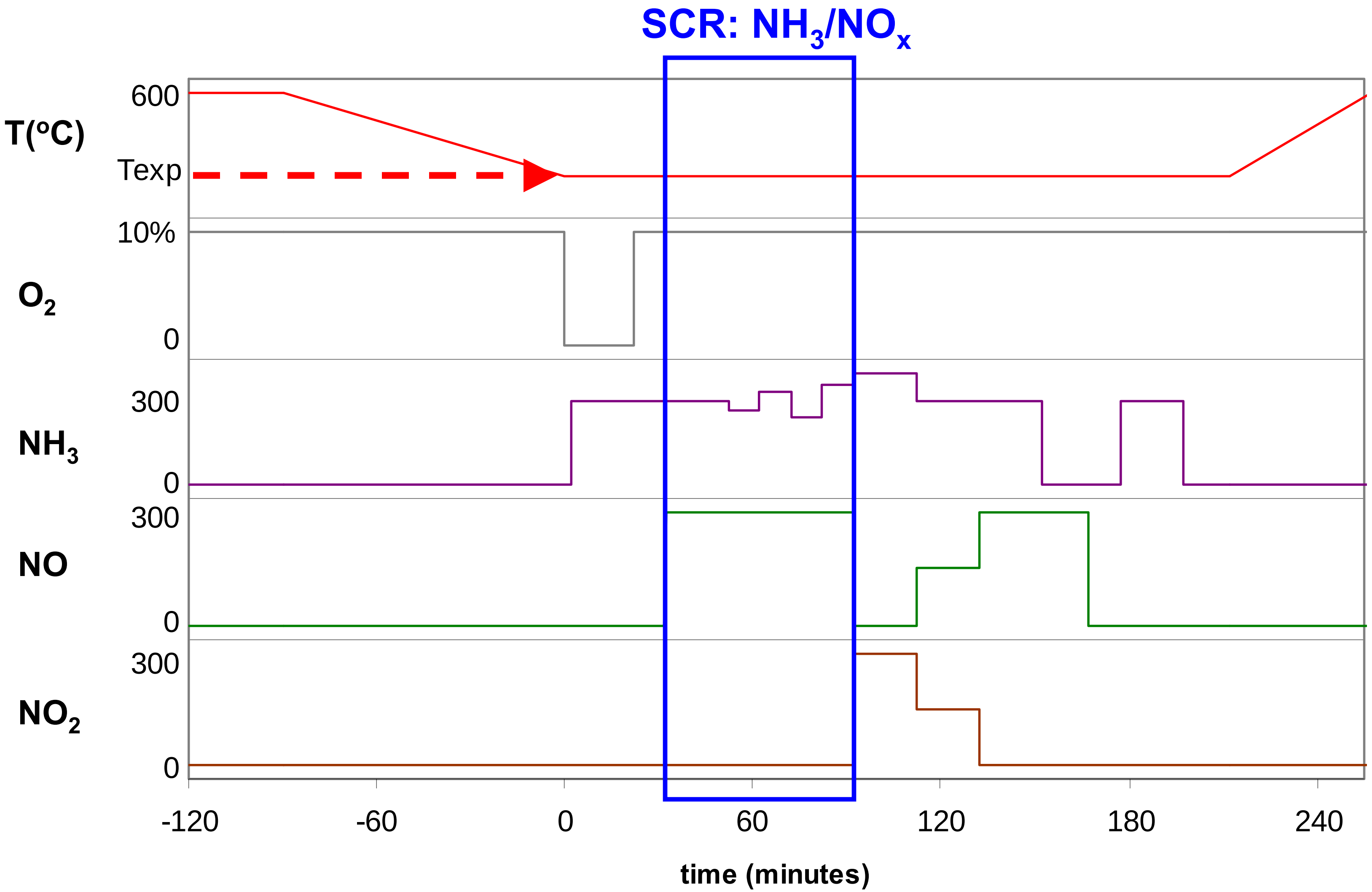
Evaluation Protocol Developed for SCR

- Measure the NH_3 oxidation behavior
  - Add 10% O_2 to the existing flow of 300 ppm NH_3 with 5% H_2O/CO_2



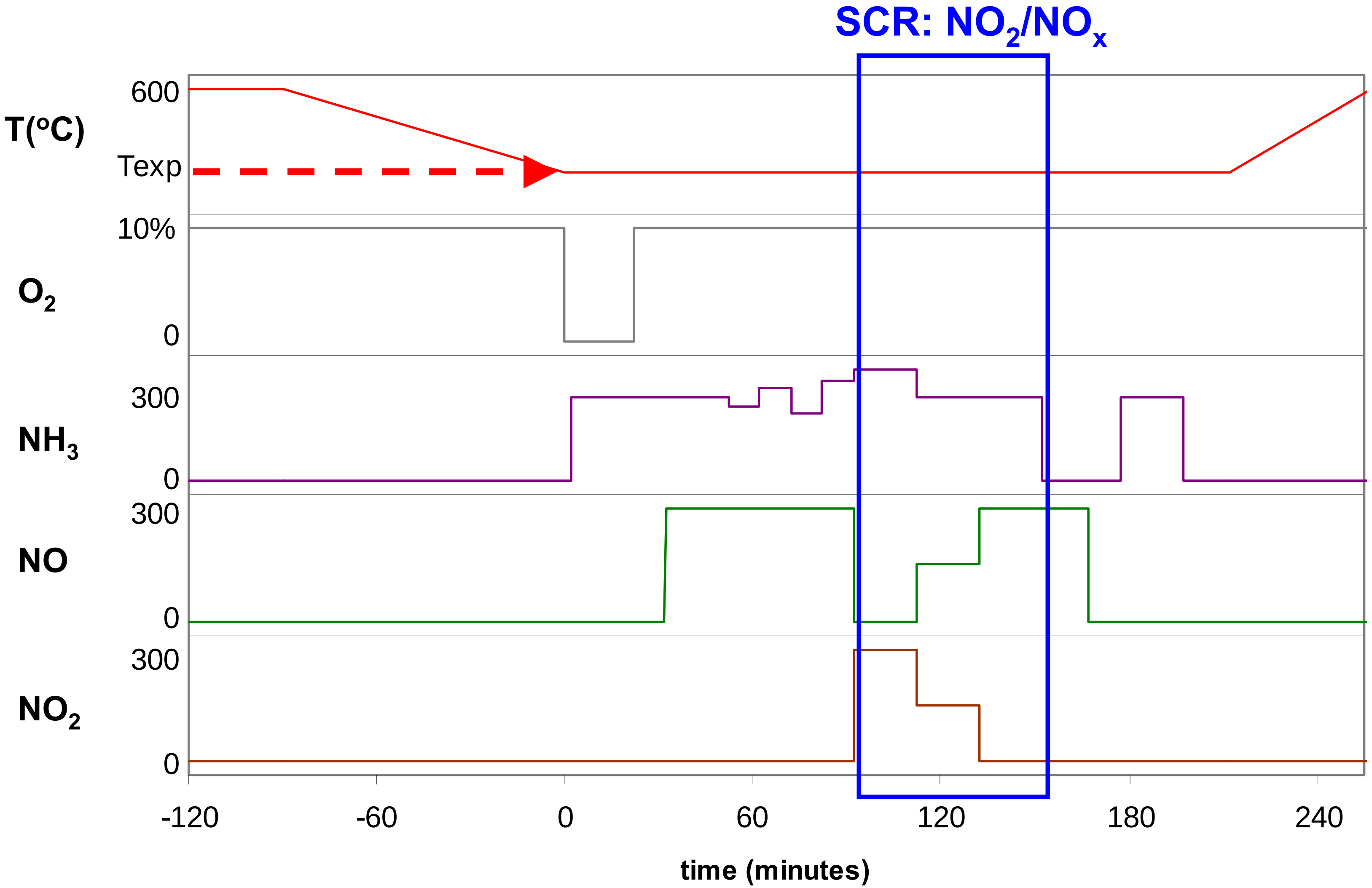
Evaluation Protocol Developed for SCR

- Measure the SCR kinetics while varying NH_3:NO ratio
  - Add 300 ppm NO, to the existing flow of 10% O_2, 300 ppm NH_3 with 5% H_2O/CO_2
  - Vary NH_3 concentration from 240 to 360 ppm (**α** = 0.8-1.2 = NH_3/NO_x)



Evaluation Protocol Developed for SCR

- Measure the SCR kinetics while varying NO_2:NO_x ratio
  - Stop NO + Introduce 300 ppm NO_2 to 10% O_2, and 5% H_2O/CO_2
  - Flow stoichiometric NH_3
    - 400 ppm NH_3 when NO_2:NO_x = 1.0; 300 ppm NH_3 for NO_2:NO_x = 0.0 and 0.5



Expected stoichiometry of SCR reactions

- NO_2-only ($NO_2/NOx = 1.0$)

$$6\ NO_2 + 8\ NH_3 \rightarrow 12\ H_2O + 7\ N_2 \qquad (NH_3{:}NO_x = 4{:}3)$$

- NO + NO_2 case ($NO_2/NOx = 0.5$)

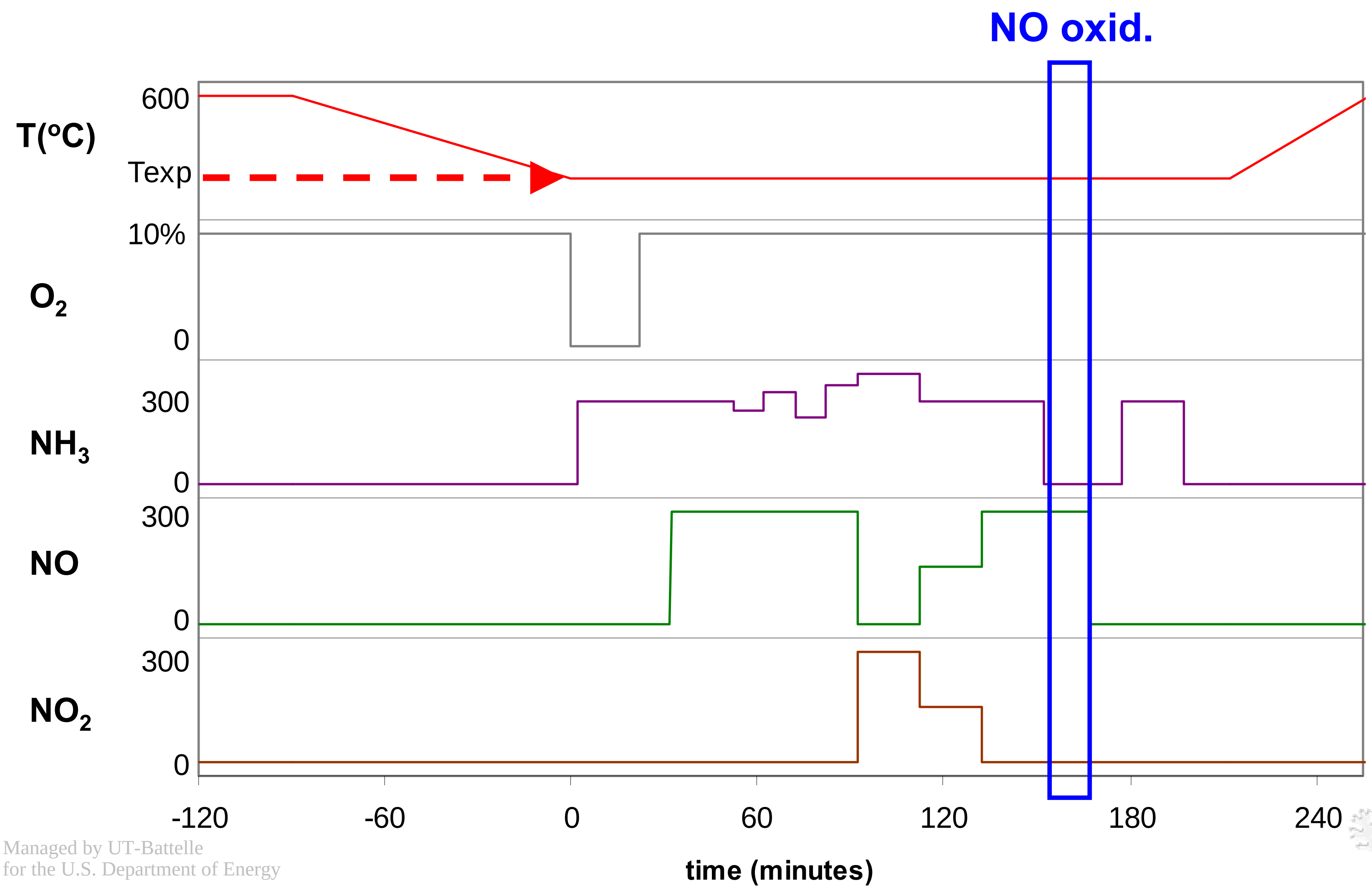
$$NO + NO_2 + 2\ NH_3 \rightarrow 3\ H_2O + 2\ N_2 \qquad (NH_3{:}NO_x = 1{:}1)$$

- NO-only ($NO_2/NOx = 0.0$)

$$4\ NO + O_2 + 4\ NH_3 \rightarrow 6\ H_2O + 4\ N_2 \qquad (NH_3{:}NO_x = 1{:}1)$$

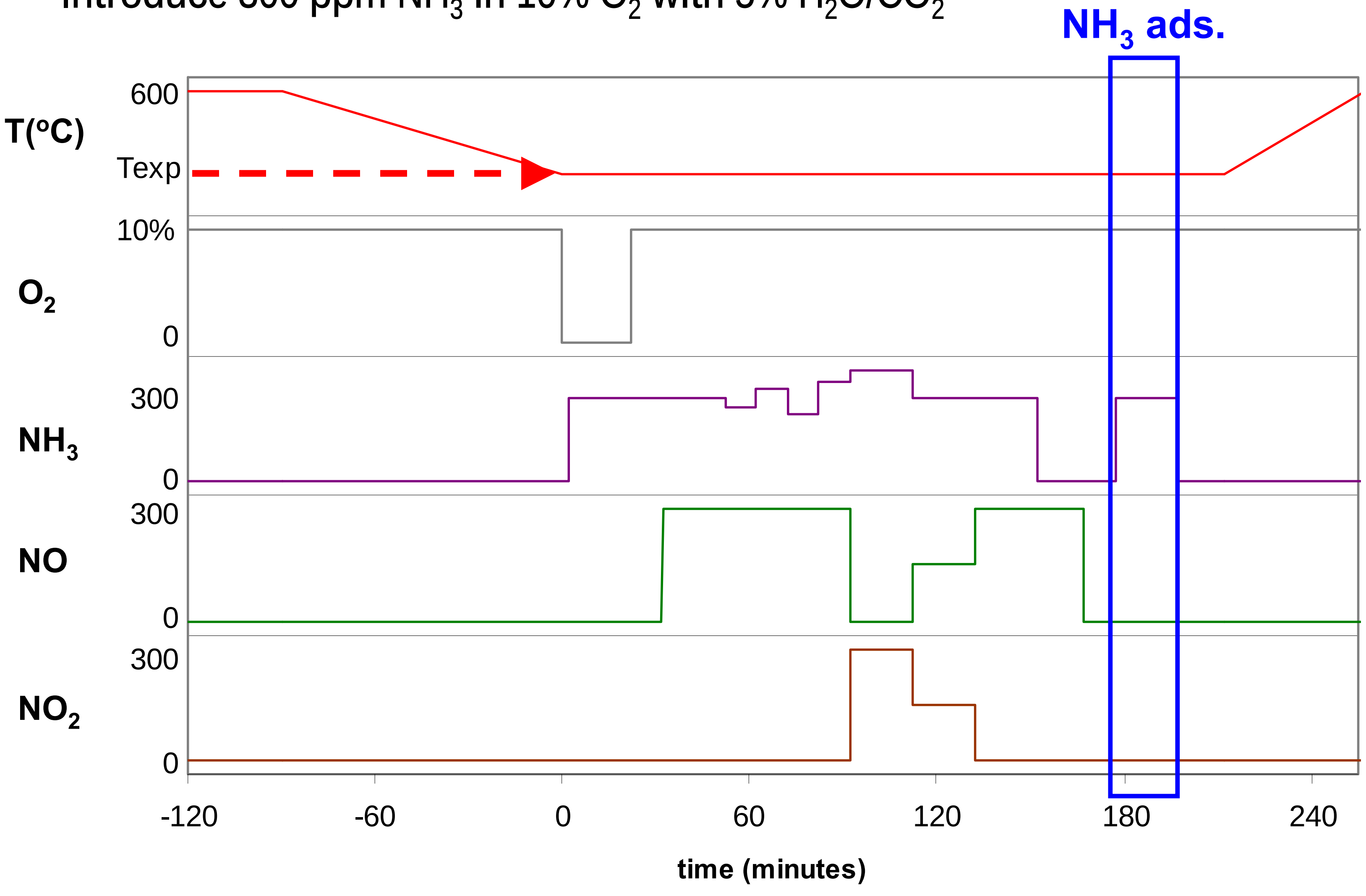
Evaluation Protocol Developed for SCR

- Measure kinetics of NO oxidation to NO_2
  - Stop 300 ppm NH_3 flow; continue to flow 10% O_2, 300 ppm NO with 5% H_2O/CO_2
- As NO value increases to steady-state value it is possible to calculate the reactivity of stored NH_3



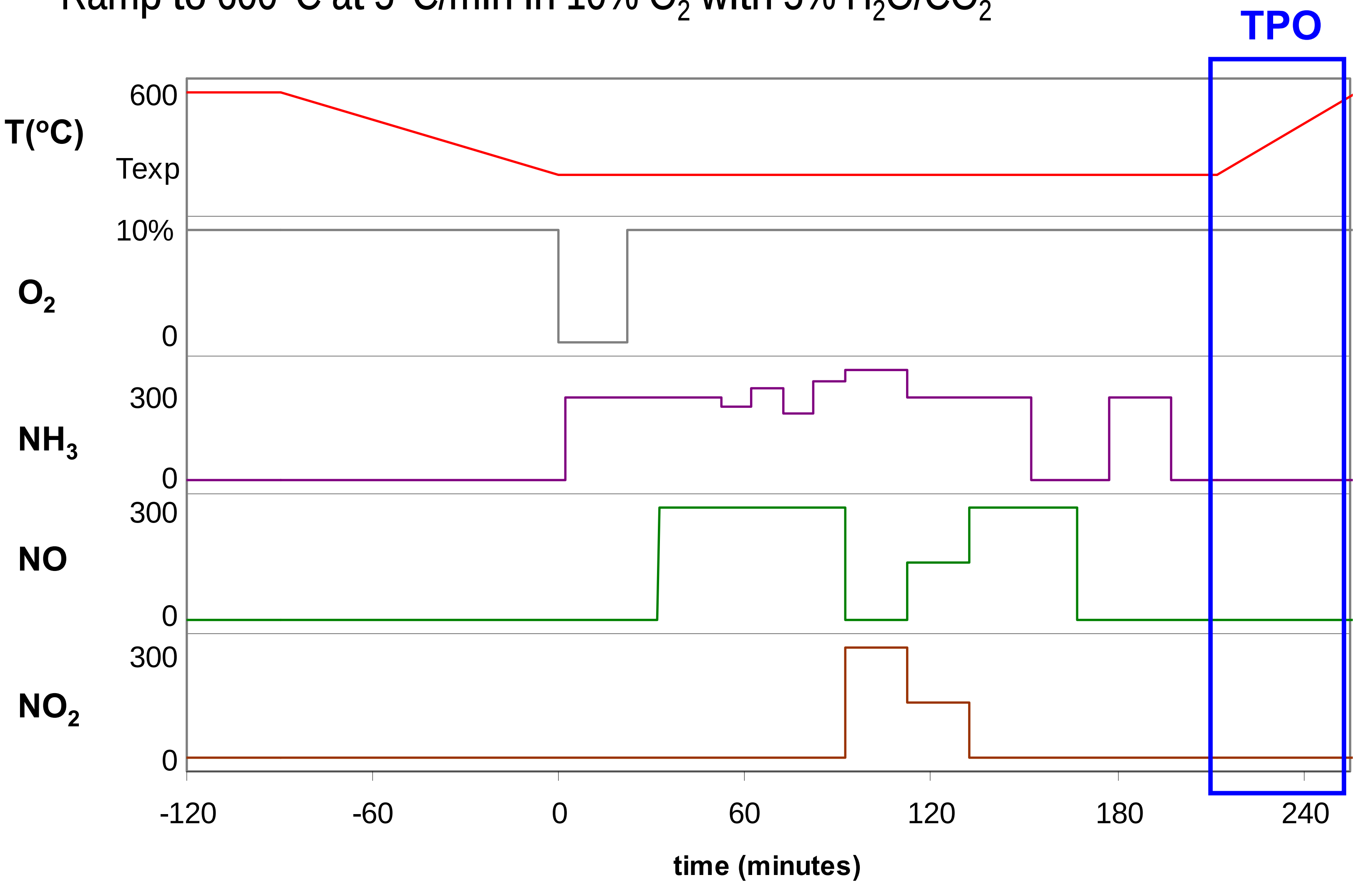
Evaluation Protocol Developed for SCR

- NH_3 storage under lean conditions
  - Turn off NO flow; wait 10 minutes
  - Introduce 300 ppm NH_3 in 10% O_2 with 5% H_2O/CO_2



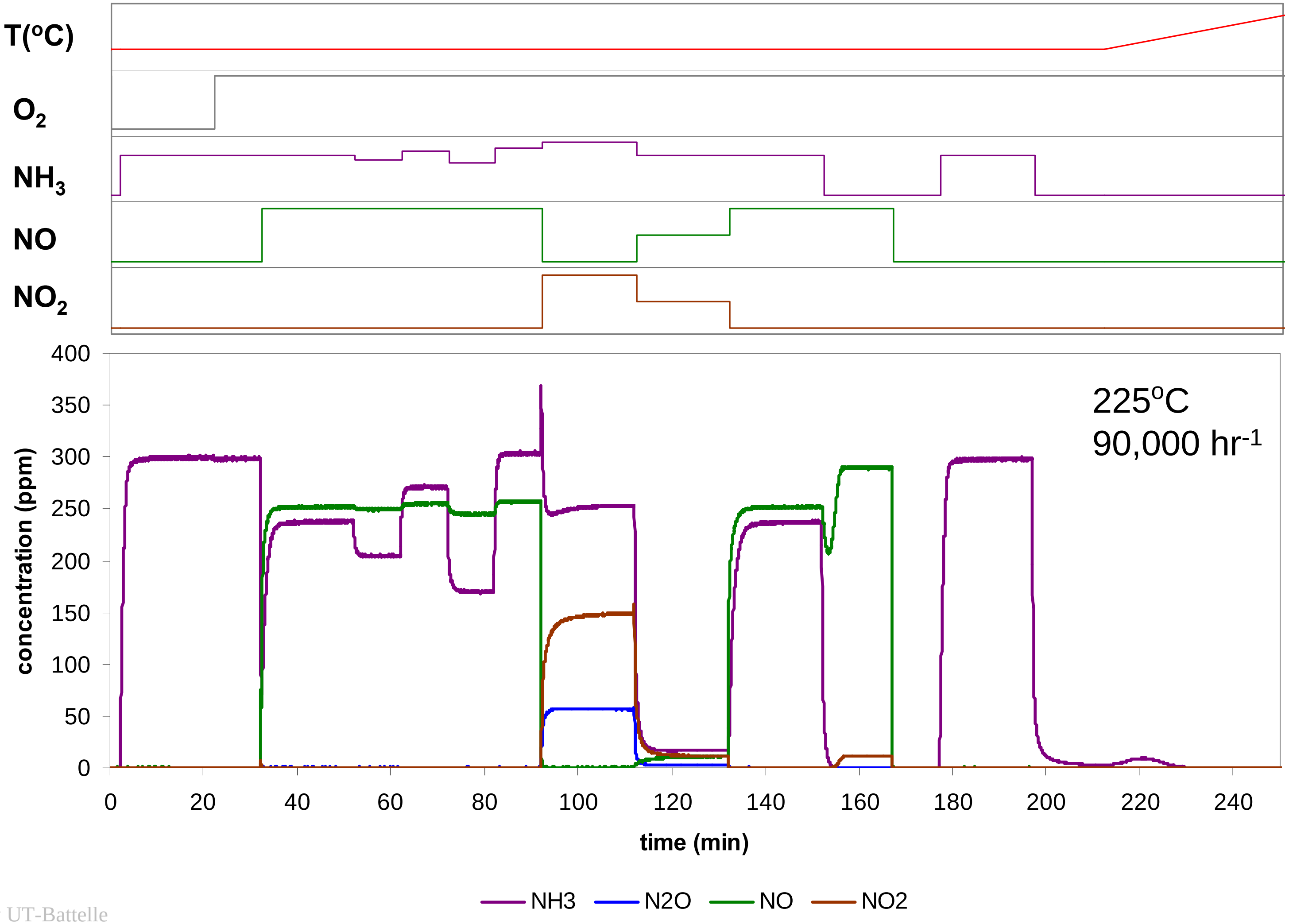
Evaluation Protocol Developed for SCR

- Temperature programmed oxidation/desorption of NH_3 stored under lean conditions
  - Turn off NH_3 flow; wait 10 minutes;
  - Ramp to 600°C at 5°C/min in 10% O_2 with 5% H_2O/CO_2



Protocol reveals characteristic transient chemistry of catalyst

- Planned protocol evaluated at 150-600°C, 60k-120k h^{-1}



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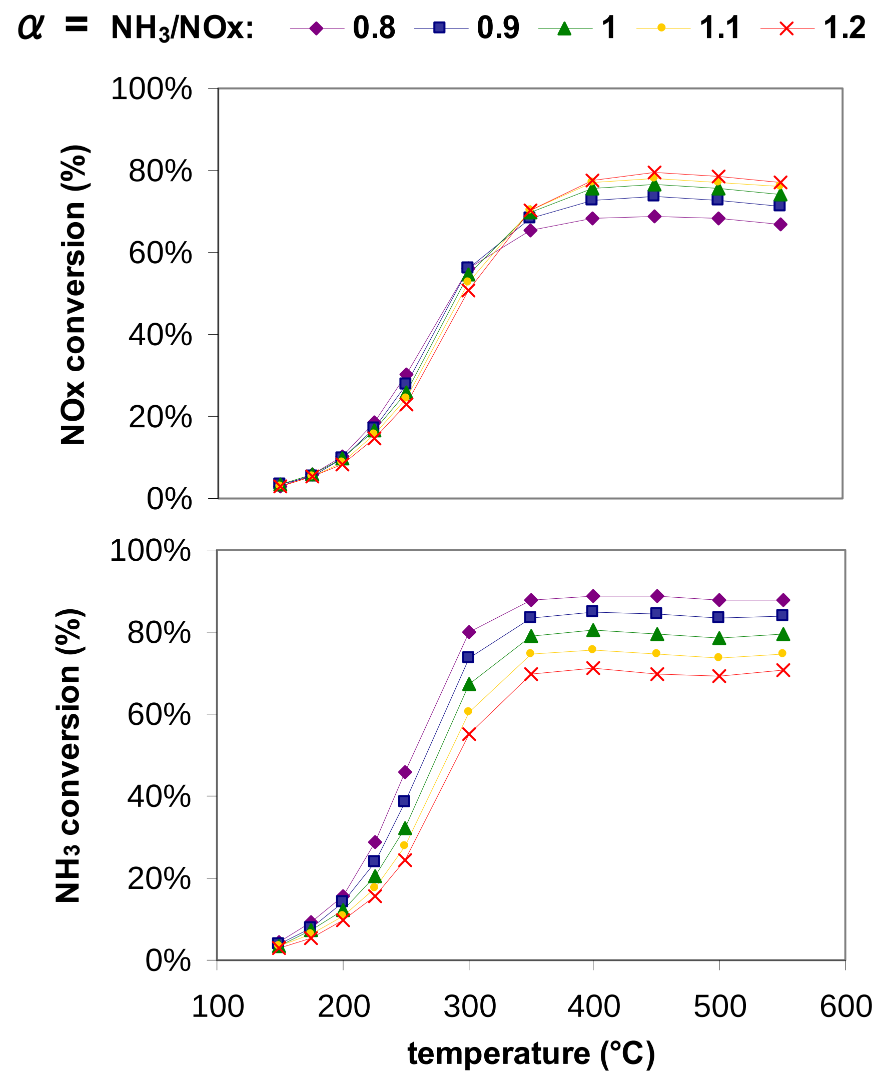
Steady-State Results

Varying NH_3/NO_x (**α**-ratio) and T demonstrate operating range of catalyst

- Generally, expected trends observed
  - With increasing temperature:
    - NO_x and NH_3 conversion increase
  - With increasing NH_3 dose (**α**-ratio):
    - NO_x conversion increases
    - NH_3 conversion decreases



Experiment conditions:

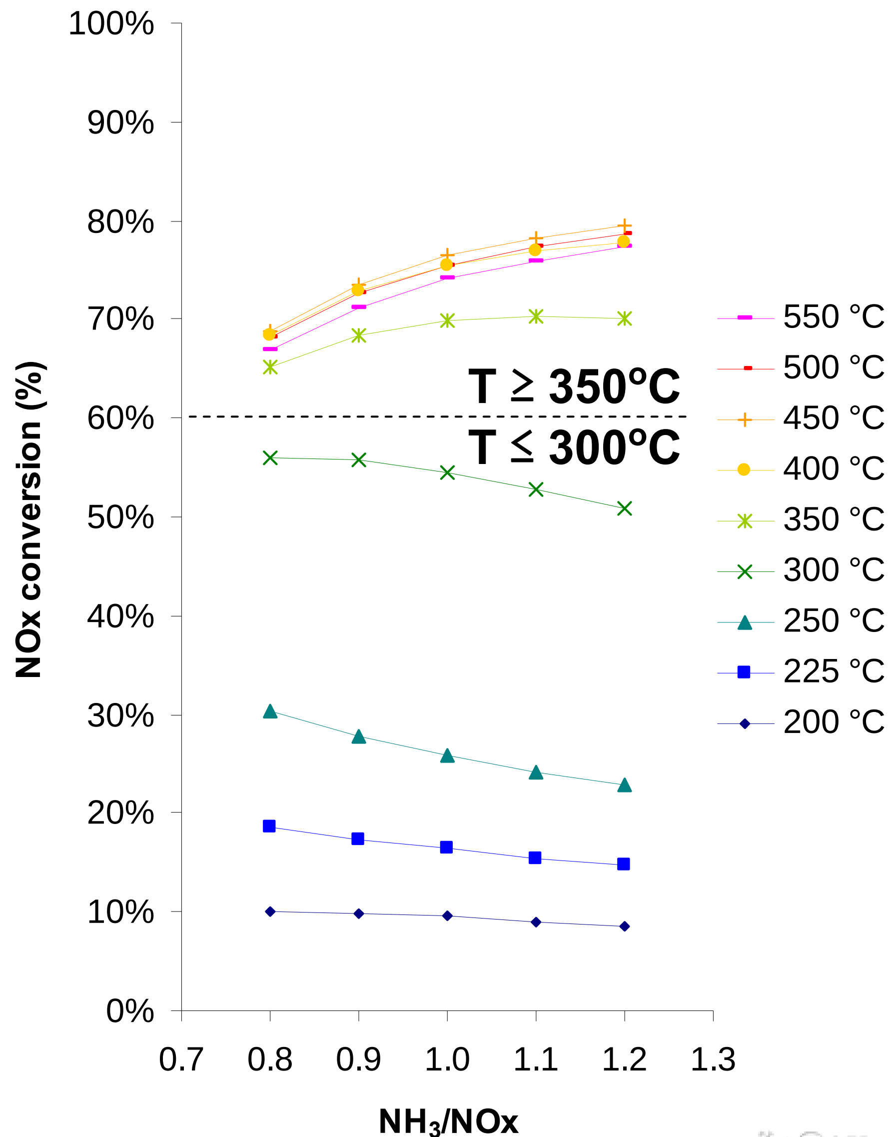
- SV = 90,000 hr^{-1}
- NO_2/NO_x = 0
- **α** = NH_3/NO_x = 0.8, 0.9, 1.0, 1.1, 1.2
- Total NO_x = 300 ppm
- 10% O_2, 5% CO_2, 5% H_2O

NH_3 inhibits NO-SCR reaction at low T

- Re-plotting data as a function of NH_3/NO_x ratio reveals NH_3 inhibition
- For T ≤ 300°C, increasing NH_3 decreases NO_x conversion
  - Indicates inhibition of NO-SCR reaction by excess NH_3 at low T
- Trend previously reported for zeolite-SCR
  - M. Wallin et al., J. Catal. 218 (2003) 354
  - A. Grossale et al., Catal. Today 136 (2008) 18
- Temperature of inhibition is catalyst dependent

Experiment conditions:

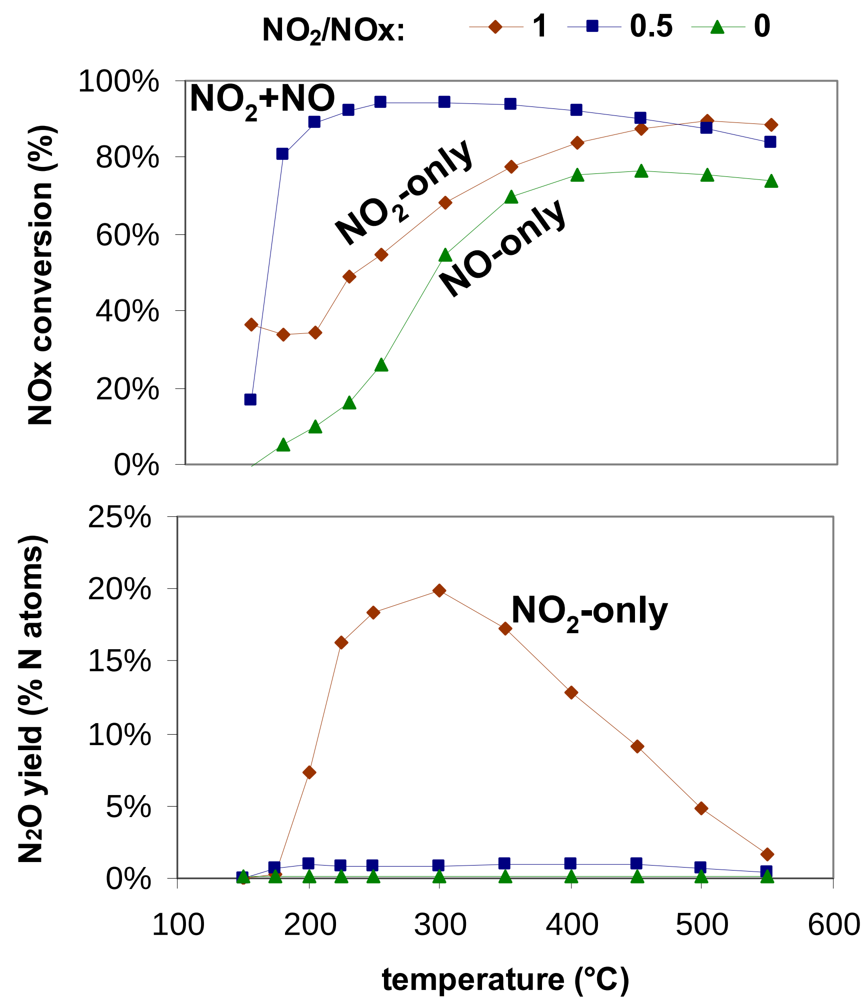
- SV = 90,000 hr^{-1}
- $NO_2/NO_x = 0$
- NH_3/NO_x = 0.8, 0.9, 1.0, 1.1, 1.2
- Total NO_x = 300 ppm
- 10% O_2, 5% CO_2, 5% H_2O



NO_2 more reactive than NO at all T

- As expected, 1:1 mixture of NO+NO_2 gives best performance
  - "Fast SCR" reaction
- However, NO_2 more reactive than NO at all temperatures
  - "Slow SCR" reaction not observed with NO_2
  - NO-only is "slowest" reaction
  - Characteristic of zeolite catalyst

    A. Grossale et al. Catal. Today 136 (2008) 18
- NO_2-SCR reaction only contributor to N_2O formation

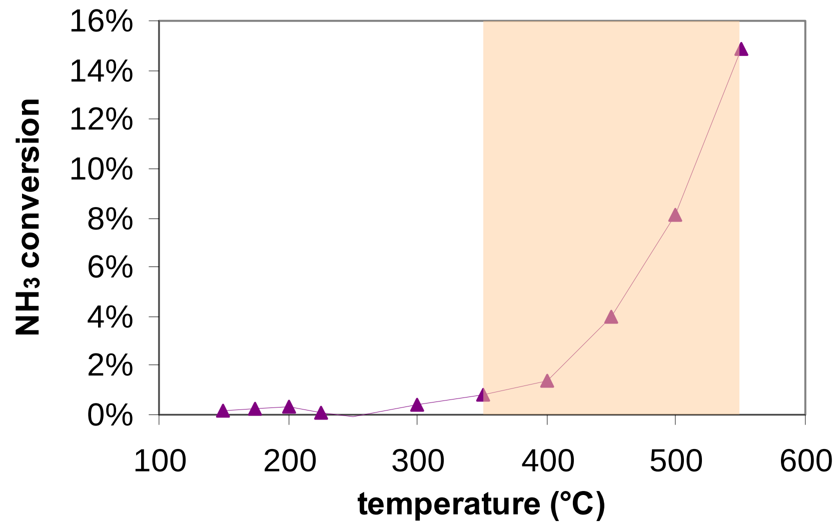


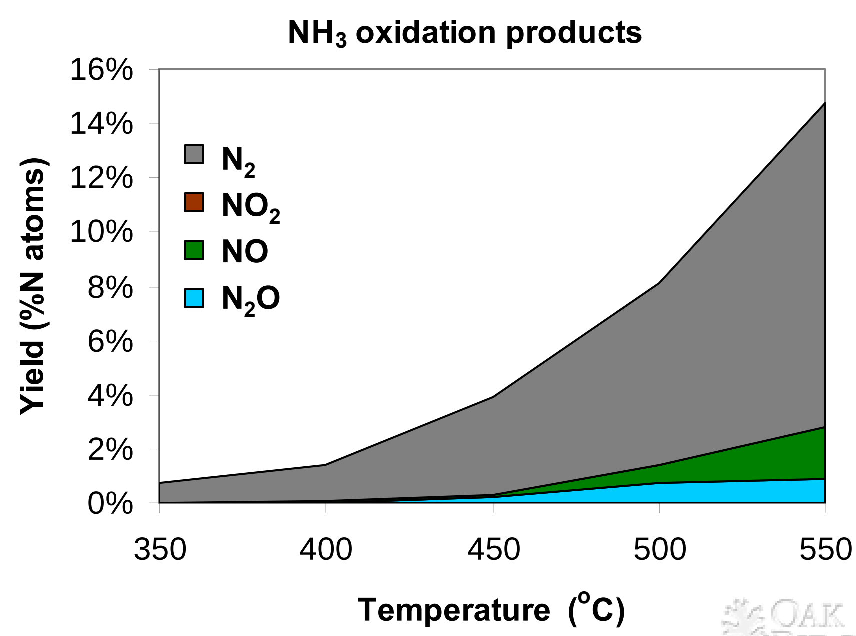
Experiment conditions

- SV = 90,000 hr^{-1}
- NO_2/NO_x = 0, 0.5, 1.0
- NH_3/NO_x = stoichiometric
- Total NO_x = 300 ppm
- 10% O_2, 5% CO_2, 5% H_2O

NH_3 oxidation observed above 350°C

- NH_3 oxidation increases rapidly above 350°C
- Catalyst selective for N_2 production from NH_3 oxidation
  - Typically oxidized to NO over precious metals
- Model must account for losses of NH_3 to direct oxidation
  - but not for additional NO formation



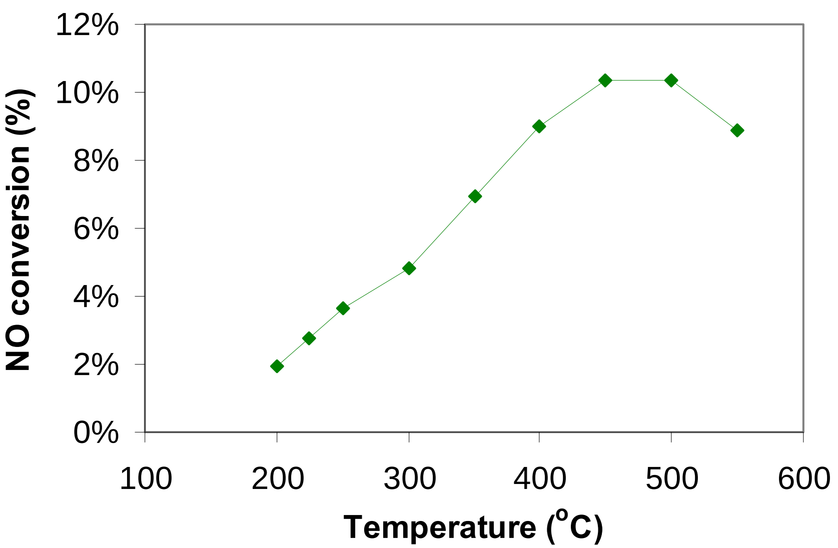


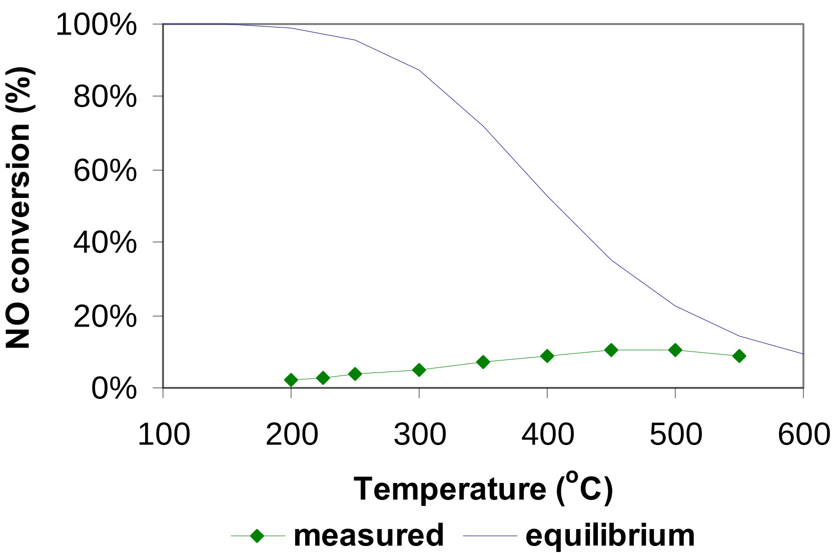
Experiment conditions

- SV = 90,000 hr^{-1}
- 300 ppm NH_3, 10% O_2, 5% CO_2, 5% H_2O

NO-oxidation peaks at 450-500°C

- NO oxidation increases with temperature up to 450°C
- Conversion decreases above 500°C
  - NO_x concentrations approach equilibrium values ∴ reaction slows





Experiment conditions

- SV = 90,000 hr^{-1}
- 300 ppm NO, 10% O_2, 5% CO_2, 5% H_2O

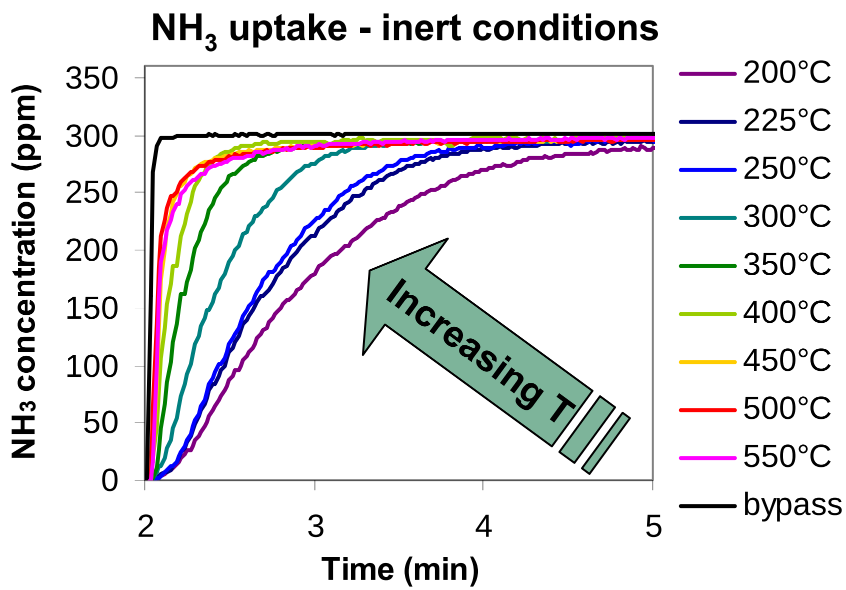
Transient Results

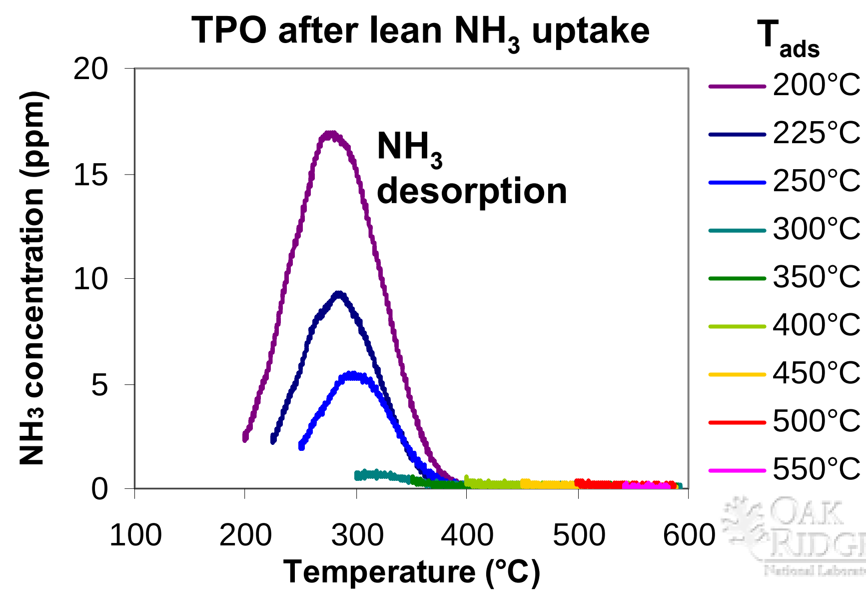
All surface NH_3 oxidizes or desorbs at temperatures above 400°C

- NH_3 storage capacity probed at two points:
  1. NH_3 uptake during step change at inlet
     - Absence of O_2
     - NH_3 stored at all temperatures
     - Storage decreases as T increases
  2. Temperature Programmed Oxidation (TPO) performed after lean NH_3 storage
     - Single desorption peak centered near 300°C
     - All NH_3 released/oxidized by 400°C
- All NH_3 stored at T ≥ 400°C oxidized by O_2 or desorbed when NH_3 flow stops

Experiment conditions

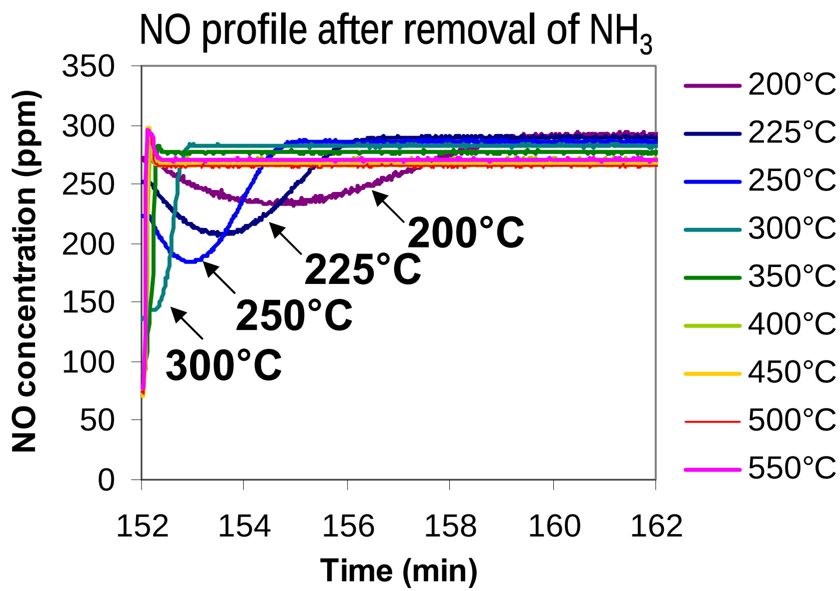
- SV = 90,000 hr^{-1}
- NH_3 Ads: 300 ppm NH_3, 0-10% O_2, 5% CO_2, 5% H_2O
- TPO: 10% O_2, 5% CO_2, 5% H_2O, 5°C/min ramp



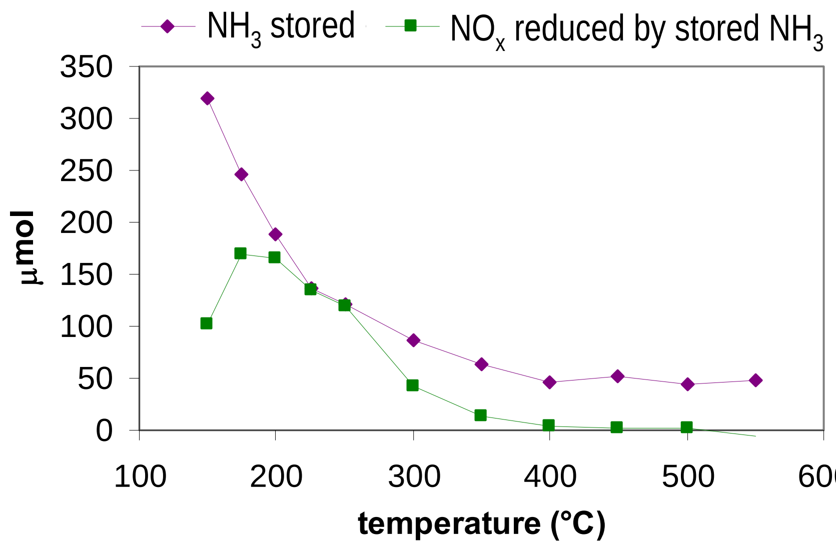


Stored NH_3 not available for subsequent NO_x reduction above 350°C

- NO oxidation step provides another measure of NH_3 storage capacity
  - NO feed constant at 300 ppm after NH_3 turned off
  - Dips in NO concentration due to conversion by stored NH_3
  - Rate of stored NH_3 consumption (depth of dip in NO) increases with T



- Comparison to NO_x uptake under inert conditions confirms oxidation or desorption of previously stored NH_3



Experiment conditions

- SV = 90,000 hr^{-1}
- 300 ppm NO, 10% O_2, 5% CO_2, 5% H_2O

Optimization of protocol necessary

- Current research plan requires ~300 hours of catalyst evaluation
  - Planned protocol evaluated at:

    150-600°C, 30k-120k h^{-1}, inlet NO_x: 150-500 ppm
  - Eight weeks of normal workday operation

- Protocol must be optimized to aid new catalyst transitions
  - Identify most critical experiments through model parameter sensitivity analysis
  - Experiments with low sensitivity are removed from the matrix

- Efforts from this project and throughout the CLEERS community to be used help guide model optimization

Something to think about…

- After completing a portion of the protocol some steps have been modified
  - Change needed to simplify transitions…
    - only one concentration change at a time
  - …or to modify parameter being measured
    - "Inert NH_3 storage→TPD" instead of "Lean NH_3 storage→TPO"
  - More changes may be necessary…

- Additional transient behavior measurements may be warranted
  - Cyclic NH_3 introduction may offer most realistic behavior for reactivity of stored NH_3
  - Inclusion will depend on the ability of the model to fit the behavior
    - Modeling results coming soon…

Summary

- Established an evaluation protocol providing both steady-state and transient chemistry
  - Optimized protocol will economize experiments
  - Starting point for validated CLEERS SCR protocol for transient behavior

- Several key SCR-chemistry findings
  - Stored NH_3 reactivity identified specifically for reactivity to NO_x reduction
  - NH_3 identified as an inhibiting species at low temperatures
  - Temperature dependent NH_3 storage identified

Acknowledgements

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