A new transient CLEERS SCR protocol

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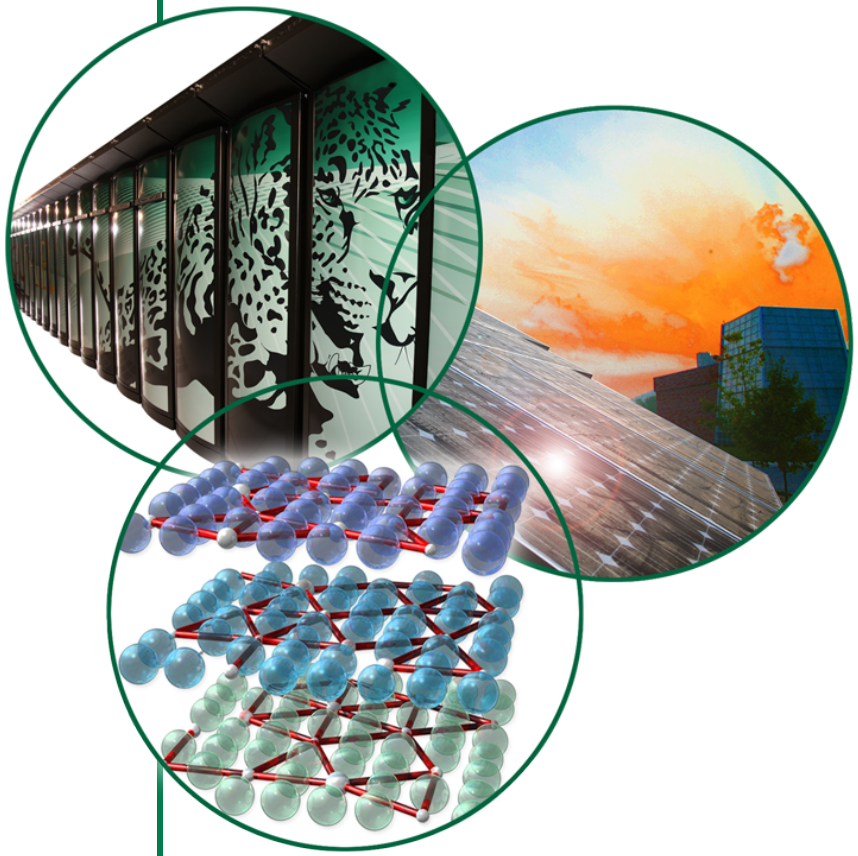

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Motivation

- Existing CLEERS protocol for urea SCR is a collection of steady state points
- It does not measure NH_3 storage and release or the reactivity of stored NH3, which are crucial to accurate device simulations
- A new transient protocol would:
  - generate well-defined data sets that could be used for parameter estimation and model validation
  - help minimize time and expense required to generate such data sets (enable rapid adaptation to changing catalyst formulations)
  - facilitate comparison of catalyst properties and kinetic data between organizations
  - avoid expense and hassle for others to build a protocol from scratch
  - held ensure the experiments we run are relevant to the needs of the aftertreatment modeling and development community

Goal: Create a general methodology for running SCR experiments that extracts necessary model parameters (reaction kinetics, storage capacities) with minimal time and expense

Approach

- Define time sequence of inlet compositions and catalyst temperatures

- Leave most operating parameters variable to allow users to customize protocol based on application requirements
  - temperatures
  - space velocities
  - step times (depend on temperatures, space velocities, catalyst formulation)
    - instead of prescribed times, allow each step to come to a steady state
    - current definition of steady state: 0.1% change in concentration per minute
  - concentrations of O_2, H_2O, CO_2, and total NOx
    - NH_3, NO, and NO_2 concentrations defined relative to total NOx in protocol

- Provide a set of suggested operating parameters

Scope of proposed protocol

- Processes included in current scope:
  - NH_3 storage capacity
  - NH_3 desorption
  - NH_3 oxidation
  - NO oxidation
  - NO only SCR kinetics, including NH_3/NO ratio impact
  - NO + NO_2 SCR kinetics
  - decomposition of surface species formed under low temperature SCR conditions

- Not currently included:
  - impact of O_2, H_2O, and CO_2 concentrations
  - dynamic (pulsed input) experiments
  - urea thermolysis/hydrolysis
  - poisons (HCs, sulfur)

Proposed CLEERS transient SCR protocol

Step	Description	NH_3	NO	NO_2	O_2	H_2O	CO_2	T
0(a)	Pretreat	0	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn+50
0(b)	T change	0	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn+50 ->T0
0(c)	NH_3 adsorption	[NOx]	0	0	0	$[H_2O]$	$[CO_2]$	T0
0(d)	NH_3 TPD (10°C/min)	0	0	0	0	$[H_2O]$	$[CO_2]$	T0–>Tn+50
0(e)	Pretreat	0	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn+50
1(a)	T change	0	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn+50 –> Tn
1(b)	NH_3 storage	[NOx]	0	0	0	$[H_2O]$	$[CO_2]$	Tn
1(c)	NH_3 oxidation	[NOx]	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn
1(d)	NO+NO2 SCR α = 1.0	[NOx]	0.5[NOx]	0.5[NOx]	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn
1(e)	NO SCR α = 1.0	[NOx]	[NOx]	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn
1(f)	NO SCR α = 0.9	0.9[NOx]	[NOx]	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn
1(g)	NO SCR α = 1.1	1.1[NOx]	[NOx]	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn
1(h)	NO oxidation, NH_3 storage	0	[NOx]	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn
2(a)	T change	0	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	Tn –> T(n-1)
…	Repeat a-h for all temperatures							T(n-1)…T0
n(h)	NH_3 storage, NO oxidation	0	[NOx]	0	$[O_2]$	$[H_2O]$	$[CO_2]$	T0
n+1(a)	TPD (10°C/min)	0	0	0	$[O_2]$	$[H_2O]$	$[CO_2]$	T0 –> Tn+50

Example operating parameters for transient CLEERS SCR protocol

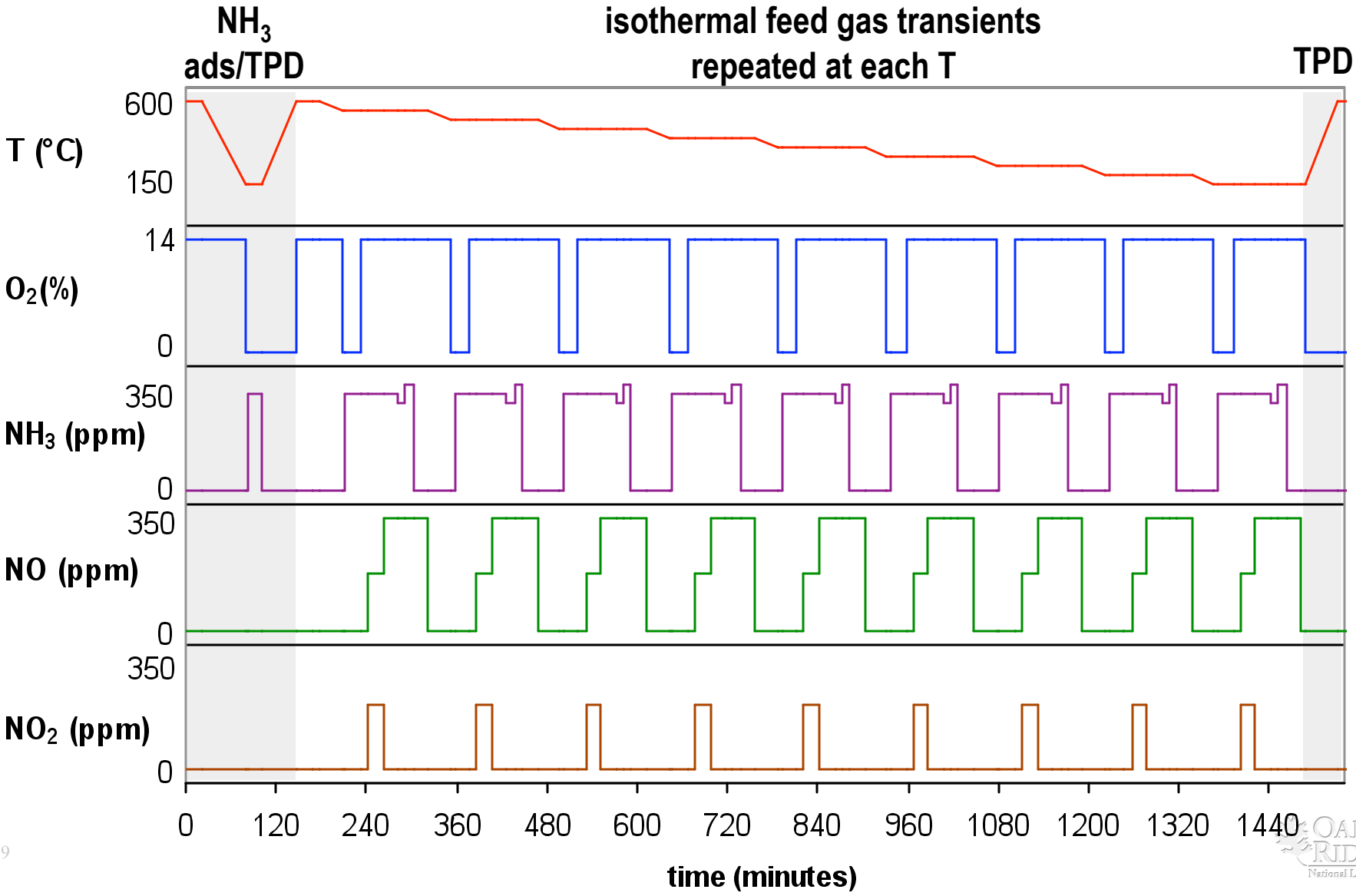
- operating temperatures: 150, 200, 250, 300, 350, 500, 450, 500, 550°C
  - n = 9
  - T0 = 150°C
  - Tn = T9 = 550°C
  - Tn+50 = 600°C

- concentrations (from steady state CLEERS SCR protocol):
  - [NOx] = 350 ppm
  - [O_2] = 14%
  - [H_2O] = 4.5%
  - [CO_2] = 5%

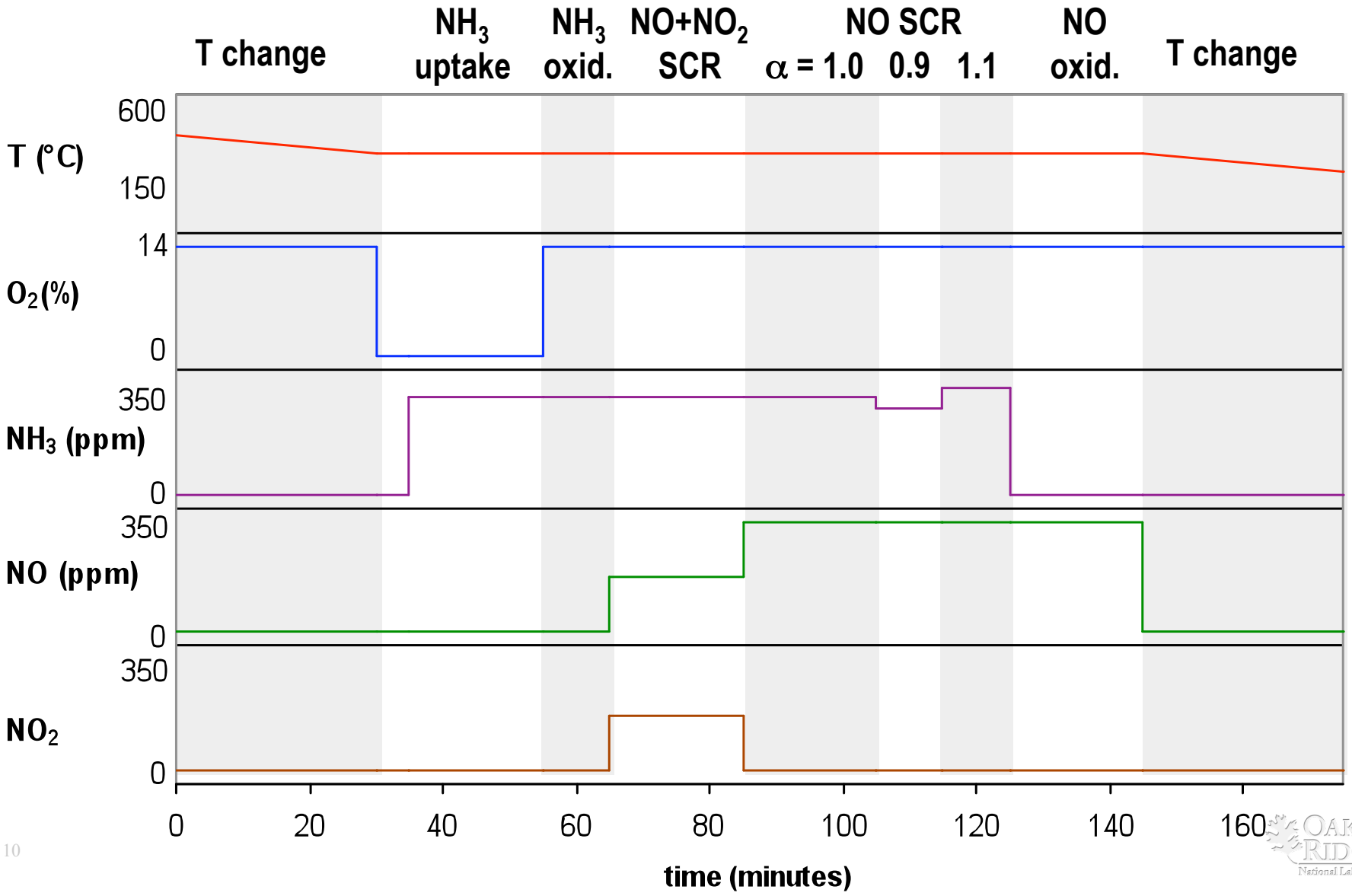
Example CLEERS transient SCR protocol

Step	Description	NH_3 (ppm)	NO (ppm)	NO_2 (ppm)	O_2 (%)	H_2O (%)	CO_2 (%)	T (°C)
0(a)	Pretreat	0	0	0	14	4.5	5	600
0(b)	T change	0	0	0	14	4.5	5	600->150
0(c)	NH_3 adsorption	350	0	0	0	4.5	5	150
0(d)	NH_3 TPD (10°C/min)	0	0	0	0	4.5	5	150–>600
0(e)	Pretreat	0	0	0	14	4.5	5	600
1(a)	T change	0	0	0	14	4.5	5	600 –> 550
1(b)	NH_3 storage	350	0	0	0	4.5	5	550
1(c)	NH_3 oxidation	350	0	0	14	4.5	5	550
1(d)	NO+NO2 SCR α = 1.0	350	175	175	14	4.5	5	550
1(e)	NO SCR α = 1.0	350	350	0	14	4.5	5	550
1(f)	NO SCR α = 0.9	315	350	0	14	4.5	5	550
1(g)	NO SCR α = 1.1	385	350	0	14	4.5	5	550
1(h)	NO oxidation, NH_3 storage	0	350	0	14	4.5	5	550
2(a)	T change	0	0	0	14	4.5	5	550 –> 450
…	Repeat a-h for all temperatures							450…150
9(h)	NH_3 storage, NO oxidation	0	175	0	14	4.5	5	150
10(a)	TPD (10°C/min)	0	0	0	14	4.5	5	150 –> 600

Example CLEERS transient SCR protocol – plot of temperatures and gas compositions



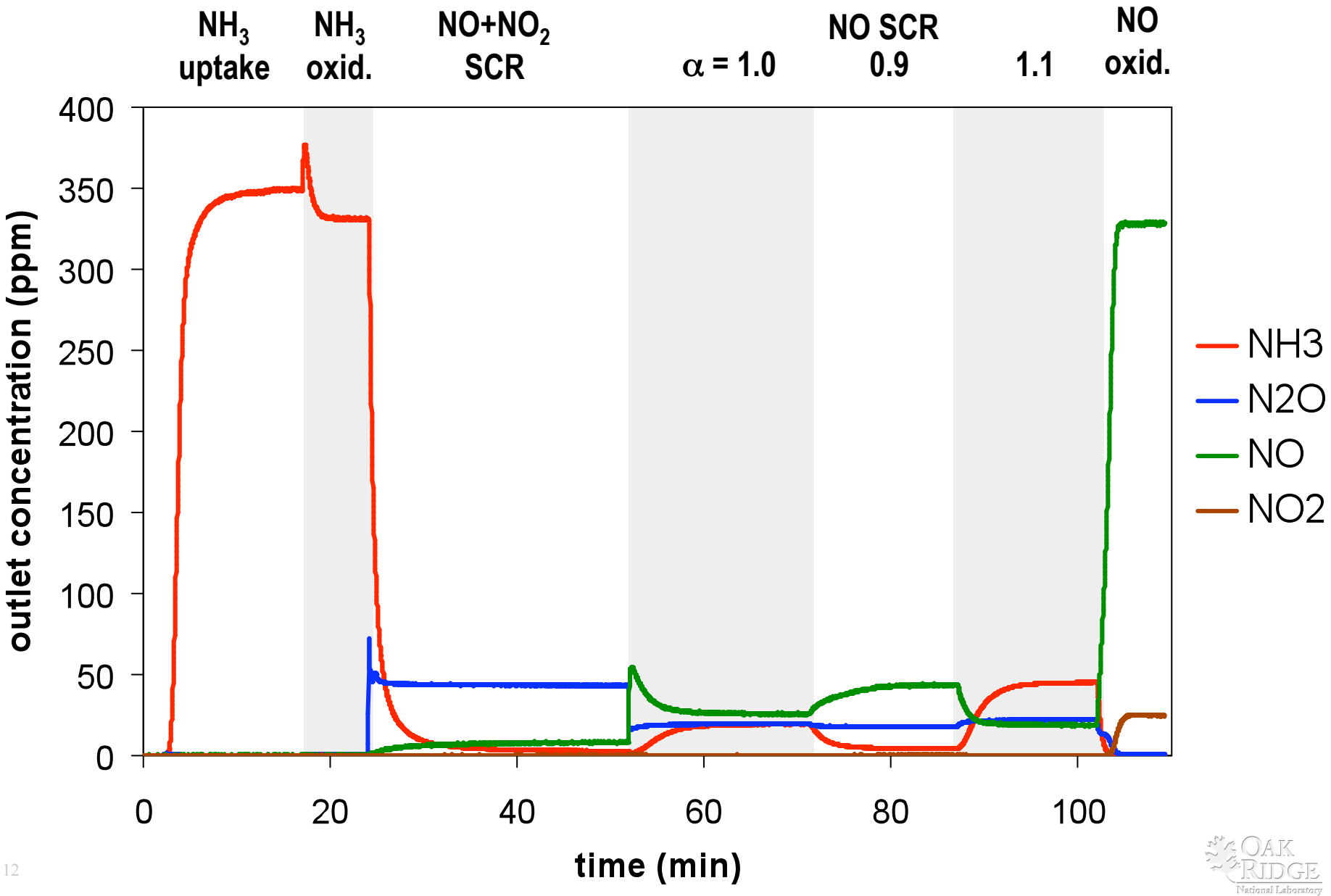
CLEERS Transient SCR Protocol – isothermal feed gas transients at each T



Other operating details

- Ran on automated flow reactor
- Used Cu zeolite core sample (1.9 cm D x 5 cm L)
- SV = 60,000 hr^{-1}
- Total run time for protocol: 21 hours

Sample data: outlet composition at 300°C

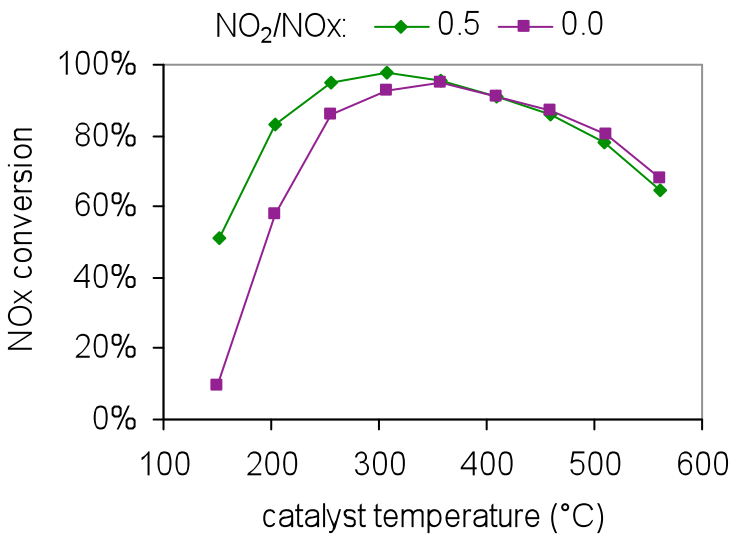


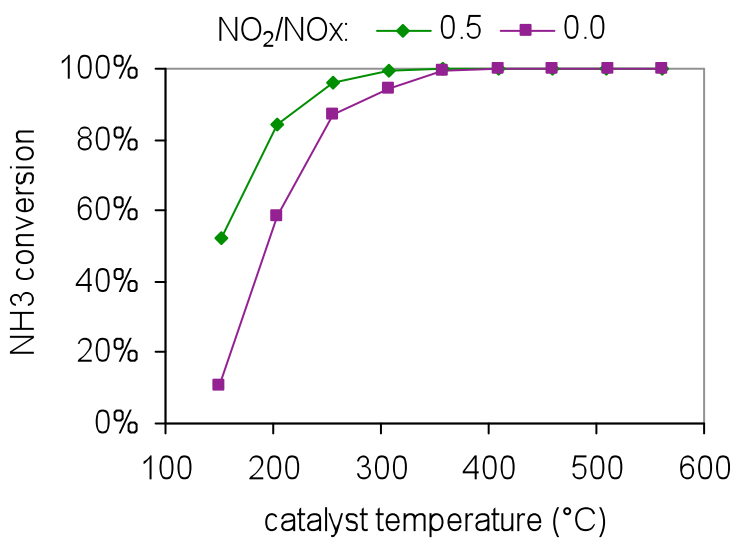
Sample results: steady state conversions

NOx conversion

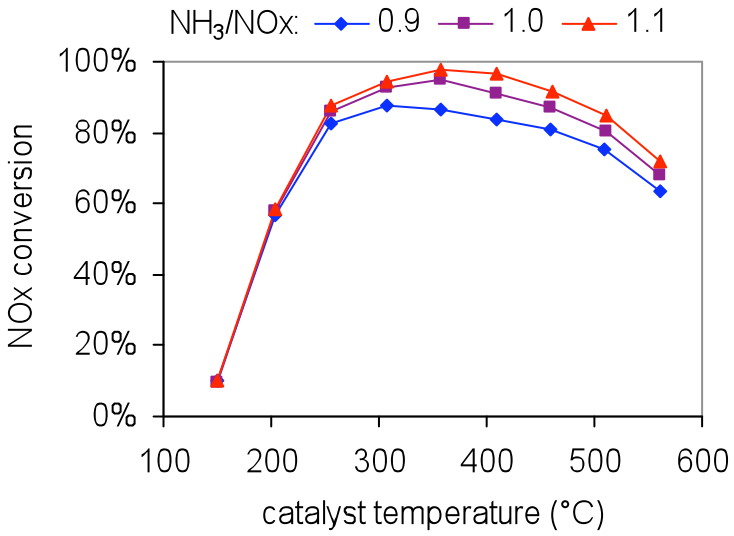
NH_3 conversion

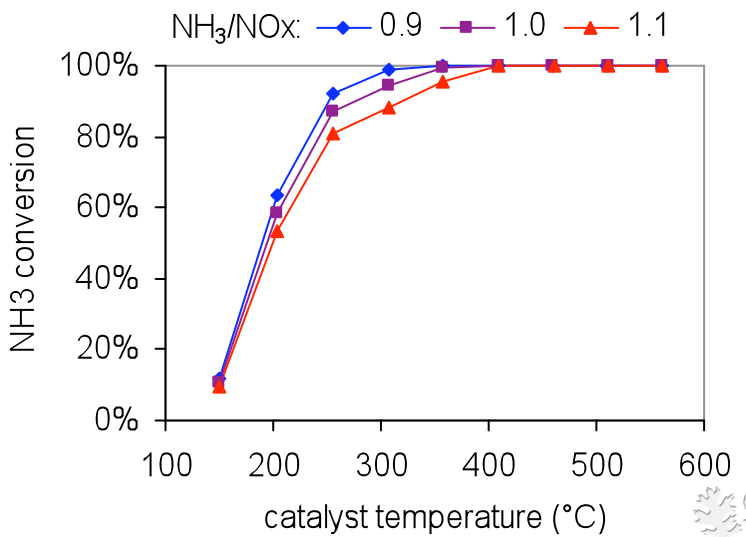
NO_2/NOx



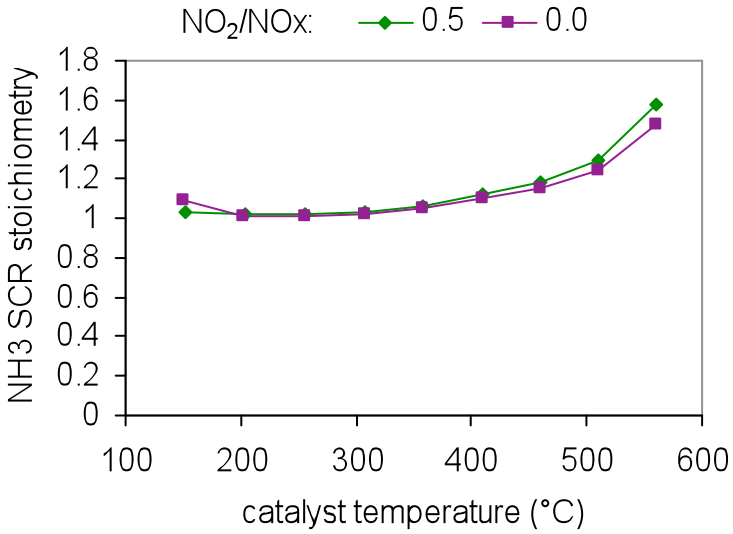


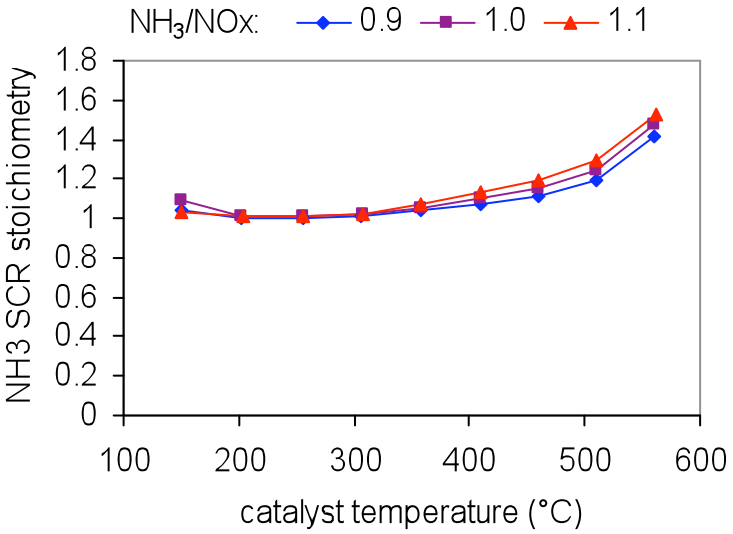
NH_3/NOx

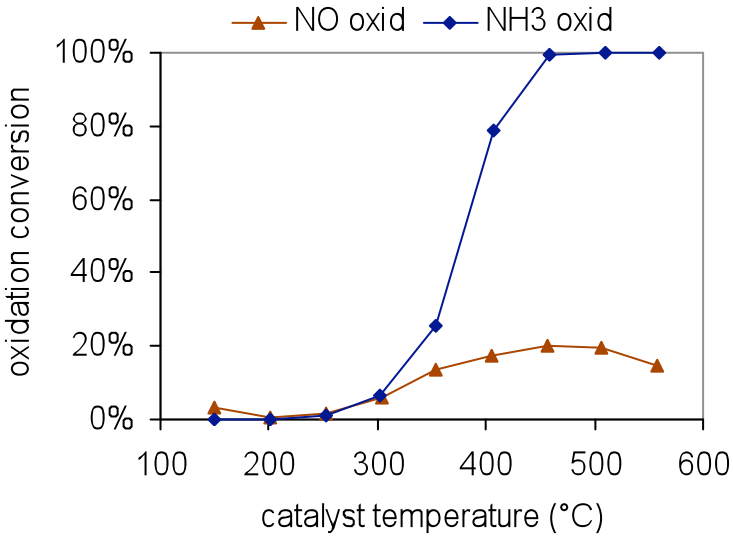




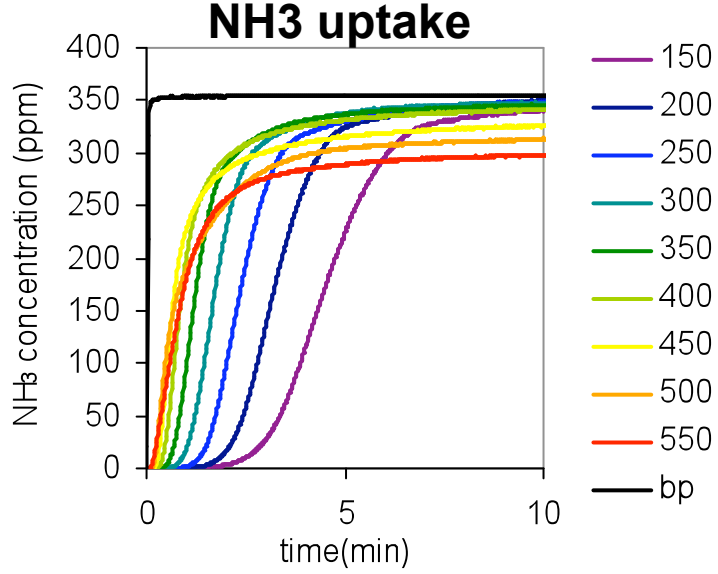
Sample results: SCR stoichiometry and oxidation conversion

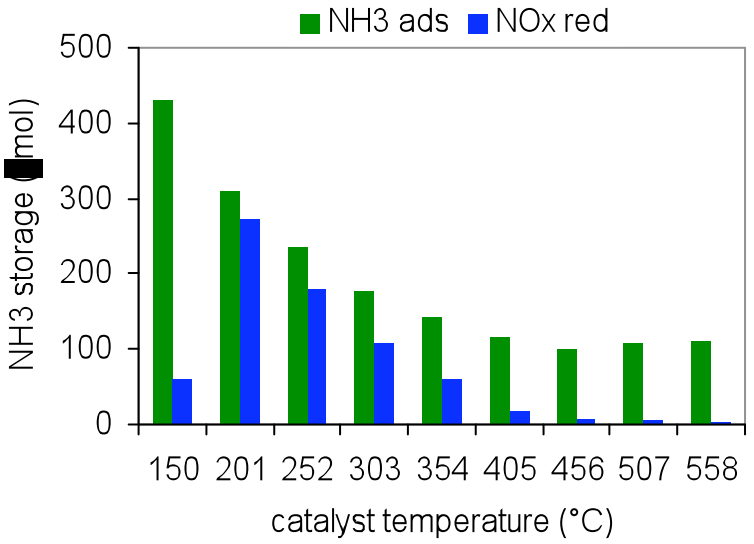


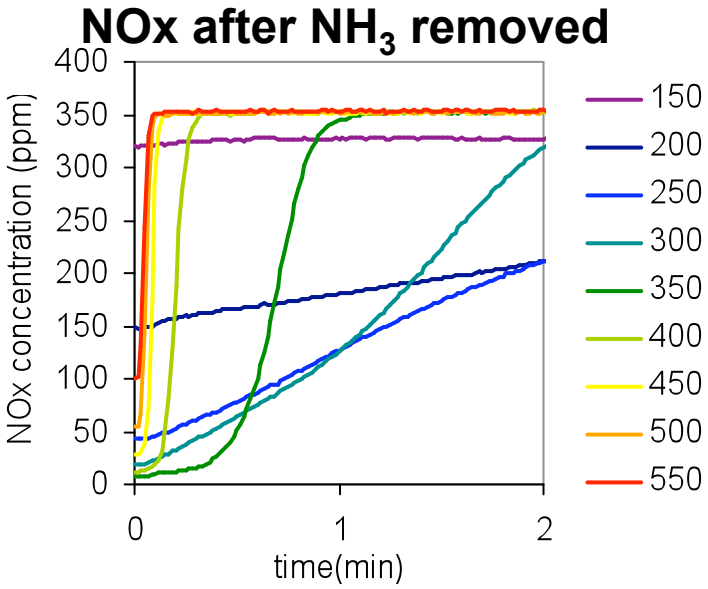


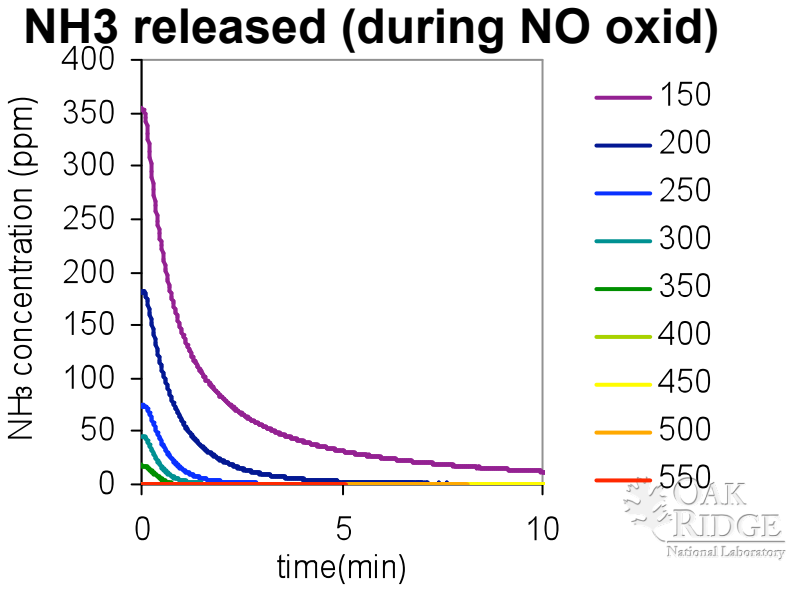


Sample results: NH_3 storage from NH_3 uptake and NOx converted by stored NH_3

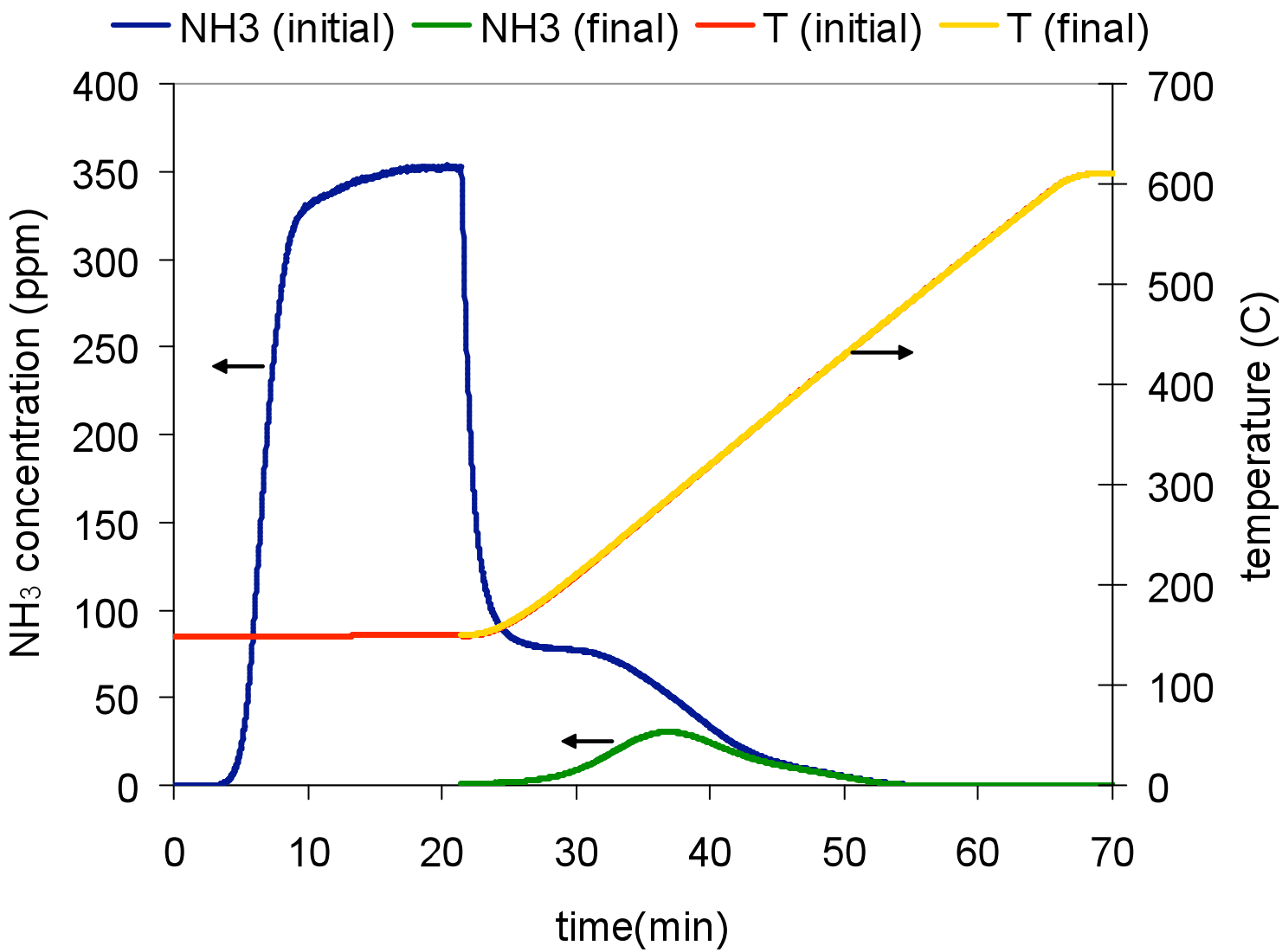








Sample results: TPDs



Questions to ponder

- Have we missed anything critical?
- Have we included anything unnecessary?
- Are either of the previous two answers dependent on the type of model the data will be used to calibrate?
  - If so, do we need more than one protocol, or perhaps a separate group of experiments to include in the protocol just for more detailed models?
- Are there any problems with the way the protocol is constructed (order of steps, variable parameters)?

Fire Away!

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