# LNT Studies at Cummins

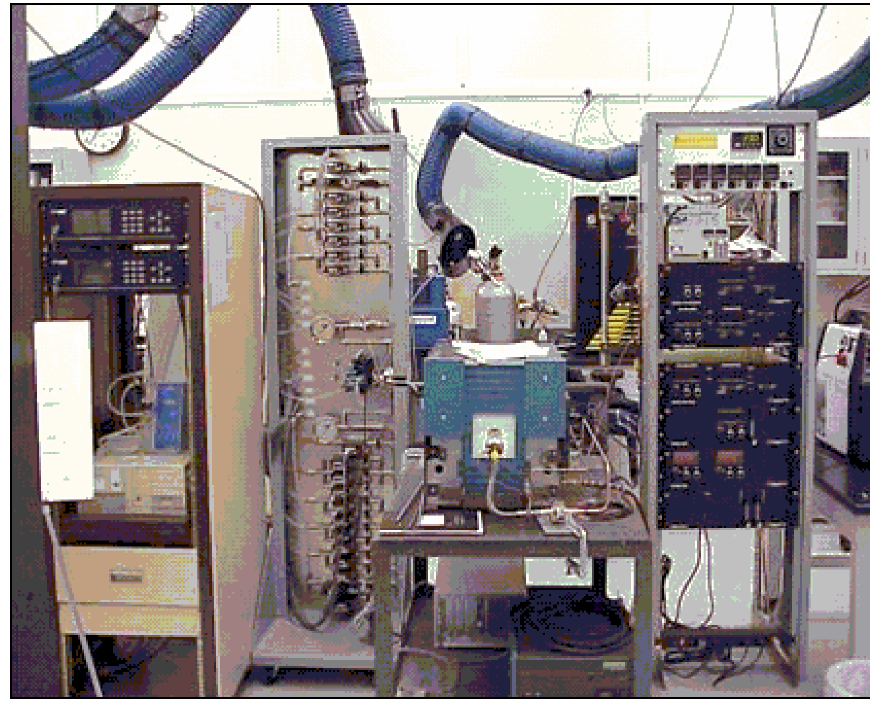
Neal Currier, Bill Epling, Aleksey Yezerets

# Objectives

- Review LNT CLEERs protocol (June 2004 draft)
- Patterns, trends that need to be captured
  - Functions of
    - Temperature
    - Reductant Amount
    - Reductant Type
    - Flow rate (space velocity)
    - $NO - NO_2$
- Identify "fingerprint" or distinct data features resulting from complex behavior
  - Transient nature of both device, engine, controls drive the need to truly understand:
    - the reaction and surface chemistry in most of its complexity,
    - fluid mechanics,
    - and heat transfer of the catalyst

# Reactor Work

- Reactor - Cummins' automated pilot scale catalyst reactor
- ~ 1 week to execute the protocol
- Instrumentation -
  - FTIR, UEGO, & NOx sensors
  - 2 Hz for IR, varied for sensors (as high as 10 Hz)
  - millisecond data rate capable (except IR)
- CLEERS LNT standard sample aged at NTRC



1" x 3" catalyst core

# Example: $H_2$/CO Reductant

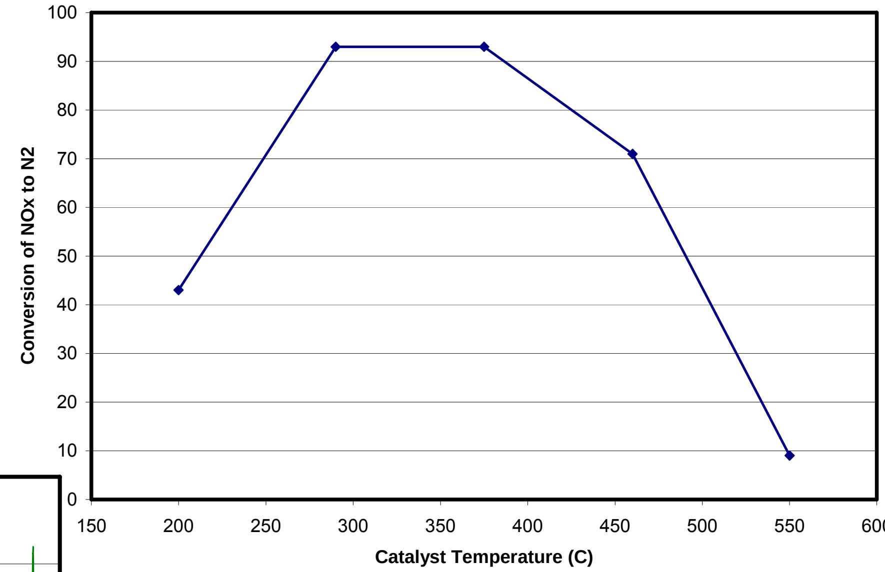
| Run No. | Temp (deg C)+ | Gas Mix++ | SV (1/hr) | Lean period (s) | Reductant* | Regen peak (ppm)** | Regen period (s)# | No. of cycles |
|---|---|---|---|---|---|---|---|---|
| 1 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 2 | 550 | 2 | 30,000 | 60 | CO/H2 | 1.8% | 5 | 30 |
| 3 | 550 | 2 | 30,000 | 60 | CO/H2 | 0.9% | 5 | 30 |
| 4 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 5 | 463 | 2 | 30,000 | 60 | CO/H2 | 1.8% | 5 | 30 |
| 6 | 463 | 2 | 30,000 | 60 | CO/H2 | 0.9% | 5 | 30 |
| 7 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 8 | 375 | 2 | 30,000 | 60 | CO/H2 | 1.8% | 5 | 30 |
| 9 | 375 | 2 | 30,000 | 60 | CO/H2 | 0.9% | 5 | 30 |
| 10 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 11 | 288 | 2 | 30,000 | 60 | CO/H2 | 1.8% | 5 | 30 |
| 12 | 288 | 2 | 30,000 | 60 | CO/H2 | 0.9% | 5 | 30 |
| 13 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 14 | 200 | 2 | 30,000 | 60 | CO/H2 | 1.8% | 5 | 30 |
| 15 | 200 | 2 | 30,000 | 60 | CO/H2 | 0.9% | 5 | 30 |
| 16 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 17 | 375 | 2 | 15,000 | 60 | CO/H2 | 1.8% | 5 | 30 |
| 18 | 550 | 1 | 30,000 | 0 | H2 | 1,000 | 900 | 1 |
| 19 | 375 | 2 | 50,000 | 60 | CO/H2 | 1.8% | 5 | 30 |

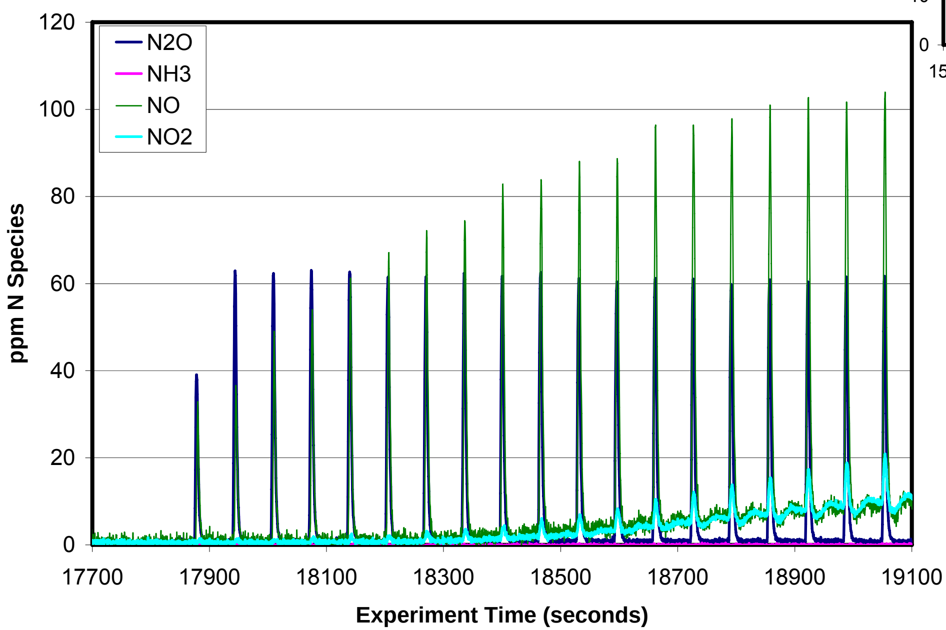
# Short Cycle Details

- Clean the sample at 550°C, $H_2$ reductant (long regeneration, 10 minutes)
- Cool to appropriate T
- 60 seconds lean, 5 seconds rich
  - Reductant level described as 2X stored $NO_X$, used 2x entering $NO_X$
- 30 cycles at this reductant level
- At end of 30th cycle, switch reductant level to 1x entering $NO_X$
- 30 cycles
- Heat to 550°C, clean

# Cycle Average Conversion

- Typical profiles and patterns
- Performance loss at "extremes"

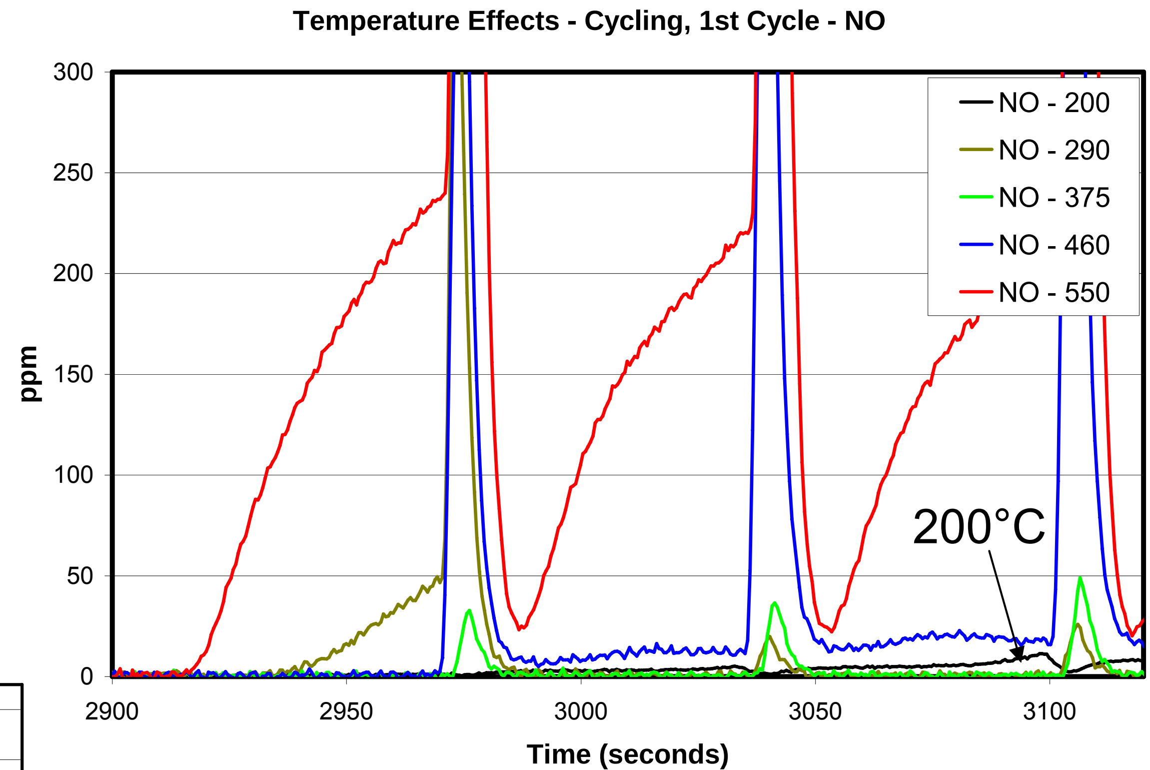


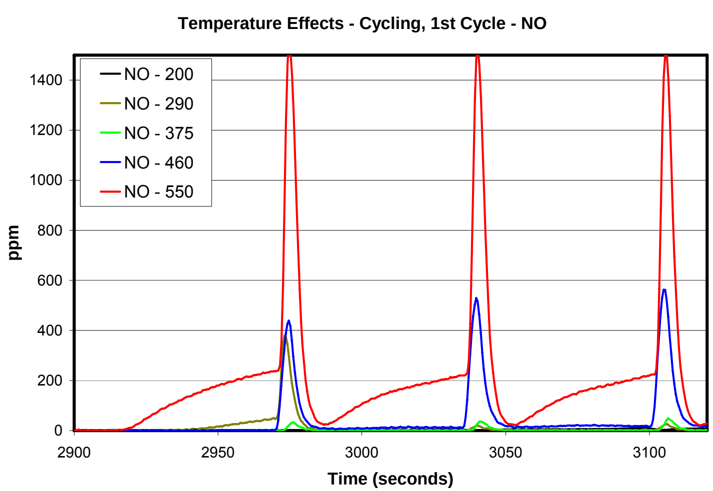




Model development requires more information – the Focus Group protocol is designed to provide some of that

# Temperature Effects – NO Slip

- Cycle average conversion not well represented by first few cycles
  - Regen changes
  - Regen efficiency
  - Surface N buildup



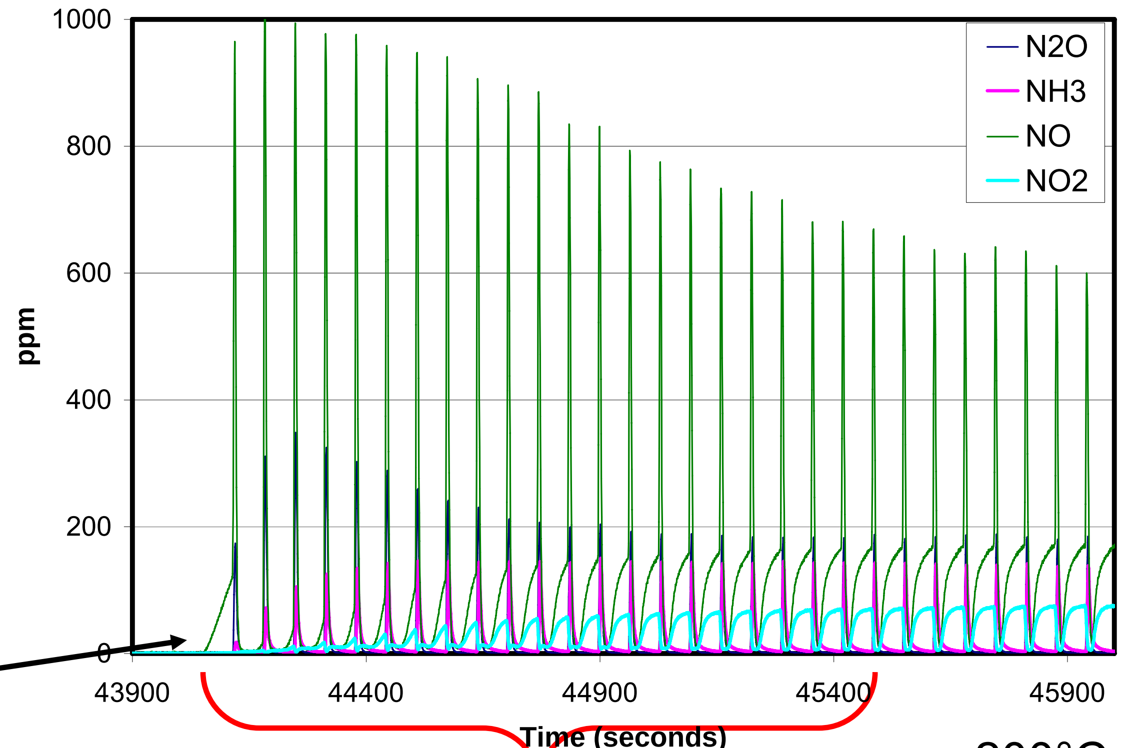




High temp – SS reached more quickly

Low temp – cycle dependent

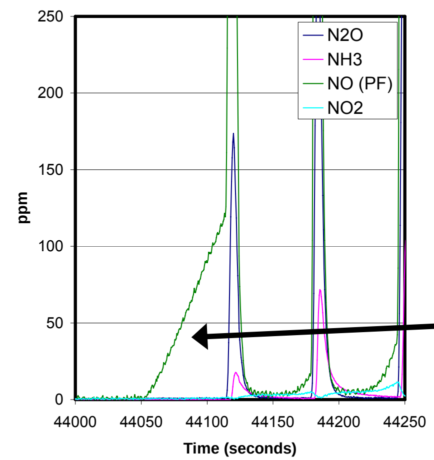
# Low Temp Experiment

Developing higher slip or breakthrough with each cycle



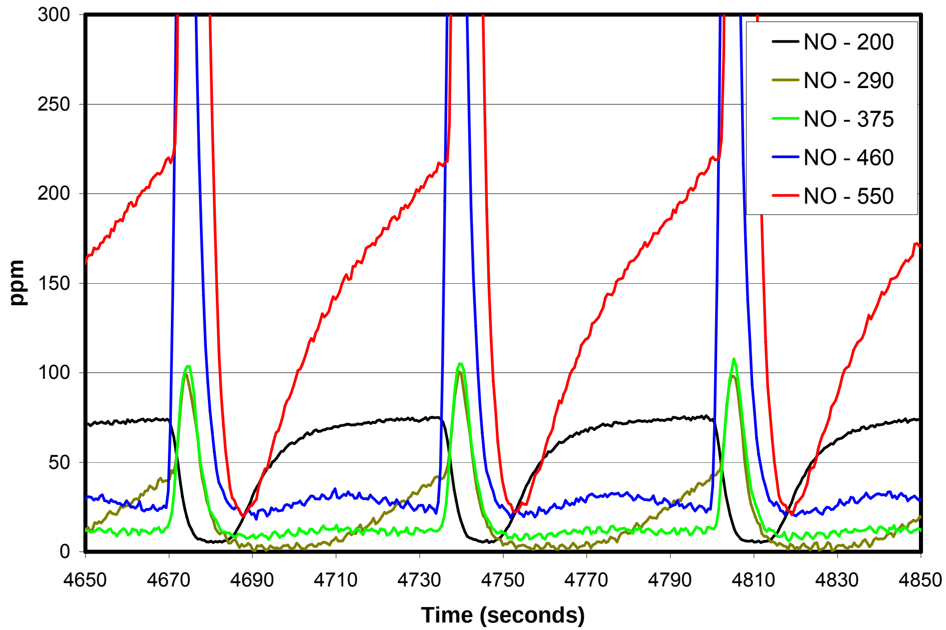

200°C

22 cycles → SS?



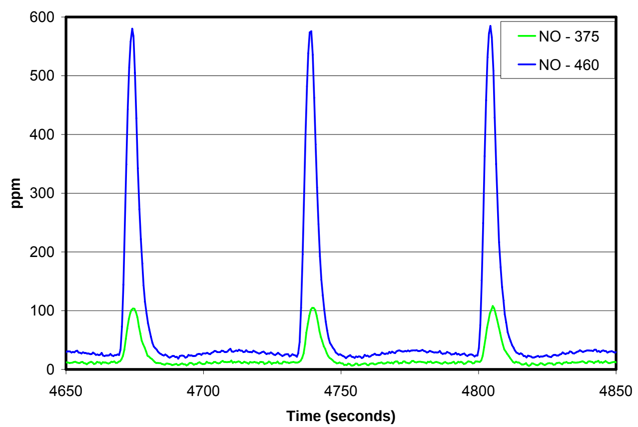

"Pretreated" surface leads to different trapping profile

# NO Slip – Last Cycles



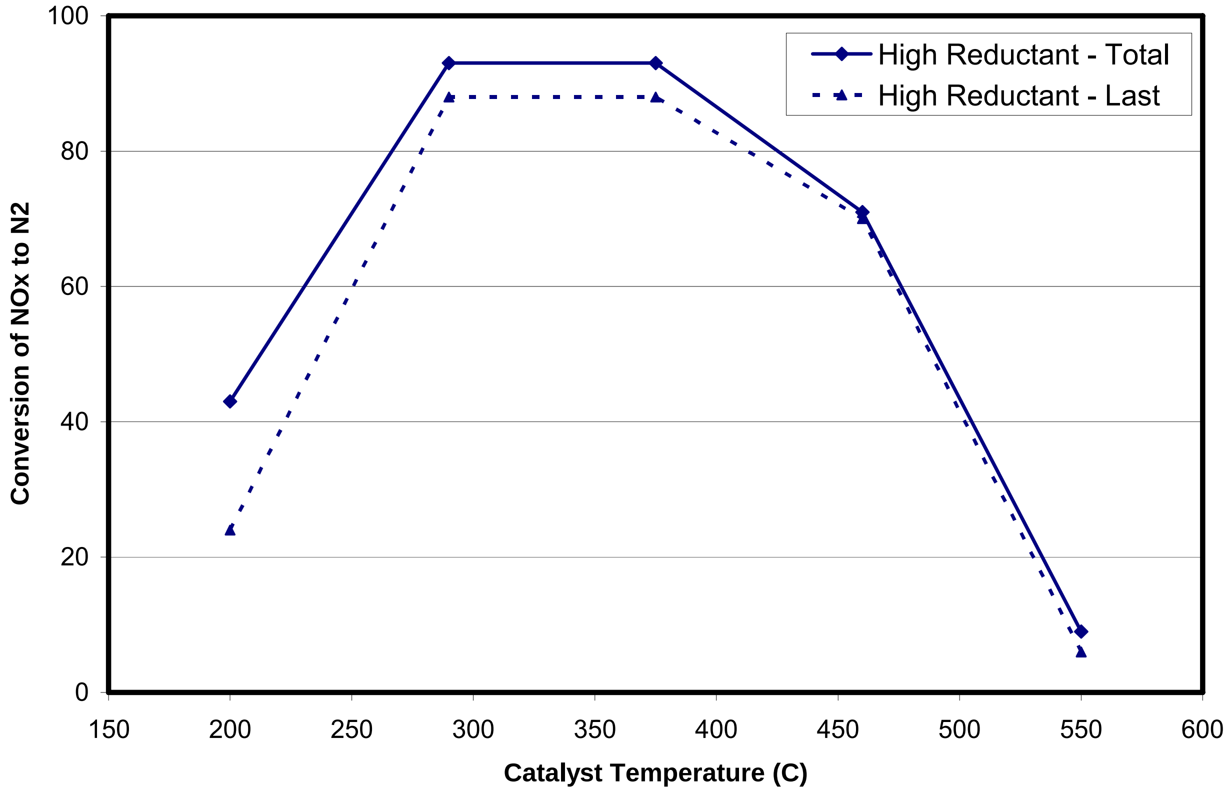

NO during regen is a f(T) → 375 vs. 460°C

- Non-linear
- Also f($NO_X$ on surface)
- Need to decouple



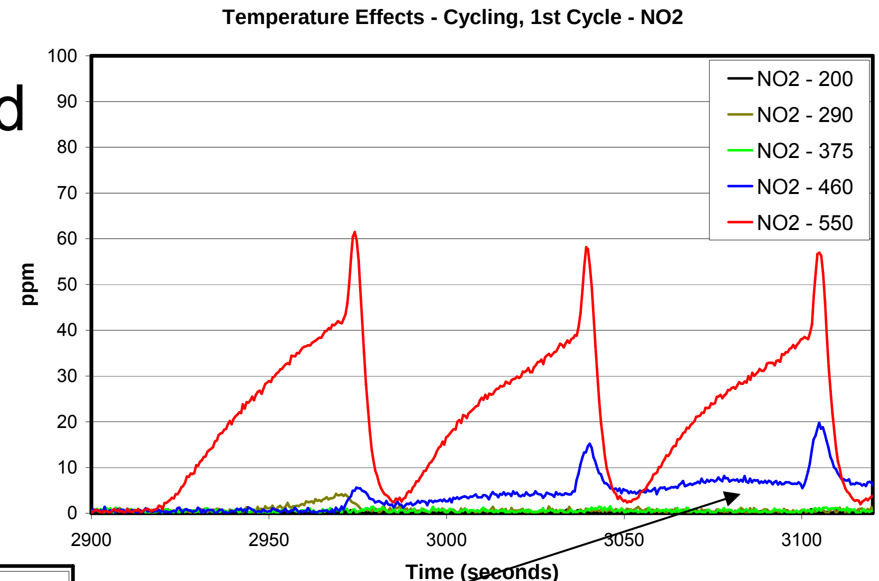
# Last Cycle Conversions

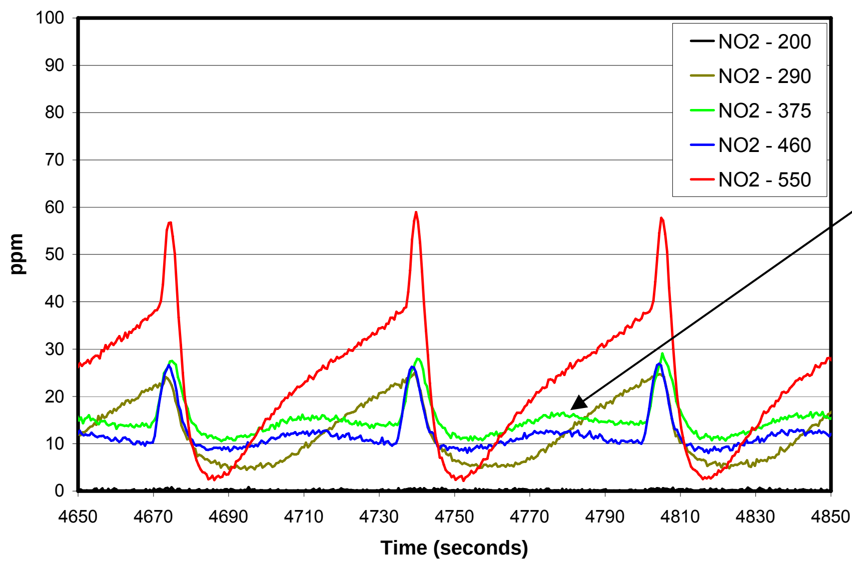
- At higher operating T – overall average and last cycle similar
- At lower T – significant difference (80%)
- Need to capture the growth of species on the surface
- T – gas/surface equilibrium



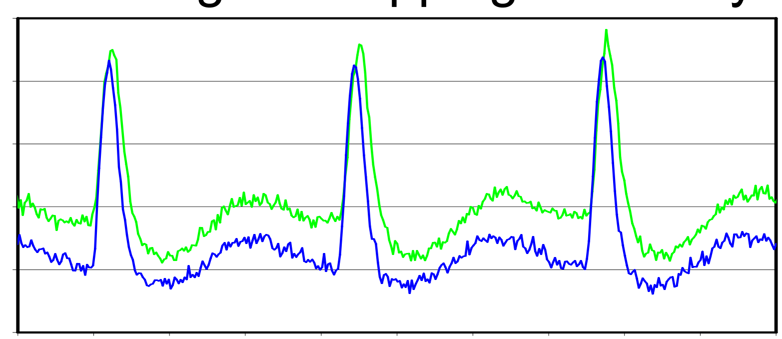
# $NO_2$

- Same trends – high temperature, SS reached more quickly
- $NO/NO_2$ equilibrium
- Evolved $NO_2$ during regen – $f(T,NO_X)$



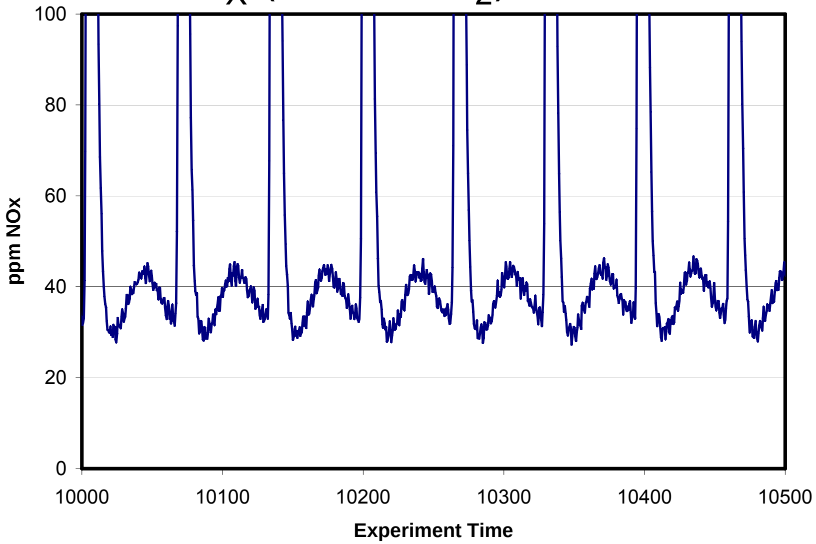




Change in trapping efficiency?



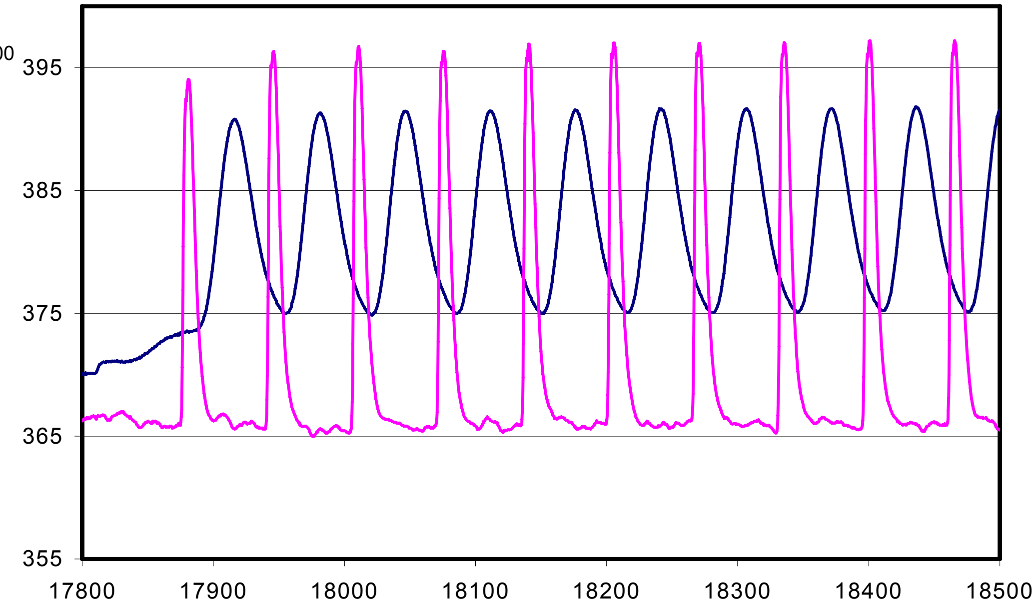
# Change in $NO_X$ Trapping – Heat Evolution

Total $NO_X$ ($NO + NO_2$)

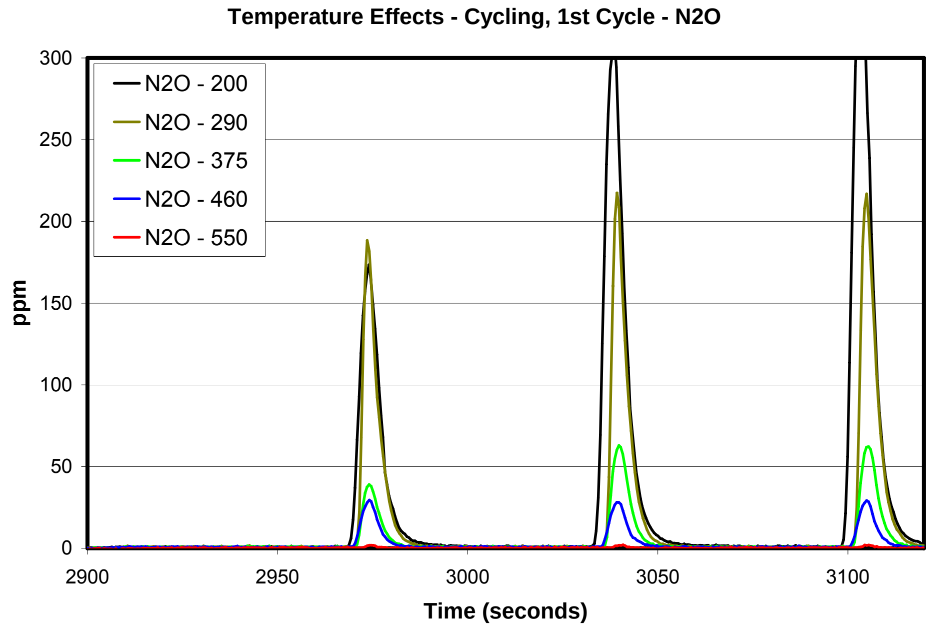



- Monitoring total $NO_X$ shows change in trapping during lean
- Temperature wave traverses catalyst length (phase shift)
- Trapping efficiency or oxidation?

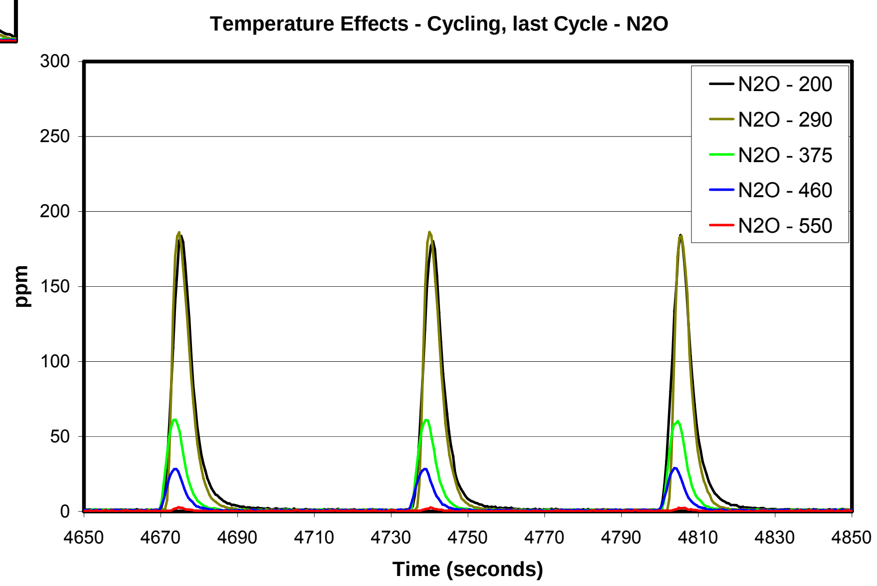
Chemistry only works if thermal is right



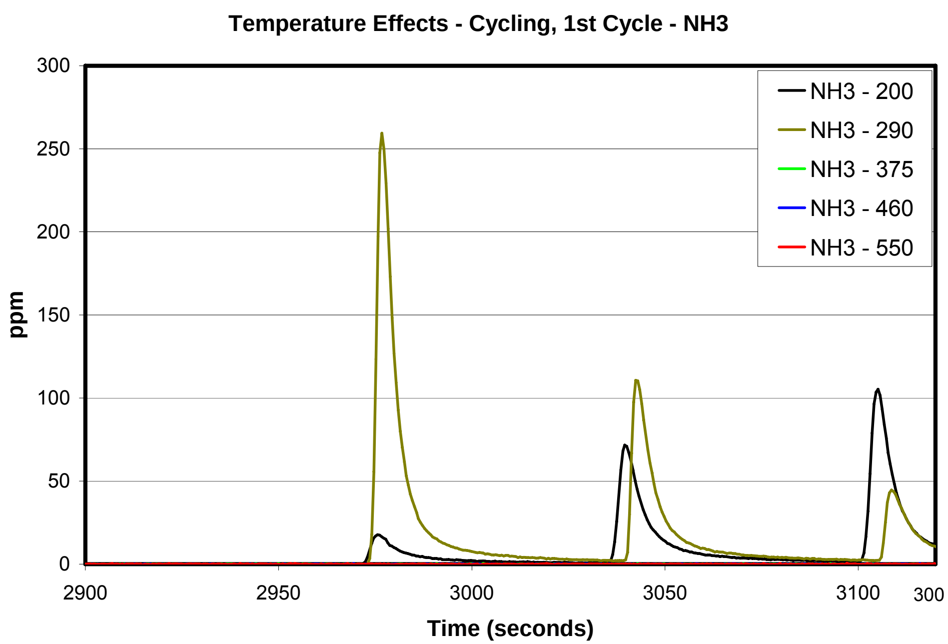
# N Byproducts – $N_2O$



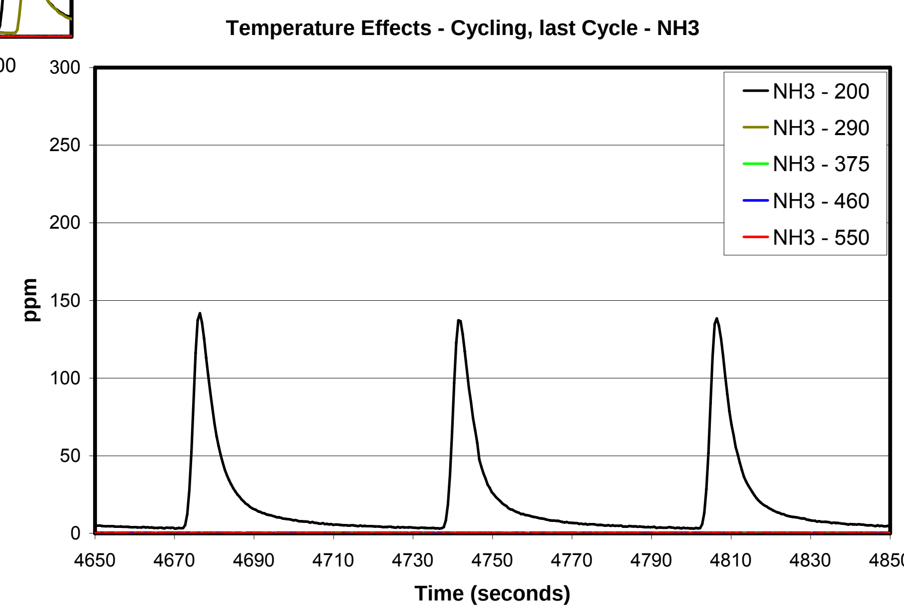

- $N_2O$ observed for all T but 550°C
- $N_2O$ release – f(T) and f(surface $NO_X$ coverage)



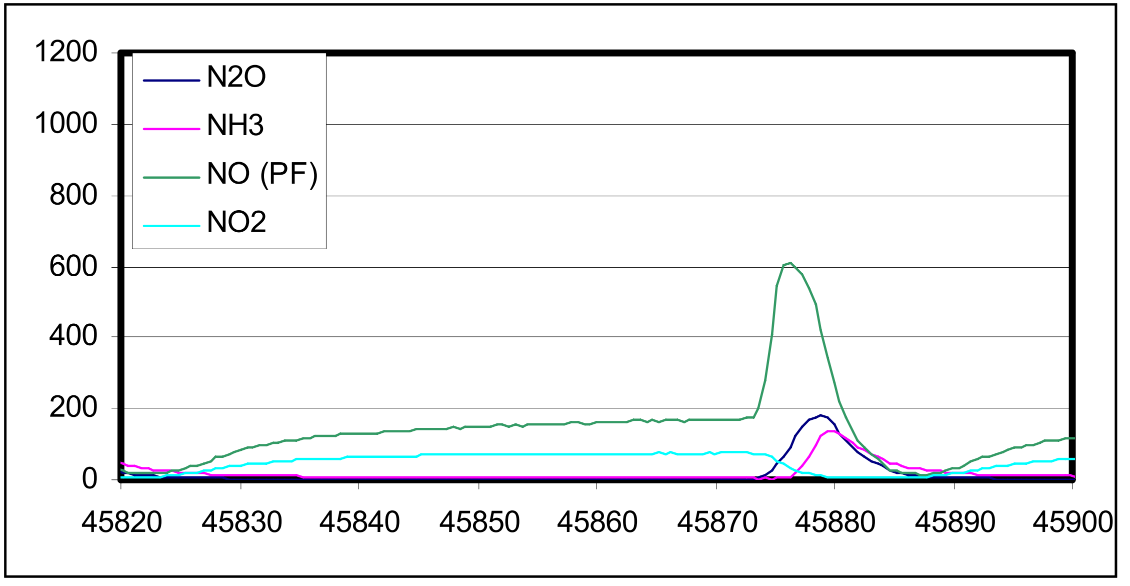
# N Byproducts – $NH_3$




- $NH_3$ present throughout cycles at 200°C
- F(?) at 290°C
  - Again, "pretreated" surface or saturation
- Fridell and coworkers



# N species release sequence

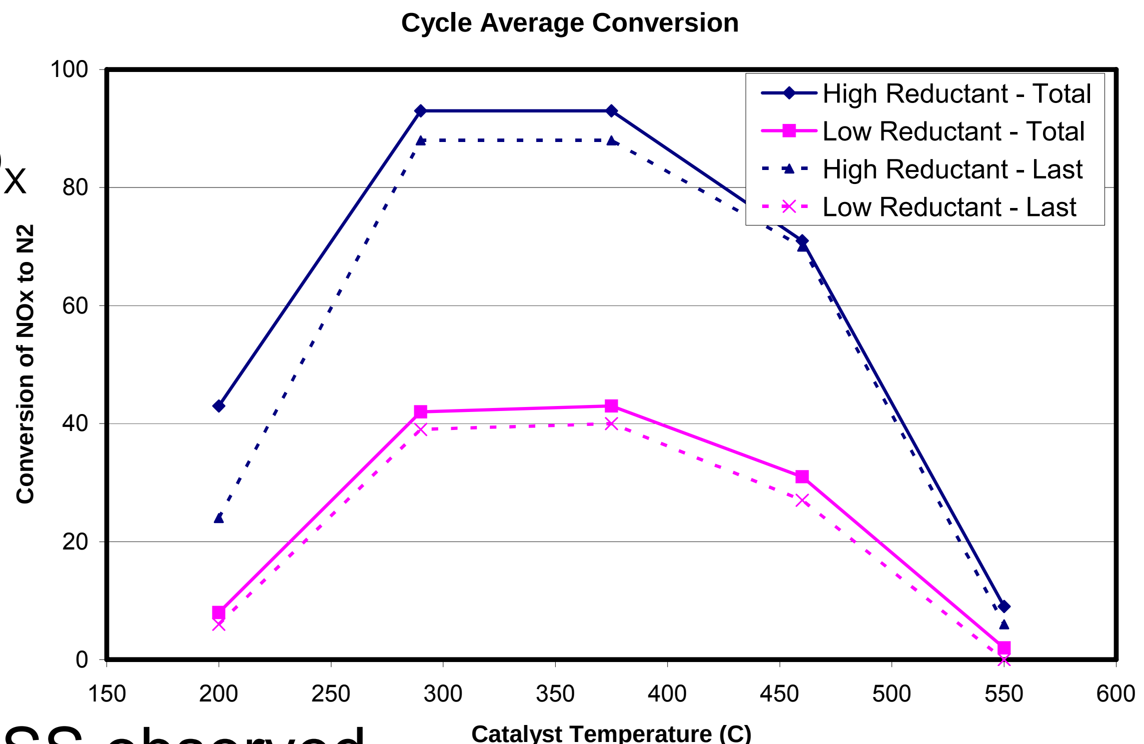



200°C Test (all species observed)

- $NO_2$ = NO → $N_2O$ → $NH_3$ at 200°C (at higher T, difficult to resolve differences between NO, $NO_2$ and $N_2O$)
- Is it less $NO_X$, more reductant; different sites; surface residence time

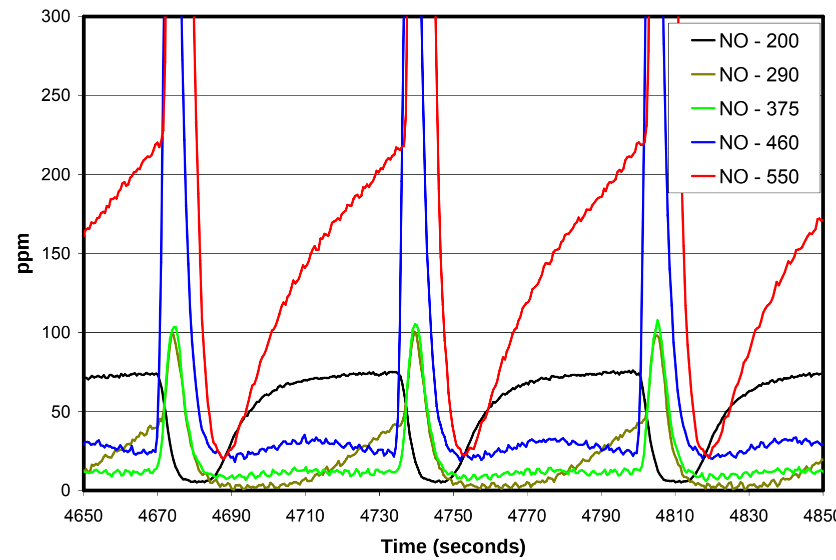
# Reductant Level

- Two levels
  - Previous data at 2x assumed stored $NO_X$ equivalent
  - Second point at 1x
- Similar pattern
  - Two “extremes” – drop off in performance observed
- Faster approach to SS observed
  - More rapid saturation
    - less reductant to clean the surface
    - *artifact of the experiment*



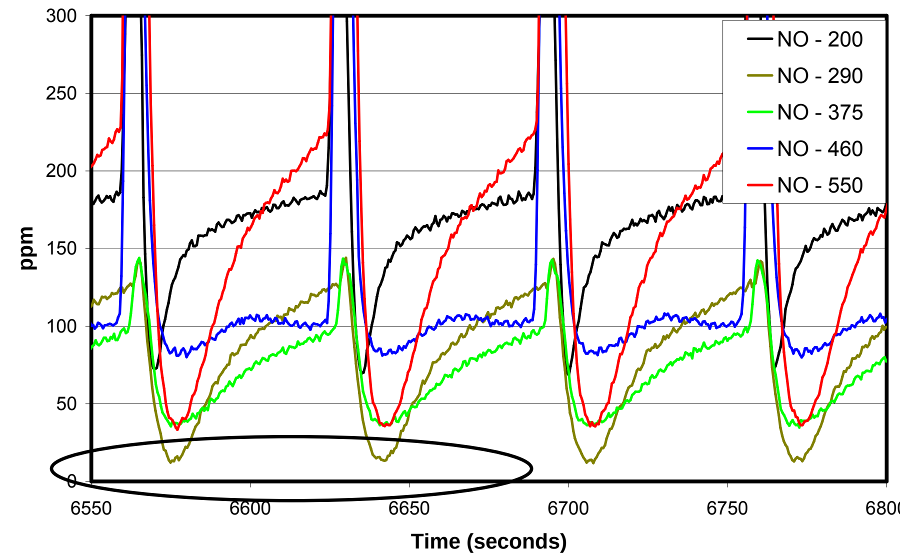
# Reductant Level Impact on NO Slip

- Further saturation
  - Only 290°C operating point approaches 0 ppm breakthrough
- NO release larger at 550, 460 and at 200°C operating conditions



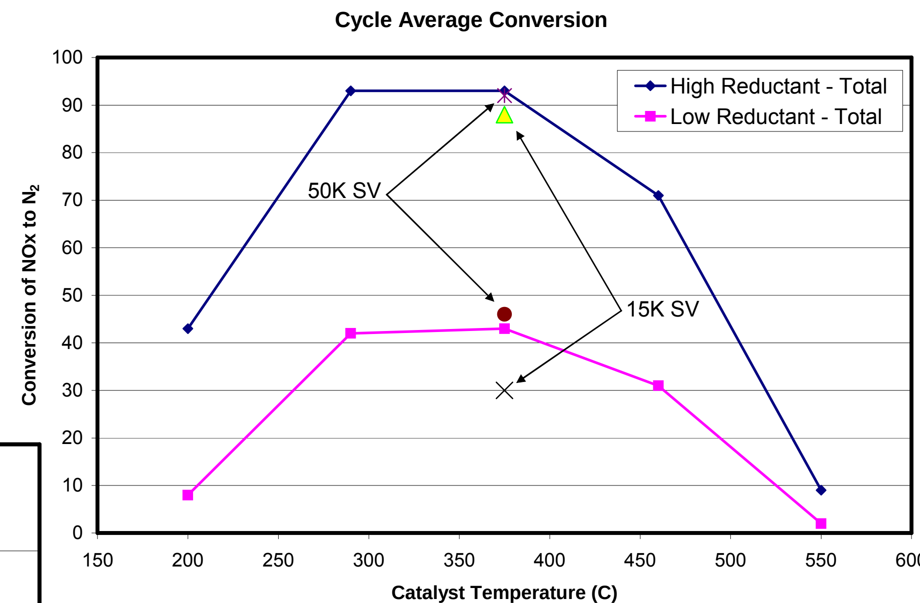

Temperature Effects - Cycling, last Cycle, low reductant level - NO

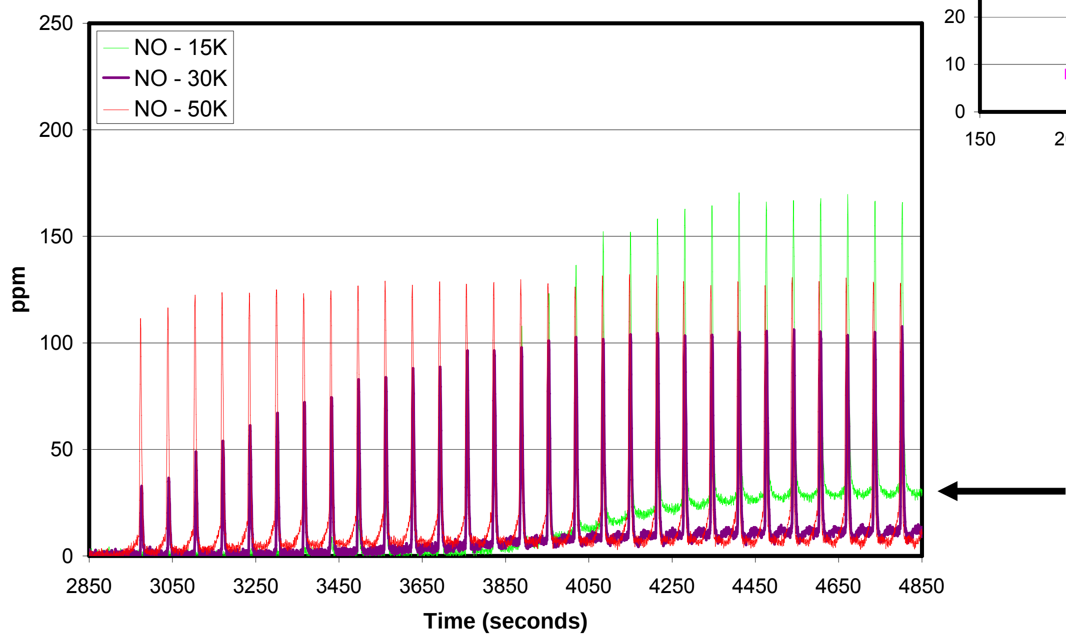
- $N_2O$ release lower throughout
- $NH_3$ release also lowered



# Space Velocity Effects

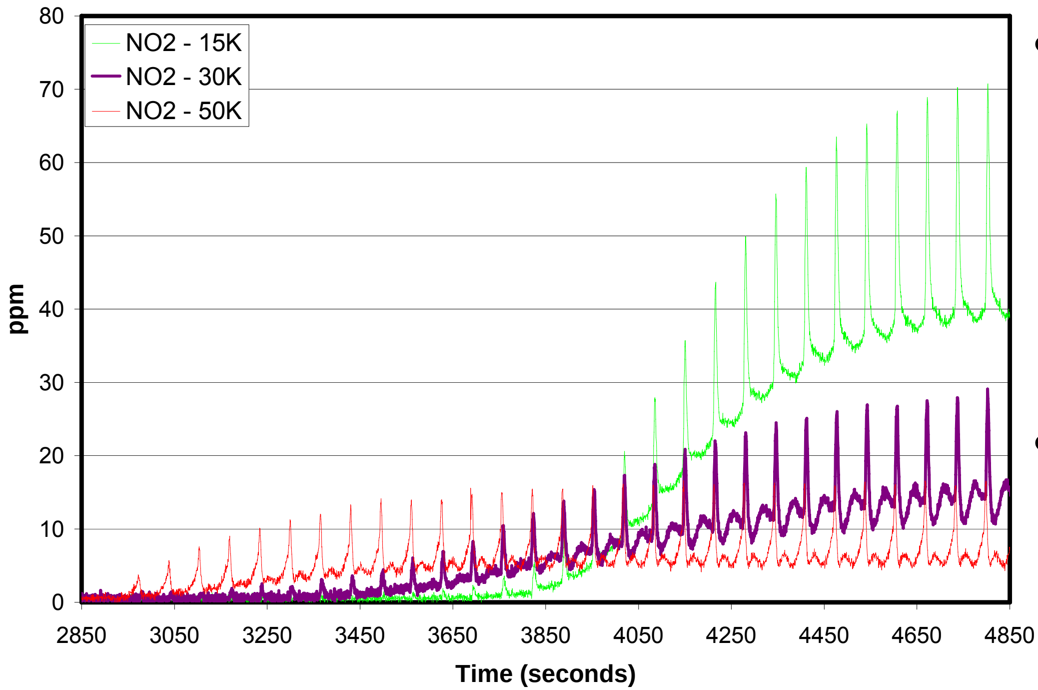
- Run at one temperature (375°C – "sweet spot")
- $NO_X$ and reductant levels not changed




- Reductant to stored $NO_X$ not constant
- Reductant to stored NOx ↑ with increased SV - oops

# $NO_2$ slip emphasizes effect

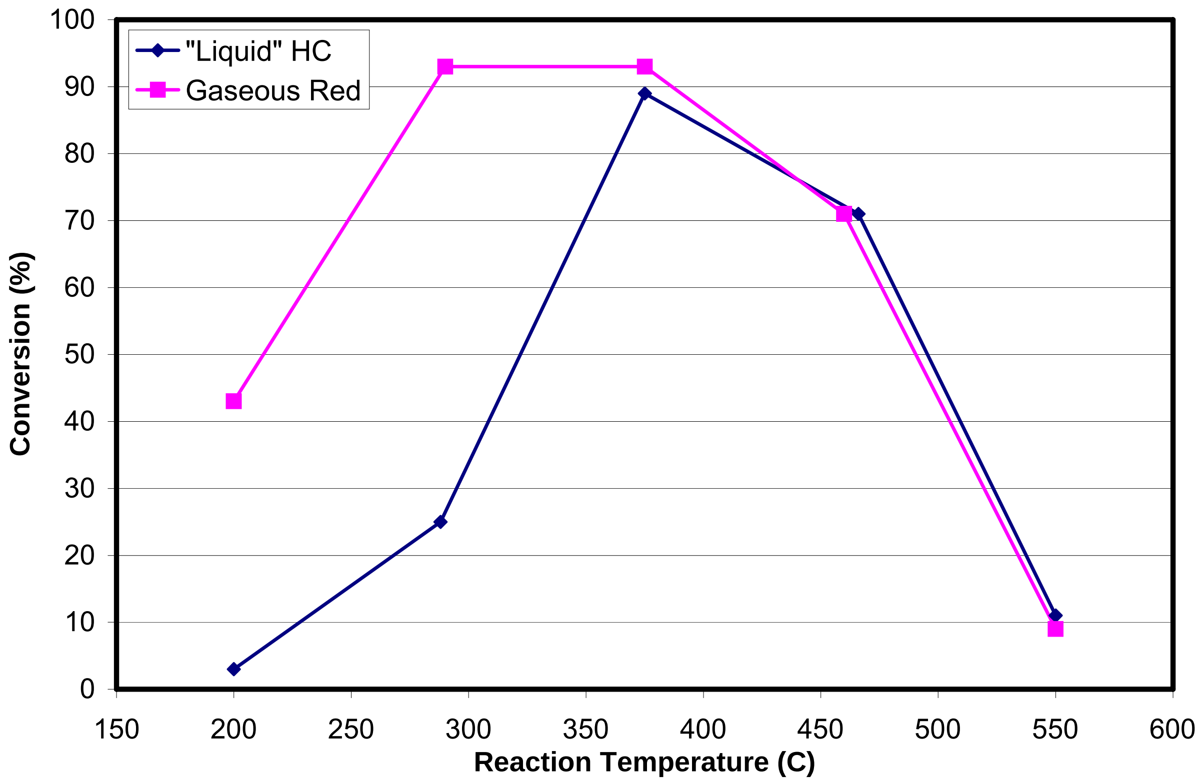



- At higher SV, observed slip begins at earlier cycle number, but at lower SV, during later cycles slip is significant
- Note curvature/shape of slip profiles – heat effects
  - More pronounced effect on $NO_2$ profile at greater saturation

SV shows no impact on $NH_3$ and $N_2O$

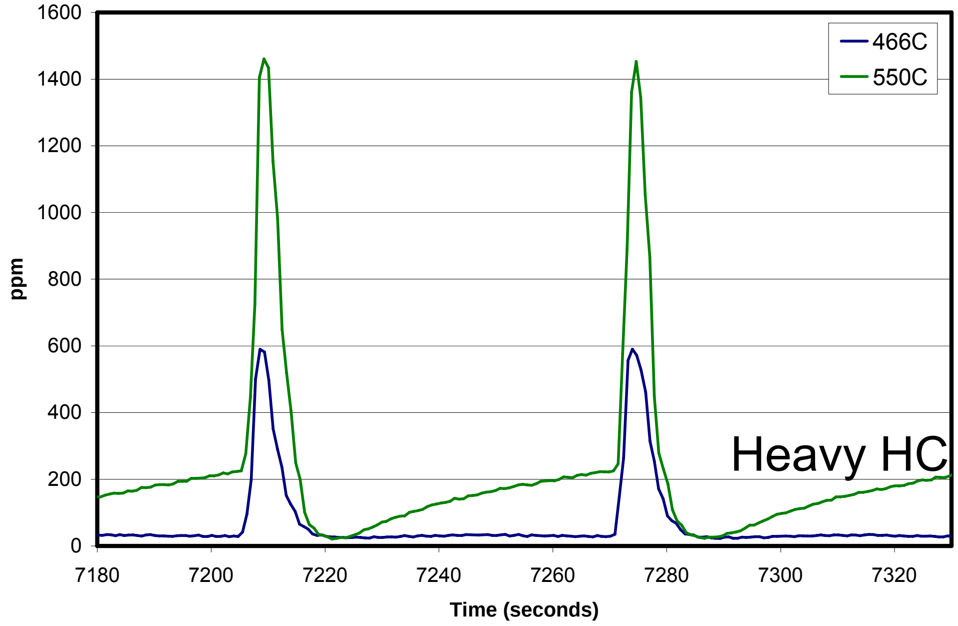
# Heavier HC as reductant

- Mixture of toluene and dodecane chosen as simulated hydrocarbon reductant for diesel

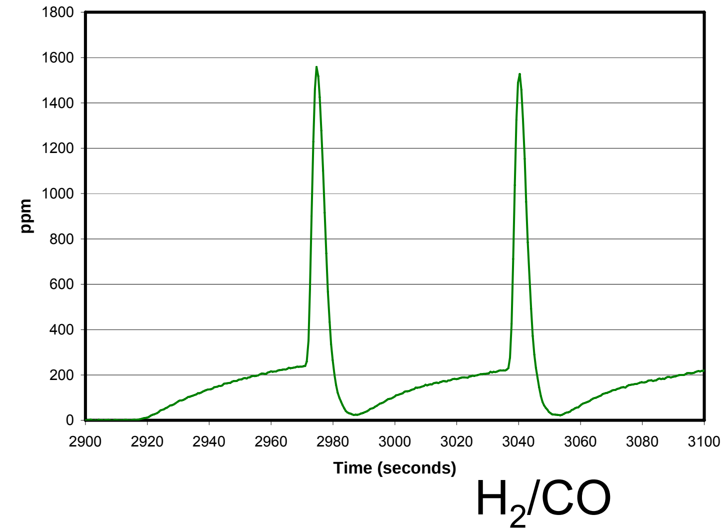



As expected, low temperature operation is decreased with heavier HC use

# High Temperature



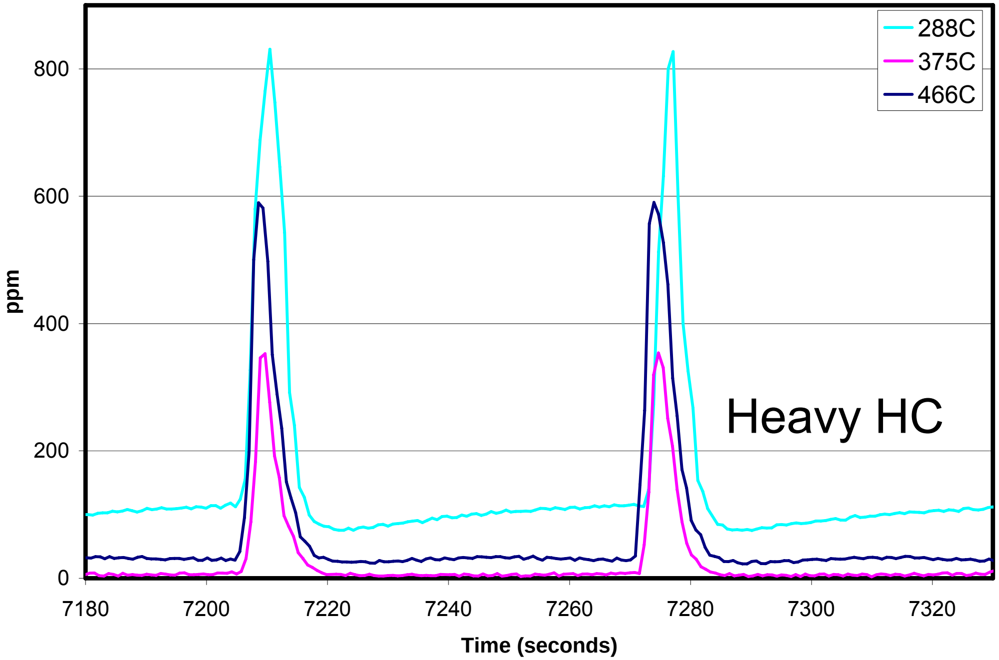

550°C profile for both reductant types - identical

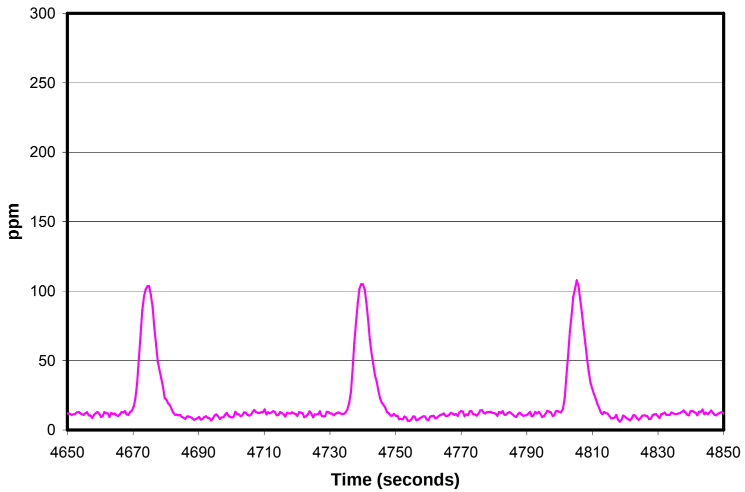



Performance at 550°C driven by nitrate stability

(no reductant effect)

# Mid Temperature

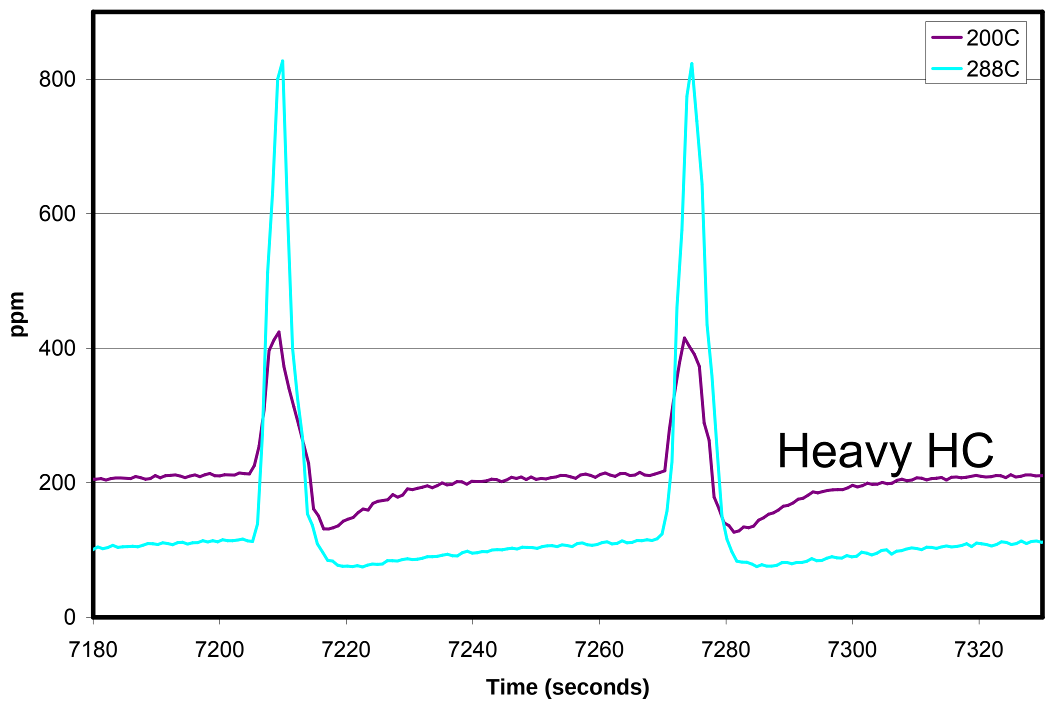


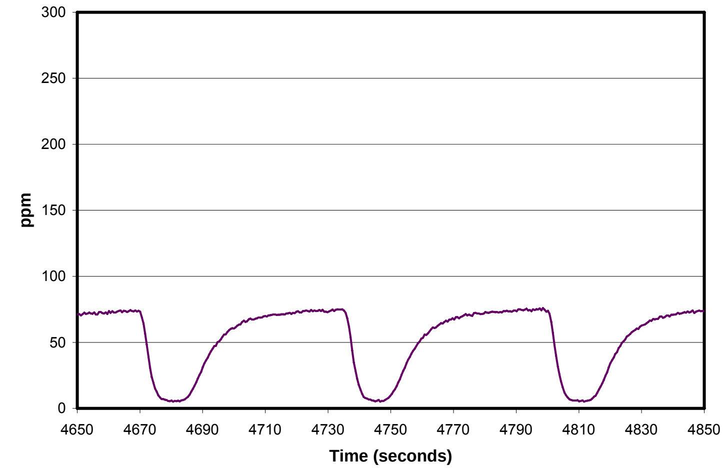




375°C operating T – performance dictated by $NO_X$ release during regeneration – trapping high, conversion high

Smaller release with $H_2$/CO mix

# Low Temperature



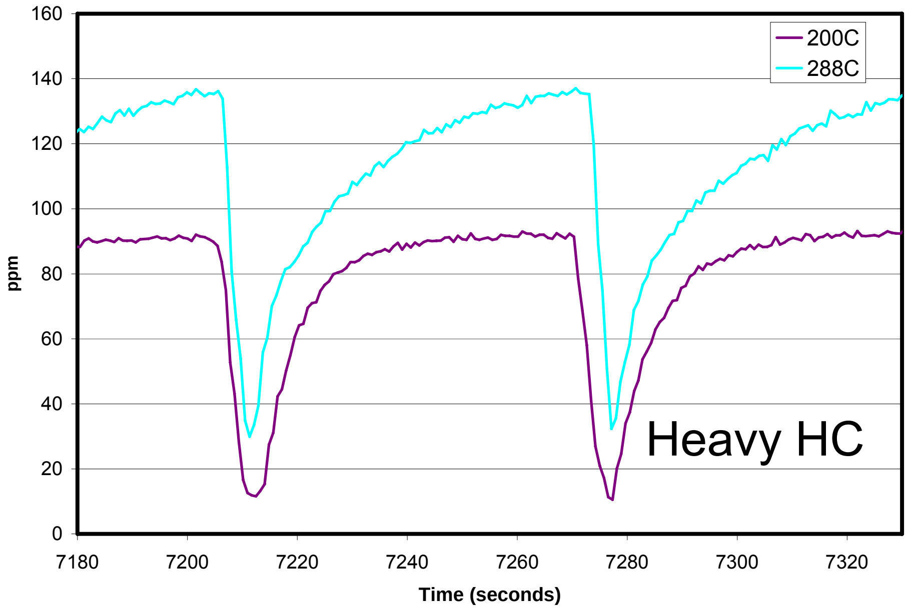

- 200°C performance
  - Surface cleaning during regeneration
  - $NO_X$ to $N_2$ reduction efficiency

As with $H_2$/CO mixture – changes occur with number of cycles

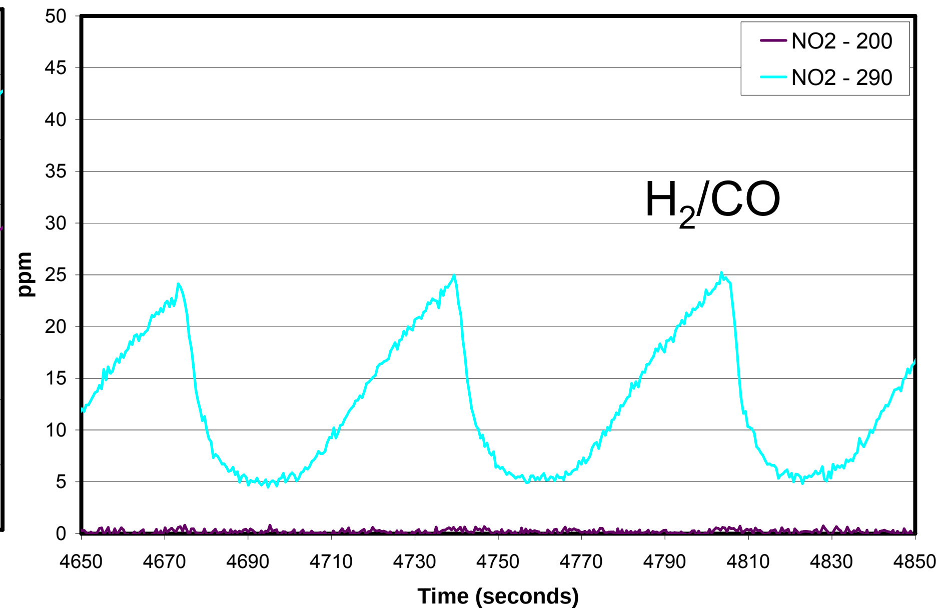
Faster approach at lower T – poor performance

# $NO_2$ Slip

- At 375°C and above – $NO_2$ trends are similar between reductant types
- Low T – surface cleaning effect emphasized



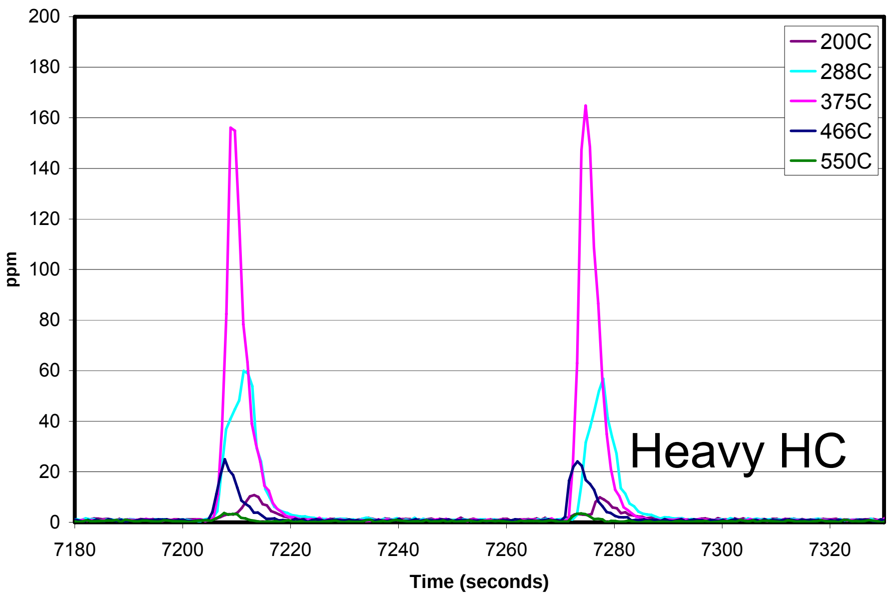

NO oxidation strong even at 200°C

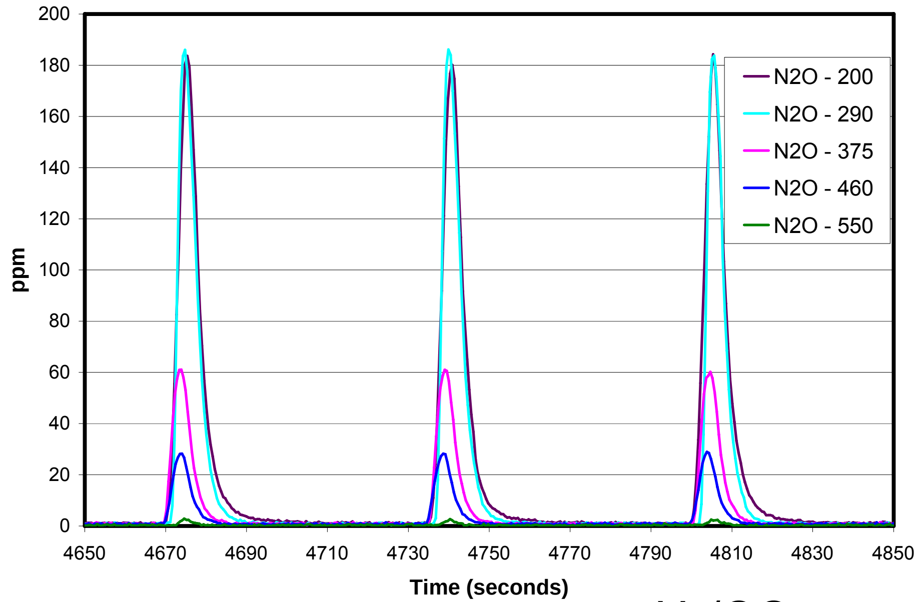



At 200°C, any $NO_2$ made is used

# N byproduct formation

- No $NH_3$ generation observed with heavy HC use
- $N_2O$
  - Lower T – less $N_2O$ with heavier HC – no surface N species
  - Higher T – Similar trends
  - Mid T – more $N_2O$ with heavier HC – still not as efficient as $H_2$/CO mix

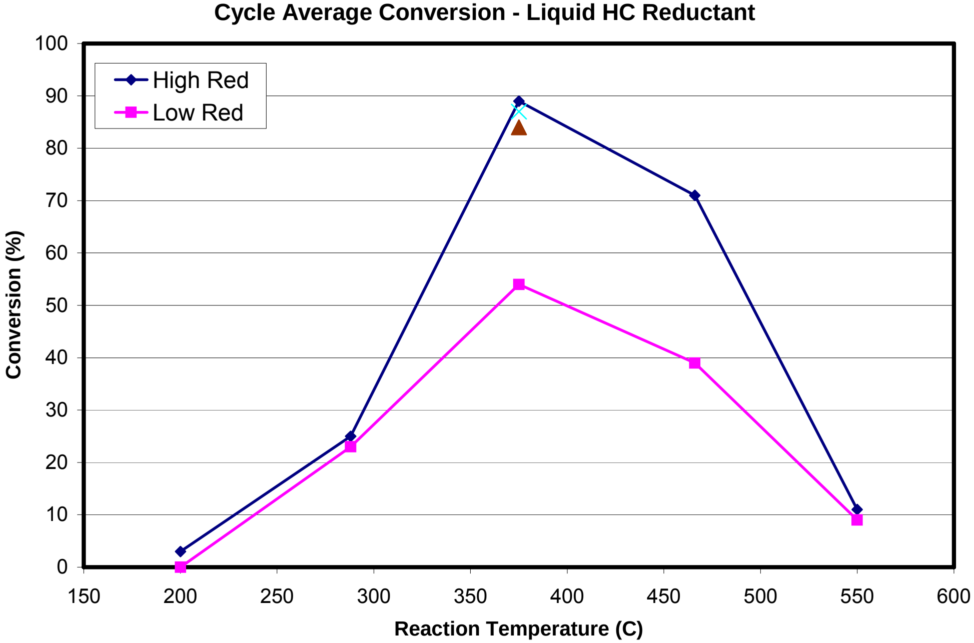



$H_2$/CO

# Less reductant

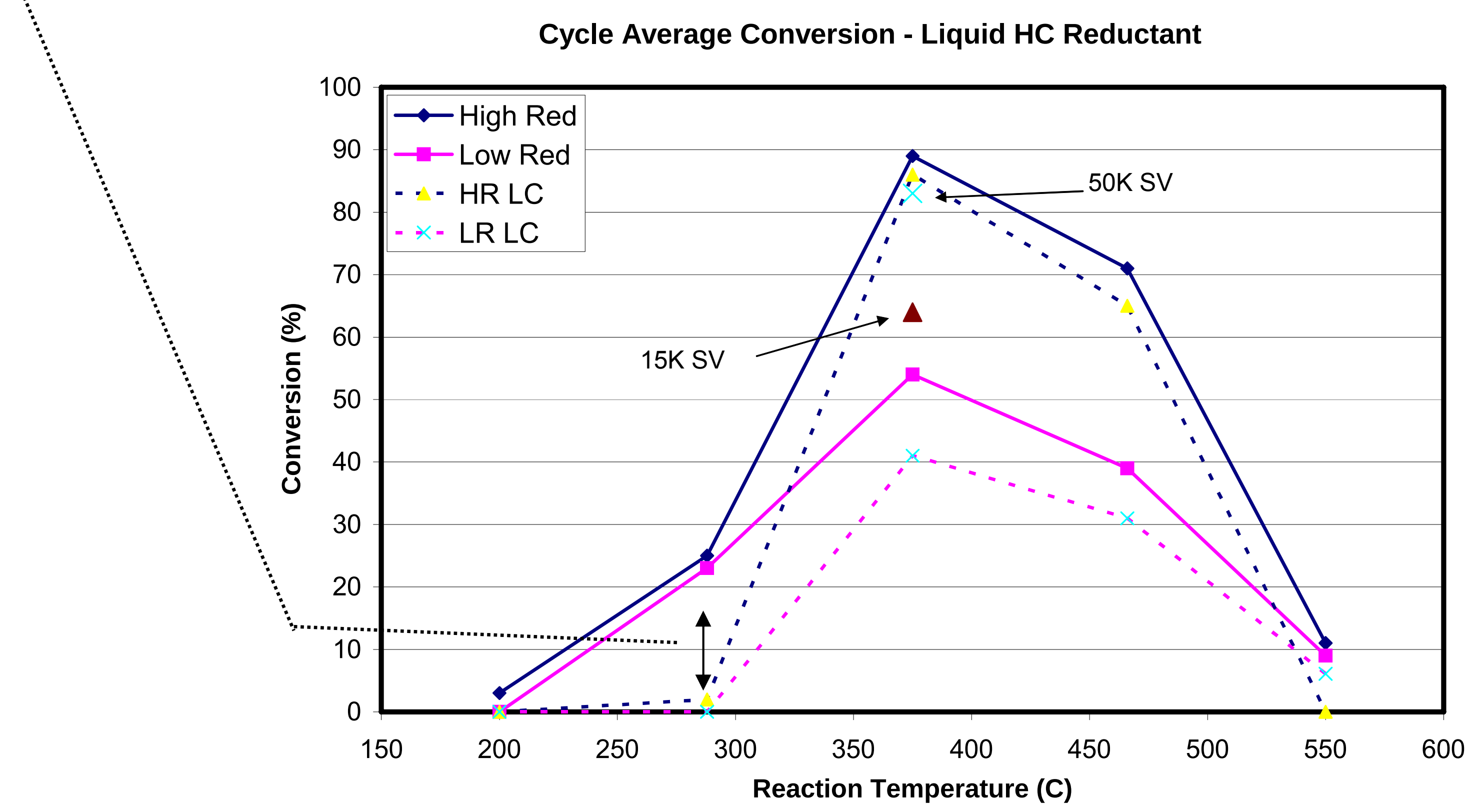
- Decreasing the amount of reductant does not affect low T performance
  - Surface is doing all it can already
- Mid-temperature points do see a change due to reductant decrease
- High temperature point not limited by reductant type or amount
  - Stability of nitrate species
- Seemingly no effect of SV on performance at the 375°C point



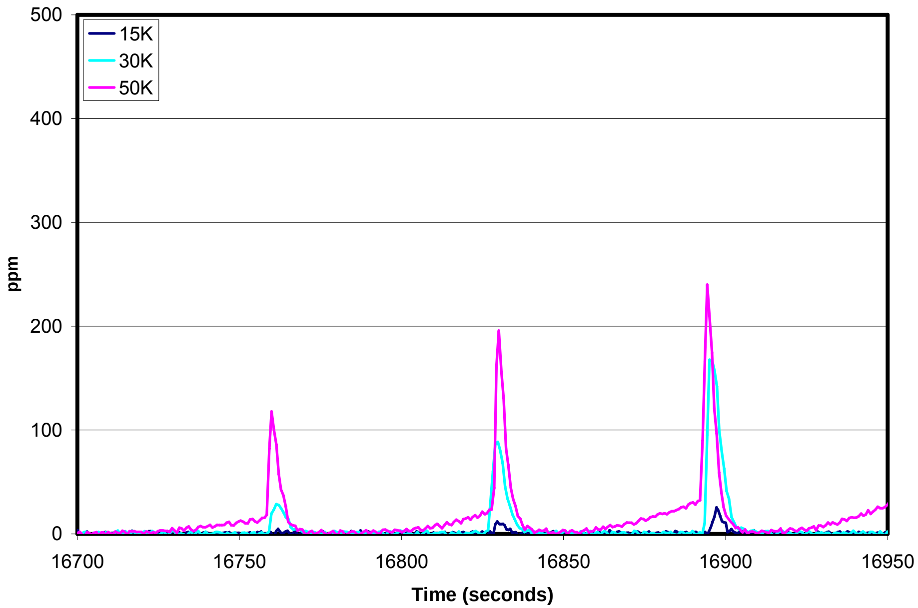
# Cycle Average vs Last Cycle

Using just the last cycle however, differences are observed – again reductant limitations for surface cleaning

Also, artifact not here– separate expts

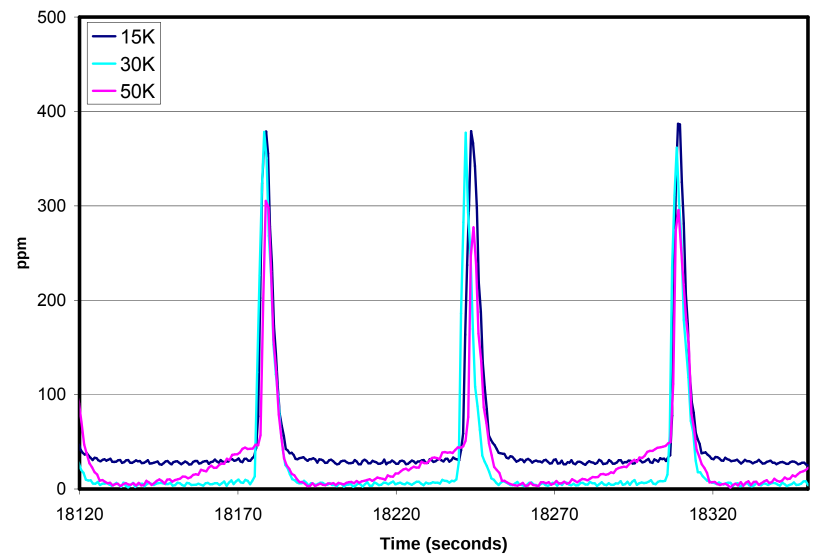


# Slip profiles




First cycles give expected results

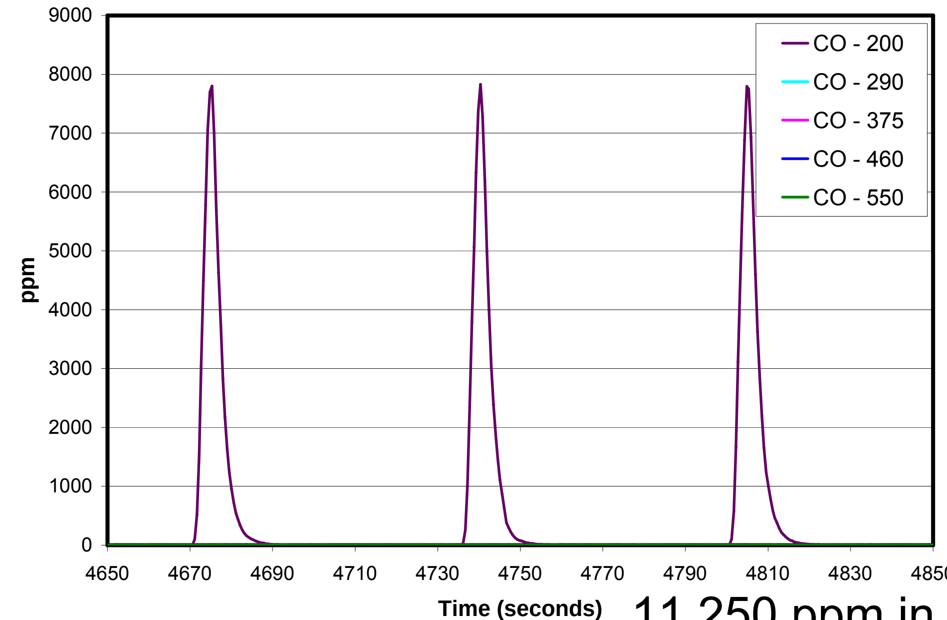
Similar trapping profiles at beginning and end of cycles for higher SV



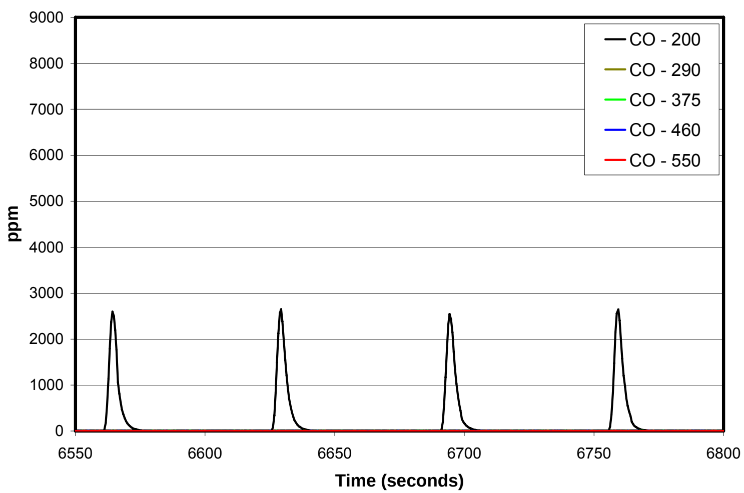

Non-zero trapping profile – due to different $NO_X$/HC, integral device or OSC?

# Reductant Usage, $H_2$/CO

- At 200°C, significant amount of CO is unused
  - Even by 280°C – all reductant now being used
- $H_2$ not measured as part of this test



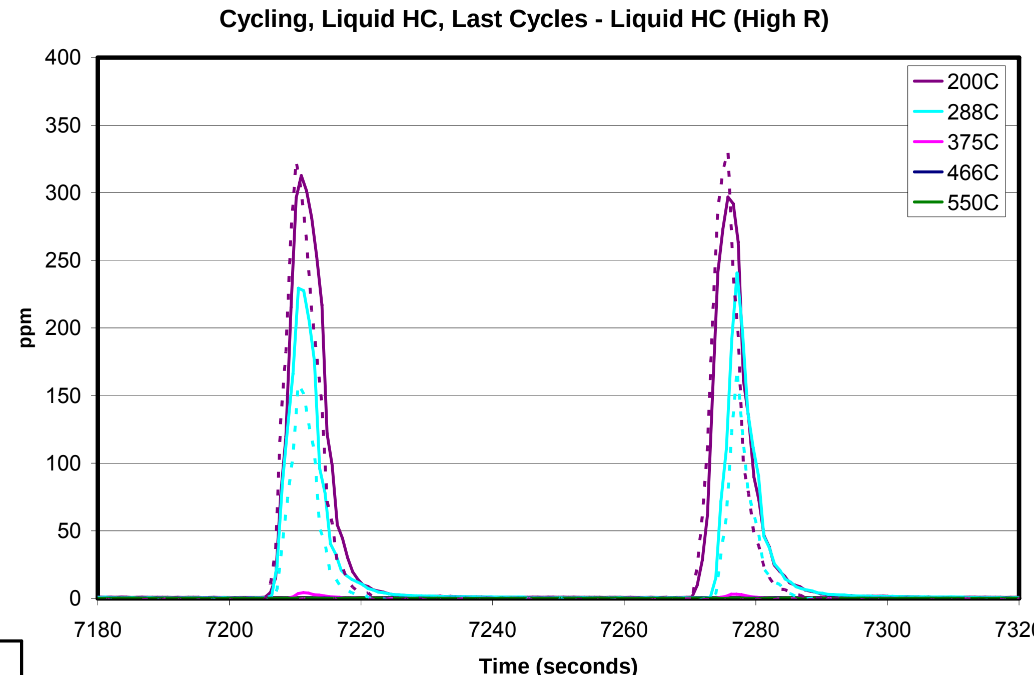

11,250 ppm in

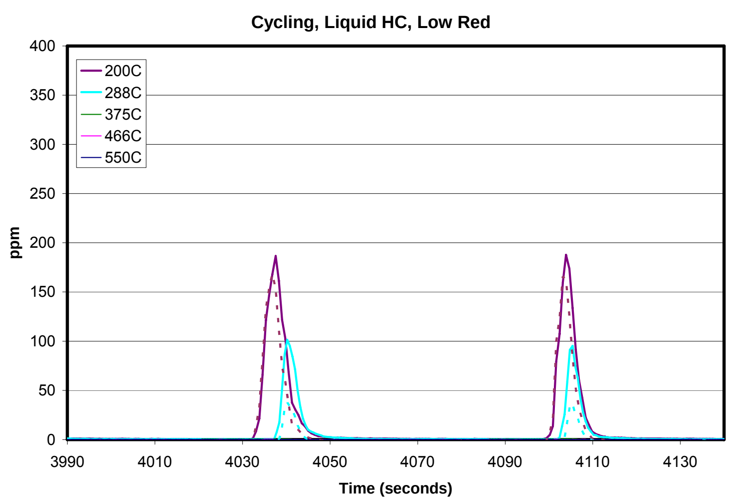



With the lower reductant amount (5625 ppm in)

# Reductant Usage, HC

- At 200°C – little/no usage of HC (total is 610 ppm in)
- At 288°C, slight
- "light-off" by 375°C



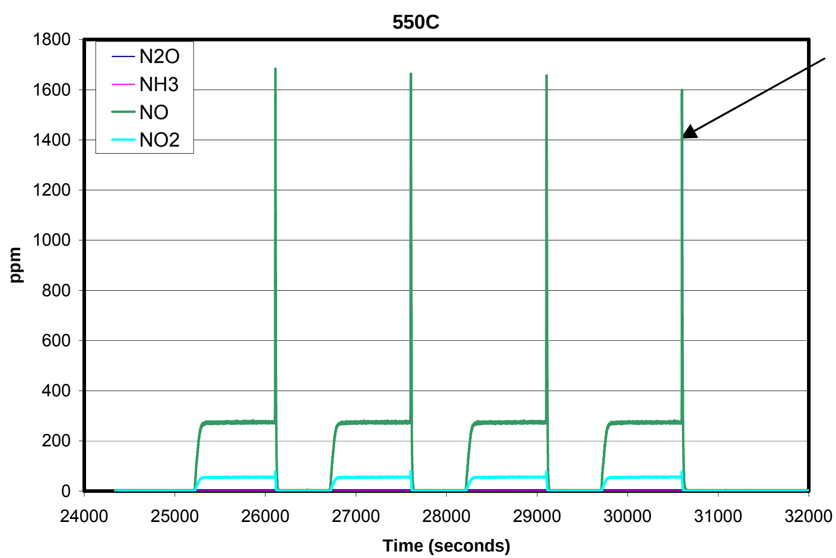

- At 288°C – some CO make (8 ppm instantaneous)
- No other HCs observed
  - $CH_4$, $C_2H_6$, $C_3H_8$, $C_2H_4$, $C_3H_6$, aldehydes monitored

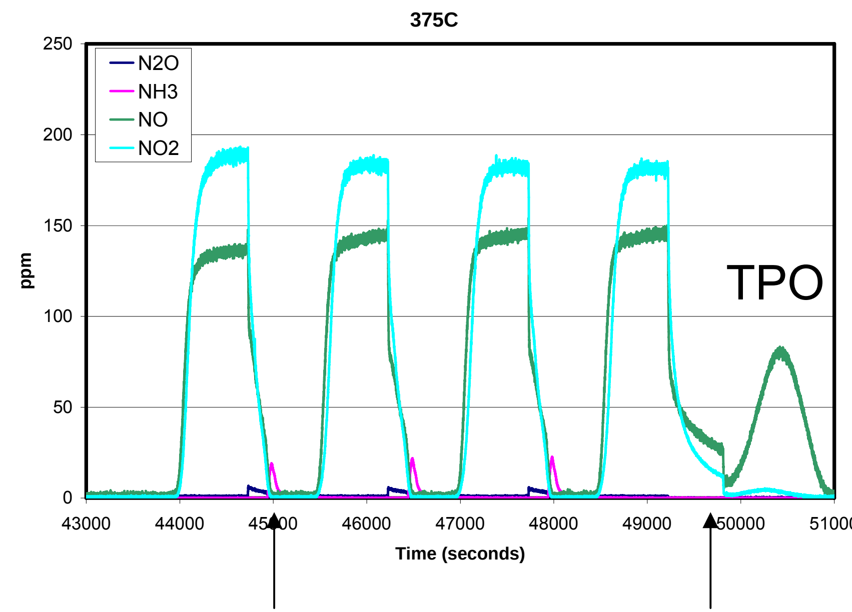
# Long Cycles

- 550°C cleaning – same as short cycle
- Cool to appropriate T
- 15 minutes lean, 10 minutes rich
- Reductant level set at 1000 ppm
- For heavier HC reductant, 1000 ppm $H_2$ (O consumption) equivalent used

# Long Cycles

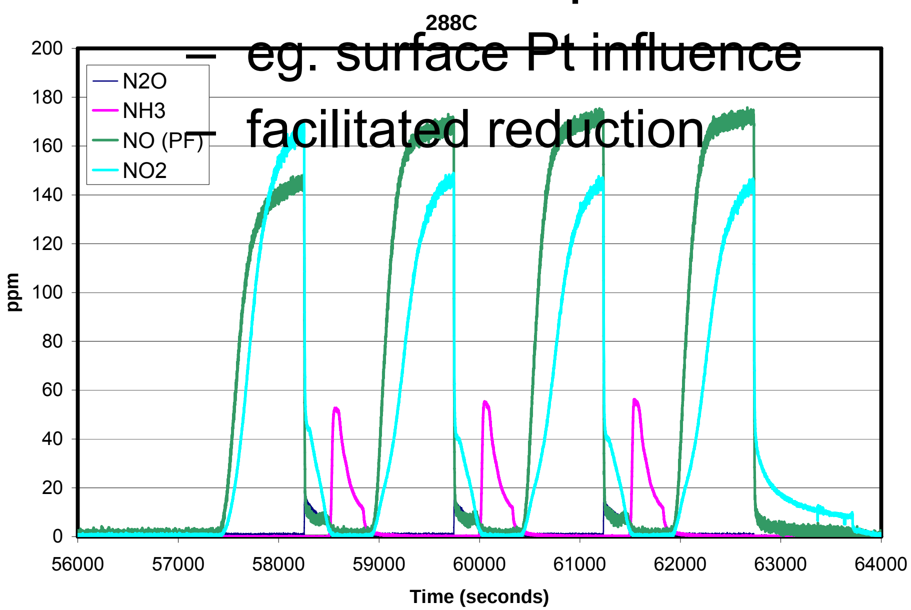
- 3 cycles with reductant in regeneration, after 4th cycle, no reductant added
- At 550°C – little trapping, large release
  - Little difference between reductant induced and thermal
- With 375°C – $NH_3$ and $N_2O$ formation becomes evident
  - Significant differences between thermal and reductant “regen”

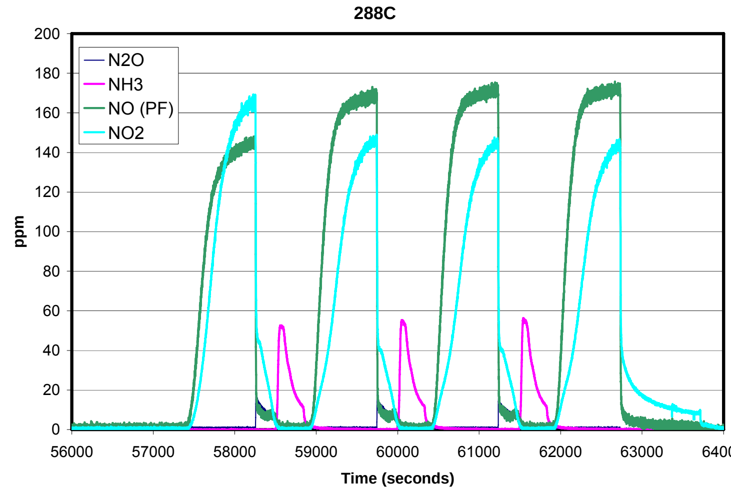


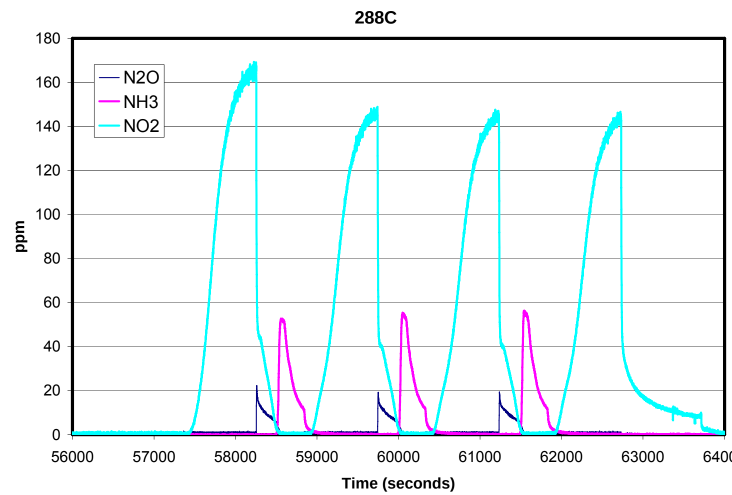



# Long cycles – low T

- $NH_3$ formation growing
- $N_2O$ release coincident with NO and $NO_2$
  - $NH_3$ after (same as cycling)
- Is such a sequence formulation dependent?
  - eg. surface Pt influence
  - facilitated reduction

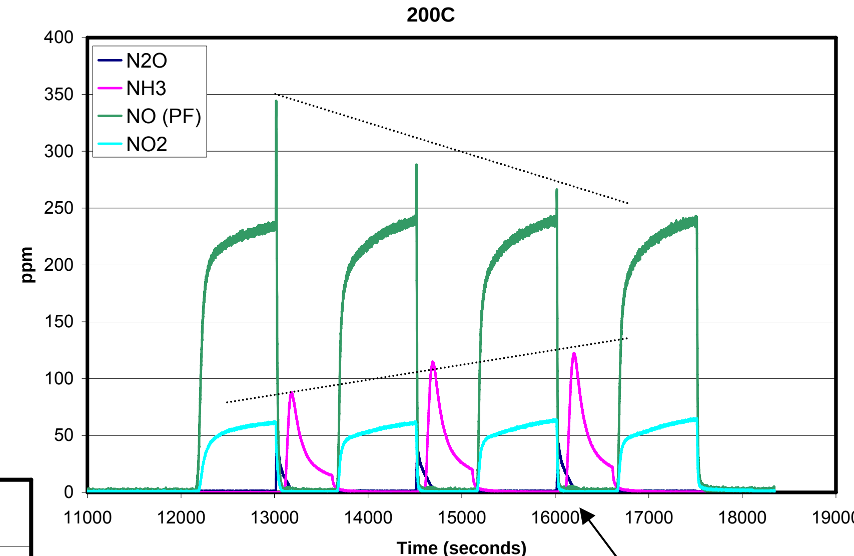


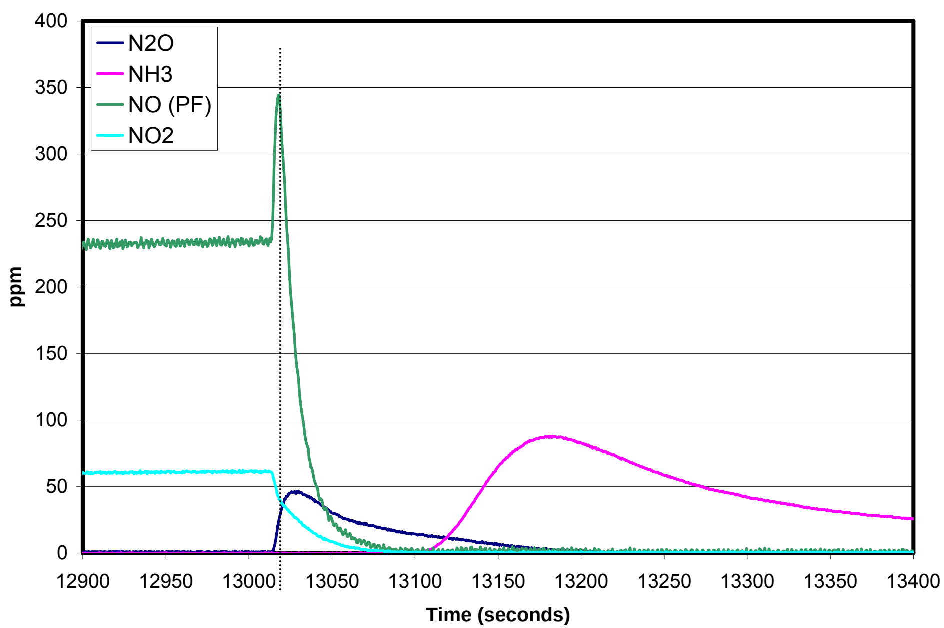



# Long cycles – 200°C

- Not at SS even after the 3 cycles – regeneration release changing

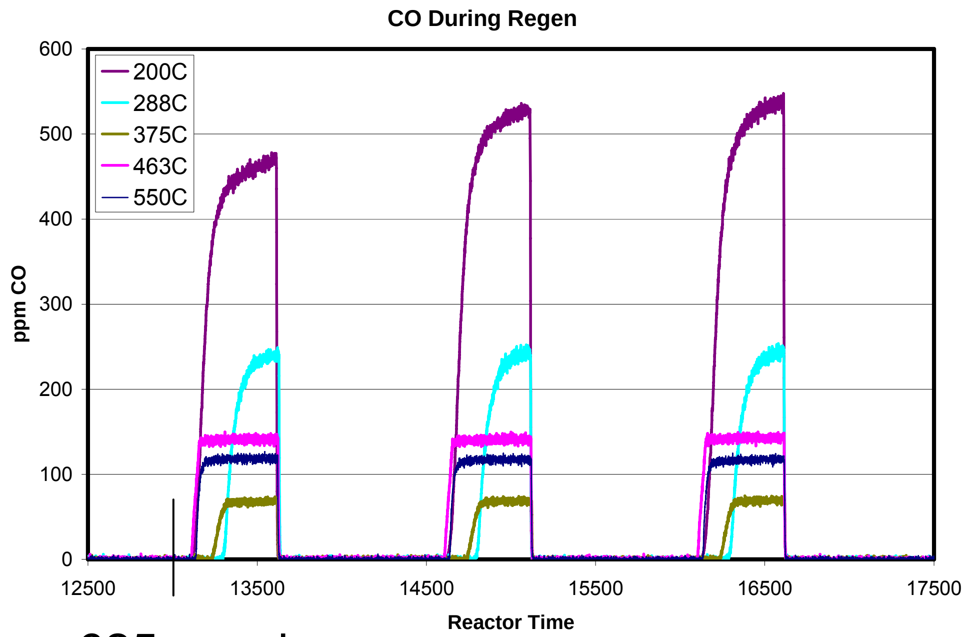



Some overlap between $N_2O$ and $NH_3$




- NO and $NO_2$ simultaneous – $N_2O$ later?

# Reductant during regen

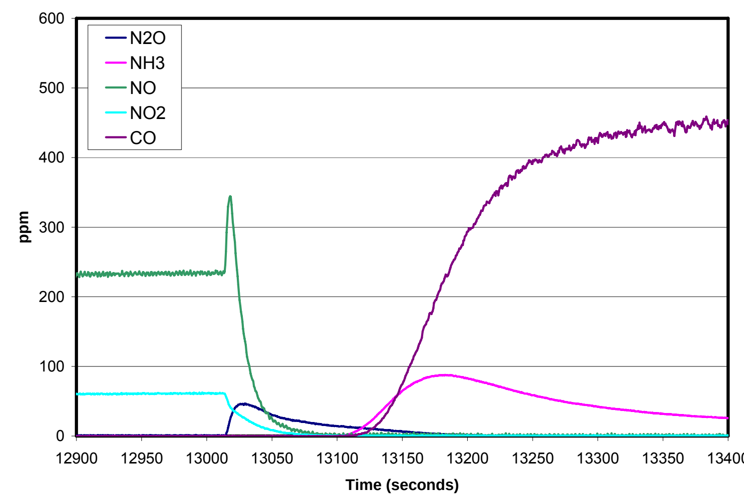



625 ppm in

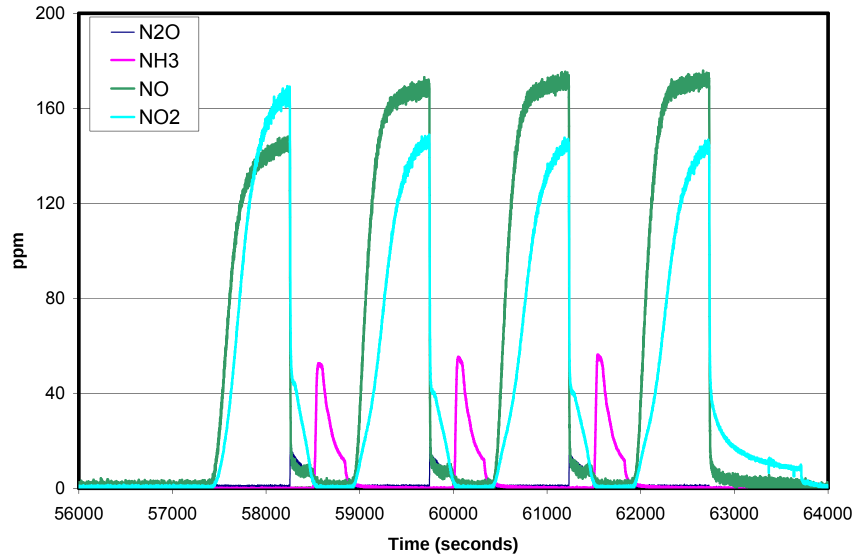
Transition as T increases

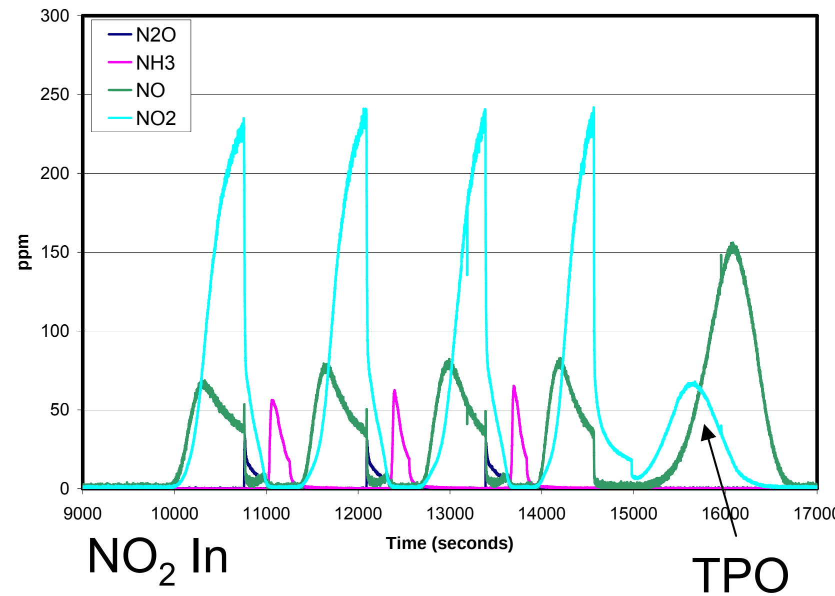
- Early usage
- Constant "use"
- OSC, $NO_X$ reduction

CO evolution coincident with $NH_3$ release!



# NO vs. $NO_2$ – 288°C

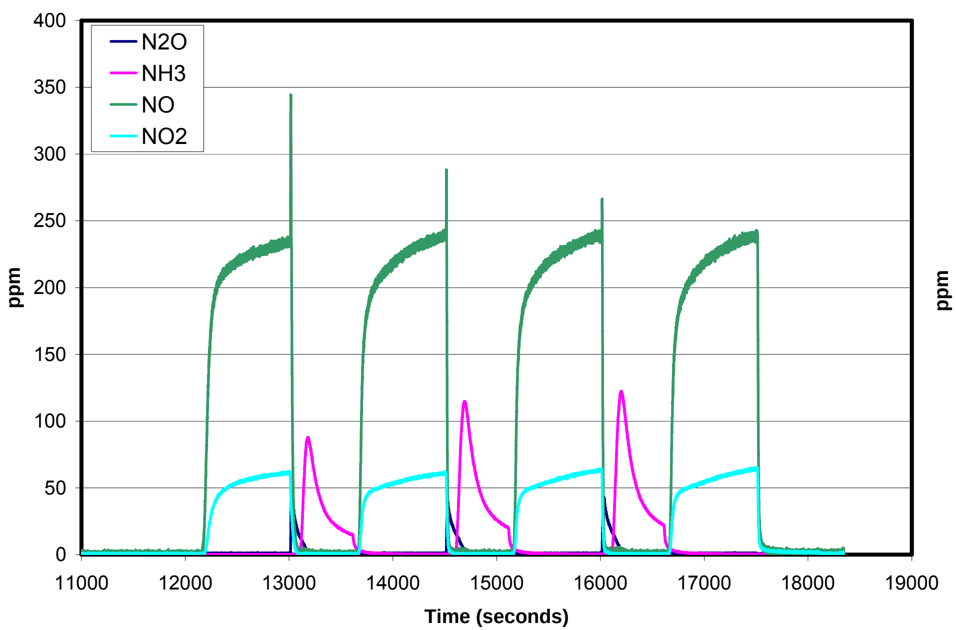


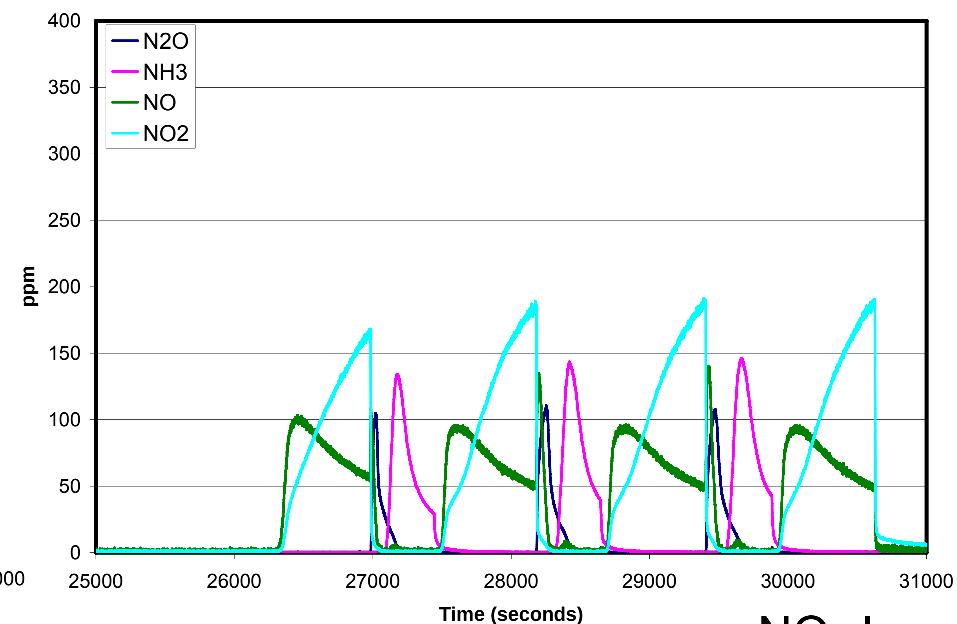




- 18.9 $cm^3$ vs. 28.6 $cm^3$
- Disproportionation mechanism more evident
  - Such data allows discrimination between disproportionation, $NO_2$ as oxidant, and $O_2$ as oxidant

# NO vs. $NO_2$ – 200°C

- 10.4 $cm^3$ vs. 29.8 $cm^3$
- Note: little change in $cm^3$ trapped between 200 and 288°C with $NO_2$ inlet (55% less with NO)
- Even with 15 minutes – chemistry not done

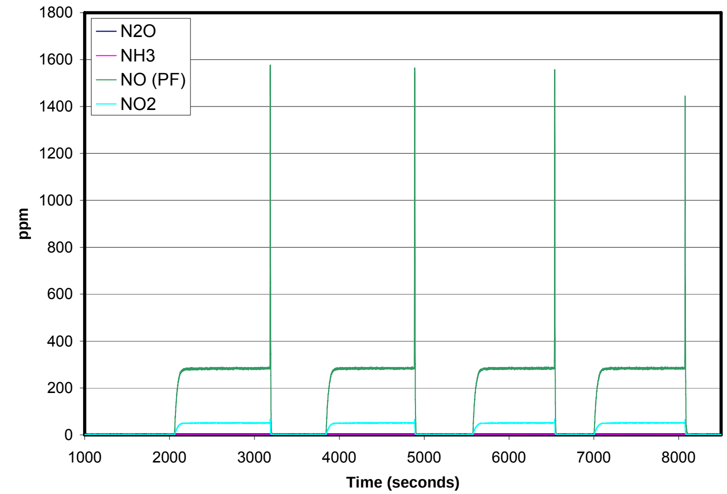


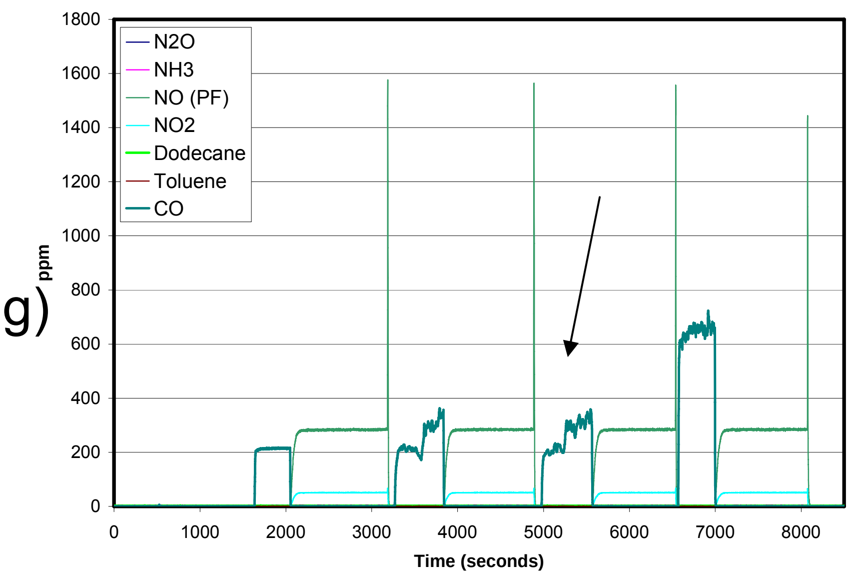

$NO_2$ In

# Long Cycle – HC reductant

- 550°C test point – same as $H_2/CO$ mixture
  - Nitrate stability



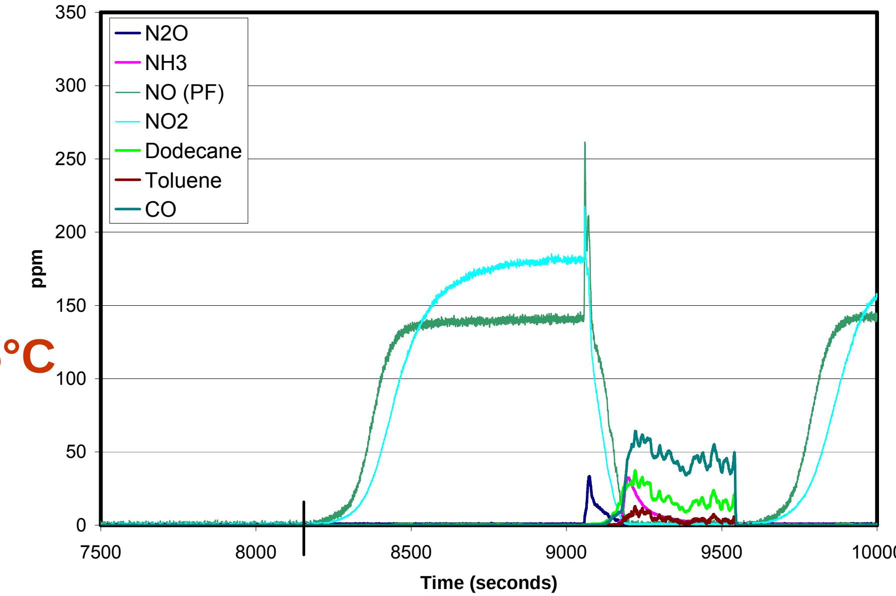

- 550°C test point
  - CO evolved
  - No HC feed seen
  - No byproducts (reforming) seen
- 470°C point similar



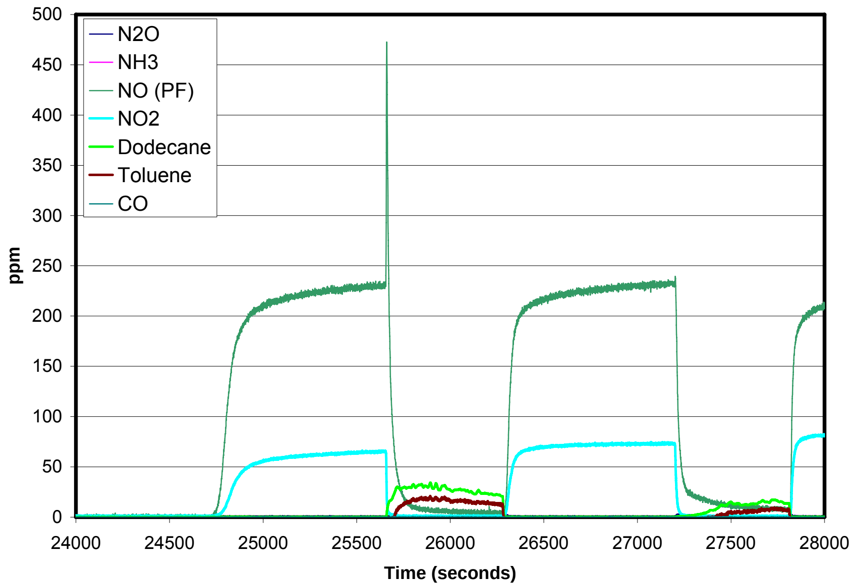
# Long Cycle – HC reductant

- Dodecane and toluene evident – as well as CO
- N byproducts – $N_2O$ prior to $NH_3$ again
  - *$NH_3$ is formed*

375°C




200°C




- Dodecane and toluene evident - no CO
- N byproducts – no $NH_3$

# Summary

- Data sets phenomenologically diverse - range of behaviors for model development
  - Predominantly reductant limited – try higher reductant levels/amount to see other limiting factors, SV effects for example
  - Need more cycles for long runs at low T
  - Need longer (more than 15 minutes) to achieve SS during long runs
- Need for tracking surface N concentration
  - Trapping and regeneration events
  - Cycle-to-cycle changes
- Need for surface oxygen/hydrocarbon interactions – OSC and HC reforming
  - Another sample with less OSC
- Need for tracking heat evolution
  - Exotherms, conduction, convection
- More to come