Kinetic and Performance Studies of the Regeneration Phase of Model Pt/Rh/Ba NOx Traps for Design and Optimization

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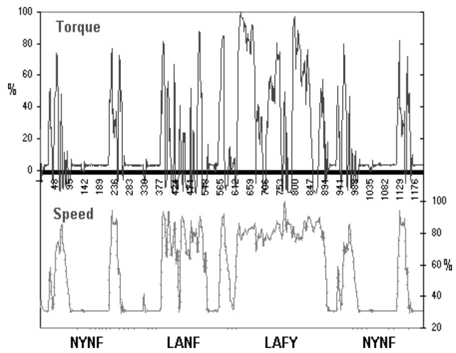
Outline

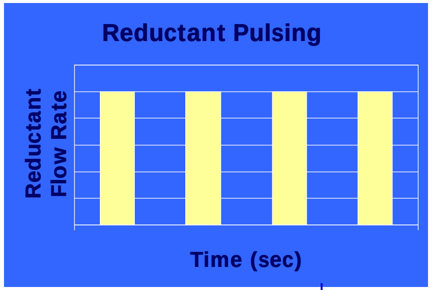
- Purpose
- Technical Barriers and Challenges
- Project Objectives
- Research Approach
- Accomplishments
- Next Steps
- Summary

Purpose of Work

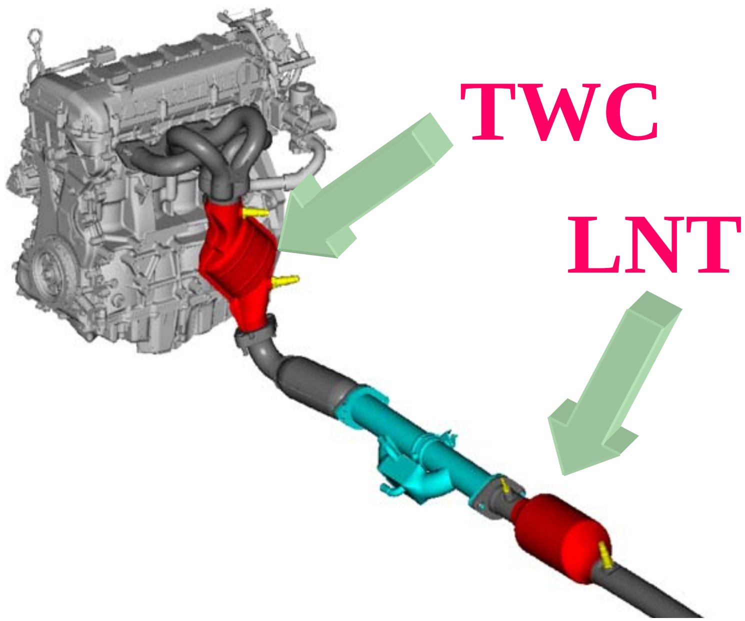
Develop, characterize, evaluate and optimize lean NOx trap catalyst and reactor designs with goal to improve the emissions performance and fuel efficiency of lean burn and diesel vehicles.

Lean NOx Trap: Adsorptive Catalytic Reactor





Engine Exhaust → LEAN NOx TRAP → Clean Exhaust



- Challenges
  - Maximize NOx conversion
  - Maximize reductant conversion
  - Minimize fuel penalty
  - Minimize deactivation
  - Achieve robust control

Major Technical Barriers & Challenges

- Lean NOx Trap: A complex periodic catalytic reactor that holds promise for lean NOx reduction in diesel exhaust
  - Transient storage & reduction produces multiple products on multi-functional catalyst
  - Reduction occurs at interface of precious metal & storage components
  - Nonlinear coupling between chemistry & transport
- *Development of a predictive LNT reactor model containing main chemistry & transport processes is critical for understanding, design, & operation*

Project Objectives

- Objective 1: *Carry out fundamental studies of the transient kinetics of LNT regeneration*
- Objective 2: *Evaluate and compare the effect of different reductants on LNT performance*
- Objective 3: *Incorporate the kinetics findings and develop and analyze a first-principles based predictive LNT model for design and optimization*
- Objective 4: *Test the new LNT designs in UH heavy-duty diesel dynamometer facility*

Research Approach

Experiments ⟷ *Modeling & Simulation*

- Lean NO_X Storage
- Steady-state lean NO_X reduction
- NO_X storage & reduction (cycling)

Transient kinetics studies (TAP)

Bench-scale Reactor Studies

Vehicle Dynamometer Testing

Implementation / Optimization of LNTs

- Develop predictive LNT models
- Optimize LNT design
- Integrate into onboard control system

Kinetic Modeling

- Micro-kinetics
- Global kinetics

Reactor Modeling

- Isothermal / short monoliths
- Non-isothermal integral monoliths

Activities

- Elucidation of data
- Bifurcation analysis

Low-dimensional models for optimization & control

Facilities Utilized in Study

- ***Bench-scale reactor system*** for atmospheric pressure steady-state & cyclic operation studies of NSR chemistries on monoliths & powders
- ***TAP reactor system*** for ultrahigh vacuum flow transient studies of NSR chemistries on powders & monoliths
- ***Catalyst characterization equipment*** for PM dispersion and particle size, surface area, etc.
- ***Computer workstations*** for microkinetic and LNT modeling studies
- ***Heavy-duty chassis dynamometer system*** for evaluation of diesel aftertreatment devices installed on vehicles (existing) and **advanced bench-scale system** utilizing exhaust side stream (under construction)

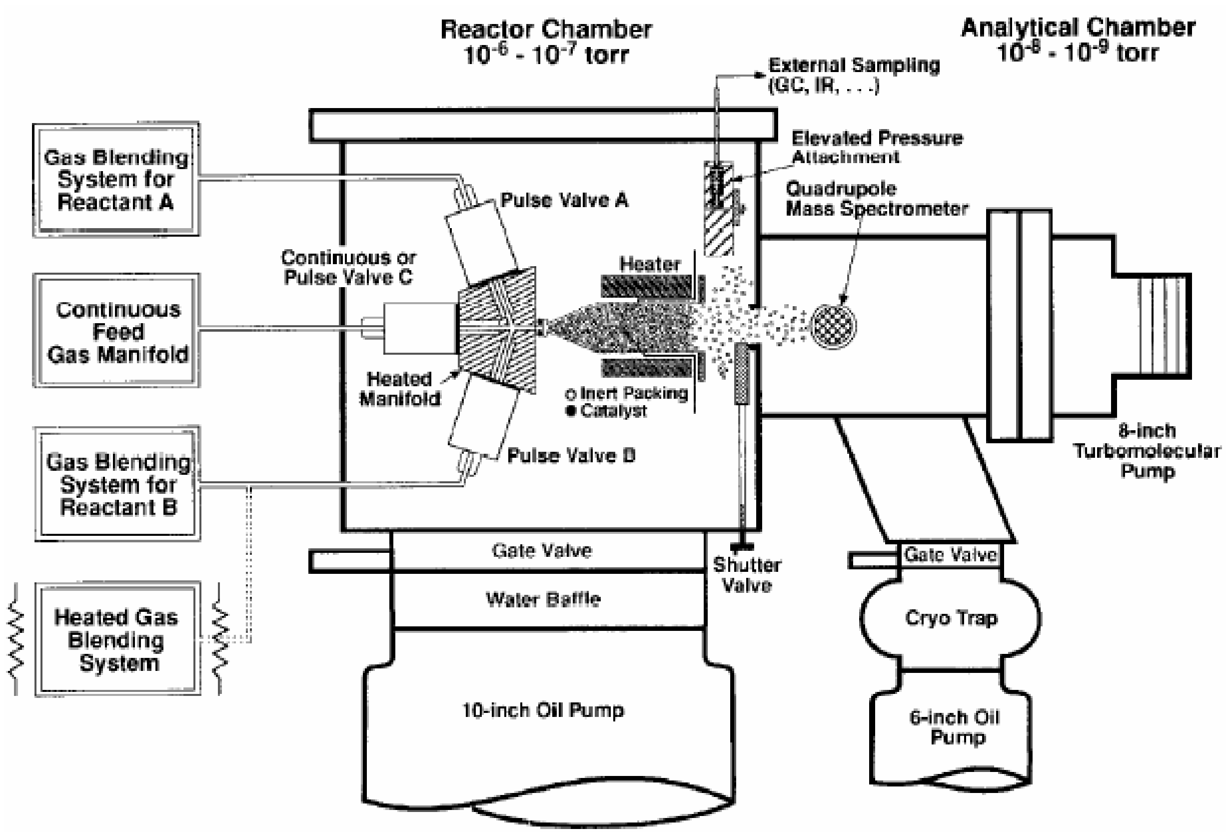
Accomplishments to Date

- TAP reactor studies
  - Carried out study of NO decomposition and NO/H_2 pump/probe on Pt/Al_2O_3 and $Pt/Ba/Al_2O_3$ catalysts
  - Developed phenomenological understanding of role of Pt/Ba coupling during storage and reduction
  - Identified conditions leading to N_2, N_2O, and NH_3 formation
  - Incorporated monolith catalyst into TAP reactor

Temporal Analysis of Products (TAP)

Advantages of TAP

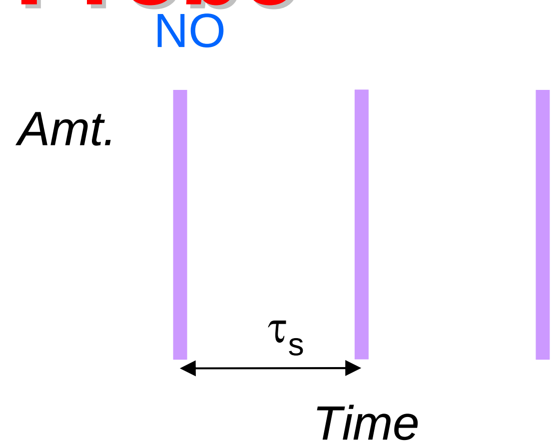
- Well characterized Knudsen diffusion
- Sub-millisecond time resolution
- Intrinsic transient kinetic measurements
- Uniform catalyst temperature



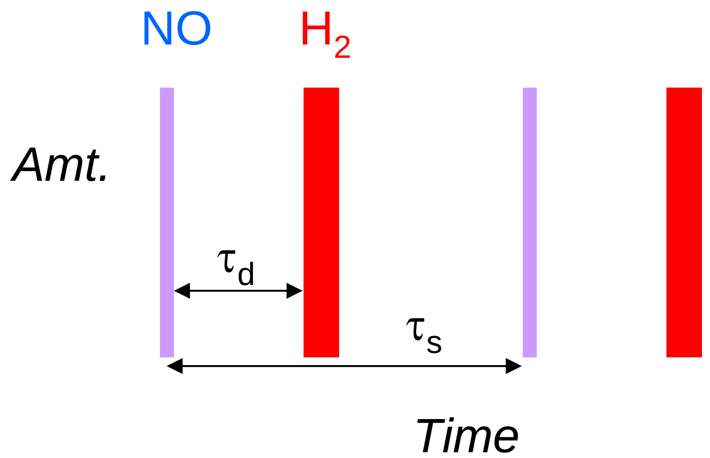
(Reference: P. Mills, DuPont)

TAP Experiments: NO Pulse & NO / H_2 Pump-Probe

- NO pulsing probes uptake & decomposition
  - Variation of pulse intensity, spacing time (τ_s)



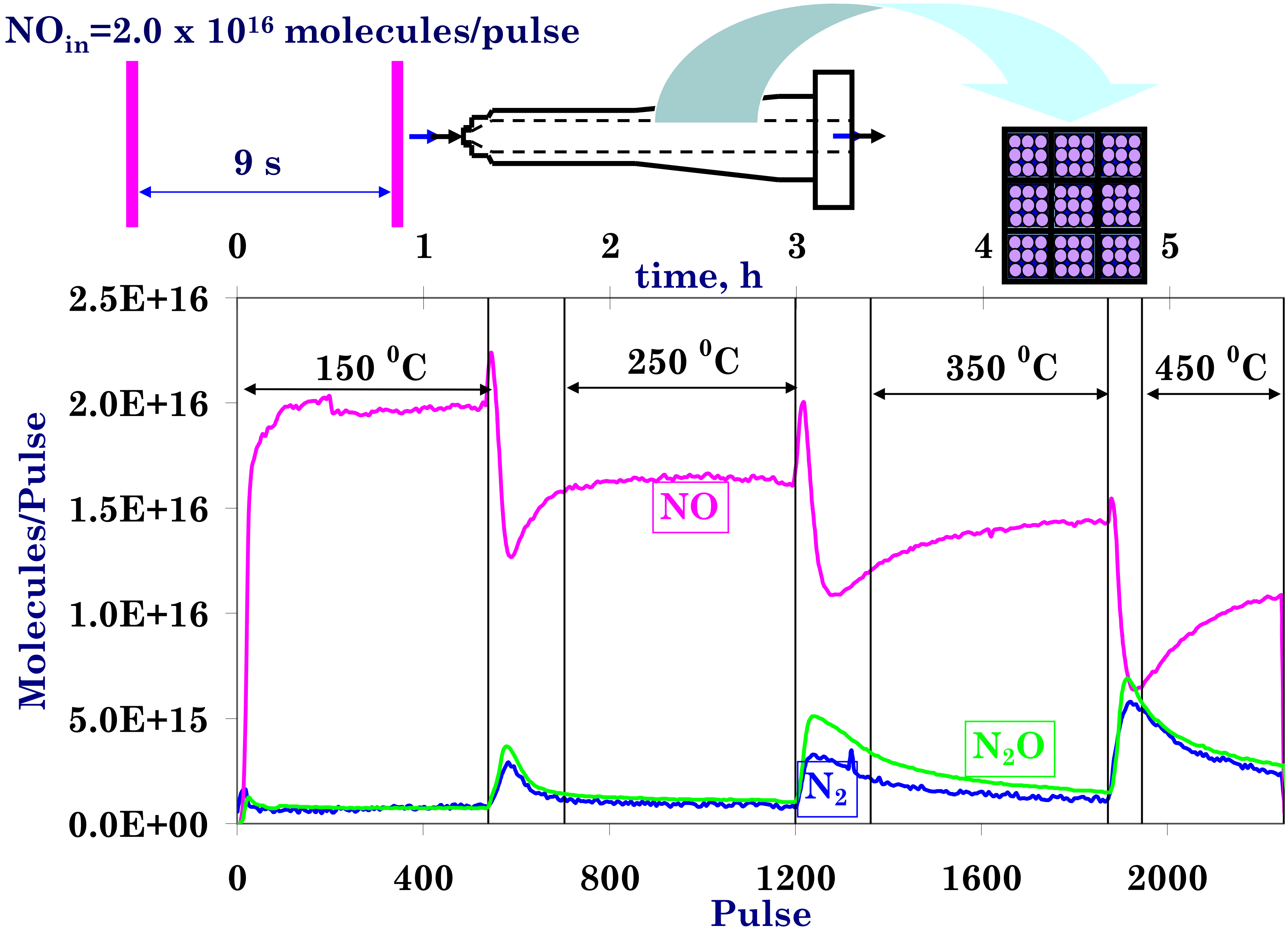
- NO and H_2 pump-probe
  - NO & H_2 pulsed alternately
  - Variation of pulse intensities, delay time (τ_d) , spacing time (τ_s)



- Feed composition*
  - Excess NO
  - Excess H_2

*Basis: $NO + H_2 \rightarrow \frac{1}{2} N_2 + H_2O$

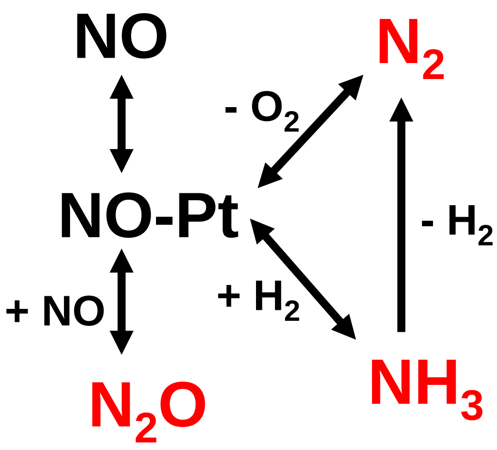
NO Pulsing Experiments on Pt / Al_2O_3



TAP Findings

- TAP studies elucidate product distribution and transient kinetics for NO + H_2 on Pt/Al_2O_3
- NH_3 and N_2O significant byproducts
- N_2O, NH_3, & N_2 selectivities depend on temperature, feed composition & pulse timing
- H_2 serves as scavenger of surface oxygen and surface nitrogen
- Micro-kinetic modeling studies ongoing to predict data trends

Mechanistic Picture of $NO + H_2$ on Pt/Al_2O_3



Mechanistic Picture of $NO + H_2$ on Pt/Al_2O_3

NO Decomposition

$NO + Pt \leftrightarrow NO-Pt$

$NO-Pt + Pt \leftrightarrow N-Pt + O-Pt$

$2\,N-Pt \leftrightarrow N_2 + 2\,Pt$

$NO\text{-}Pt + N\text{-}Pt \leftrightarrow N_2O + 2\,Pt$

$2\,NO\text{-}Pt \leftrightarrow N_2O + O-Pt + Pt$

H_2 Oxidation

$H_2 + 2\,Pt \leftrightarrow 2\,H\text{-}Pt$

$H-Pt + O-Pt \leftrightarrow HO\text{-}Pt + Pt$

$H-Pt + HO-Pt \leftrightarrow H_2O + 2\,Pt$

NH_3 Formation

$H-Pt + NO-Pt \leftrightarrow HO\text{-}Pt + N\text{-}Pt$

$H-Pt + N-Pt \leftrightarrow NH-Pt$

$H-Pt + NH-Pt \leftrightarrow NH_2-Pt + Pt$

$H-Pt + NH_2-Pt \leftrightarrow NH_3-Pt + Pt$

$NH_3-Pt \leftrightarrow NH_3 + Pt$

NH_3 Decomposition

NO-Pt; NO; N_2; $-O_2$; N_2O; +NO; $+H_2$; NH_3; $-H_2$

Mechanistic Picture of $NO + H_2$ on Pt/Ba/Al_2O_3

NO Decomposition

$NO + Pt \leftrightarrow NO-Pt$

$NO-Pt + Pt \leftrightarrow N-Pt + O-Pt$

$2\,N-Pt \leftrightarrow N_2 + 2\,Pt$

$NO\text{-}Pt + N\text{-}Pt \leftrightarrow N_2O + 2\,Pt$

$2\,NO\text{-}Pt \leftrightarrow N_2O + O-Pt$

Storage Chemistry

$NO + O_2 \rightarrow NO_2$

$3NO_2 + BaO \rightarrow Ba(NO_3)_2 + NO$

H_2 Oxidation

$H_2 + 2\,Pt \leftrightarrow 2\,H\text{-}Pt$

$H-Pt + O-Pt \leftrightarrow HO\text{-}Pt + Pt$

$H-Pt + HO-Pt \leftrightarrow H_2O + 2\,Pt$

NH_3 Formation

$H-Pt + NO-Pt \leftrightarrow HO\text{-}Pt + N\text{-}Pt$

$H-Pt + N-Pt \leftrightarrow NH-Pt$

$H-Pt + NH-Pt \leftrightarrow NH_2-Pt + Pt$

$H-Pt + NH_2-Pt \leftrightarrow NH_3-Pt + Pt$

NH_3 Decomposition

$NH_3-Pt \leftrightarrow NH_3 + Pt$

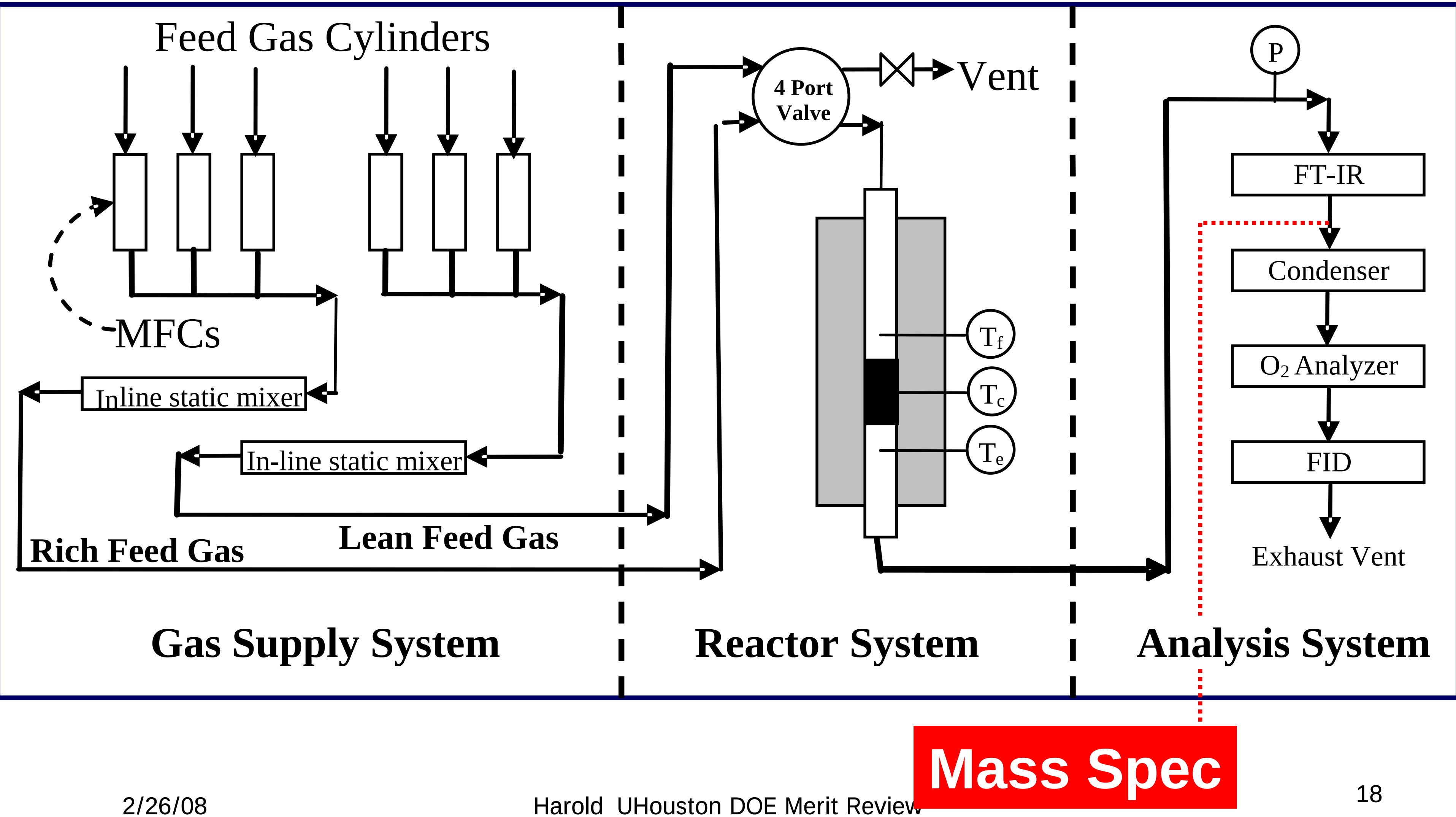
Pt/BaO Interface

Stored NOx spillover $Ba(NO_3)_2 + 4\,Pt \leftrightarrow 2\,NO\text{-}Pt + BaO_2 + 2\,O-Pt$

Accomplishments to Date, cont.

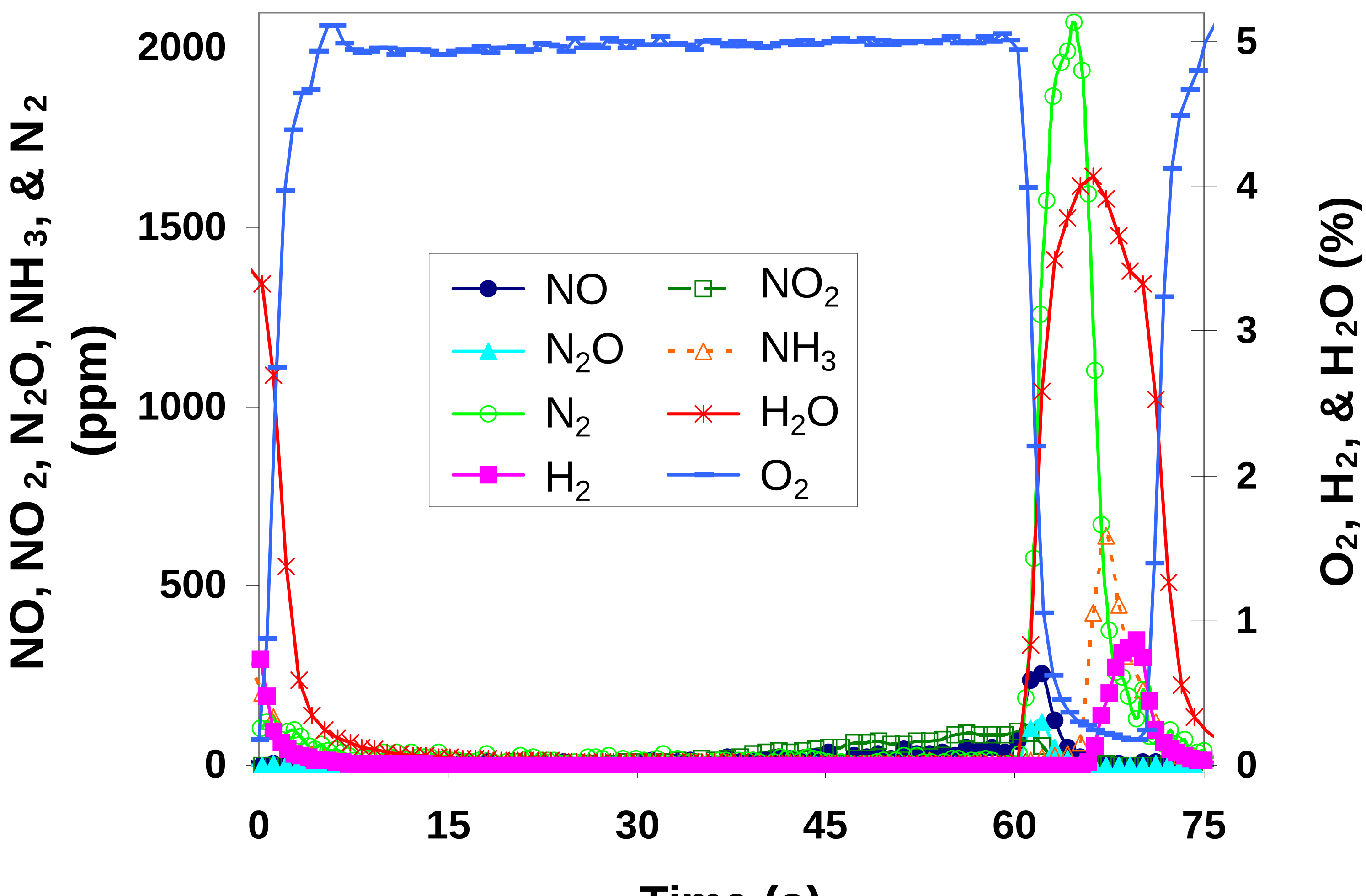
- Bench-scale reactor studies
  - Comprehensive study of *steady-state* operation using H_2 as reductant on model Pt/Al_2O_3, $Pt/BaO/Al_2O_3$, and BaO/Al_2O_3 catalysts
    - Identified major reaction pathways to N_2, N_2O, and NH_3
    - Compared activity of Pt, Pt/BaO and BaO
    - Provided basic data for development of microkinetic model
  - Comprehensive study of *cyclic* operation with H_2 as reductant on Pt/Al_2O_3 , $Pt/BaO/Al_2O_3$, BaO/Al_2O_3 catalysts
    - Quantified cycle-averaged conversions & and selectivities as function of feed composition. lean/rich cycling, and temperature
    - Conducted varied-length reactor experiments to determine how ammonia is formed and consumed
    - Provided basic data for evaluation of transient lean NOx trap

Bench-Scale Reactor System



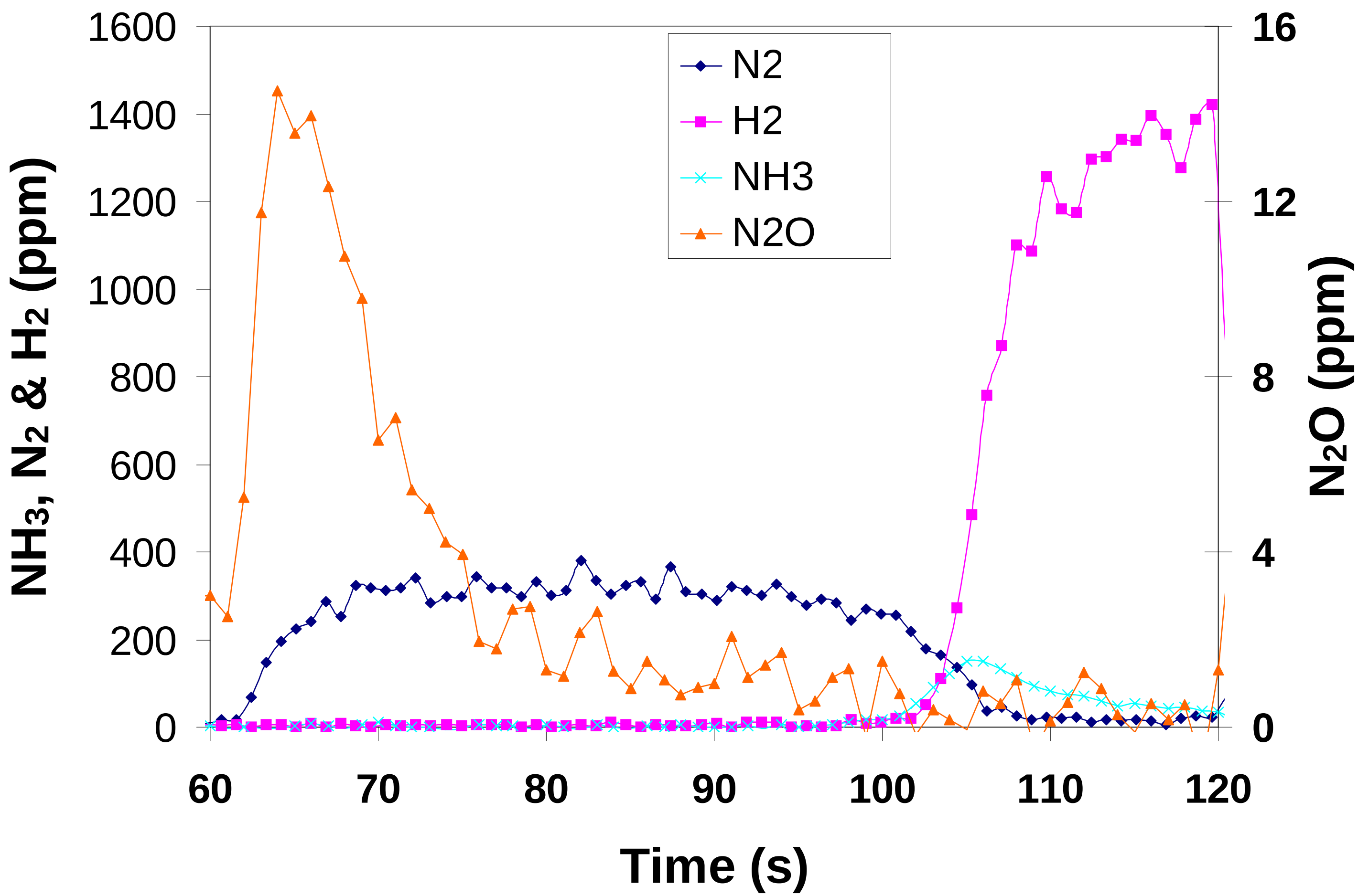
Effluent Composition versus Time: Storage and Reduction

Lean: 500 ppm NO and 5% O_2 (60s); **Rich:** 4.3% H_2 1.5% O_2 $S_{N,p}$ = 0.7 (10s)

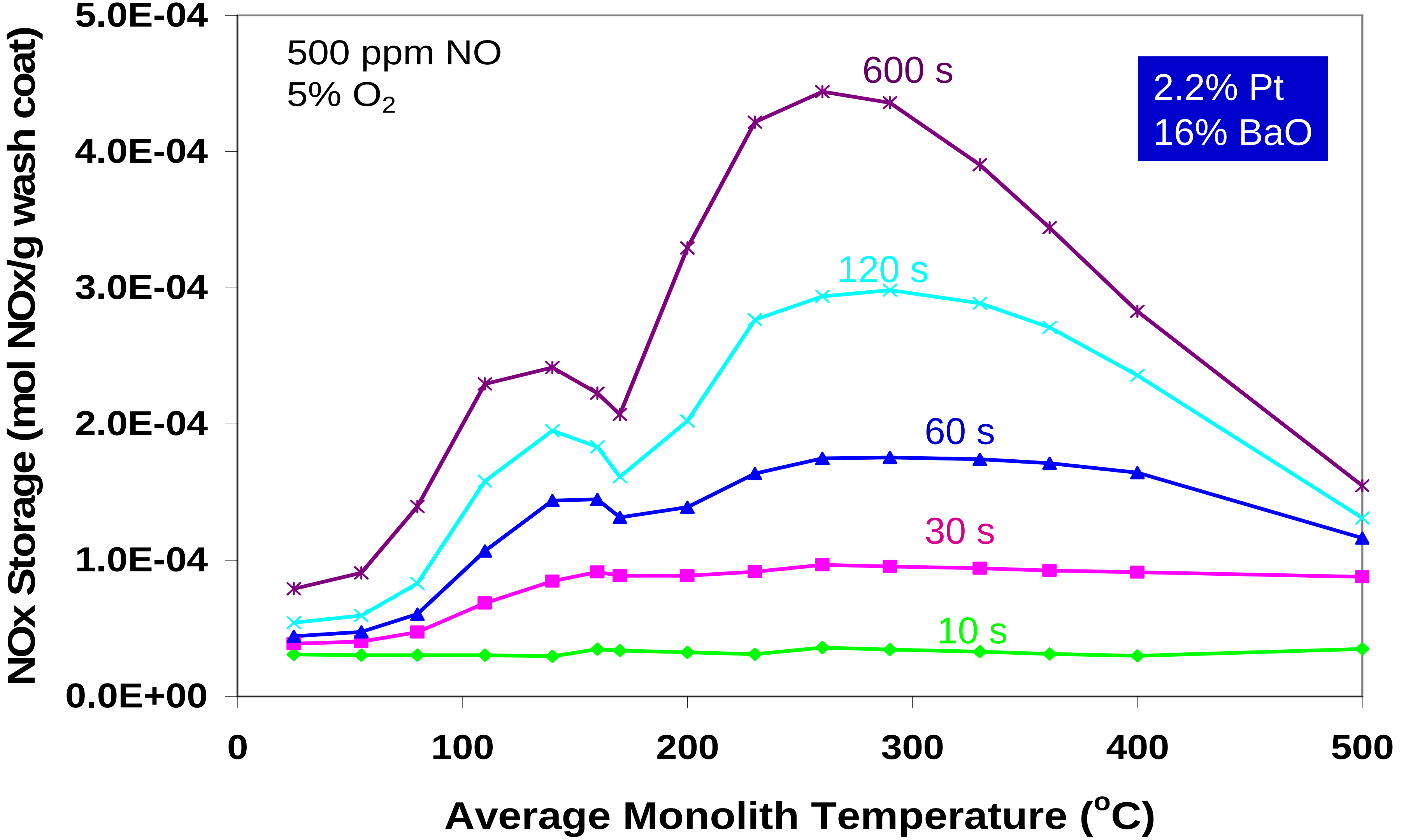


Regeneration of Stored NOx: Effluent Composition versus Time

- Lean: 500 ppm NO and 5% O_2 (60s);
- Rich: 0.15% H_2 (60s)

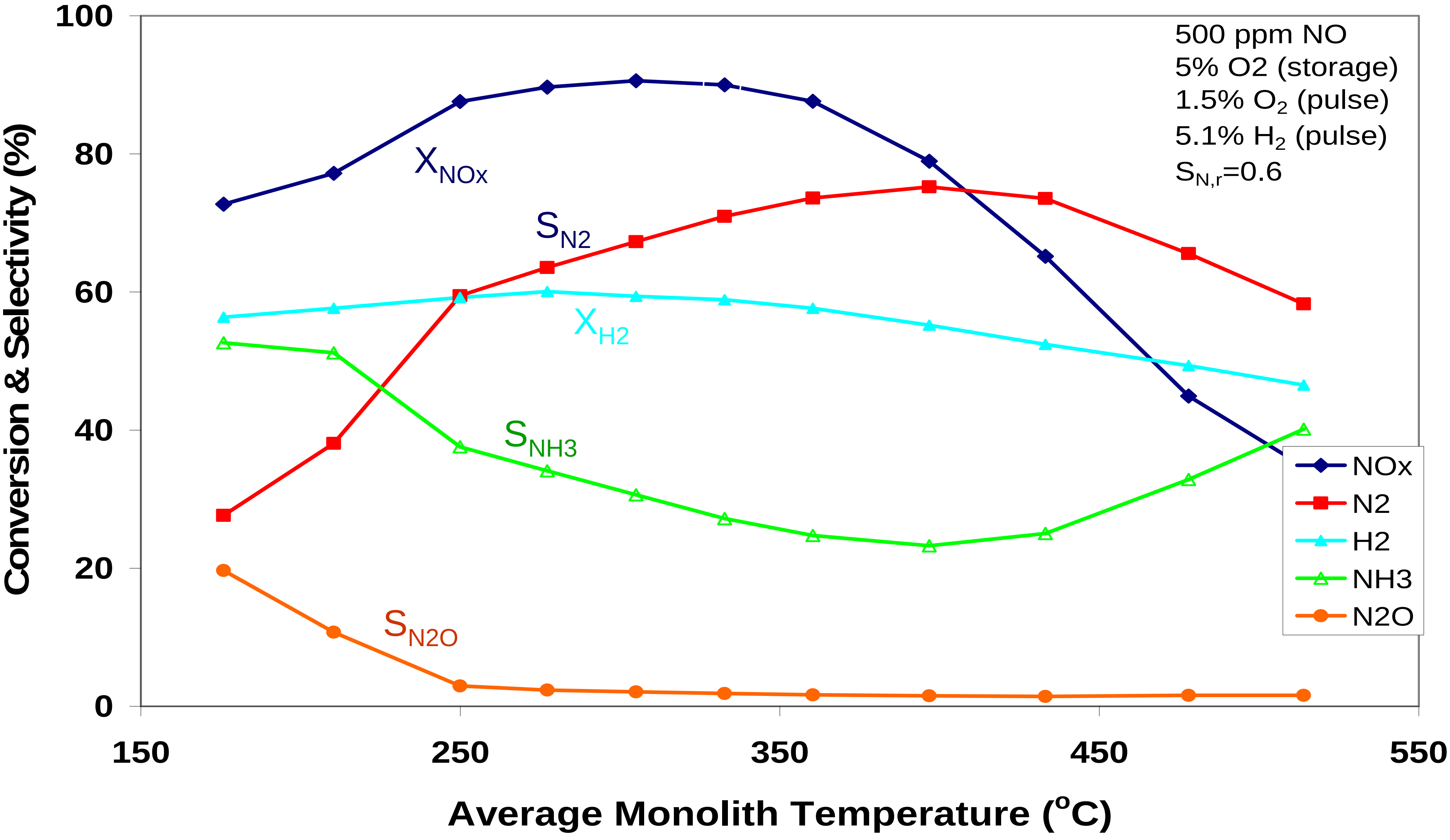


NOx Storage



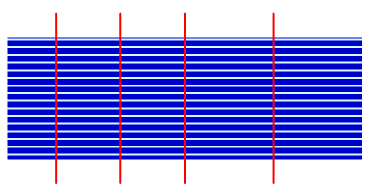
500 ppm NO
5% O_2
600 s
120 s
60 s
30 s
10 s
2.2% Pt
16% BaO
NOx Storage (mol NOx/g wash coat)
5.0E-04
4.0E-04
3.0E-04
2.0E-04
1.0E-04
0.0E+00
0
100
200
300
400
500
Average Monolith Temperature (^oC)

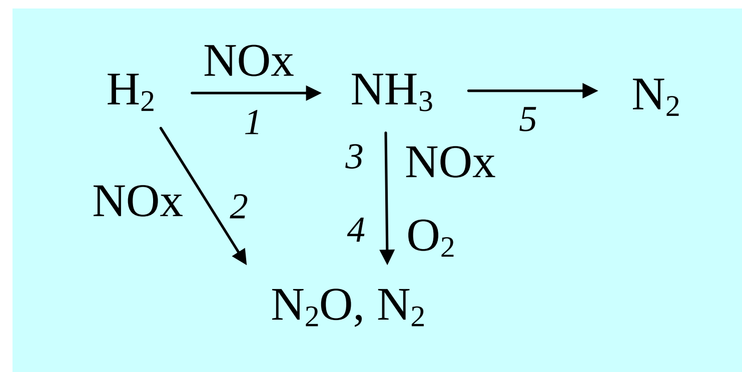
Cycle-Averaged Results

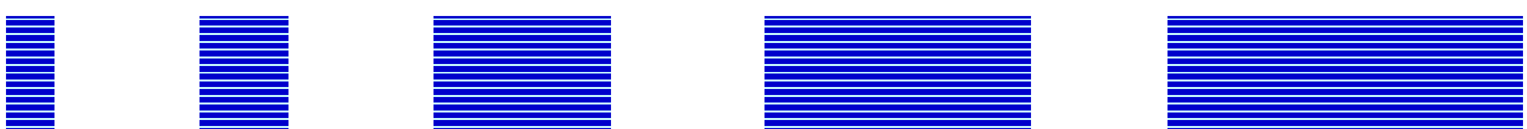


Varied Monolith Length Experiments

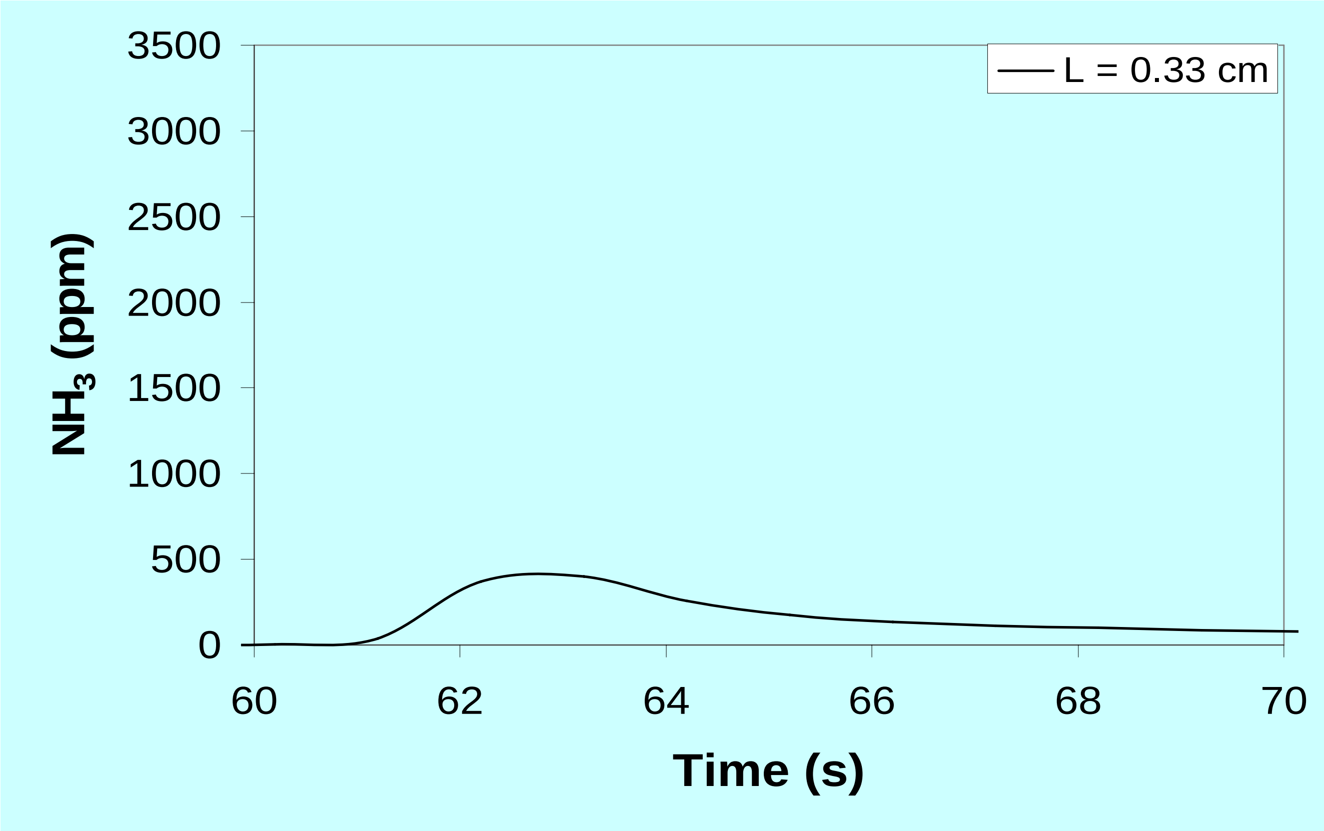
- Approach
  - Divide original monolith into progressively smaller sections
  - Replicate experiments to generate spatio-temporal concentration profiles



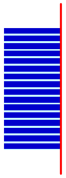




Effect of Length on Ammonia Production: Aerobic Pulse



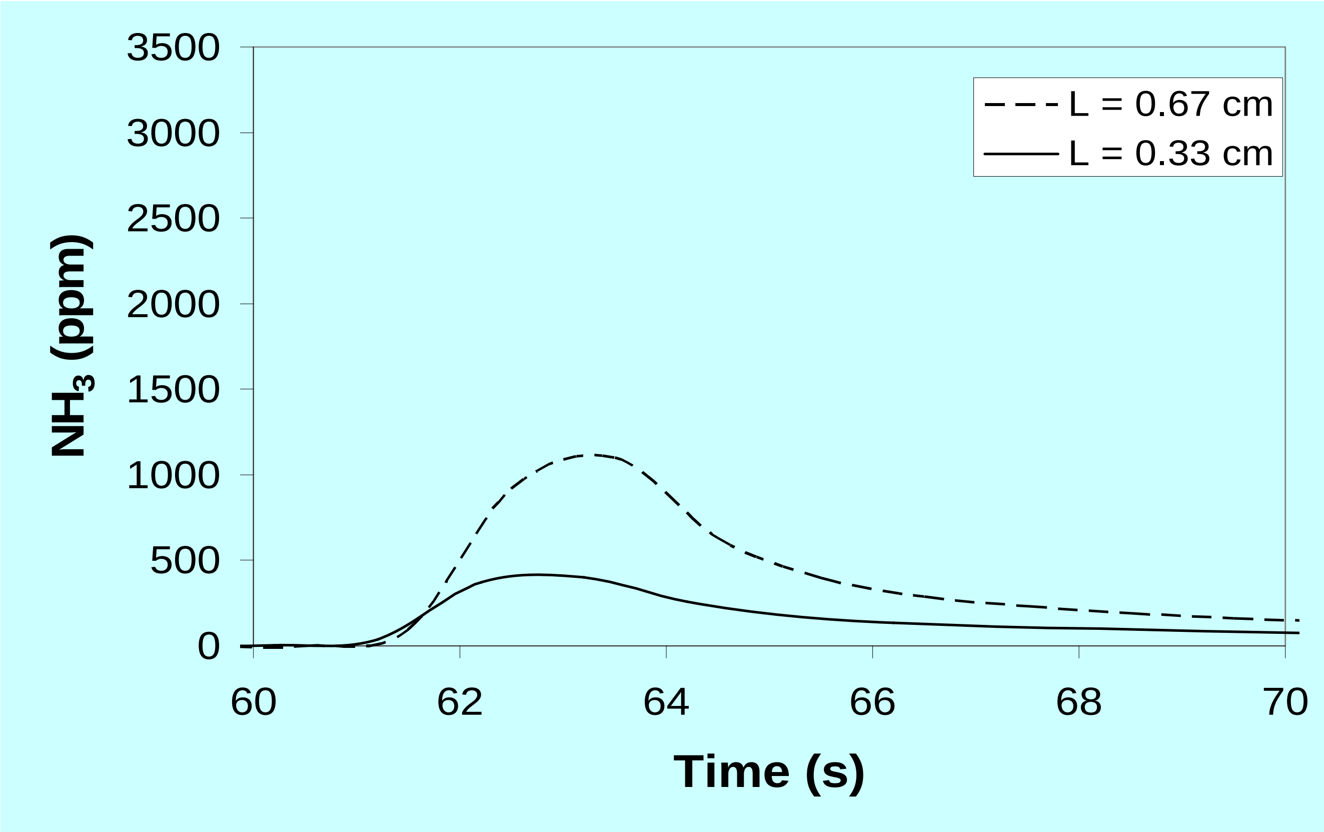
(T_f = 100 ºC)



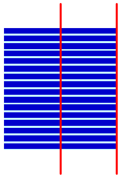
Lean: 500 ppm NO and 5% O_2 (60s);

Rich: 4.35% H_2 and 1.5% O_2 (10s); $S_{N,P}$=0.7

Effect of Length on Ammonia Production: Aerobic Pulse



(T_f = 100 ^{o}C)



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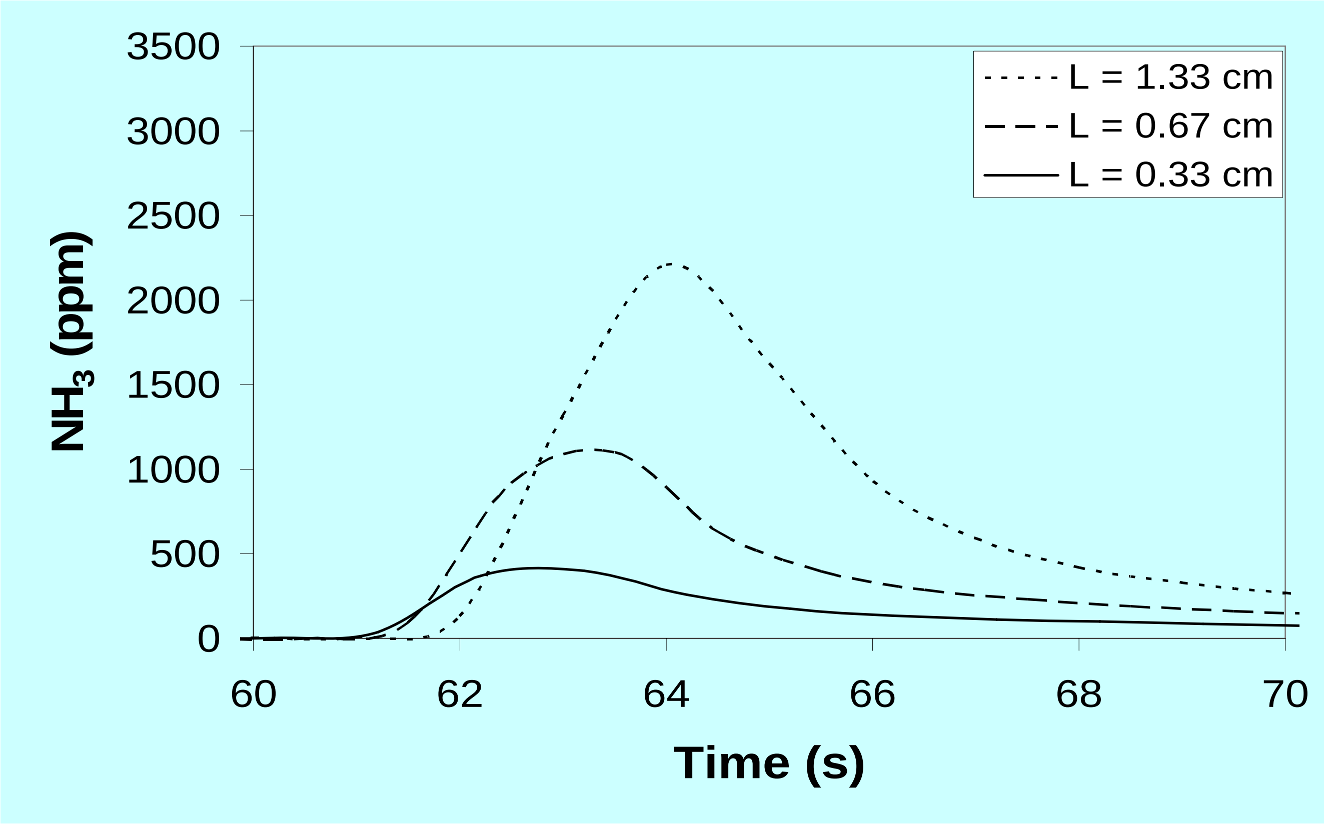
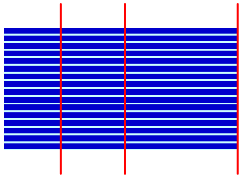


(T_f = 100 ^{o}C)



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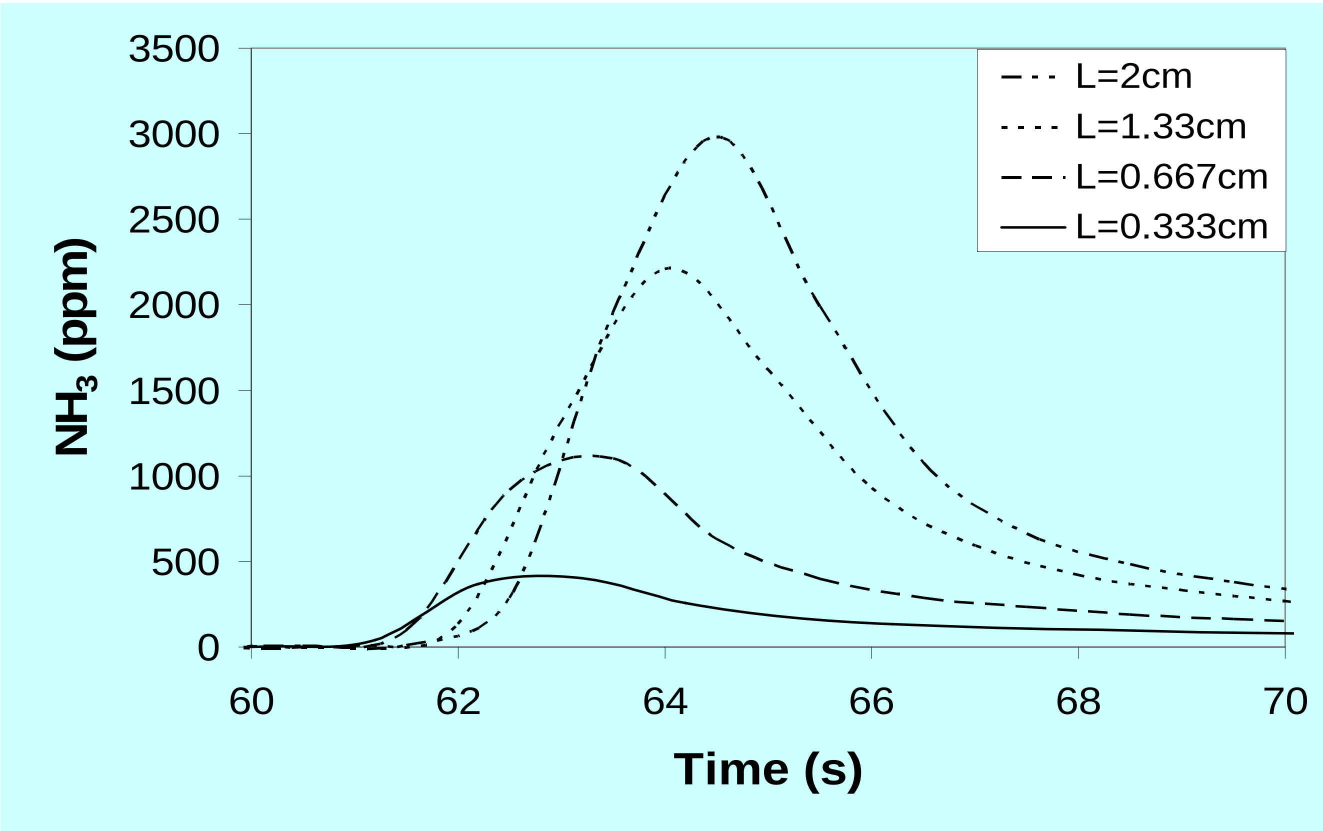
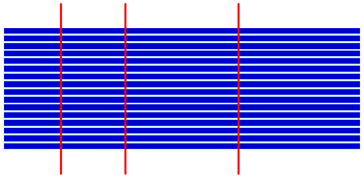


(T_f = 100 ^oC)



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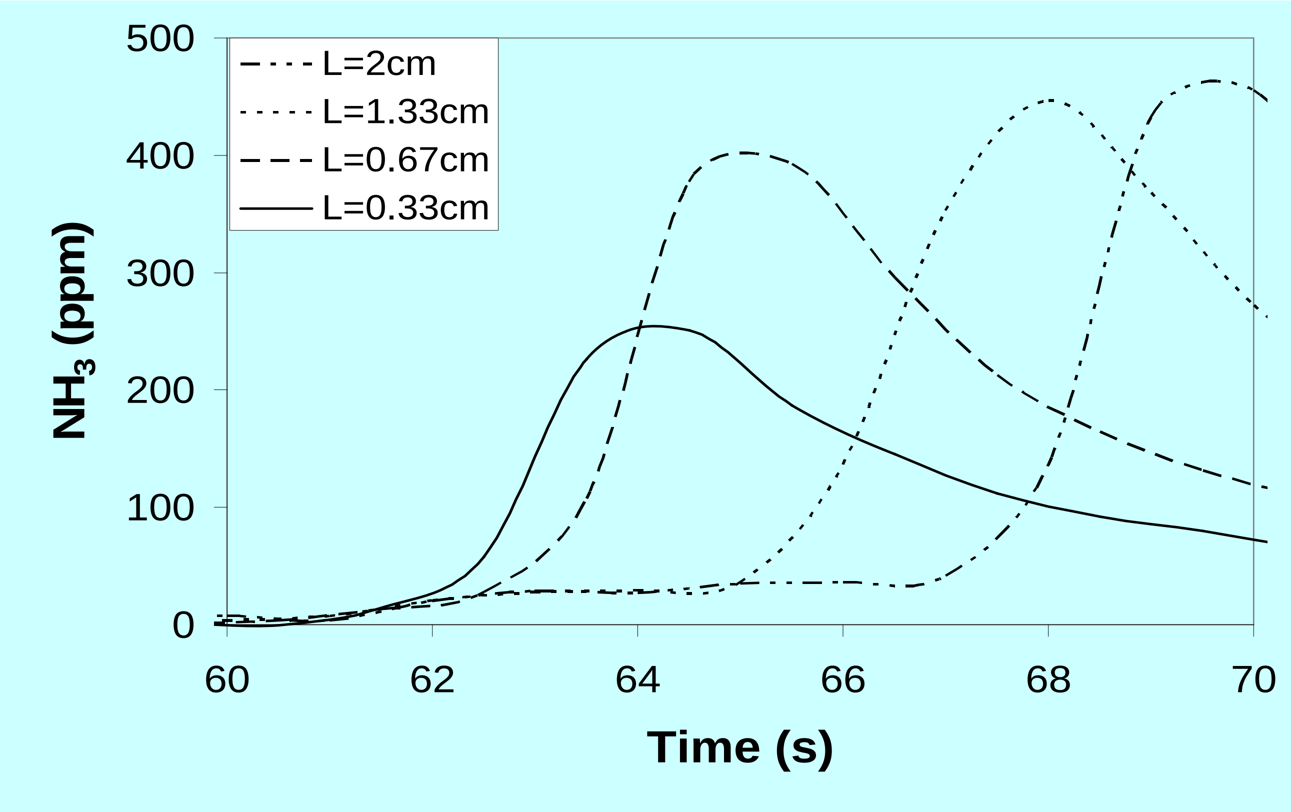
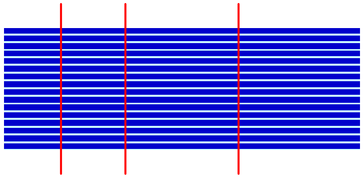
Effect of Length on Ammonia Production: Aerobic Pulse



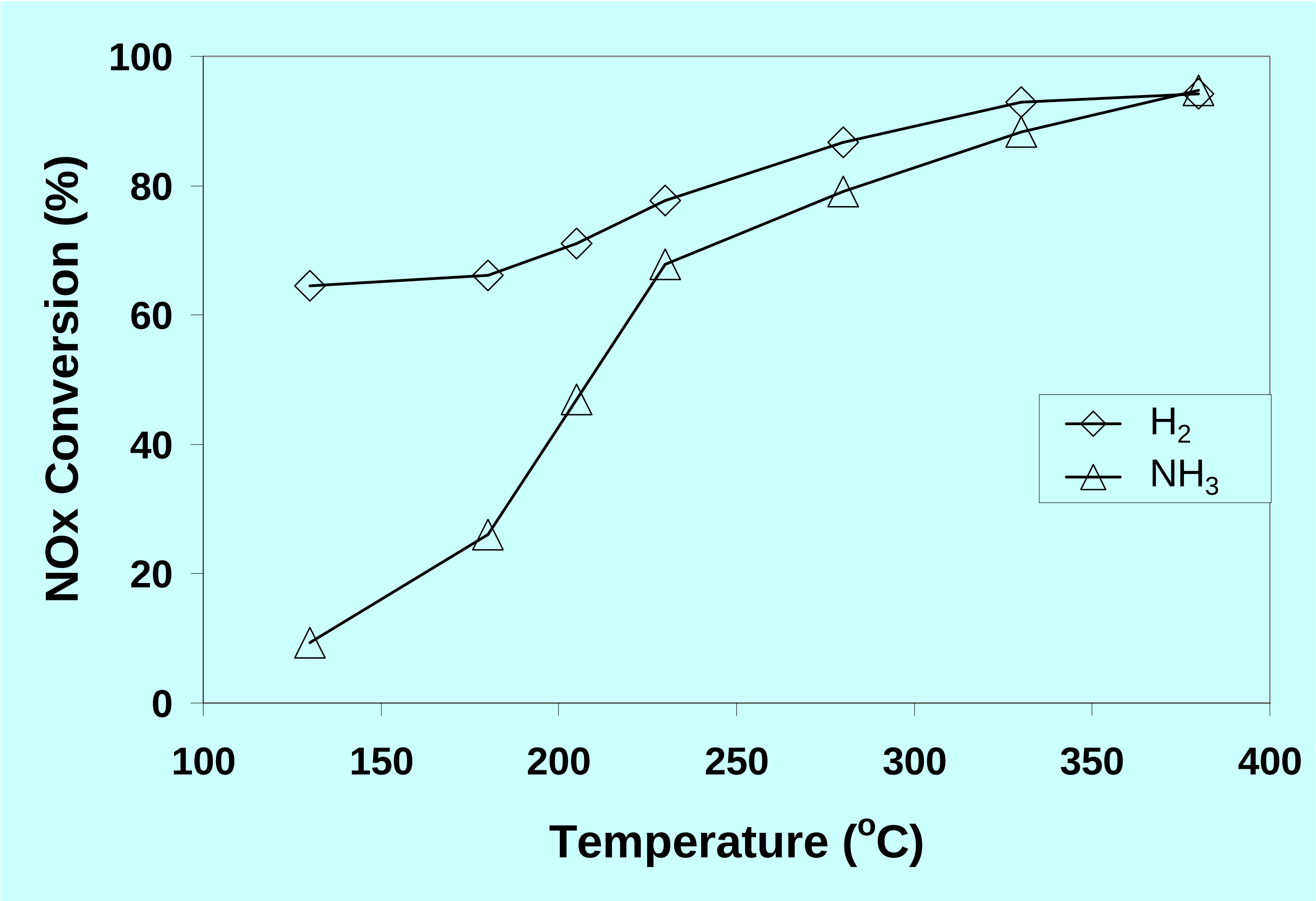
$(T_f = 320\ ^oC)$



Lean: 500 ppm NO and 5% O_2 (60s);

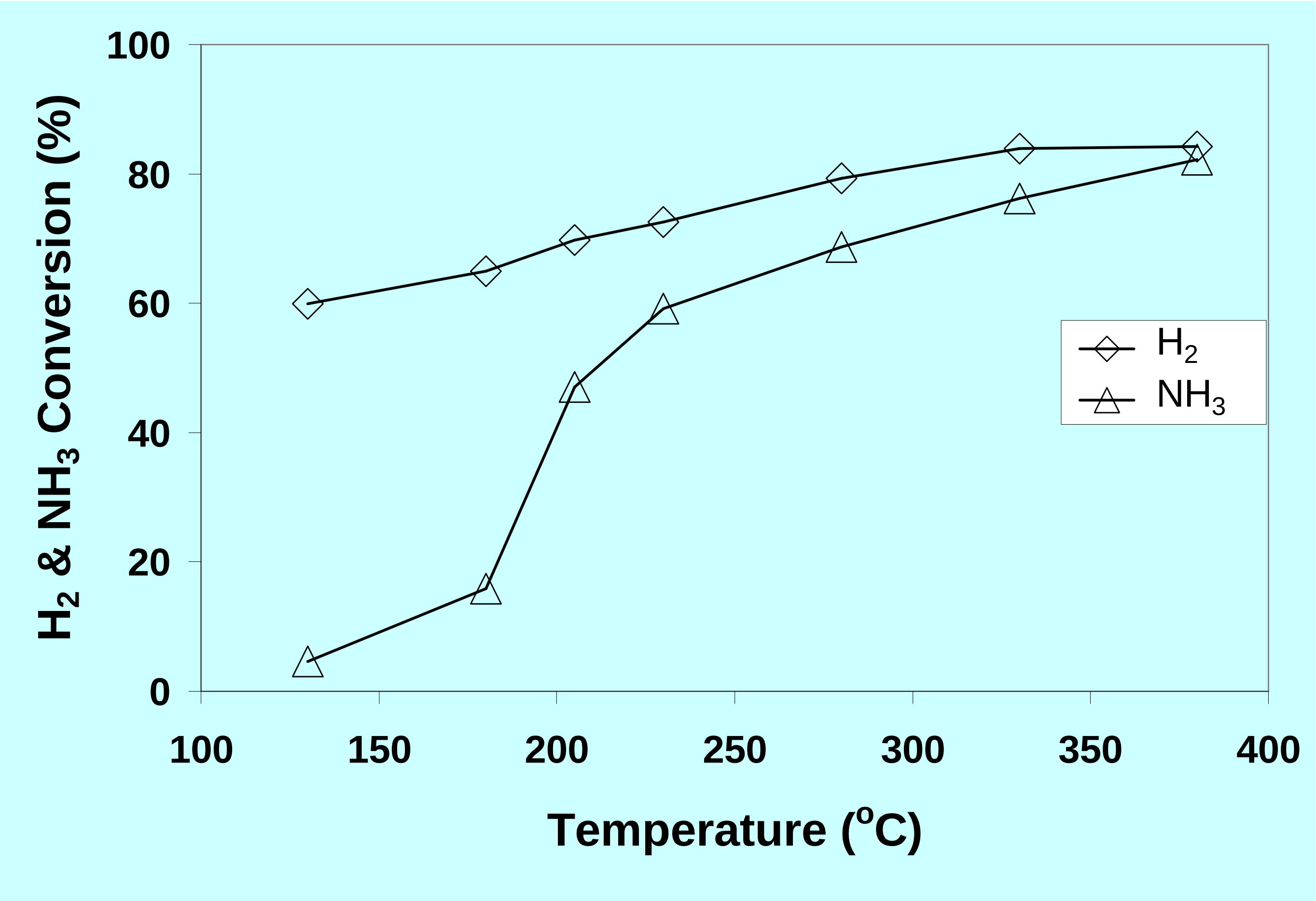
Rich: 4.35% H_2 and 1.5% O_2 (10s); $S_{N,P}$=0.7

Rapid Pulsing Experiments



- Lean: 500 ppm NO and 5% O_2 (60s);
- Rich: 4% H_2 or 2.67% NH_3 (3.33s);

Rapid Pulsing Experiments

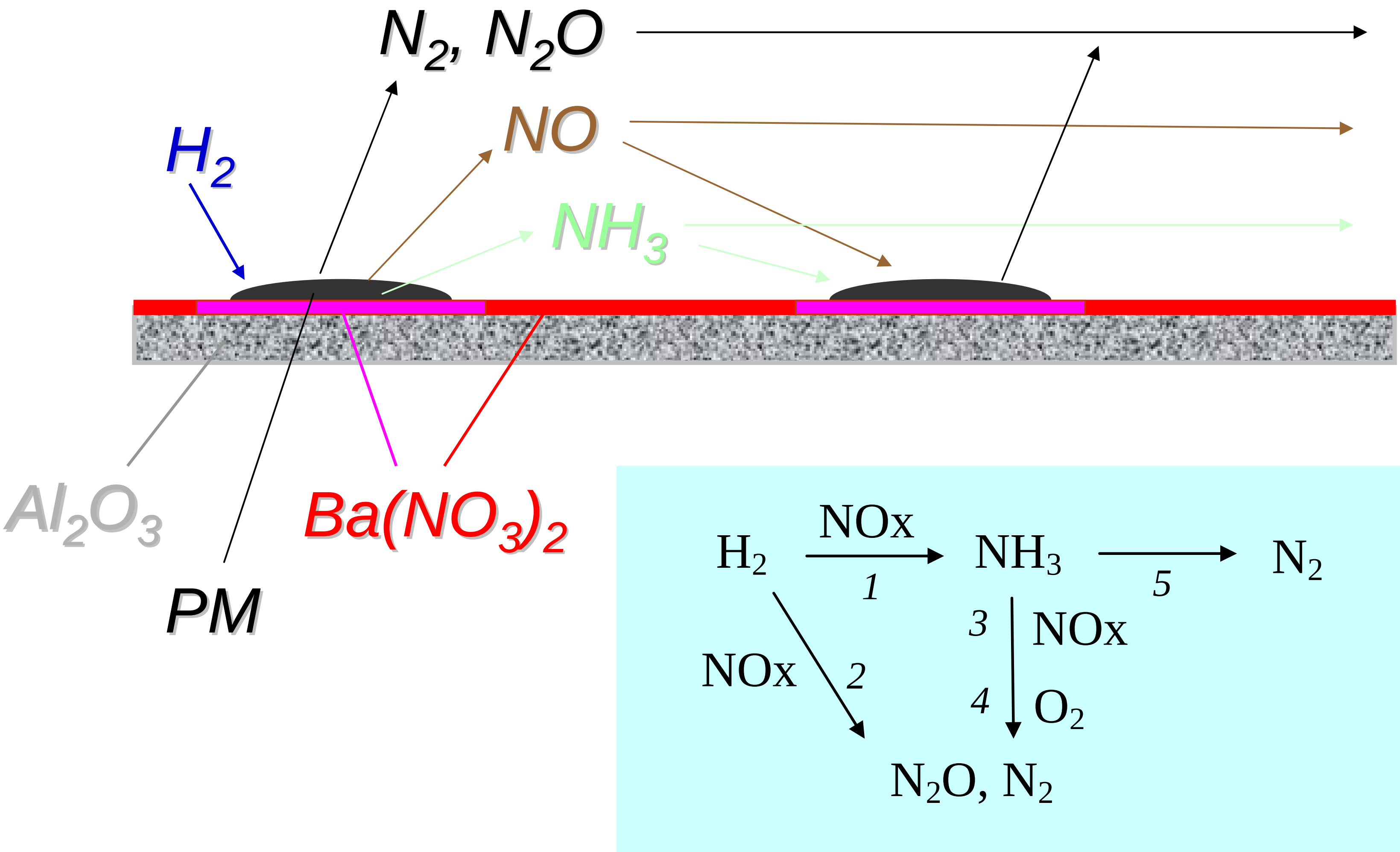


- Lean: 500 ppm NO and 5% O_2 (60s);
- Rich: 4% H_2 or 2.67% NH_3 (3.33s);

Summary ($NO/H_2/NH_3$ System)

- H_2 and NH_3 serve as reductants during NSR
  - H_2 is a superior reductant under steady-state conditions and below 380 ºC during cycling
- Formation of N_2 can occur through four different reaction routes; two primary routes
  - Direct : $H_2 + NOx \rightarrow N_2$
  - Indirect: $H_2 + NOx \rightarrow NH_3$ and $NH_3 + NOx \rightarrow N_2$
- Regeneration initially feed rate limited by H_2
- Rate limiting step switches from a feed rate limited state to one in which the supply of NOx from the storage phase to Pt is limiting

Picture of NSR With H_2 as Reductant



Accomplishments to Date, cont.

- Kinetic & Reactor Modeling
  - Microkinetic modeling
    - Developed microkinetic model for H_2/NO/O_2 on Pt based on TAP & bench-scale data trends
    - Incorporated microkinetic model into TAP model simulation for further upgrading
  - NOx trap reactor modeling
    - Incorporated NO oxidation and storage with propylene as reductant; simulated multiple states during steady state & cyclic operation
    - Incorporated microkinetic model into short monolith model; predicted most features of steady-state H_2/NO on Pt from bench-scale study

LNT Monolith Model Features

Fluid Phase

Mass balances ***(for species j)***

$$\frac{\partial X_{jm}}{\partial t} + \bar{u}_f \frac{\partial X_{jm}}{\partial Z} = -k_{jc} \frac{1}{R_\Omega}(X_{jm} - X_{js})$$

Energy Balance

$$\rho_f c_{pf} \left(\frac{\partial T_m}{\partial t} + \bar{u}_f \frac{\partial T_m}{\partial Z} \right) = -h_f \frac{1}{R_\Omega}(T_m - T_s)$$

Solid Phase

Surface balances ***(for species j on site i)***

$$C_i \frac{\partial \theta_{ji}}{\partial t} = R^j{}_{adi} - R^j{}_{dei} - \sum \nu_j R_{rxn}$$

Energy Balance

$$\delta_W \rho_W c_{pW} \frac{\partial T_s}{\partial t} = \delta_W k_W \frac{\partial^2 T_s}{\partial Z^2} - h_f (T_s - T_m) + \delta_c \left((-\Delta H_{rxn}) R_{rxn} \right)_{Pt}$$

Interphase

$$C_o k_{jc} (X_{jm} - X_{js}) = \delta_c (R^j{}_{ad} - R^j{}_{de})_{BaO} + \delta_c (R^j{}_{ad} - R^j{}_{de})_{Pt}$$

Site Balance

$$\sum \theta_{ji} + \theta_{vi} = 1$$

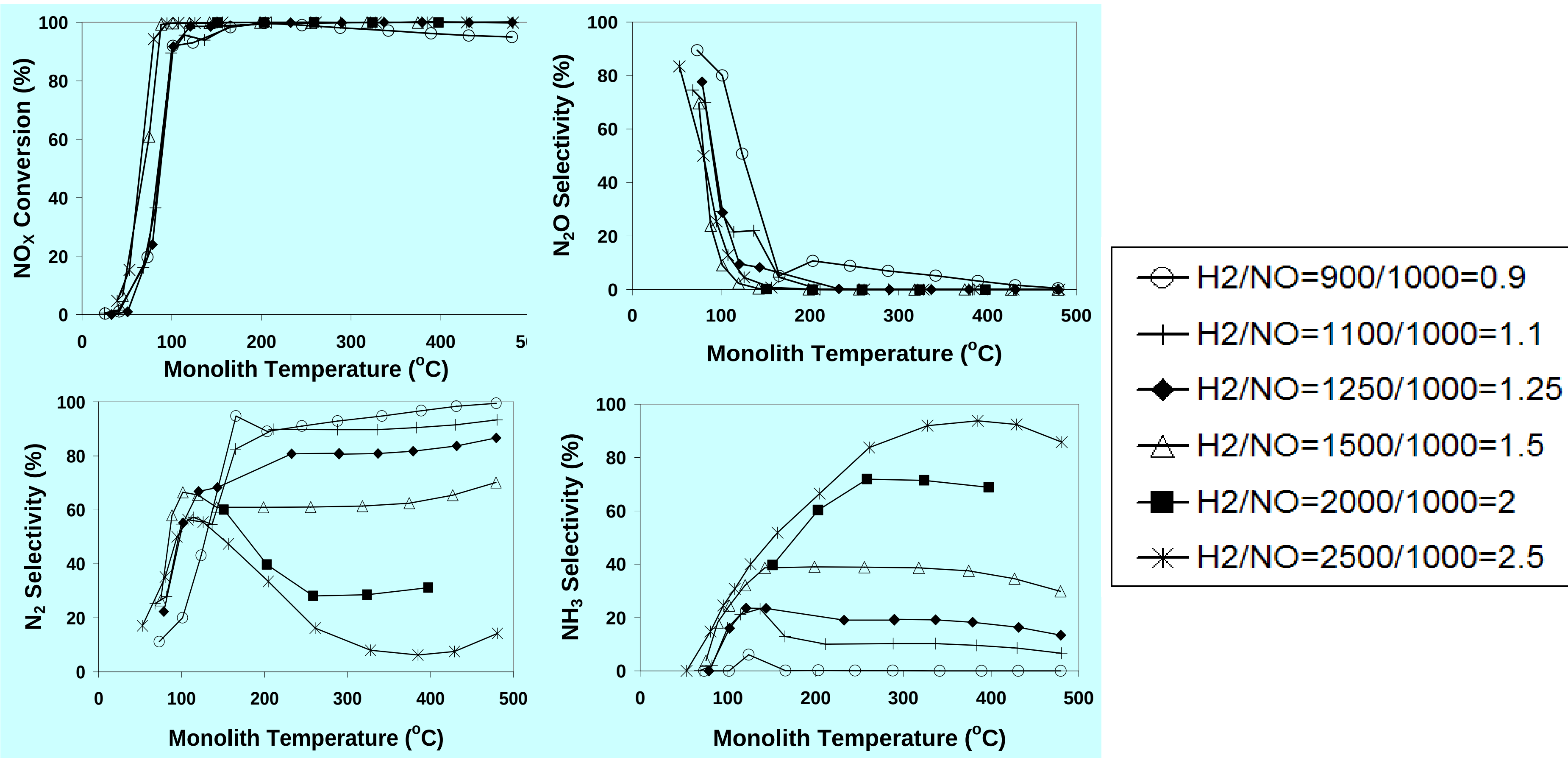
Reaction System Mechanism: Steady-State NO + H_2 on Pt / Al_2O_3

$$S1:\ NO + Pt \leftrightarrow NO-Pt$$
$$S2:\ H_2 + 2Pt \leftrightarrow 2H-Pt$$
$$S3:\ NO-Pt + H-Pt \leftrightarrow N-Pt + OH-Pt$$
$$S4:\ N_2O + 2Pt \leftrightarrow NO-Pt + N-Pt$$
$$S5:\ H-Pt + O-Pt \leftrightarrow OH-Pt + Pt$$
$$S6:\ H-Pt + OH-Pt \rightarrow H_2O + 2Pt$$
$$S7:\ N_2 + 2Pt \leftarrow 2N-Pt$$
$$S8:\ NO-Pt + Pt \leftrightarrow N-Pt + O-Pt$$
$$S10^*:\ N-Pt + 3H-Pt \leftrightarrow NH_3-Pt + 3Pt$$
$$S13:\ NH_3 + Pt \leftrightarrow NH_3-Pt$$
$$S14:\ O_2 + 2Pt \leftrightarrow 2O-Pt$$
$$S15:\ NO-Pt + O-Pt \leftrightarrow NO_2-Pt + Pt$$
$$S16:\ NO_2 + Pt \leftrightarrow NO_2-Pt$$

Steps:

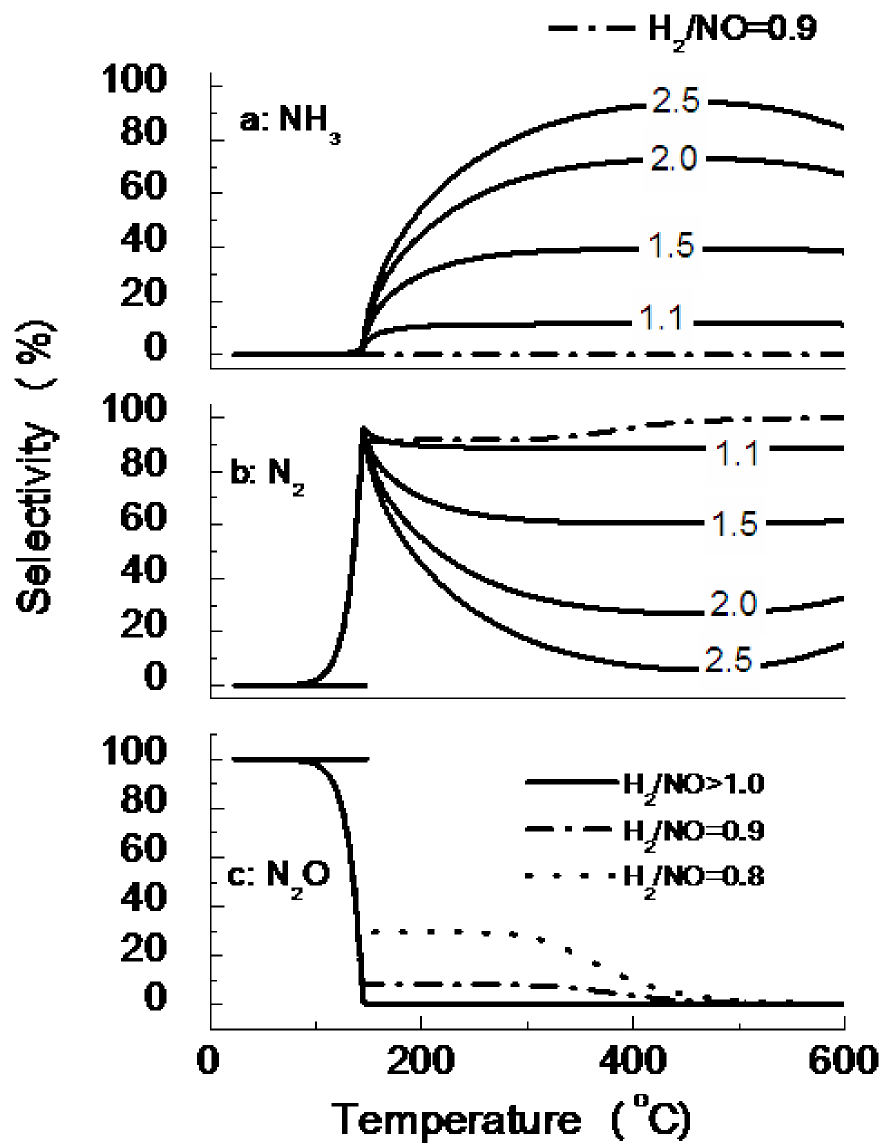
- Formulate main mechanism based on data trends
- Utilize literature kinetics where possible
- Do sensitivity analysis; tune key parameters

Steady-State NO + H_2 on Pt/BaO: Effect of Temperature



Selectivities vs Temperature

- Main trends in data captured by model



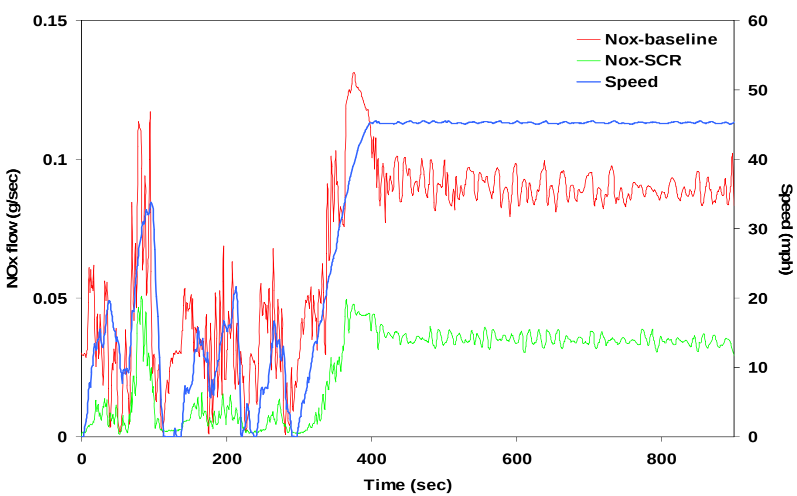
Next Steps: Year 3 of 4

- Experiments
  - Conduct bench-scale and TAP experiments on additional catalyst types
    - Effect of Pt dispersion for Pt/BaO catalysts
    - Systematic Pt/Ba interfacial perimeter for Pt/BaO catalysts
    - Effect of Rh in Pt/Rh/Ba catalysts
- Modeling
  - Further upgrade microkinetic model through specific kinetic measurements in bench-scale & TAP reactors
  - Incorporate upgraded kinetic model into integral transient LNT monolith reactor
  - Use LNT model with microkinetics to investigate different NOx trap operating strategies and designs

Synergistic Studies

- State of Texas/BASF Catalysts LLC (Engelhard Inc.)
  - State of Texas/Engelhard project ($200K funding; >$50K in-kind)
  - BASF provided all catalysts used in study
- Ford Motor Company (Chemical Engineering group)
  - $100K funding over last three years
  - Develop computationally efficient "low dimensional" NOx trap model for design and on-vehicle use
- City of Houston: 5-year project ($3.8 million 2002-2008): UH Diesel Emission Research & Testing Facility
- State of Texas (TCEQ; $8.8 - $10.3 million; 2 years)
  - Expansion of facility into "Texas Diesel Testing & Research Center" in support of "New Technology Research & Development" (NTRD) program focused on diesel retrofit technologies for NOx and particulates reduction

Heavy-Duty Chassis Dynamometer Facility



- Technology verification/testing
- Demonstration projects
- Elements:
  - 500HP AC Chassis Dyno (Burke Porter)
  - Partial Flow Dilution Tunnel (Horiba)
  - Raw exhaust gas analyzer (Horiba)
  - FTIR exhaust gas analyzer (MKS)
  - Exhaust Flow meter (Rosemount)
  - Fuel column
  - Data Acquisition/Control software

Active Collaborations

- BASF Catalysts LLC (formerly Engelhard Inc.)
  - Dr. Stan Roth, Dr. C.Z. Wan
  - Builds off State of Texas / Engelhard funded project
  - 10 refereed publications on LNTs from 2004-2006
  - BASF provided several series of model catalysts: Pt, Pt/Ba, Rh, Pt/Rh/Ba
- Ford Motor Company
  - Dr. Bob McCabe, Dr. Joseph Theis
  - Development of low-dimensional models of TWC and LNT converters for on-vehicle use
  - Regular technology exchanges

Summary

- Growth of diesel-powered vehicles requires cost-effective & reliable lean NOx reduction
- Key hurdle to application of LNT is its complexity in terms of periodic operation
- Multi-faceted experimental & modeling: Focus on building mechanistic understanding through bench-scale and TAP experiments
- Project on track
  - Predictive LNT reactor model with microkinetics
  - Year 3 plans will provide important information about chemistry/kinetics at Pt/Ba interface

Refereed Publications

Task (a) Kinetic Models for NOx storage and reduction on Pt/Rh/Ba

- **Paper 1:** Medhekar, V., V. Balakotaiah, and M.P. Harold, "TAP Study of NOx Storage and Reduction on Pt/Al_2O_3 and $Pt/Ba/Al_2O_3$," Catalysis Today, **121**, 226-236 (2007).
- **Paper 3:** Xu, J., R.D. Clayton, V. Balakotaiah and M.P. Harold, "Experimental and Microkinetic Modeling of Steady-State NO Reduction by H_2 on $Pt/BaO/Al_2O_3$ Monolith Catalysts," Appl. Catal. B. Environmental, 77, 395-408 (2008).
- **Paper 7:** Kumar, A., V. Medhekar, M.P. Harold, and V. Balakotaiah, "NOx Reduction Studies on Pt/Al_2O_3 Powder and Monolith Catalyst using Temporal Analysis of Products," Appl. Catal. B. Environmental, Catalysis Today, to be submitted (March, 2008).

Task (b) Bench scale studies of NOx reduction & NSR

- **Paper 2:** Sharma, M., R.D. Clayton, M.P. Harold, and V. Balakotaiah, "Multiplicity in Lean NOx Traps," Chem. Engng. Science, **62**, 5176-5181 (2007).
- **Paper 4:** Clayton, R.D.., M.P. Harold, and V. Balakotaiah, "Selective Catalytic Reduction of NO by H_2 in O_2 on $Pt/BaO/Al_2O_3$ Monolith NOx Storage Catalysts," Appl. Catal. B. Environmental, to appear (2008): doi:10.1016/j.apcatb.2007.11.038.
- **Paper 5:** Clayton, R.D.., M.P. Harold, and V. Balakotaiah, "NOx Storage and Reduction with H_2 on $Pt/BaO/Al_2O_3$ Monolith: Spatio-Temporal Resolution of Product Distribution ," Appl. Catal. B. Environmental, submitted (2007).
- **Paper 6:** Clayton, R.D.., M.P. Harold, and V. Balakotaiah, "NOx Storage and Reduction with H_2 on $Pt/BaO/Al_2O_3$ Monolith: Performance Studies," Appl. Catal. B. Environmental, to be submitted (March, 2008).

Presentations to Date: 10

- 2005 International Symposium of Chemical Reaction Engineering (Berlin): 1 presentation
- 2006 AIChE Meeting (San Francisco): 3 presentations
- 2007 North American Symposium of Chemical Reaction Engineering (Houston): 2 presentations (1 invited)
- 2007 North American Catalysis Society Meeting (Houston): 2 presentations
- 2007 AIChE Meeting (Salt Lake City): 2 presentations