Elucidating the Mechanism of NOx Storage and Reduction

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** Now with Caterpillar Inc.*

http://www.nasa.gov/vision/earth/everydaylife/archives/HP_ILP_Feature_03.html

Acknowledgements
DOE-NETL, BASF Catalysts LLC, Ford Motor Company, NSF

Diesel Emission Research at UH

Experiments

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

Transient kinetics studies (TAP)

IR Imaging

Bench-scale Reactor Studies

Chassis & Engine Dynamometer Testing

Modeling & Simulation

Kinetic Modeling

- Microkinetics
- Global kinetics

Reactor Modeling

- Isothermal / short monoliths
- Non-isothermal integral monoliths

Activities

- Elucidation of data
- Bifurcation analysis
- Low-D models for optimization & control

Implementation / Optimization of LNTs

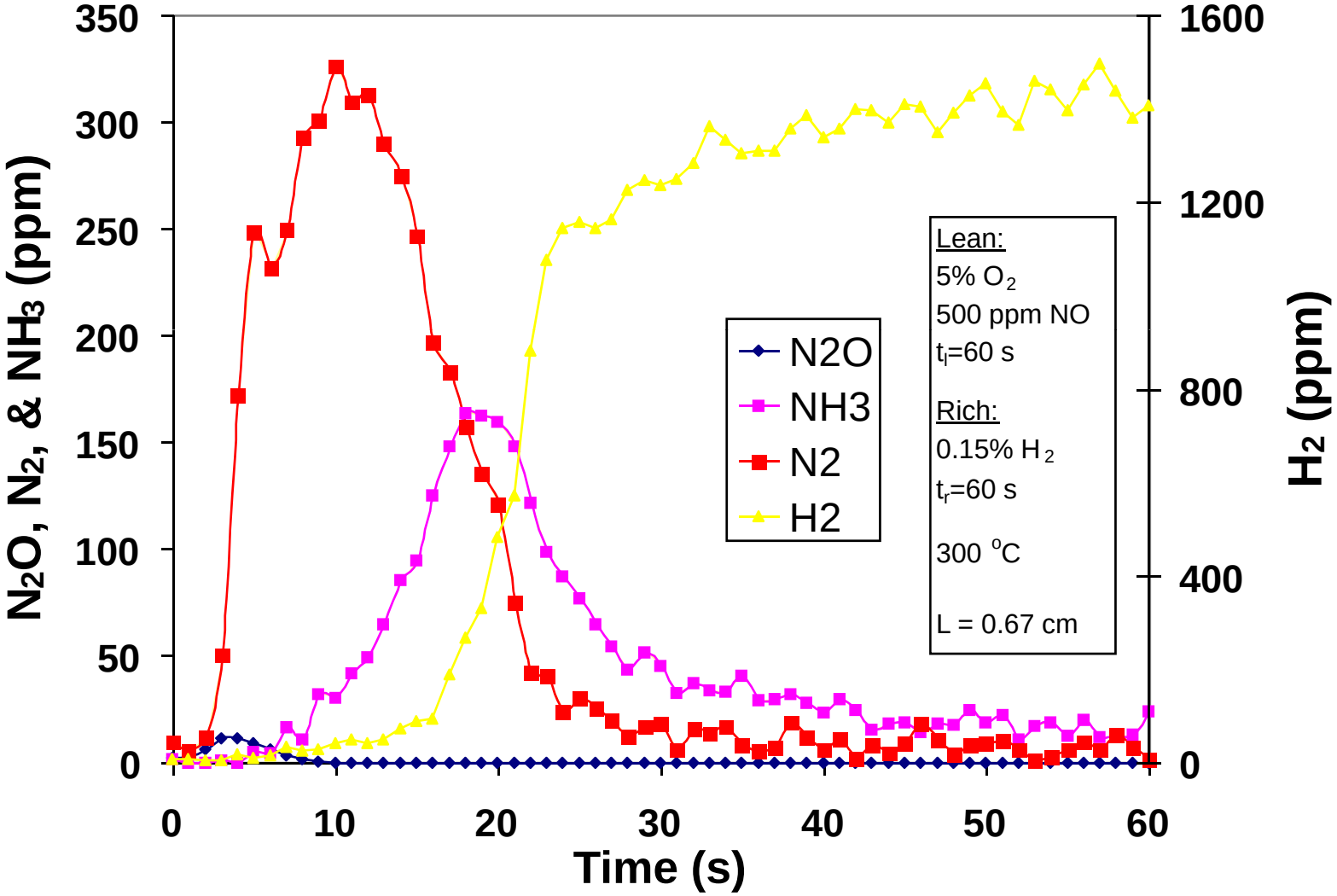
- Develop predictive LNT models
- Optimize LNT design
- Integrate into onboard control system

Overview

<u>Objective:</u> Gain fundamental understanding of NSR mechanism through focused experiments and capture that understanding in predictive LNT models for design, optimization, and control

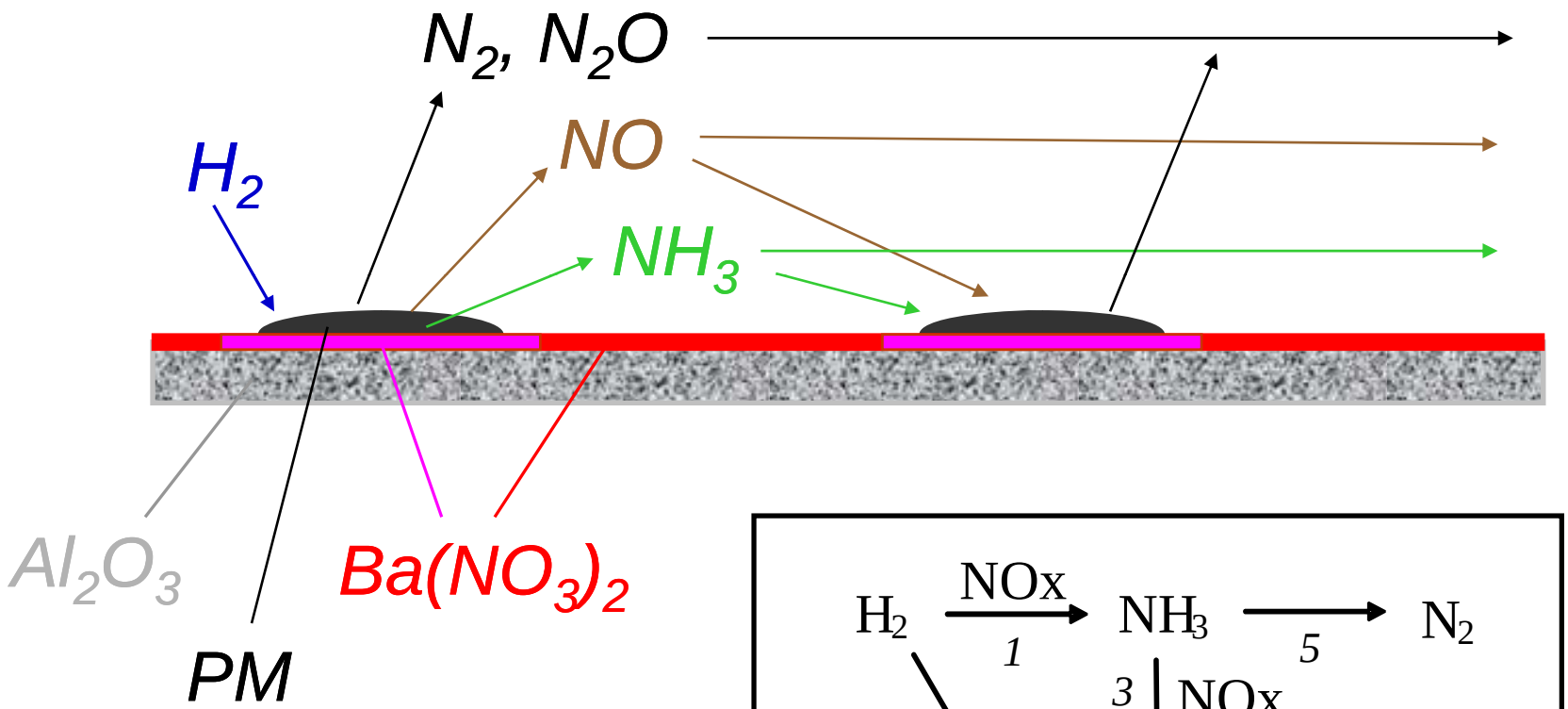
- Spatio-temporal effects
- Global reaction LNT model
- Effect of Pt dispersion
- Isotopic TAP experiments

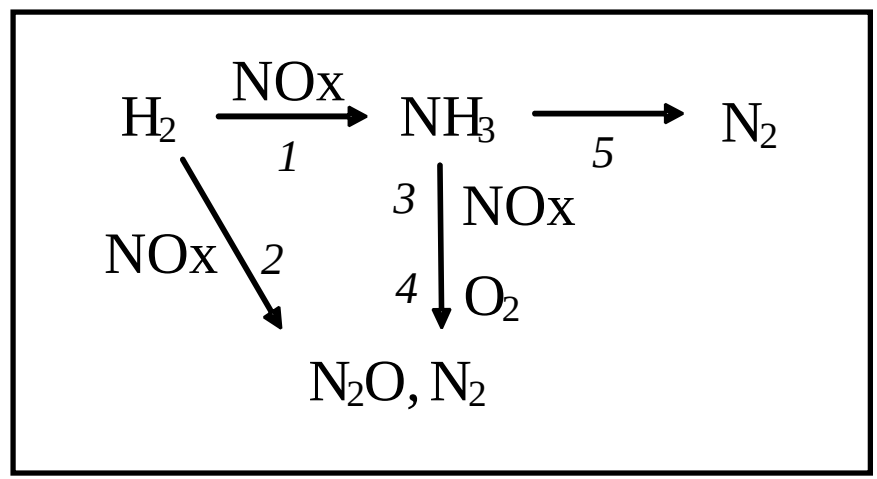
Typical Anaerobic Regeneration



Clayton, R.D.., M.P. Harold, and V. Balakotaiah, "Performance Features of Pt/BaO Lean NOx Trap with Hydrogen as Reductant," AIChE J., ***55****, 687-700 (2009).*

Phenomological Picture of NSR with H_2 as Reductant



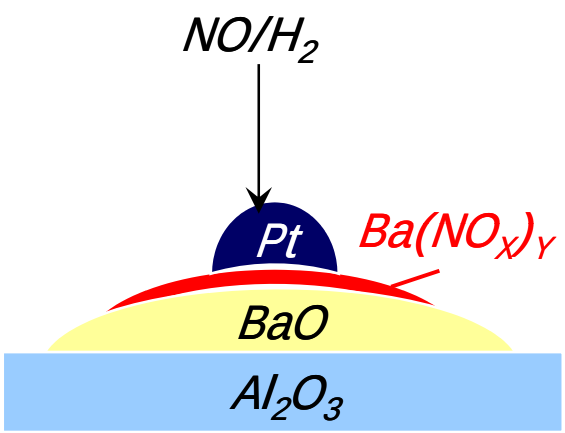


Global Kinetic Model for NOx Storage & Reduction: Storage

1. $NO + 1/2O_2 \longleftrightarrow NO_2$

2. $3NO_2 + BaO(f) \rightarrow Ba(NO_3)_2(f) + NO$

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



$$R_{v1} = k_{f2} X_{O_2,wc} \left[1 - \left(\frac{X_{NO_2,wc}}{K_{eq}\sqrt{X_{O_2,wc}}\, X_{NO,wc}} \right)^2 \right] \frac{1}{K_1 X_{NO,wc} + \frac{1}{K_3} \frac{K_4 X_{NO_2,wc}}{K_1 X_{NO,wc}}}$$

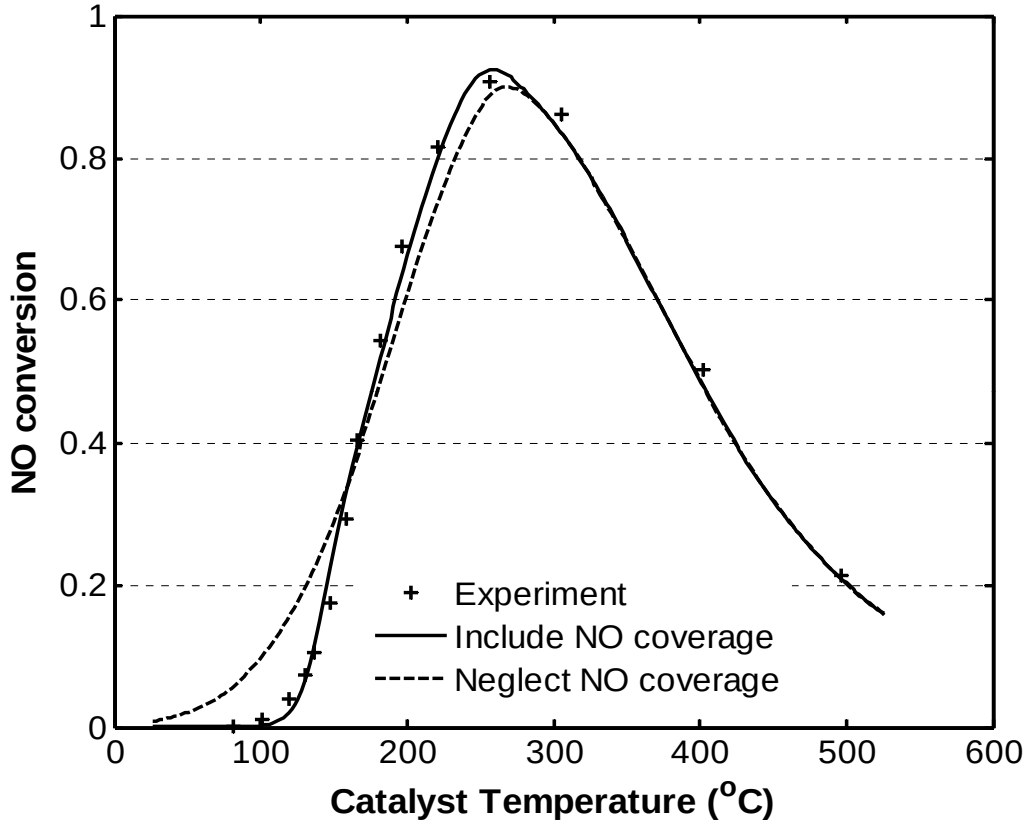
$$R_{v2} = k_2 X_{NO_2,wc} c_{BaO}(f) \theta_v(f)$$

$$R_{v3} = k_3 X_{NO_2,wc} c_{BaO}(s) \theta_v(s)$$

NO Oxidation on Pt Catalysts

NO oxidation rate on Pt/Al_2O_3 & $Pt/BaO/Al_2O_3$:

- Rate inhibited by NO and NO_2
- Rate limited by kinetic (O_2 adsorption) and thermodynamic factors
- Global kinetic model developed
- Transient kinetics complicated by uptake of NO_2 on Al_2O_3 & BaO and oxidation of Pt



$$1: NO + Pt \longleftrightarrow NO - Pt$$

$$2: O_2 + Pt \longleftrightarrow O_2 - Pt$$

$$3: NO - Pt + O - Pt \longleftrightarrow NO_2 - Pt + Pt$$

$$4: NO_2 + Pt \longleftrightarrow NO_2 - Pt$$

$$5: O_2 - Pt + Pt \longleftrightarrow 2O - Pt$$

$$R_{v,NO\_ox} = k_{f2} X_{O_2,s} \left[1 - \frac{1}{X_{O_2,s} K_2 K_5} \left(\frac{1}{K_3} \frac{K_4 X_{NO_2,s}}{K_1 X_{NO,s}} \right)^2 \right] \frac{1}{K_1 X_{NO,s} + \frac{1}{K_3} \frac{K_4 X_{NO_2,s}}{K_1 X_{NO,s}}}$$

Bhatia, D., V. Balakotaiah, M.P. Harold, and R. McCabe, "Experimental and Kinetic Study of NO Oxidation on Model Pt Catalysts," J. Catalysis, under review (2009).

LNT Monolith Model

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

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

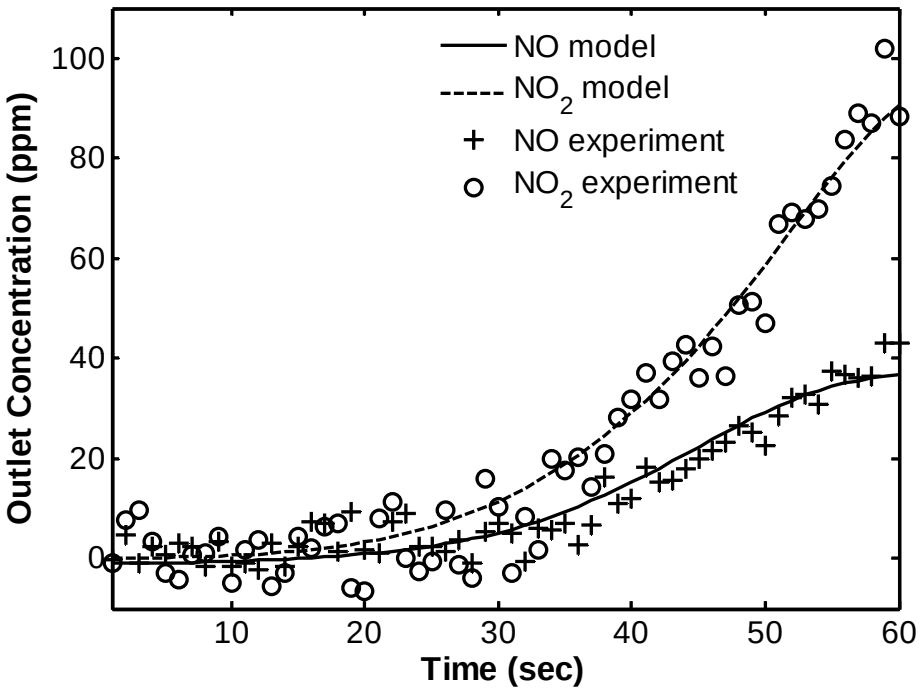
Interphase

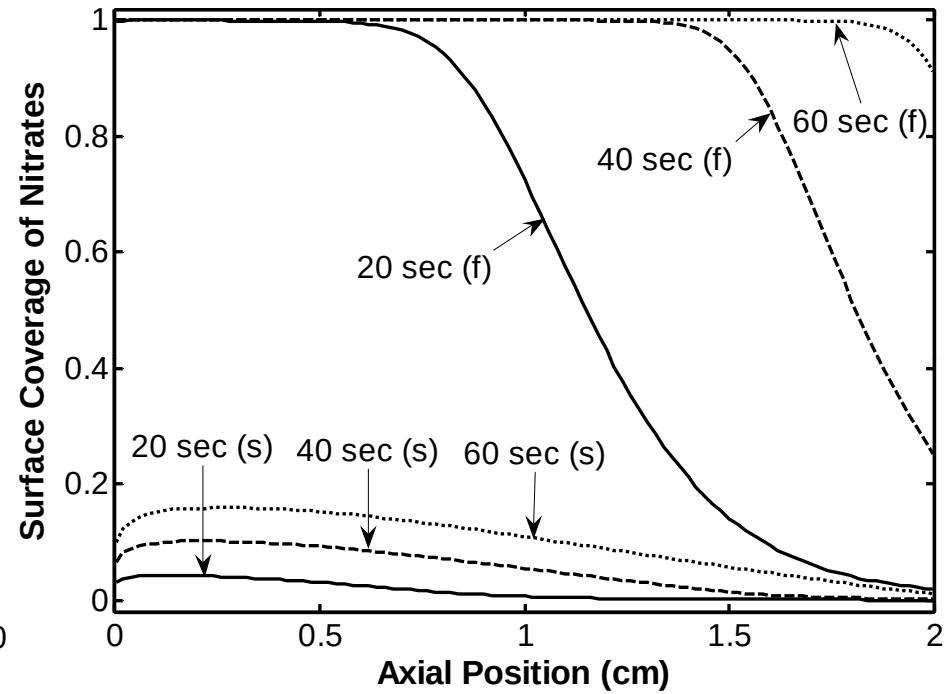
$$C_o k_{jc} (X_{jm} - X_{js}) = \delta_c (R^j{}_{ad} - R^j{}_{de})_{BaO} + \delta_c (R^j{}_{ad} - R^j{}_{de})_{Pt}$$

Site Balance

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

Model vs. Experiment: Storage



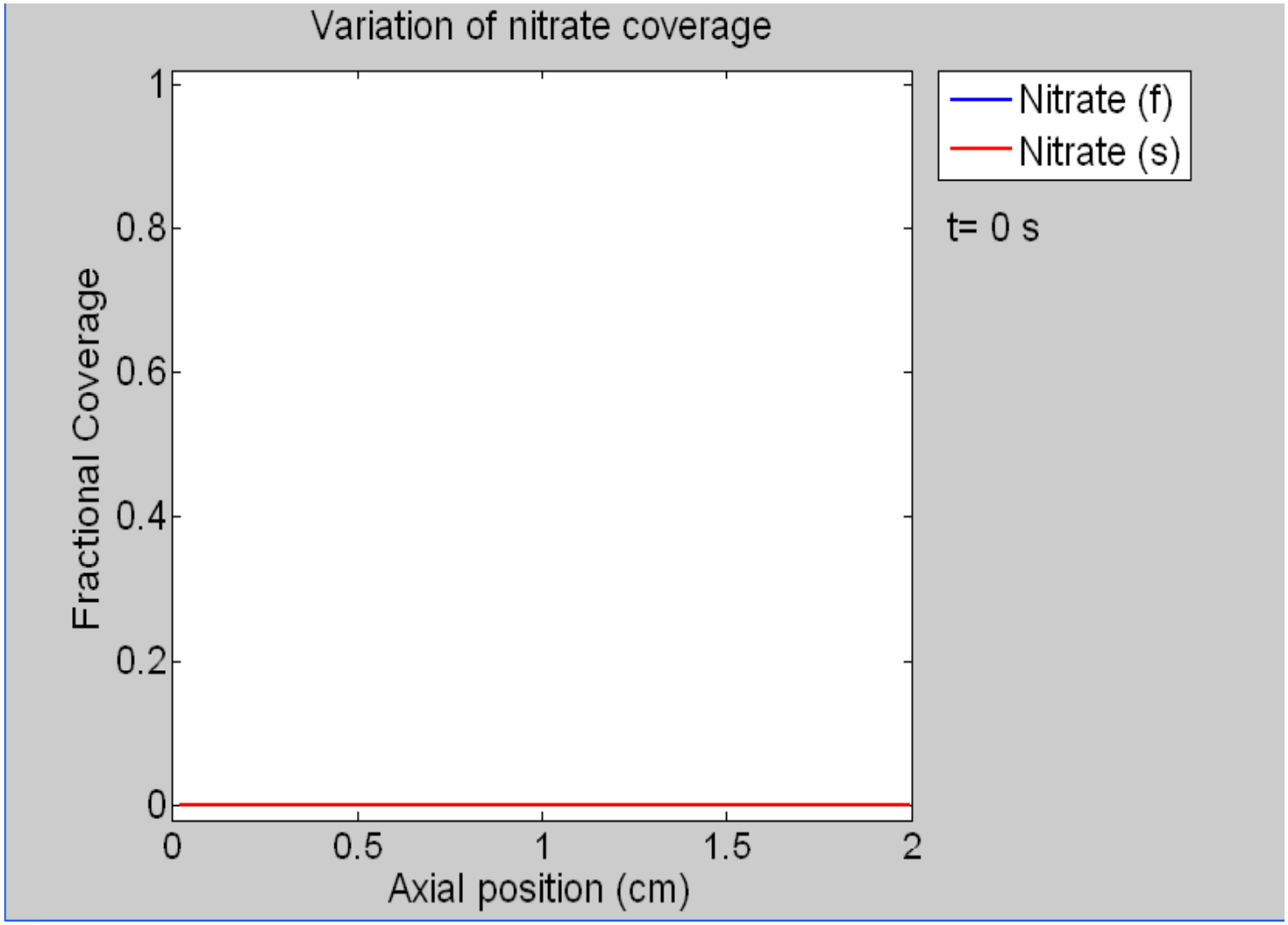


Conditions: T = 275 °C
Lean: 500 ppm NO, 5%O_2
Rich: 1500 ppm H_2, balance Ar (100 s)
Pt, BaO: 2.70 wt.%, 14.6 wt.%

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, ***84****, 616-630 (2008).*

Bhatia, D., M.P. Harold, and V. Balakotaiah, "A Global Kinetic Model for NOx Storage and Reduction on Pt/BaO/Al_2O_3 Monolithic Catalysts, Catalysis Today, under review (2009).

Animated Storage



Global Kinetic Model for NOx Storage & Reduction: Regeneration

4. $8H_2 + Ba(NO_3)_2(f) \rightarrow 5H_2O + BaO(f) + 2NH_3$

$$R_{v4} = k_4 X_{H_2,wc} c_{BaO}(f)\theta_{Ba(NO_3)_2}(f)$$

5. $8H_2 + Ba(NO_3)_2(s) \rightarrow 5H_2O + BaO(s) + 2NH_3$

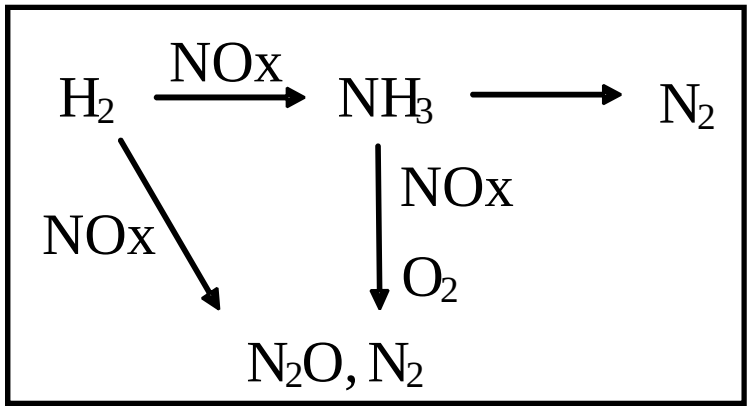
$$R_{v5} = k_5 X_{H_2,wc} c_{BaO}(s)\theta_{Ba(NO_3)_2}(s)$$

6. $\frac{10}{3}NH_3 + Ba(NO_3)_2(f) \rightarrow 5H_2O + BaO(f) + \frac{8}{3}N_2$

7. $\frac{10}{3}NH_3 + Ba(NO_3)_2(s) \rightarrow 5H_2O + BaO(s) + \frac{8}{3}N_2$

8. $H_2O + Al_2O_3 \Leftrightarrow H_2O - Al_2O_3$

9. $NH_3 + Al_2O_3 \Leftrightarrow NH_3 - Al_2O_3$



Global Kinetic Model for NOx Storage & Reduction: Regeneration

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5. $8H_2 + Ba(NO_3)_2(s) \rightarrow 5H_2O + BaO(s) + 2NH_3$

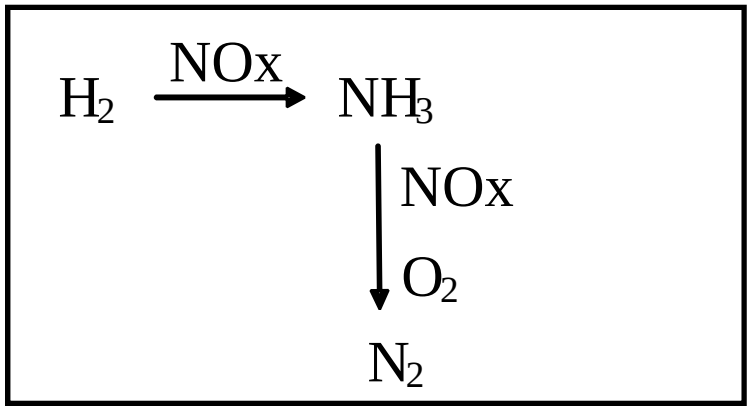
$$R_{v5} = k_5 X_{H_2,wc} c_{BaO}(s)\theta_{Ba(NO_3)_2}(s)$$

6. $\frac{10}{3}NH_3 + Ba(NO_3)_2(f) \rightarrow 5H_2O + BaO(f) + \frac{8}{3}N_2$

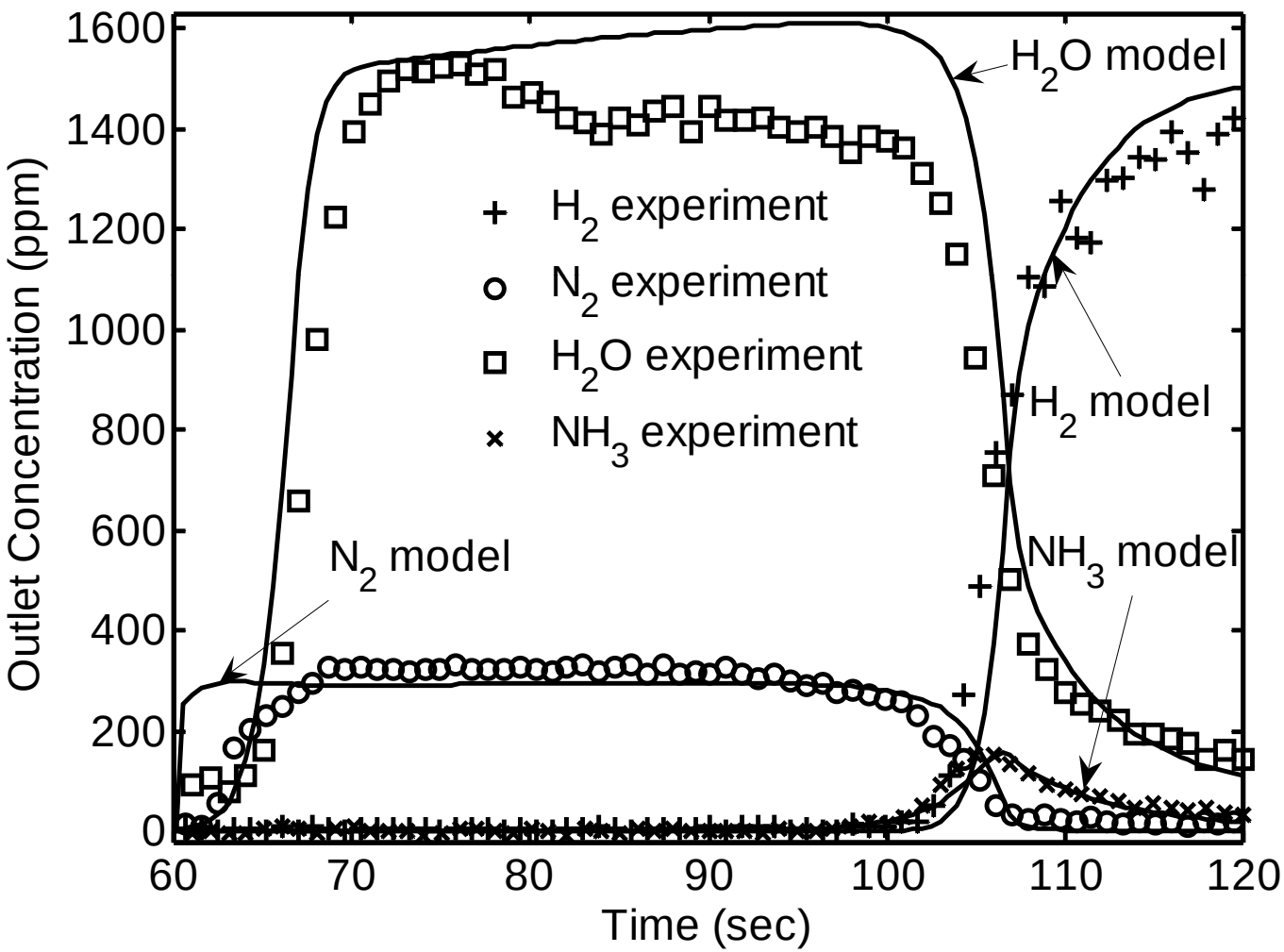
7. $\frac{10}{3}NH_3 + Ba(NO_3)_2(s) \rightarrow 5H_2O + BaO(s) + \frac{8}{3}N_2$

8. $H_2O + Al_2O_3 \Leftrightarrow H_2O - Al_2O_3$

9. $NH_3 + Al_2O_3 \Leftrightarrow NH_3 - Al_2O_3$



Model vs. Experiment: Regeneration

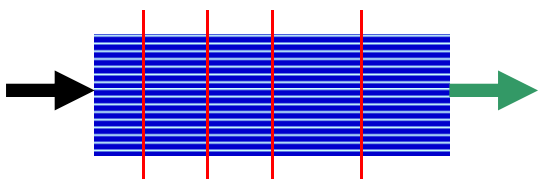


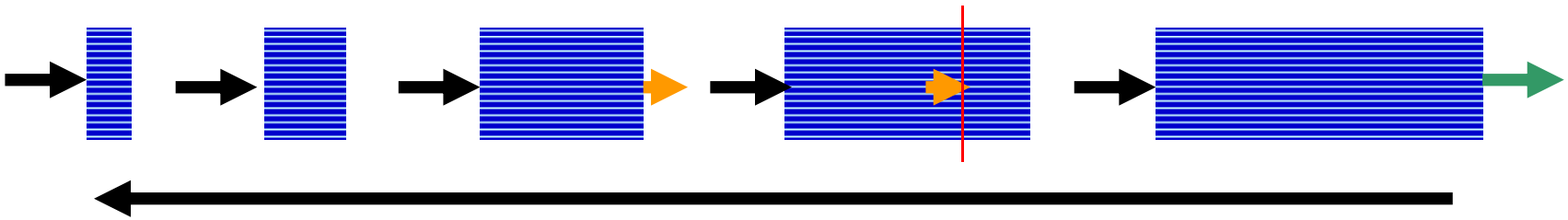
Conditions:
Lean: 500 ppm NO, 5%O_2
Rich: 1500 ppm H_2, balance Ar (100 s)
Pt, BaO: 2.70 wt.%, 14.6 wt.%
T = 275 ^oC

Varied Length Experiments

Approach:

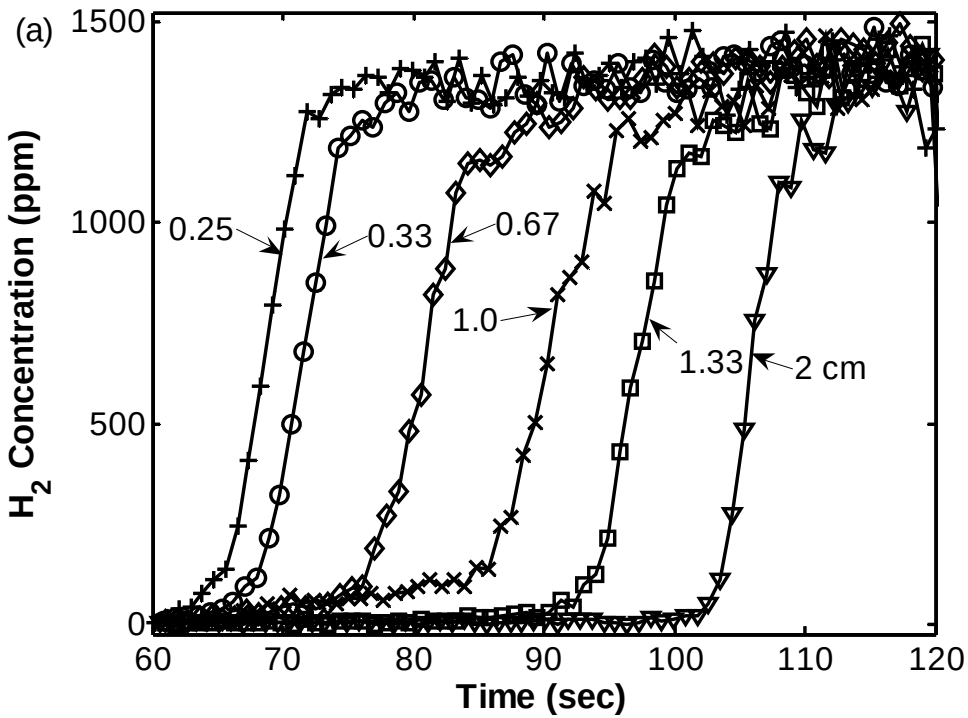
- Divide original monolith into progressively smaller sections
- Replicate experiments to generate spatio-temporal concentration profiles

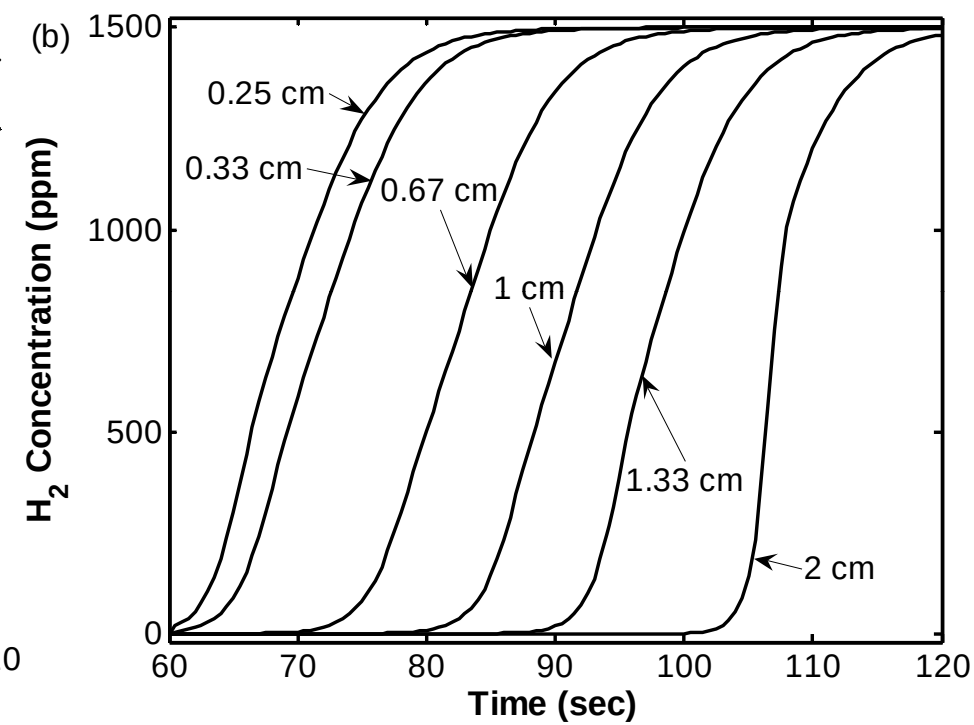




Monolith Length Reduction

Effluent H_2 Transient

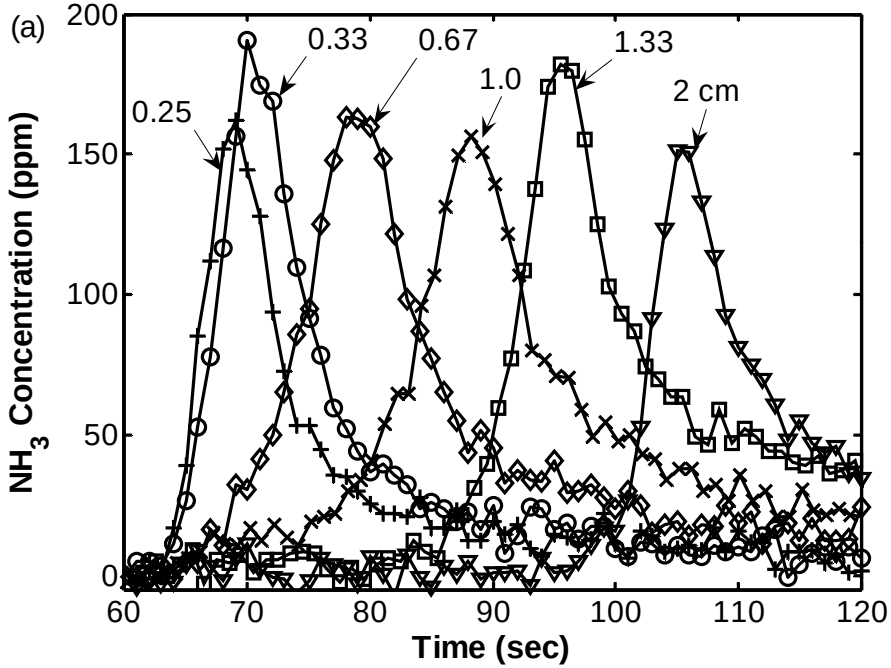


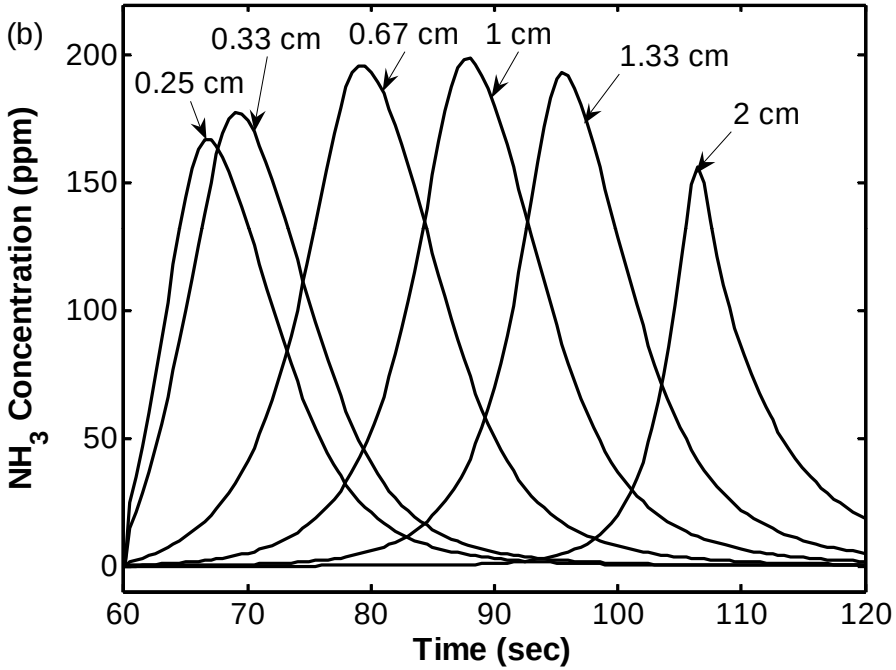


Experiment

Model

Effluent NH_3 Transient

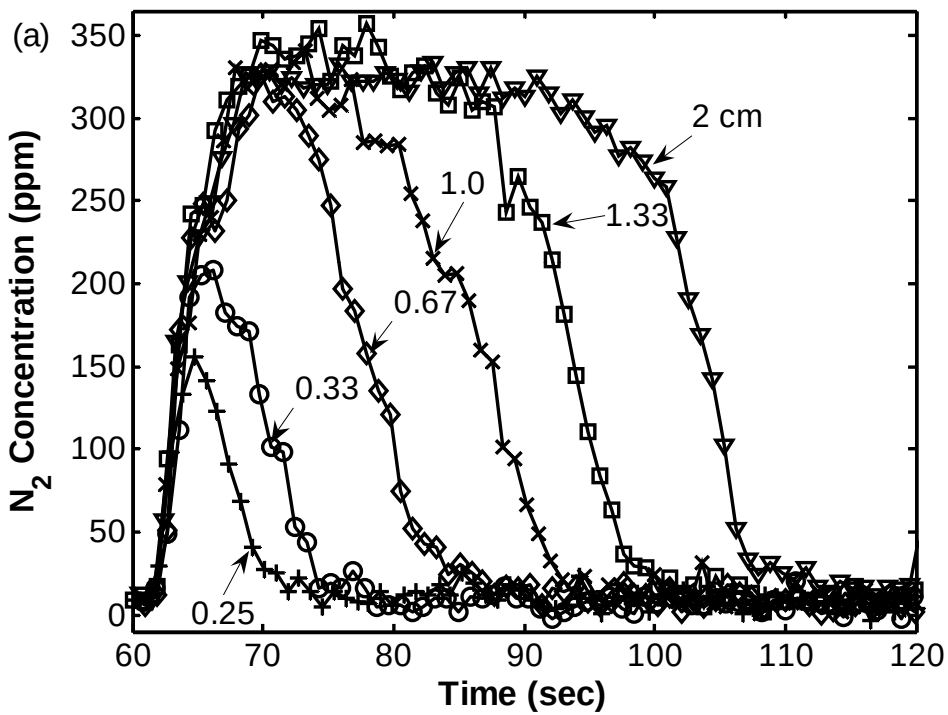


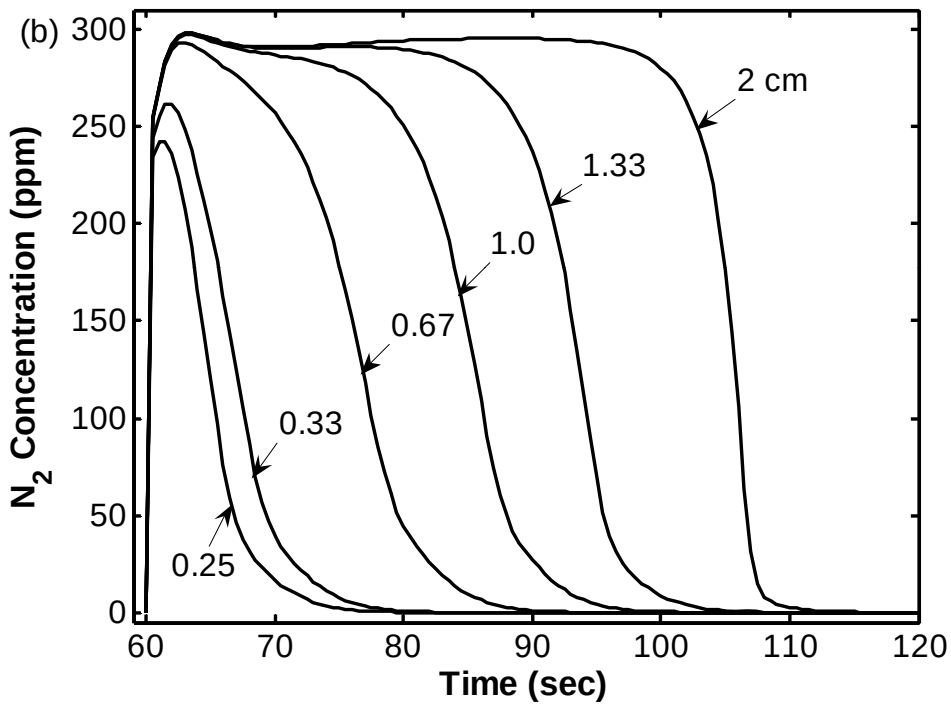


Experiment

Model

Effluent N_2 Transient

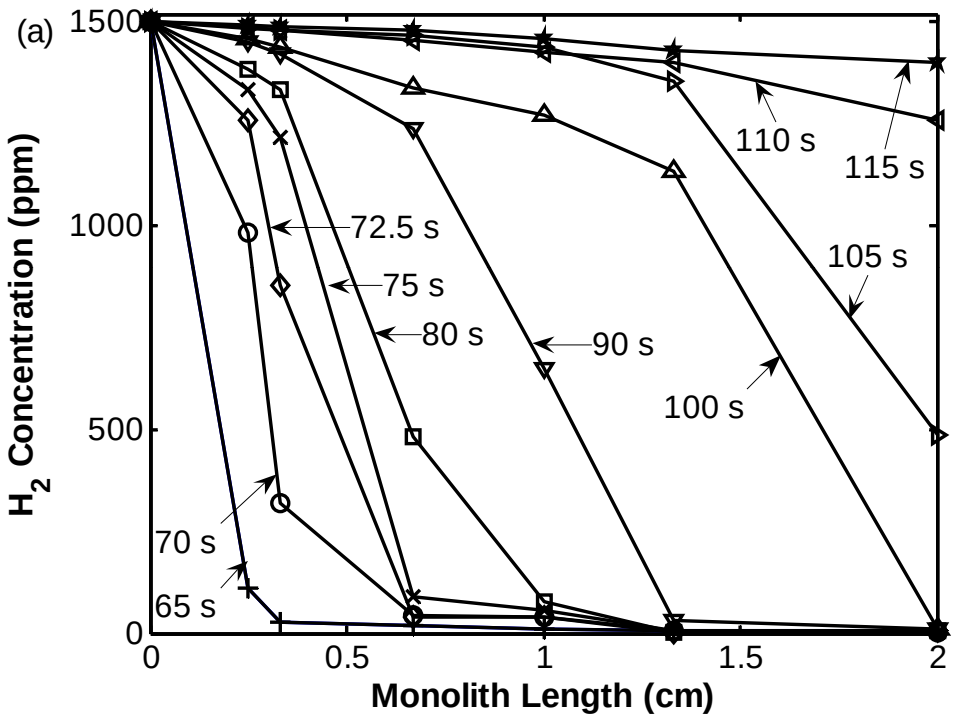


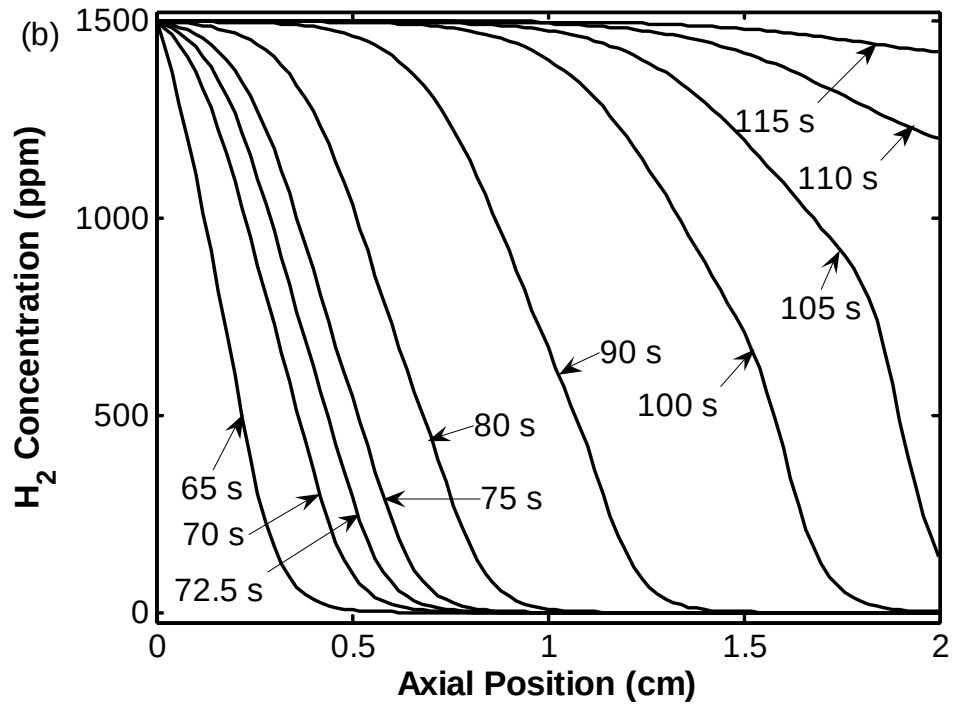


Experiment

Model

Traveling H_2 Front

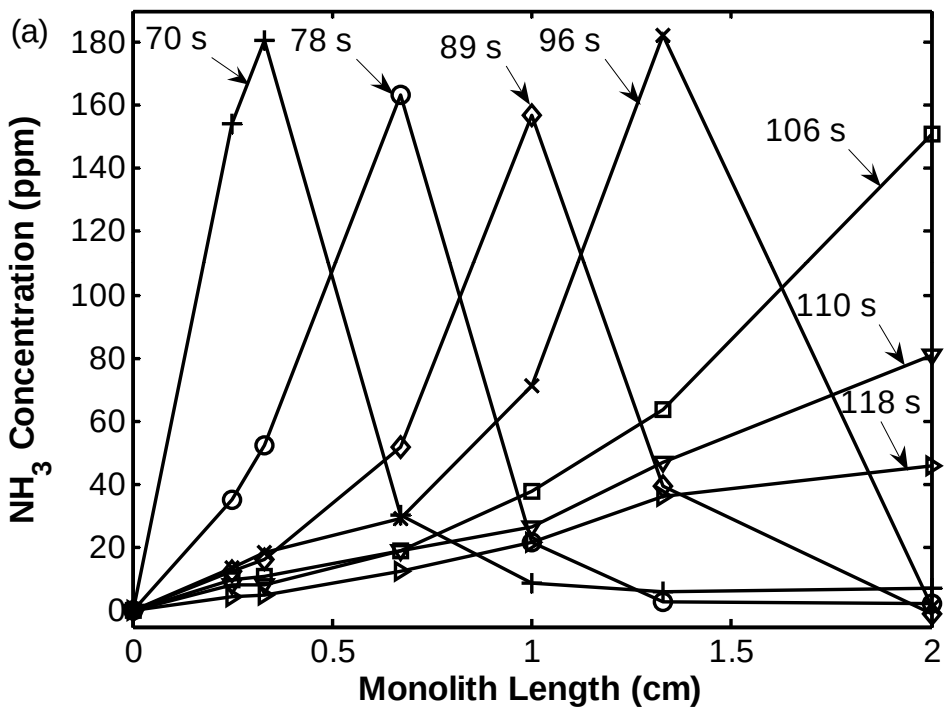


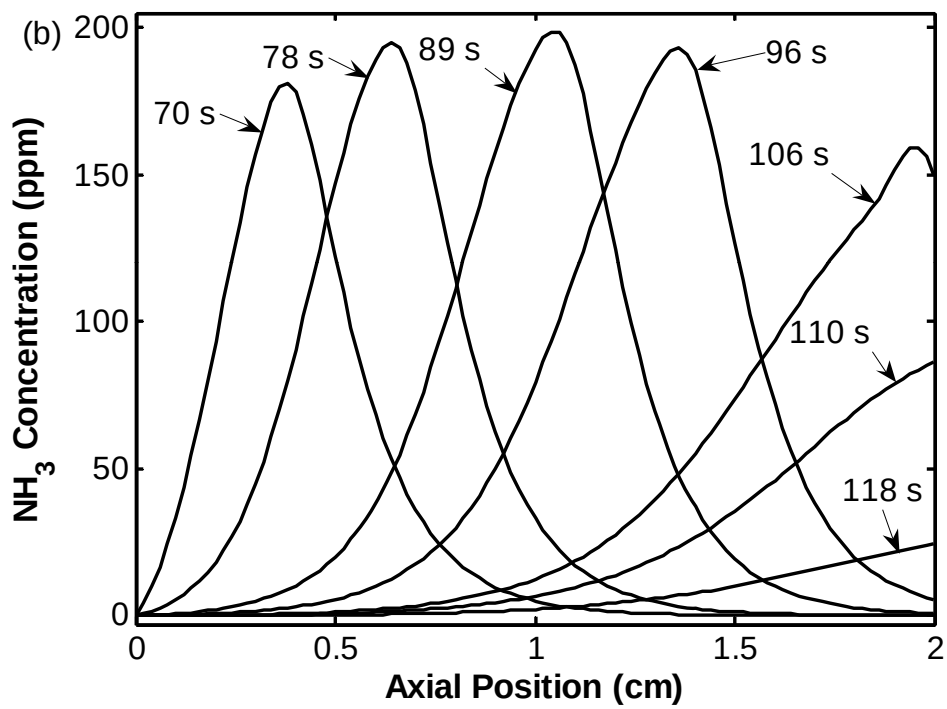


Experiment

Model

Traveling NH_3 Front

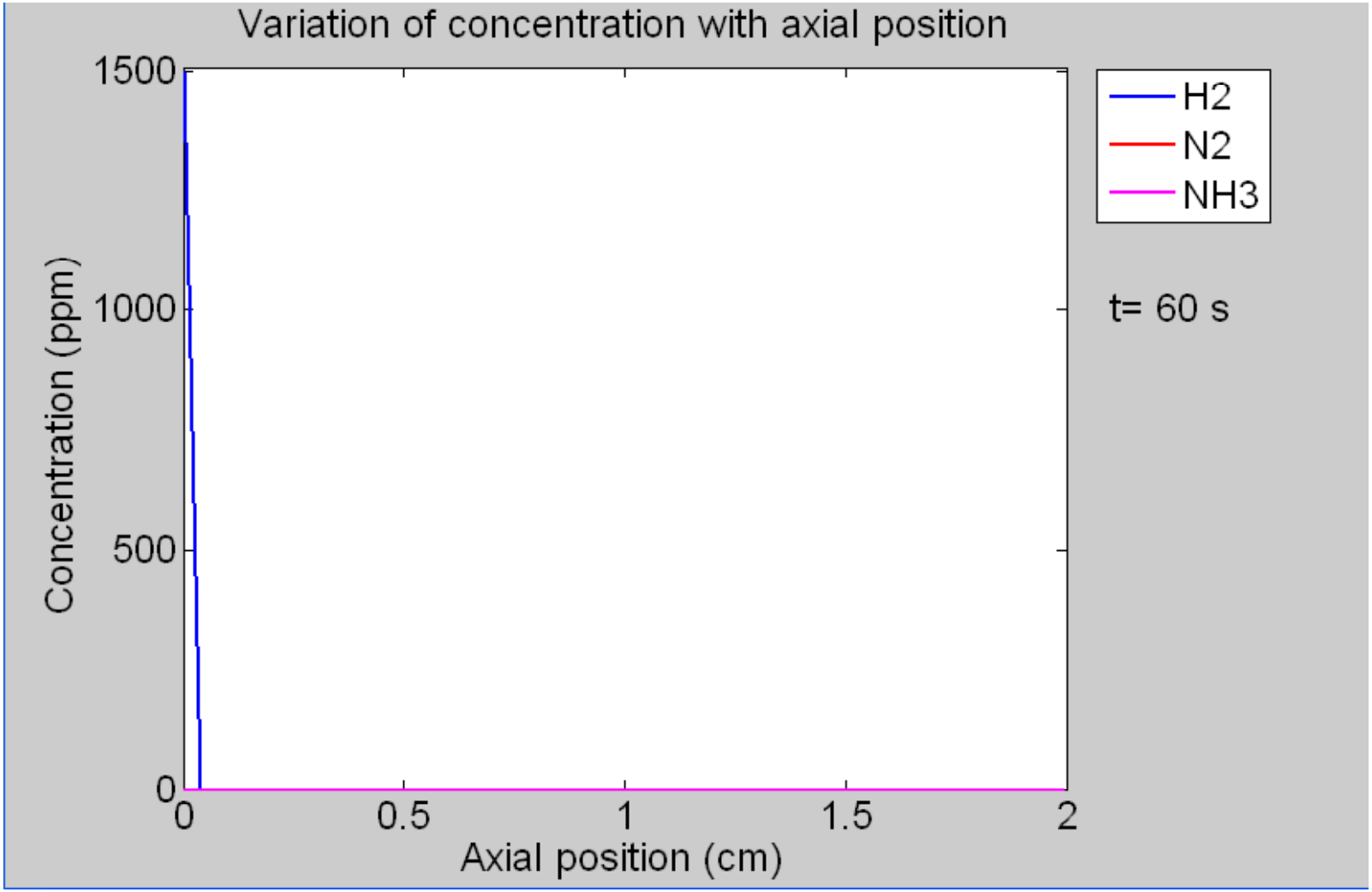




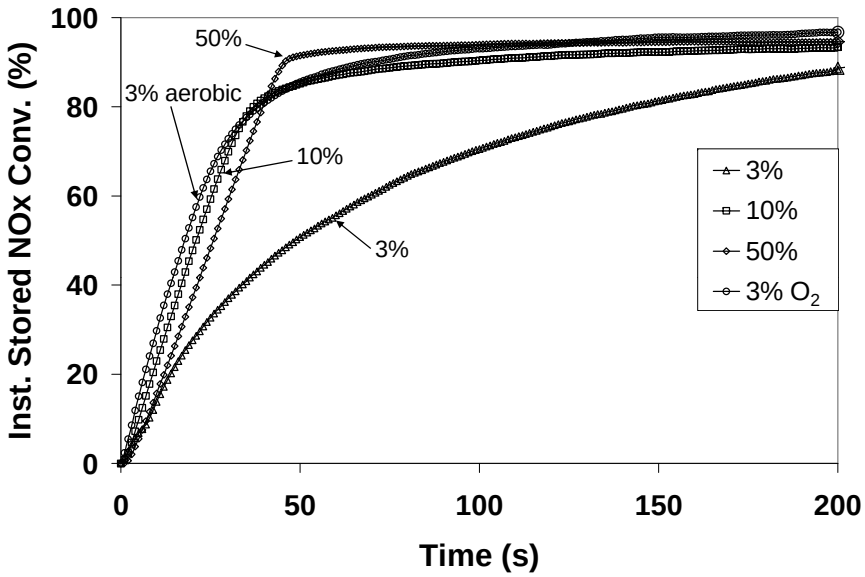
Experiment

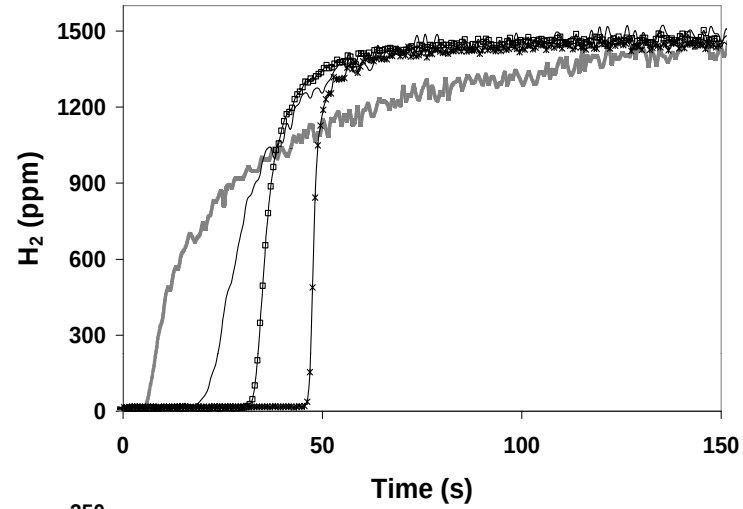
Model

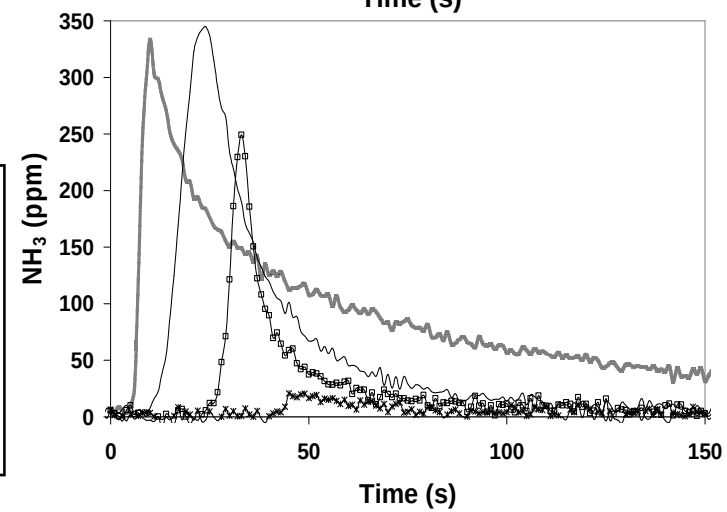
Animated Regeneration



Transient Reduction: Effect of Pt Dispersion with Fixed Stored NOx



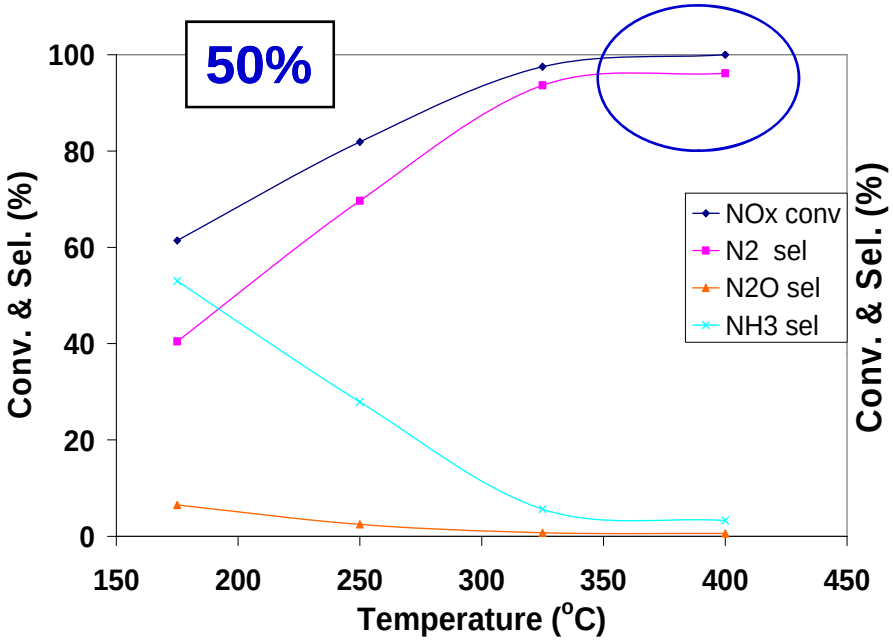


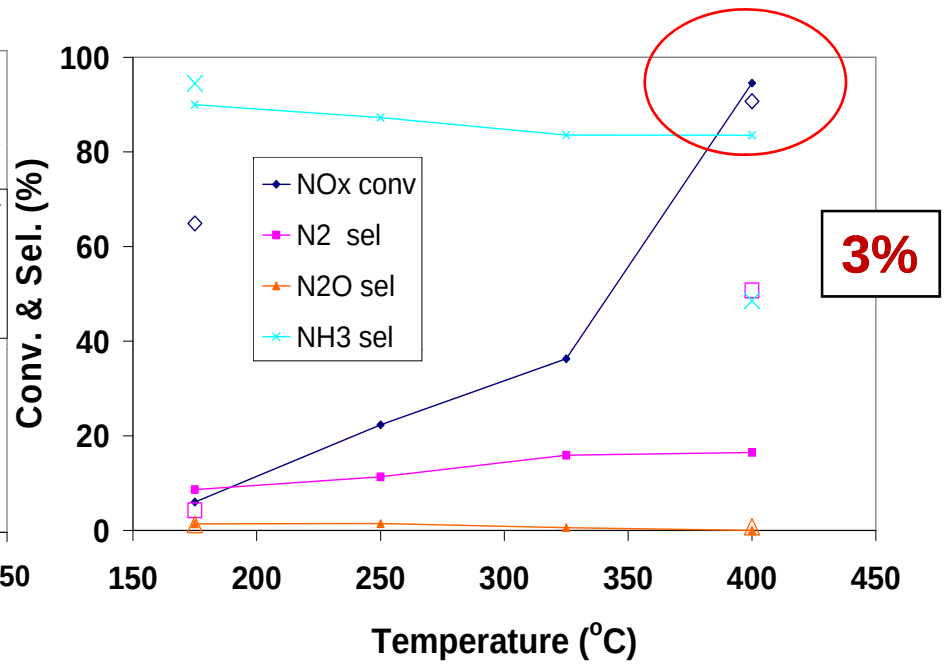


Conditions:
Lean: Fixed Stored NOx 1.3 x 10^{-5} mole N
Rich: 1500 ppm H_2, balance Ar (200 s)
Pt, BaO loading: 2.70 wt.%, 14.6 wt.%
T = 400 ^{o}C

- *High dispersion: faster reduction & N_2*
- *Low dispersion: slower reduction to NH_3*

Effect of Pt Dispersion: Fixed Stored NOx





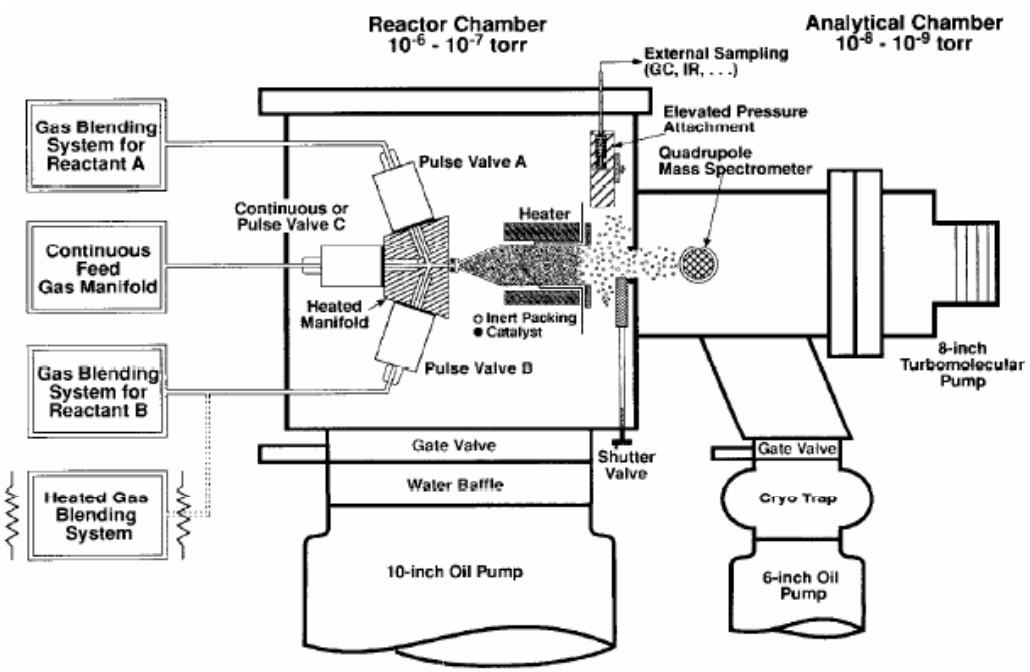
High dispersion: NOx to N_2

Low dispersion: NOx to NH_3

Conditions:
Lean: Fixed Stored NOx 1.3 x 10^{-5} mole N
Rich: 1500 ppm H_2, balance Ar
Pt, BaO loading: 2.70 wt.%, 14.6 wt.%

Clayton, R.D., M.P. Harold, V. Balakotaiah, C.Z. Wan, "Effect of Pt Dispersion on NOx Storage and Reduction in Pt/BaO/Al_2O_3 Catalyst," Appl. Catal. B. Environmental, in press (2009).

Temporal Analysis of Products (TAP)

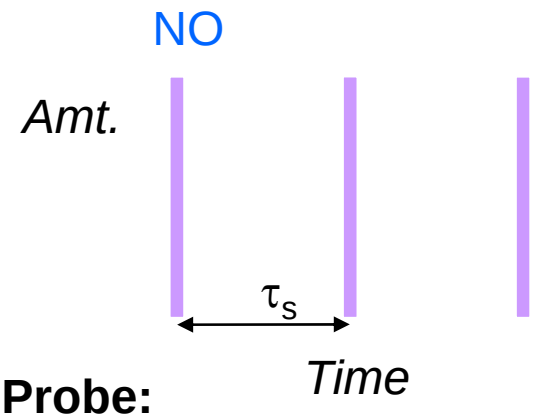


(Reference: P. Mills, DuPont)

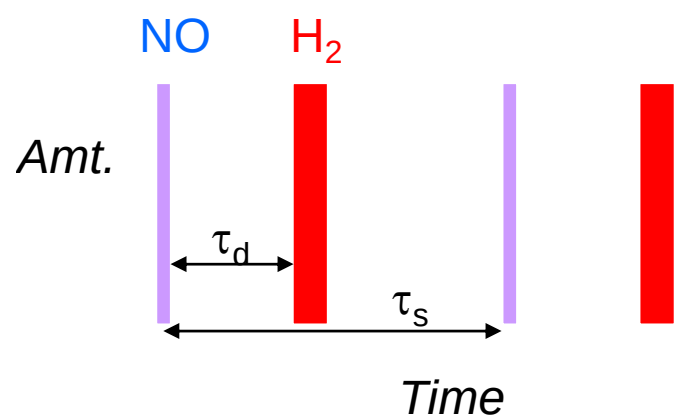
Medhekar, V., V. Balakotaiah, and M.P. Harold, "TAP Study of NOx Storage and Reduction on Pt/Al2O3 and Pt/Ba/Al_2O_3," Catalysis Today, ***121****, 226-236 (2007).*

Kumar, A., V. Medhekar, M.P. Harold, and V. Balakotaiah, "NO Decomposition and Reduction Studies on Pt/Al2O3 Powder and Monolith Catalysts Using the TAP Reactor," Appl. Catal. B. Environmental, to appear (2009).

Multi-Pulse:



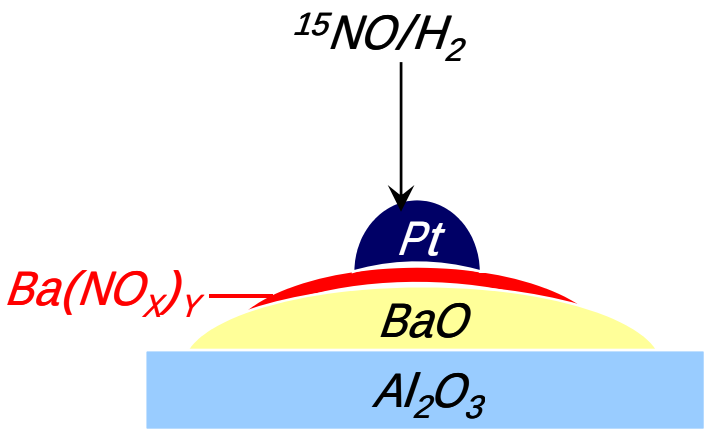
Pump-Probe:



Isotopic TAP Study: $^{15}NO/H_2$ Pump-Probe on Pre-nitrated $Pt/BaO/Al_2O_3$

$NO \rightarrow {}^{15}NO/H_2$

<u>Objective:</u> Follow formation of N_2 and NH_3 during ^{15}NO and H_2 pulses to quantify source of products (i.e. stored NO_x or gas phase NO)



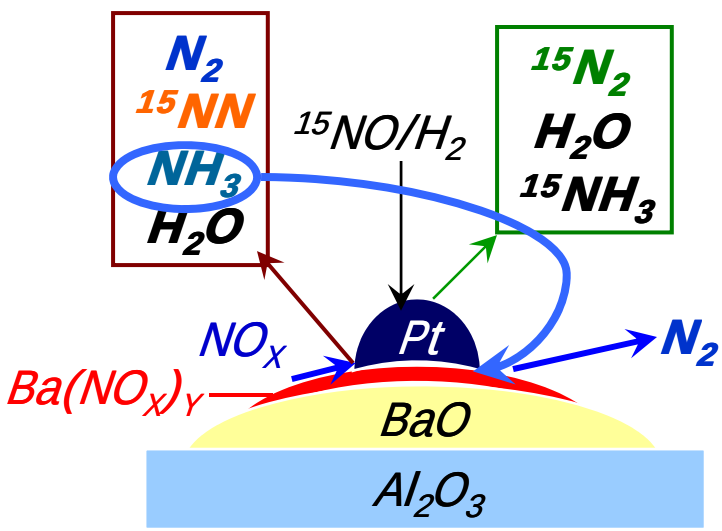
Kumar, A., M.P. Harold, and V. Balakotaiah, "Isotopic TAP Studies of NOx Storage and Reduction," J. Catalysis, to be submitted (2009).

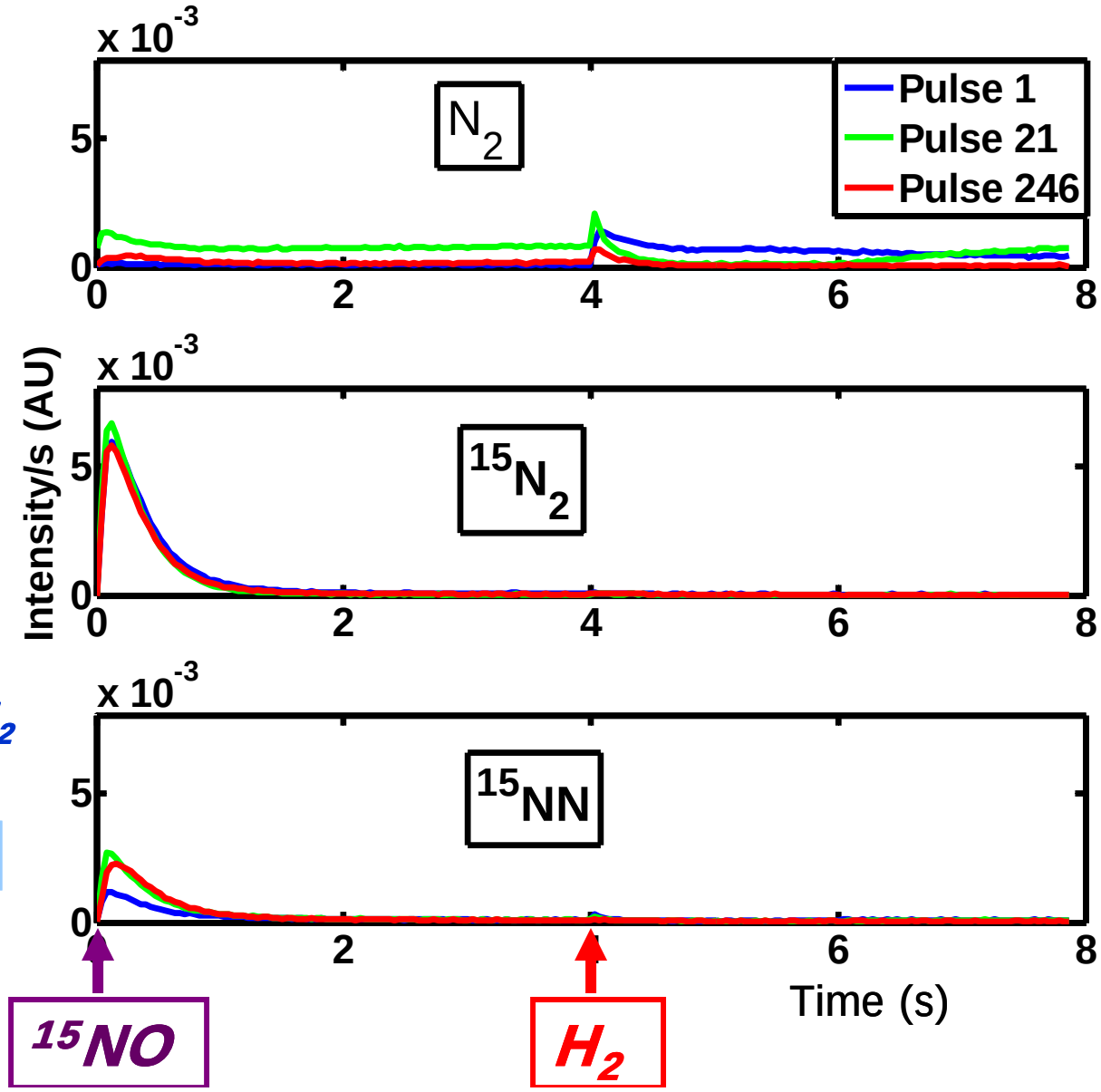
$^{15}NO/H_2$ Pump-Probe on Pre-nitrated $Pt/BaO/Al_2O_3$: Instantaneous Results

T = 250 °C

$H_2/^{15}NO$ = 4.4

$NO \rightarrow {}^{15}NO/H_2$



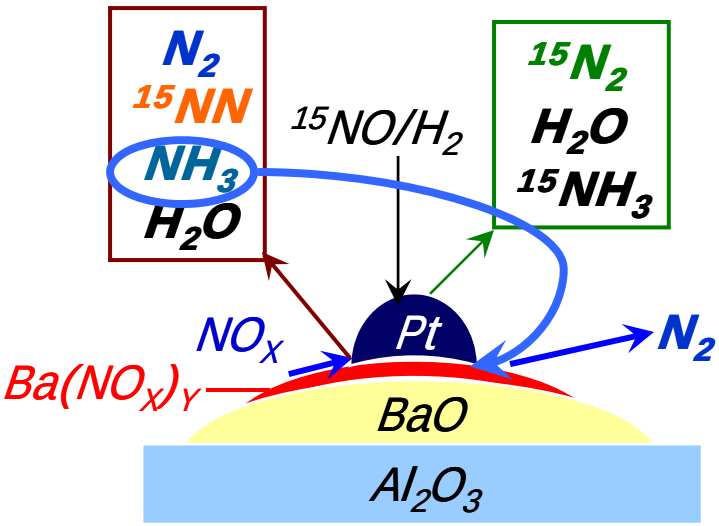


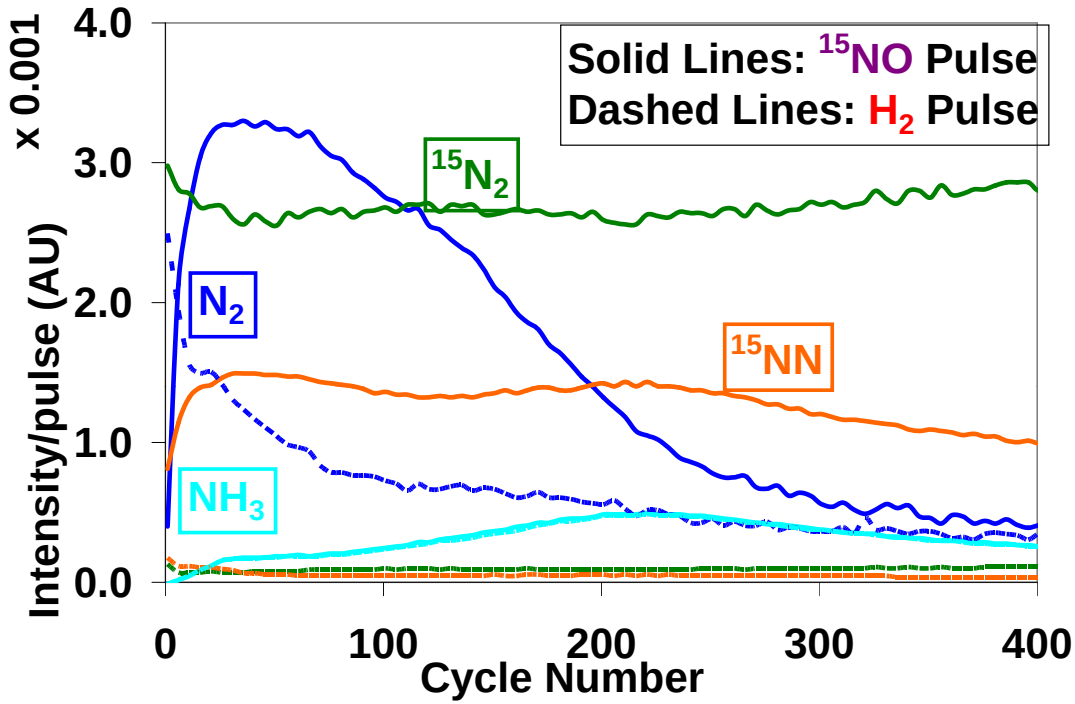
$^{15}NO/H_2$ Pump-Probe on Pre-nitrated $Pt/BaO/Al_2O_3$: Integral Results

T = 250 °C

$H_2/^{15}NO$ = 4.4

NO → ***$^{15}NO/H_2$***





<u>Data reveal following chemistry:</u>

- *$^{15}N_2$ produced by ^{15}NO decomposition on clean Pt (H_2 scavenges O-Pt)*
- *N_2, ^{15}NN produced at Pt/BaO interface via spillover chemistry*

H-Pt + $Ba(NO_3)_2$ + ^{15}N-Pt

Microkinetic Model Used for LNT Model Development

Pt Chemistry

$O_2(g)+2Pt=2O\text{-}Pt$
$H_2(g)+2Pt=2H\text{-}Pt$
$NO(g)+Pt=NO\text{-}Pt$
$2N\text{-}Pt=N_2(g)+2Pt$
$NO_2(g)+Pt=NO_2\text{-}Pt$
$O\text{-}Pt+H\text{-}Pt=OH\text{-}Pt+Pt$
$OH\text{-}Pt+H\text{-}Pt=H_2O(g)+2Pt$
$NO\text{-}Pt+Pt=N\text{-}Pt+O\text{-}Pt$
$O\text{-}Pt+NO\text{-}Pt=NO_2\text{-}Pt+Pt$
$N\text{-}Pt+3H\text{-}Pt=NH_3\text{-}Pt+3Pt$
$NO\text{-}Pt+3H\text{-}Pt=NH_3\text{-}Pt+O\text{-}Pt+2Pt$
$NH_3(g)+Pt=NH_3\text{-}Pt$
$NO\text{-}Pt+H\text{-}Pt=N\text{-}Pt+OH\text{-}Pt$
$N_2O(g)+2Pt=NO\text{-}Pt+N\text{-}Pt$
$NH_3\text{-}Pt+3NO\text{-}Pt+3Pt=4N\text{-}Pt+3OH\text{-}Pt$
$NH_3\text{-}Pt+3OH\text{-}Pt=3H_2O+N\text{-}Pt+3Pt$
$NH_3\text{-}Pt+3O\text{-}Pt=N\text{-}Pt+3OH\text{-}Pt$

Storage Chemistry w/ & w/o Pt

$NO_2(g)+BaO=BaO\text{-}NO_2$
$BaO\text{-}O+NO(g)=BaO\text{-}NO_2$
$BaO\text{-}O+NO_2(g)=BaO\text{-}NO_3$
$BaO\text{-}NO_3+NO_2(g)=Ba(NO_3)_2$
$2BaO+O_2(g)=2BaO\text{-}O$

Spillover Chemistry at Pt/Ba Interface

$NO_2\text{-}BaO+Pt=BaO\text{-}O+NO\text{-}Pt$

- Pt chemistry from Xu et al. (2009)
- BaO chemistry is from literature (Olsson et al., 2001)
- Storage & spillover reactions provide Pt/BaO coupling effects

Xu, J., M.P. Harold, and V. Balakotaiah, "Microkinetic Modeling of Steady-State $NO/H_2/O_2$ on $Pt/BaO/Al_2O_3$ Monolith Catalysts," Appl. Catal. B. Environmental, in press(2009).

*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).*

Conclusions

- Simple global kinetic model predicts main trends of storage & anaerobic reduction with H_2
- Significant effect of Pt dispersion on regeneration activity & product distribution
- Isotopic TAP studies reveal multiple pathways to N_2
- Microkinetic model under development to capture Pt/Ba interface and Pt dispersion effects

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

$$S1: \quad NO + Pt \leftrightarrow NO - Pt$$

$$S2: \quad H_2 + 2Pt \leftrightarrow 2H - Pt$$

$$S3: \quad NO - Pt + H - Pt \leftrightarrow N - Pt + OH - Pt$$

$$S4: \quad N_2O + 2Pt \leftrightarrow NO - Pt + N - Pt$$

$$S5: \quad H - Pt + O - Pt \leftrightarrow OH - Pt + Pt$$

$$S6: \quad H - Pt + OH - Pt \rightarrow H_2O + 2Pt$$

$$S7: \quad N_2 + 2Pt \leftarrow 2N - Pt$$

$$S8: \quad NO - Pt + Pt \leftrightarrow N - Pt + O - Pt$$

$$S10^*: \quad N - Pt + 3H - Pt \leftrightarrow NH_3 - Pt + 3Pt$$

$$S13: \quad NH_3 + Pt \leftrightarrow NH_3 - Pt$$

$$S14: \quad O_2 + 2Pt \leftrightarrow 2O - Pt$$

$$S15: \quad NO - Pt + O - Pt \leftrightarrow NO_2 - Pt + Pt$$

$$S16: \quad NO_2 + Pt \leftrightarrow NO_2 - Pt$$

<u>Model Development Steps:</u>

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

Reaction System: Steady State $NO + H_2 + O_2$ on Pt/Al_2O_3

- Four additional hybrid steps involving NH_3:

S17 $NH_3 - Pt + 3O - Pt \rightarrow N - Pt + 3OH - Pt$

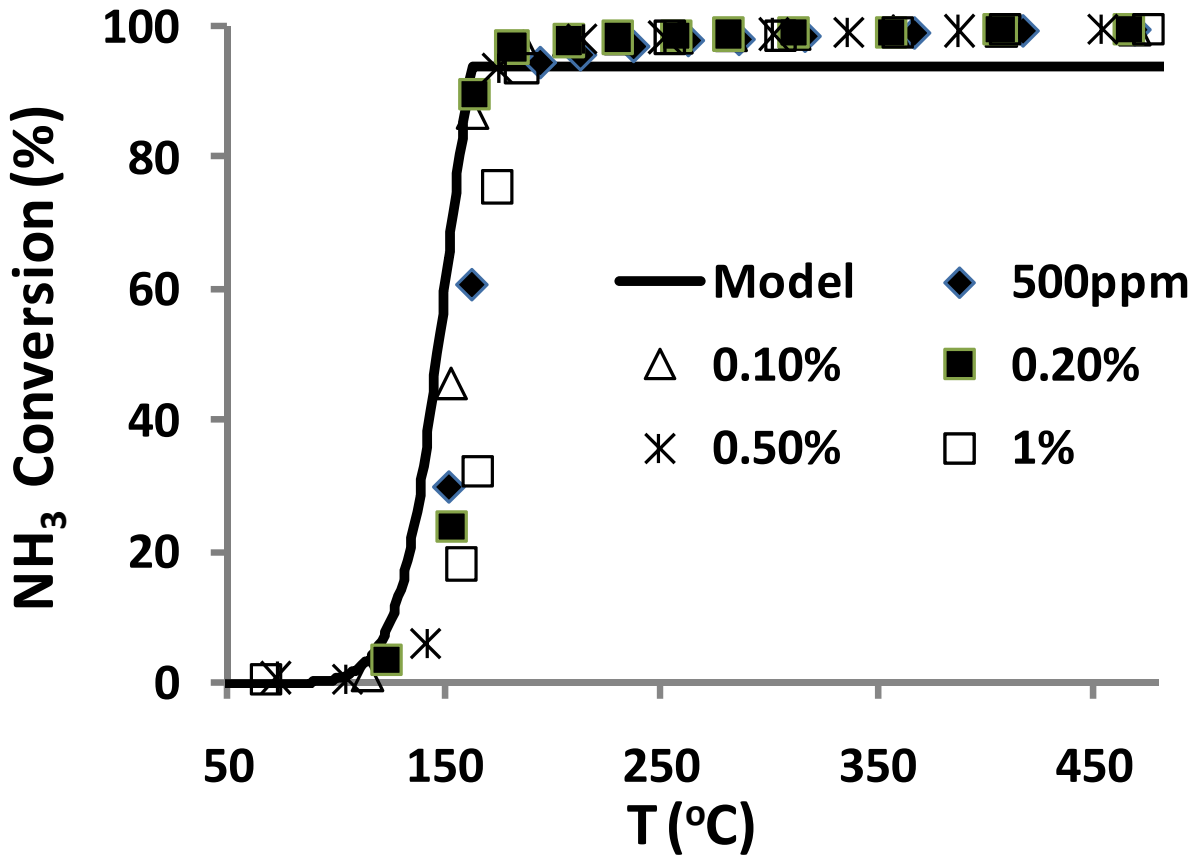
S18 $NH_3 - Pt + 3OH - Pt \rightarrow N - Pt + 3H_2O + 3Pt$

NH_3 oxidation

S19 $NH_3 - Pt + 3NO - Pt + 3Pt \rightarrow 4N - Pt + 3OH - Pt$ NH_3 oxidation by NO

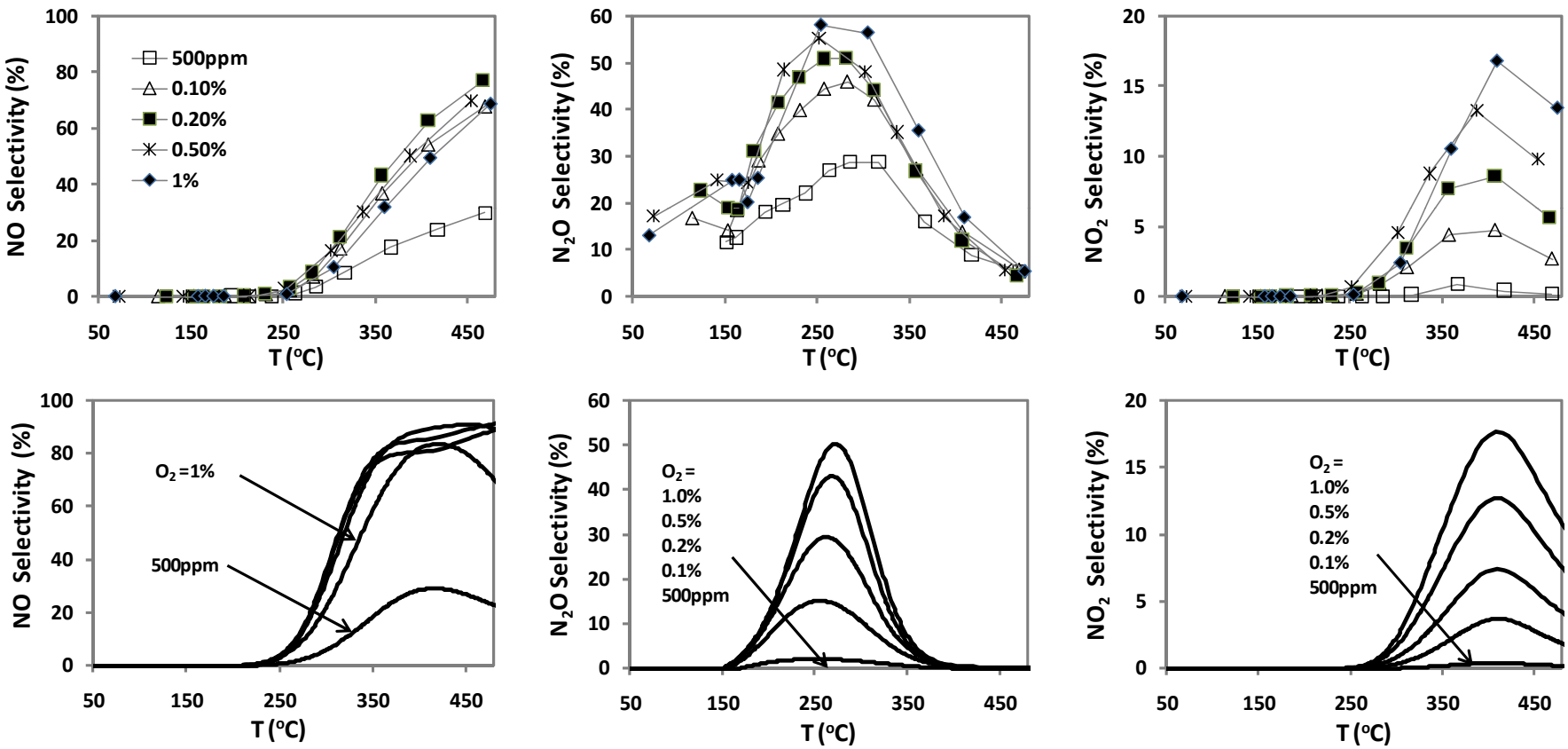
S20 $NO - Pt + 3H - Pt \leftrightarrow NH_3 - Pt + O - Pt + 2Pt$ NH_3 formation by NO+ H_2

Comparison of Experiment & Model: NH_3 + O_2 on Pt: Ammonia Conversion



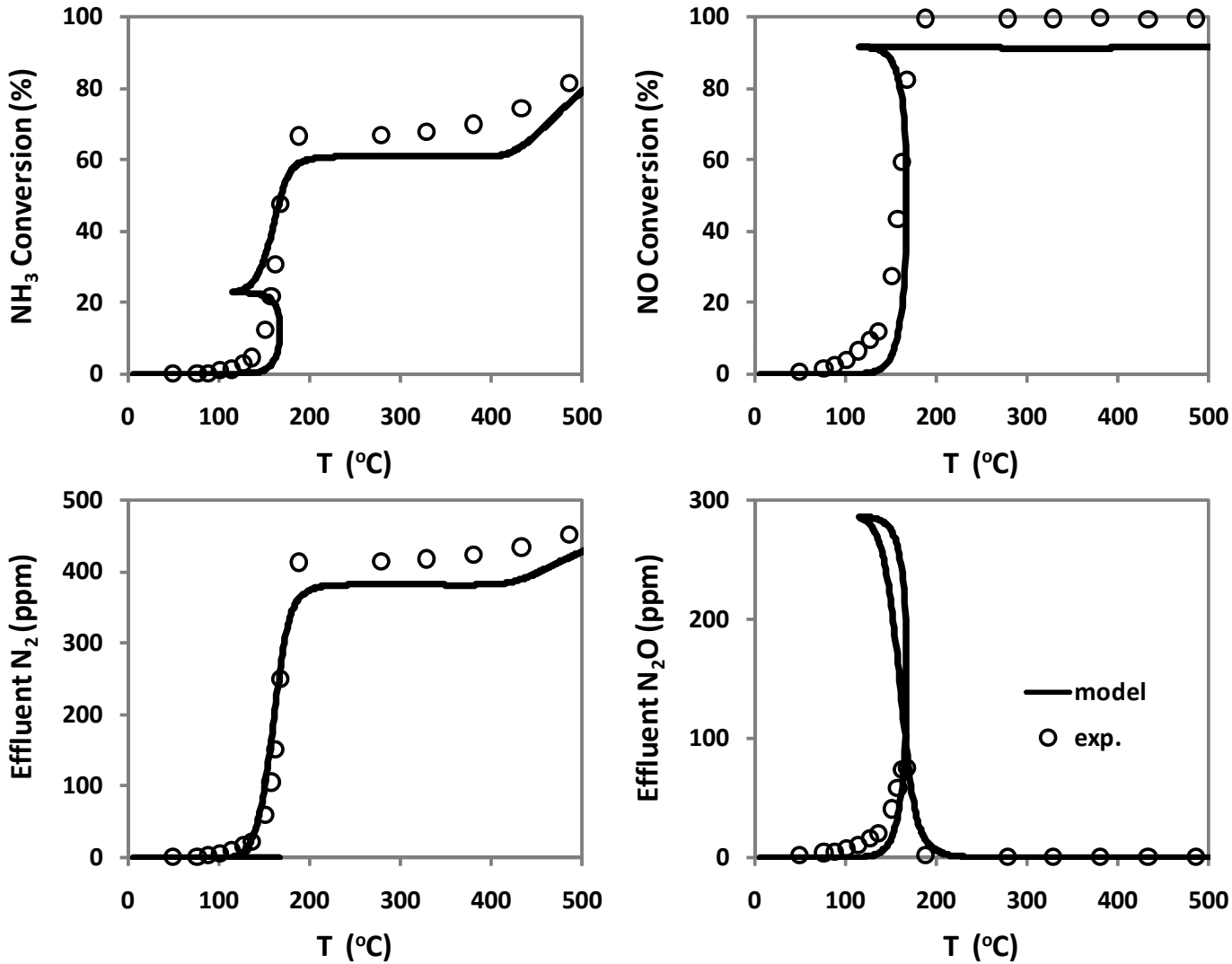
- *Model captures light-off & insensitivity to O_2 concentration*

Comparison of Experiment & Model: NH_3 + O_2 on Pt - Product Selectivities



- *Model captures trends in product selectivities*

Comparison of Experiments & Model: NH_3 + NO on Pt



- *Model captures nonlinear trends with temperature*

Summary

- Project on track:
  - Regeneration of model Pt/BaO LNTs: Combined experiments & modeling reveal complex spatio-temporal effects and close coupling between Pt & BaO
  - 9 refereed publications (plus 4 under review)
- Near-term (FY09) challenges:
  - Converge on microkinetic treatment of Pt/BaO interface
  - Utilize LNT model for optimization
  - Conduct testing with diesel engine exhaust
  - Complete several more manuscripts