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

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

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Overview

Timeline

- Start: Oct. 1, 2005
- End: Sept. 30, 2009
- 80% complete

Budget

- Total project funding
  - DOE: $715,661
  - UH: $189,699
- Funding received
  - FYO8: $188,819
  - FYO9: $245,778

Barriers

- Mechanism & kinetics of LNT storage & regeneration not known
- Predictive LNT model needed for optimization

Partners

- Active collaborations
  - Ford Motor Company
  - BASF Catalysts LLC

Technical Barriers & Challenges

- Lean NOx Trap: 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

Project Premise: Development of predictive LNT reactor model containing main chemistry & transport processes is critical for understanding, design, & operation of lean NOx traps

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*

Project Milestones & Tasks

- **Task 1:** *Carry out comprehensive mechanistic study of the regeneration of model Pt/Rh/Ba NSR catalysts with reductants H_2 and CO in the TAP reactor and TGA/DSC systems.*
- ***Task 2:*** *Evaluate performance of the model NSR catalysts in a bench-scale NOx trap using synthetic lean burn and diesel exhaust, with particular attention placed on differences in reductant type and injection protocols.*
- ***Task 3:*** ***a.*** *Develop and analyze a first-principles based predictive lean NOx trap model that incorporates a detailed understanding of the chemistry and transport processes.*

  b. *Compare alternative NOx trap configurations and identify optimal designs and operating strategies.*
- ***Task 4:*** *Test prototype NSR device in the exhaust stream of a diesel vehicle.*

	0-6	6-12	12-18	18-24	24-30	31-36	37-42	43-48
Task 1	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX
Task 2		XXX	XXX	XXX	XXX	XXX	XXX	Done
Task 3a	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XX
Task 3b								XX
Task 4								XX

LNT 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

- Microkinetics
- Global kinetics

Reactor Modeling

- Isothermal / short monoliths
- Non-isothermal integral monoliths

Activities

- Elucidation of data
- Bifurcation analysis

Low-dimensional models for optimization & control

Active Collaborations

- **BASF Catalysts LLC** (formerly Engelhard)
  - Dr. Stan Roth, Dr. C.Z. Wan
  - Builds off State of Texas / Engelhard funded project (2003-2006)
  - 10 refereed publications on LNTs from 2004-2006
  - BASF provided several series of model catalysts: Pt, Pt/Ba, Rh, Pt/Rh/Ba, Pt/Rh/Ba/Ce, Rh/Ce, etc.

- **Ford Motor Company**
  - Dr. Bob McCabe, Dr. Joseph Theis
  - Grant: Development of low-dimensional models of TWC and LNT converters for on-vehicle use
  - Student intern during Summer 08: Divesh Bhatia

Facilities Utilized in Study

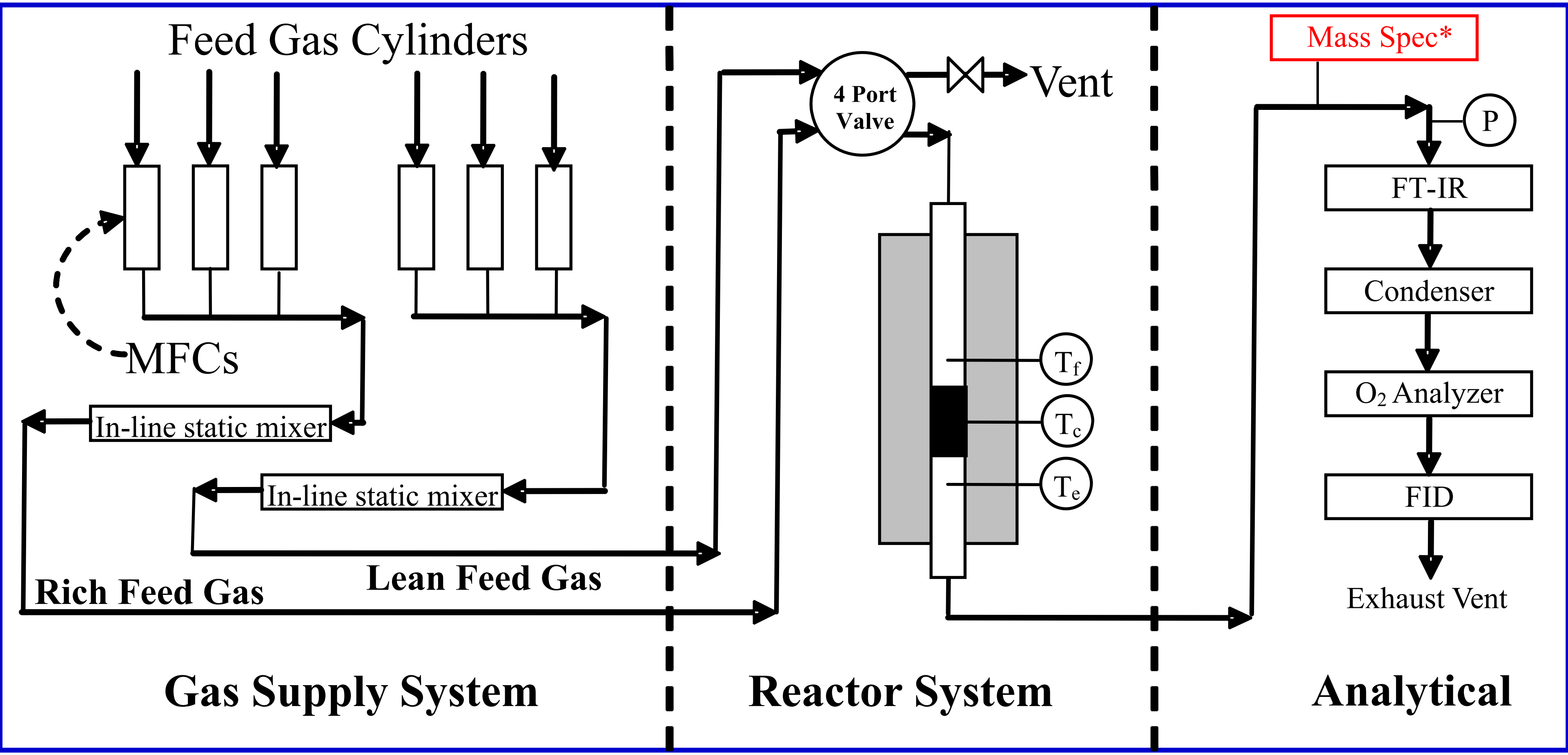
- ***Bench-scale reactor system*** for atmospheric pressure steady-state & cyclic operation studies of NSR chemistries on monoliths & powders
- ***TAP reactor system*** for ultrahigh vacuum flow transient studies of NSR chemistries on powders & monoliths
- ***Catalyst characterization equipment*** for 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 (near completion)

Experimental Studies

Accomplishments in FY08

- Bench-scale reactor studies:
  - 3 papers published
    - R4: 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, **81**, 161-181 (2008).
    - R5: 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).
    - R6: 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).
  - Carried out detailed kinetics study of NO oxidation on Pt/Al_2O_3 & Pt/BaO/Al_2O_3
    - Identified issues of Pt deactivation & rate inhibition effects (NO, NO_2)
    - Data used to develop predictive kinetic model
    - Paper under review (R11: Bhatia, D., V. Balakotaiah, M.P. Harold, and R. McCabe, "Experimental and Kinetic Study of NO Oxidation on Model Pt Catalysts," J. Catalysis, submitted (March, 2009).
  - Carried out systematic study of effect of Pt dispersion in Pt/BaO/Al_2O_3 on LNT performance
    - Compared storage, activity, and selectivity effects
    - Identified catalyst & conditions giving low or high NH_3 yield
    - Revisions to paper pending (R10: 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, revisions pending (March, 2009).

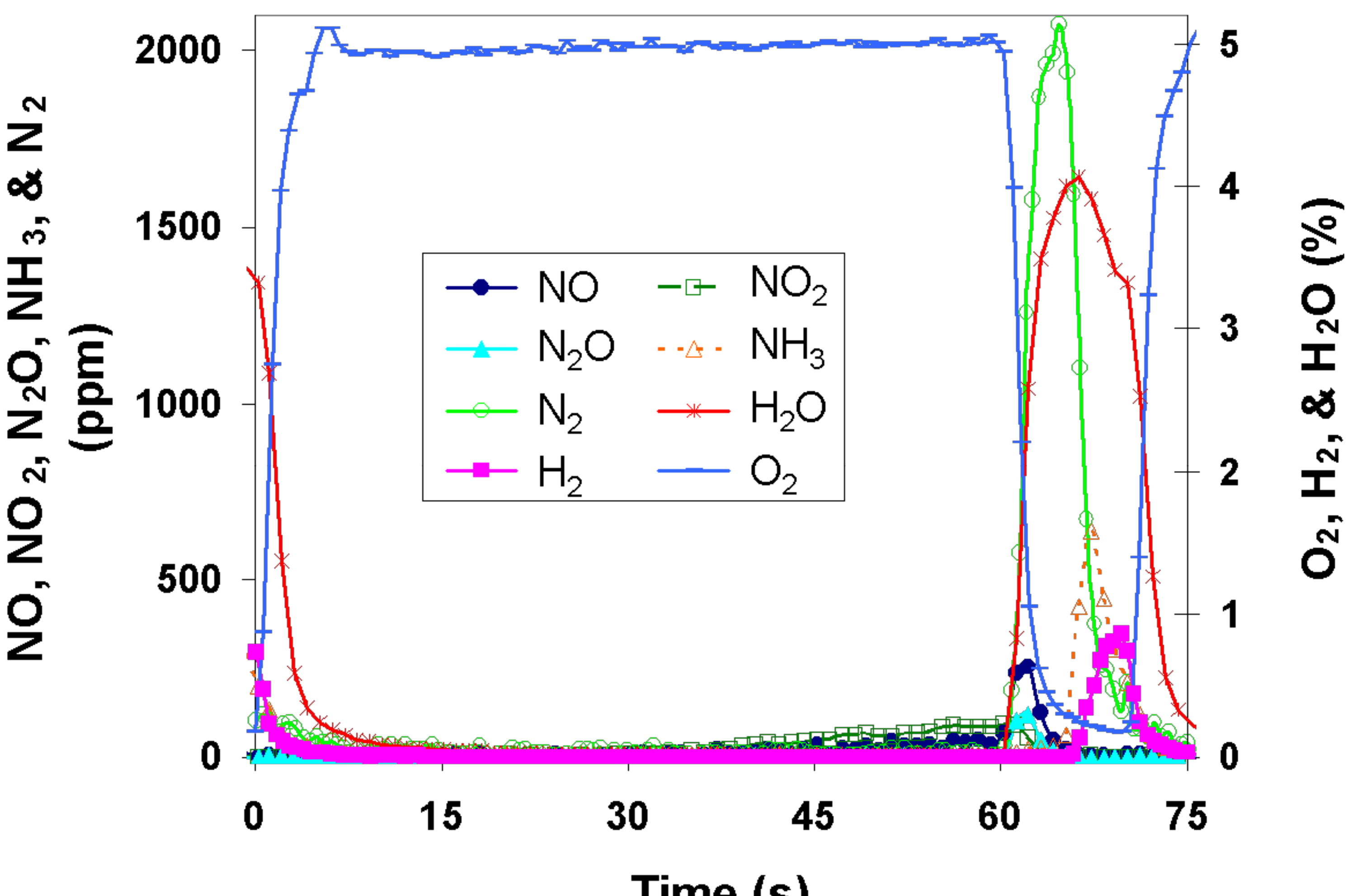
Bench-Scale Reactor System



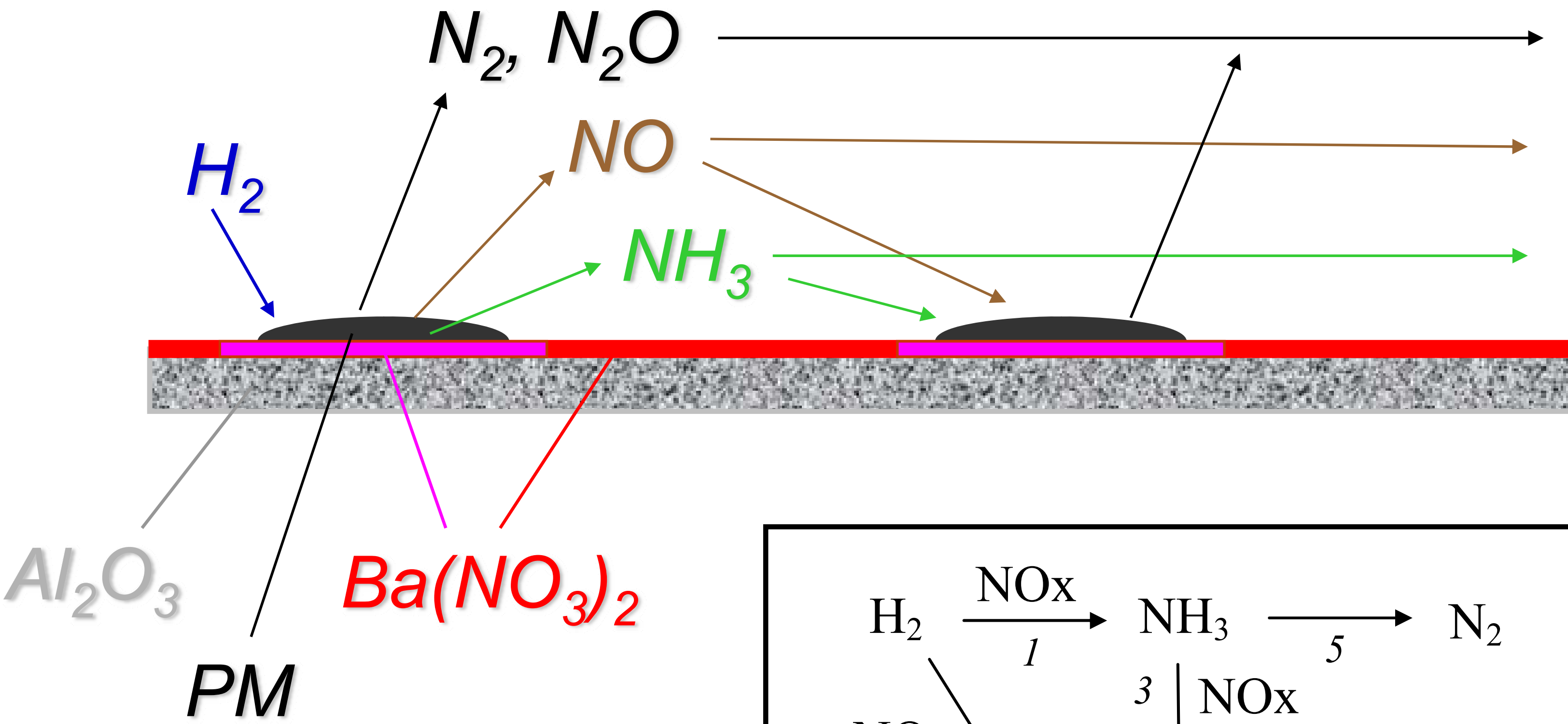
* Mass spec installed 6/07

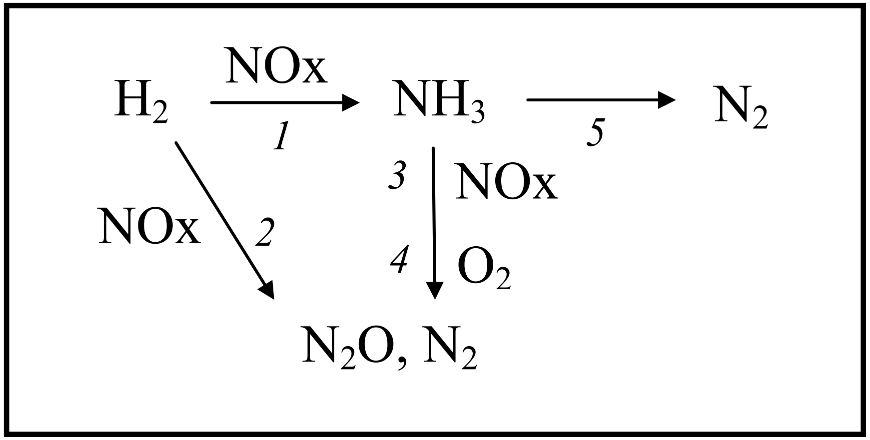
Effluent Composition versus Time: Storage and Reduction

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

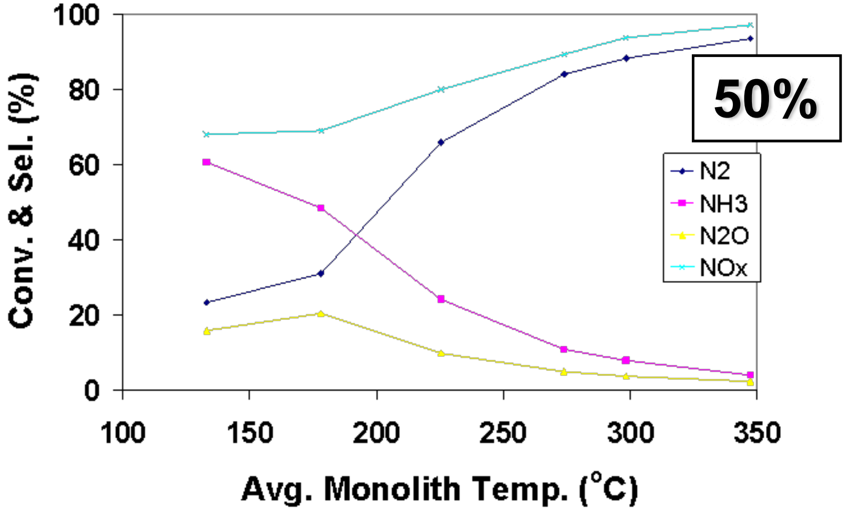


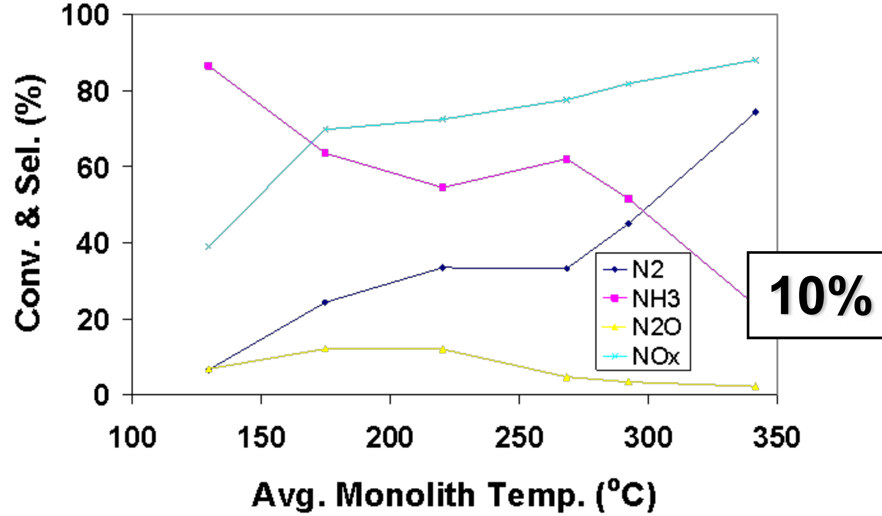
Phenomological Picture of NSR with H_2 as Reductant

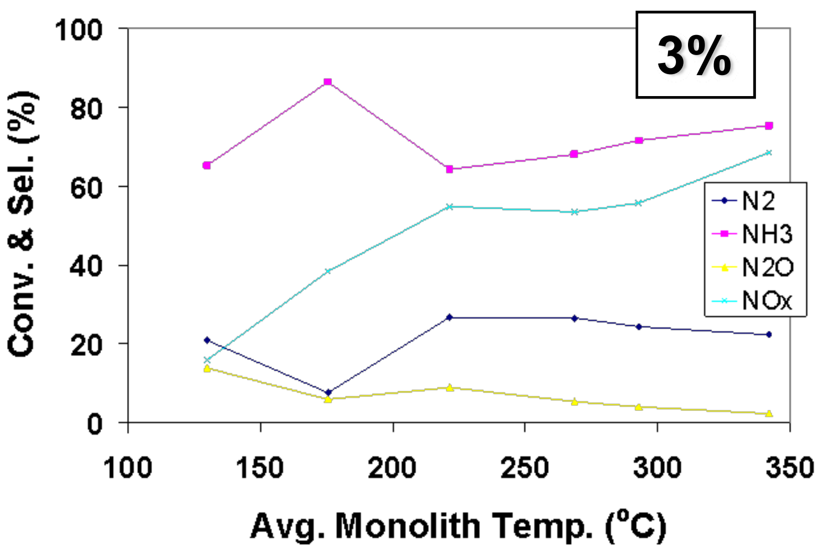




Effect of Pt Dispersion







<u>Conditions:</u>

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

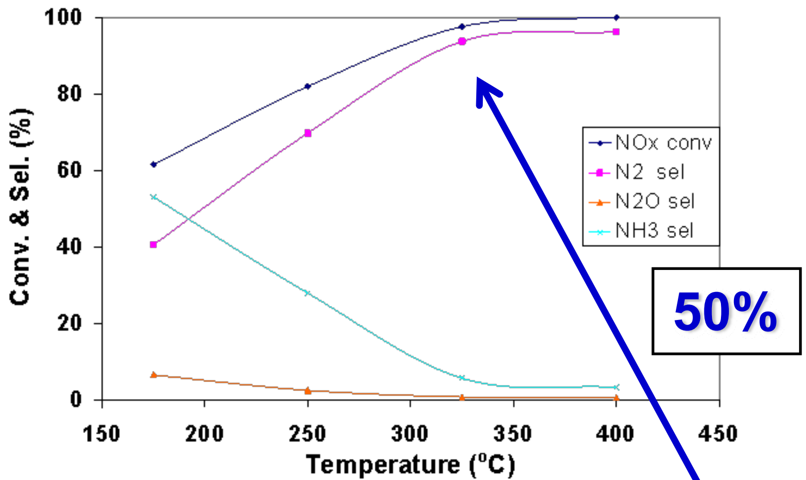
Rich: 2% H_2, 0.5% O_2, balance Ar (30 s)

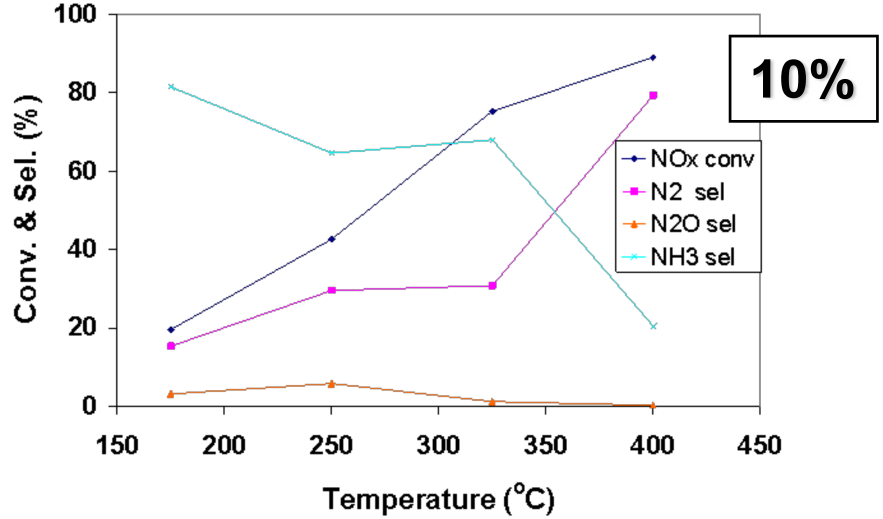
Pt loading: 2.70 wt.%

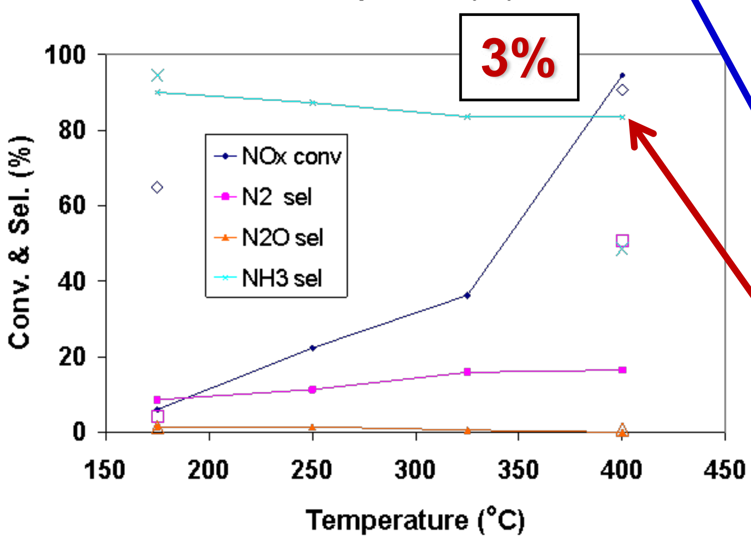
BaO loading: 14.6 wt.%

- *Significant effect of Pt dispersion on conversion & selectivity*

Effect of Pt Dispersion: Fixed Stored NOx







Conditions:

Lean: Fixed Stored NOx 1.3 x 10^{-5} mole N

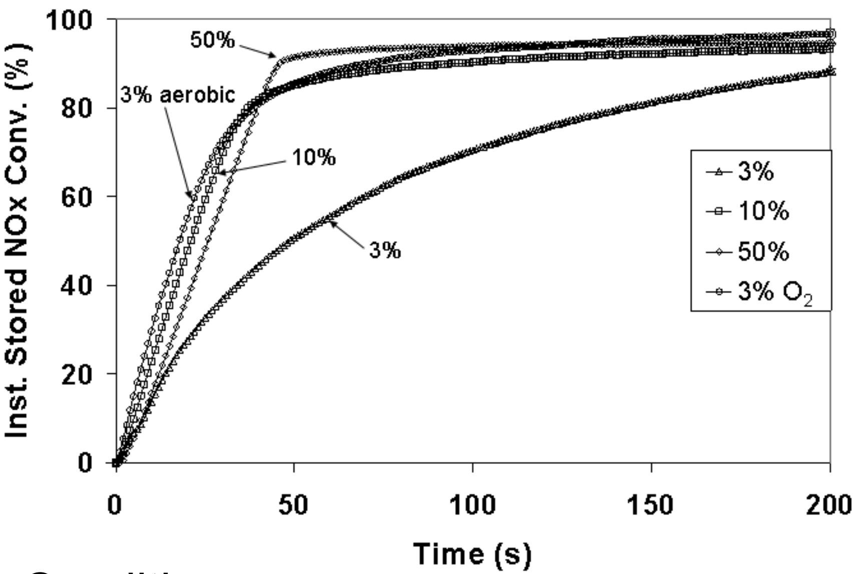
Rich: 1500 ppm H_2, balance Ar

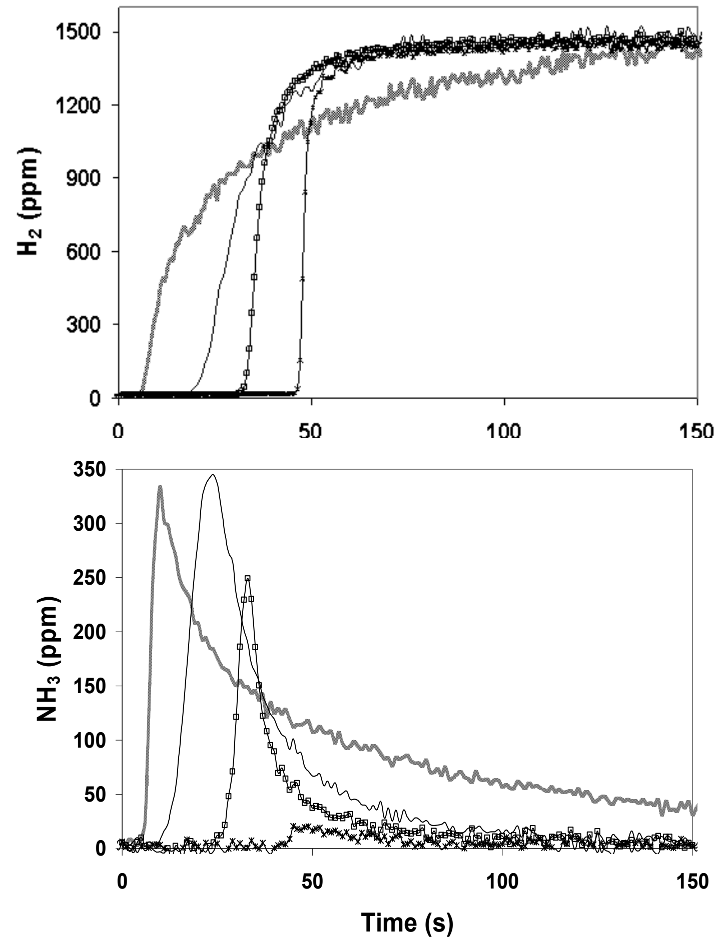
Pt, BaO loading: 2.70 wt.%, 14.6 wt.%

High dispersion: NOx to N_2

Low dispersion: NOx to NH_3

Transient Reduction: Effect of Pt Dispersion with Fixed Stored NOx





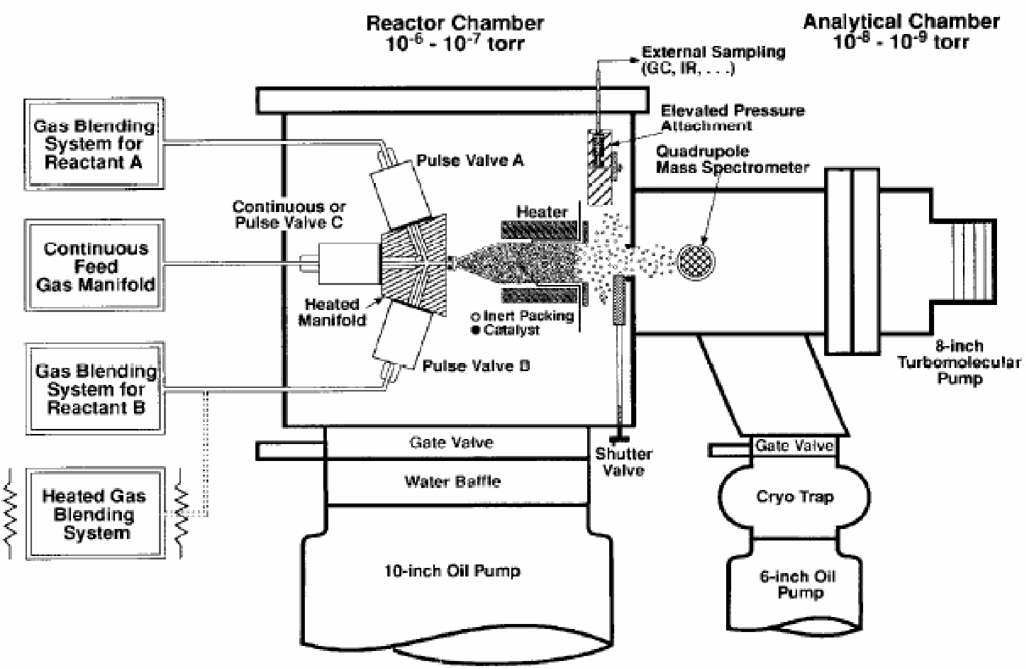
Conditions:
Lean: Fixed Stored NOx 1.3 x 10^{-5} mole N
Rich: 1500 ppm H_2, balance Ar (200 s)
Pt, BaO loading: 2.70 wt.%, 14.6 wt.%

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

Accomplishments in FY08, cont.

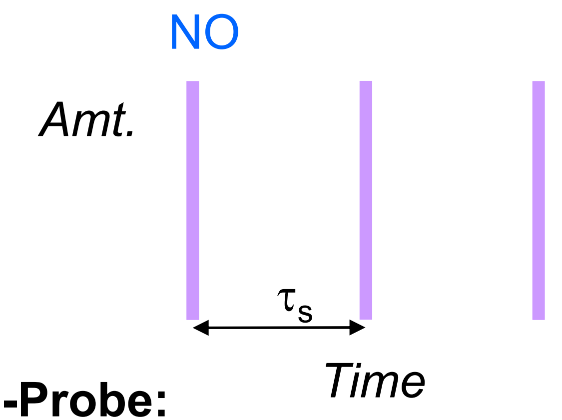
- TAP reactor studies
  - Paper under review (R9: Kumar, A., V. Medhekar, M.P. Harold, and V. Balakotaiah, "NO Decomposition and Reduction Studies on Pt/Al_2O_3 Powder and Monolith Catalysts Using the TAP Reactor," Appl. Catal. B. Environmental, revisions pending; March, 2009).
  - Demonstrated use of monolith catalyst in TAP reactor for first time (R9)
  - Provided performance data of Pt/BaO/Al_2O_3 catalysts for microkinetic models
  - Isotopic $^{18}O_2$ study of NO oxidation and NOx storage
  - Isotopic ^{15}NO decomposition and $^{15}NO + H_2$ pump-probe experiments provided insight about pathways for N_2, NH_3 production & Pt/BaO coupling effects

Temporal Analysis of Products (TAP)

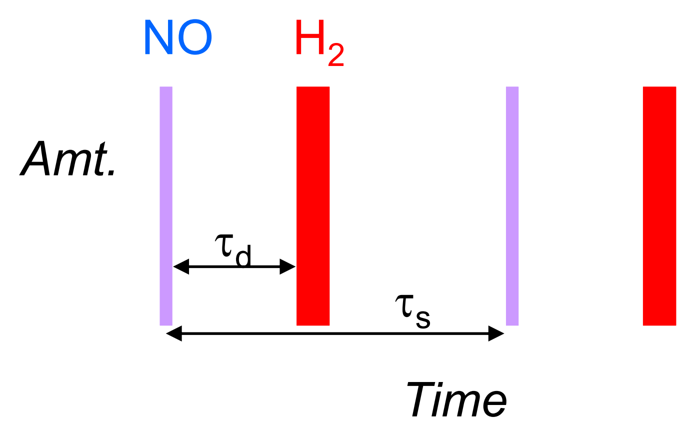


(Reference: P. Mills, DuPont)

Multi-Pulse:



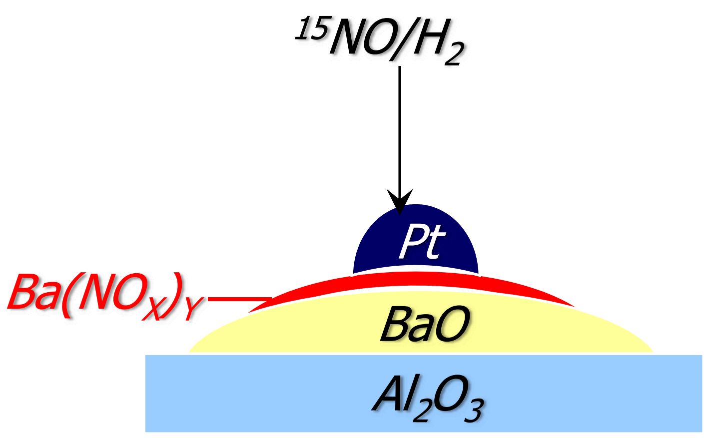
Pump-Probe:



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

NO → **$^{15}NO/H_2$**

Objective: 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)

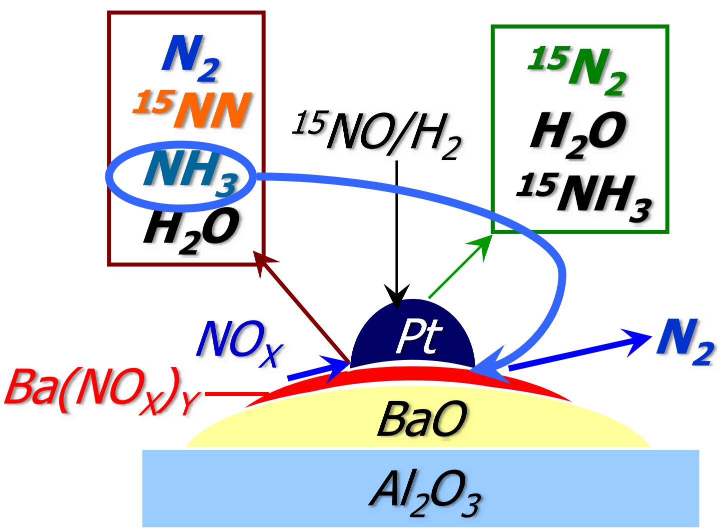


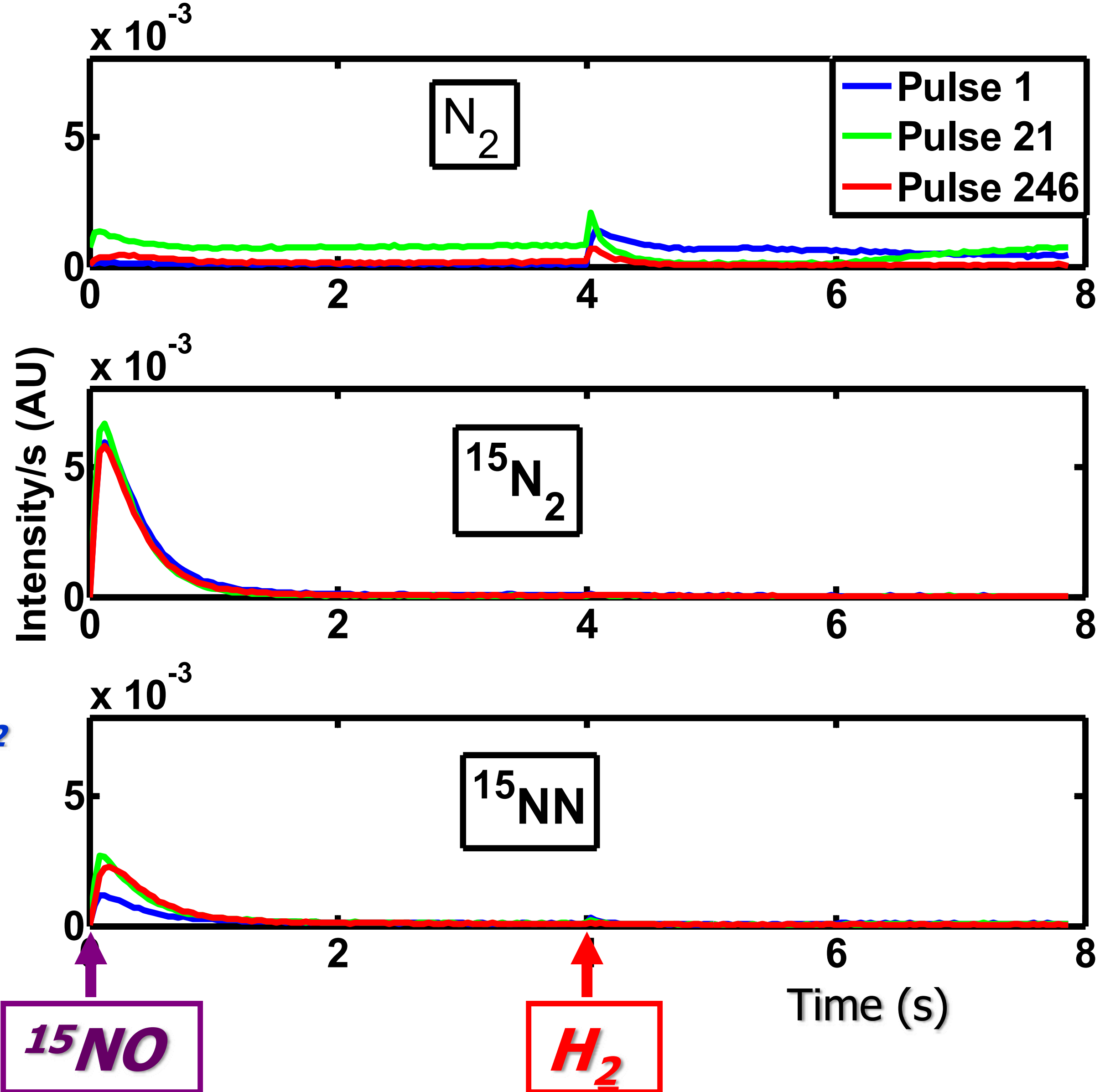
$^{15}NO/H_2$ Pump-Probe on Pre-nitrated $Pt/BaO/Al_2O_3$: Instantaneous Results

T = 250 °C

$H_2/^{15}NO = 4.4$

NO → $^{15}NO/H_2$



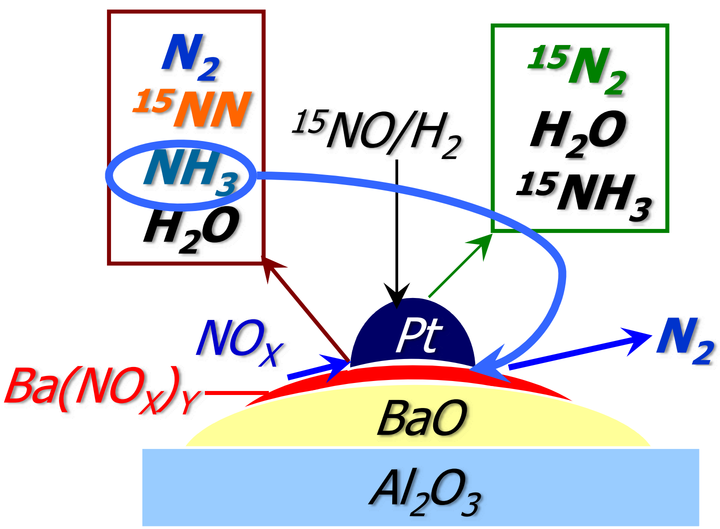


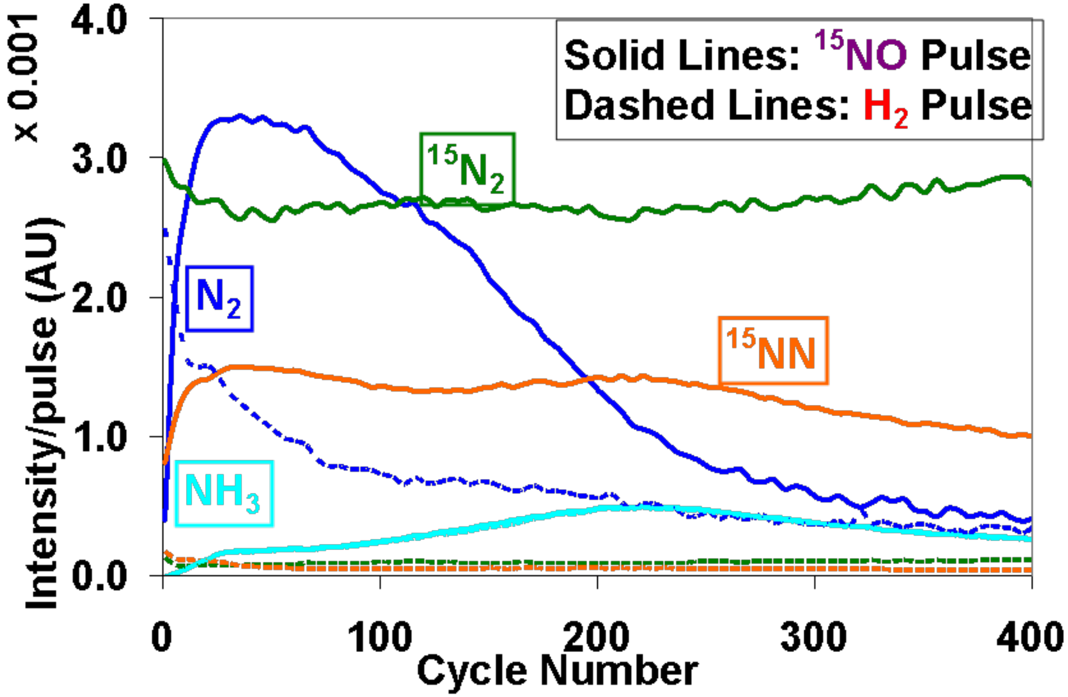
$^{15}NO/H_2$ Pump-Probe on Pre-nitrated Pt/BaO/Al_2O_3: Integral Results

T = 250 °C

$H_2/^{15}NO$ = 4.4

NO → $^{15}NO/H_2$





Data reveal following chemistry:

- *$^{15}N_2$ 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*

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

Modeling Studies

Accomplishments in FY08

- Modeling
  - 3 papers published
    - R3: 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).
    - R7: Bhatia, D., V. Balakotaiah and M.P. Harold, "Bifurcation Analysis of CO and H_2 Oxidation on Pt/Al_2O_3 Monolith Reactors." Chem. Eng. Sci. **64**, 1544-1558 (2009).
    - R8: 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, doi:10.1016/j.apcatb.2008.11.017 (2008), in press.
  - Kinetic modeling
    - Developed microkinetic model for H_2/NO/O_2 on Pt (R3)
    - Developed micro & global kinetics for NO oxidation on Pt (R11)
    - Developed micro & global kinetics for co-oxidation of H_2 & CO on Pt (R7)
  - NOx trap reactor modeling
    - Incorporated microkinetic model into short monolith model; predicted steady-state H_2/NO/O_2 on Pt from earlier bench-scale study (R3)
    - Incorporated H_2/NO/O_2 microkinetic model into LNT model with NO/O_2 oxidation and stored NOx chemistry; currently evaluating model vs. LNT bench-scale data
    - Developed low dimensional monolith reactor model for steady-state and transient operation of monolith reactors (R13)

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

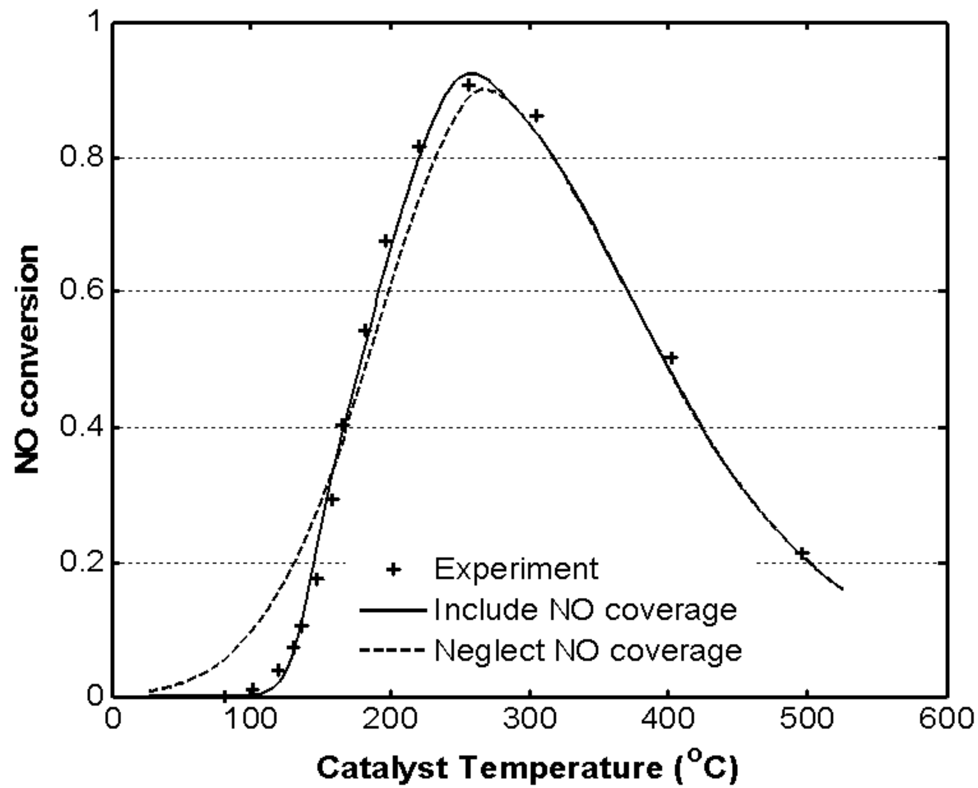
$$C_o k_{jc}(X_{jm} - X_{js}) = \delta_c (R^j{}_{ad} - R^j{}_{de})_{BaO} + \delta_c (R^j{}_{ad} - R^j{}_{de})_{Pt}$$

Site Balance

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

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



$$1: NO + Pt \longleftrightarrow NO - Pt$$
$$2: O_2 + Pt \longleftrightarrow O_2 - Pt$$
$$3: NO - Pt + O - Pt \longleftrightarrow NO_2 - Pt + Pt$$
$$4: NO_2 + Pt \longleftrightarrow NO_2 - Pt$$
$$5: O_2 - Pt + Pt \longleftrightarrow 2O - Pt$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

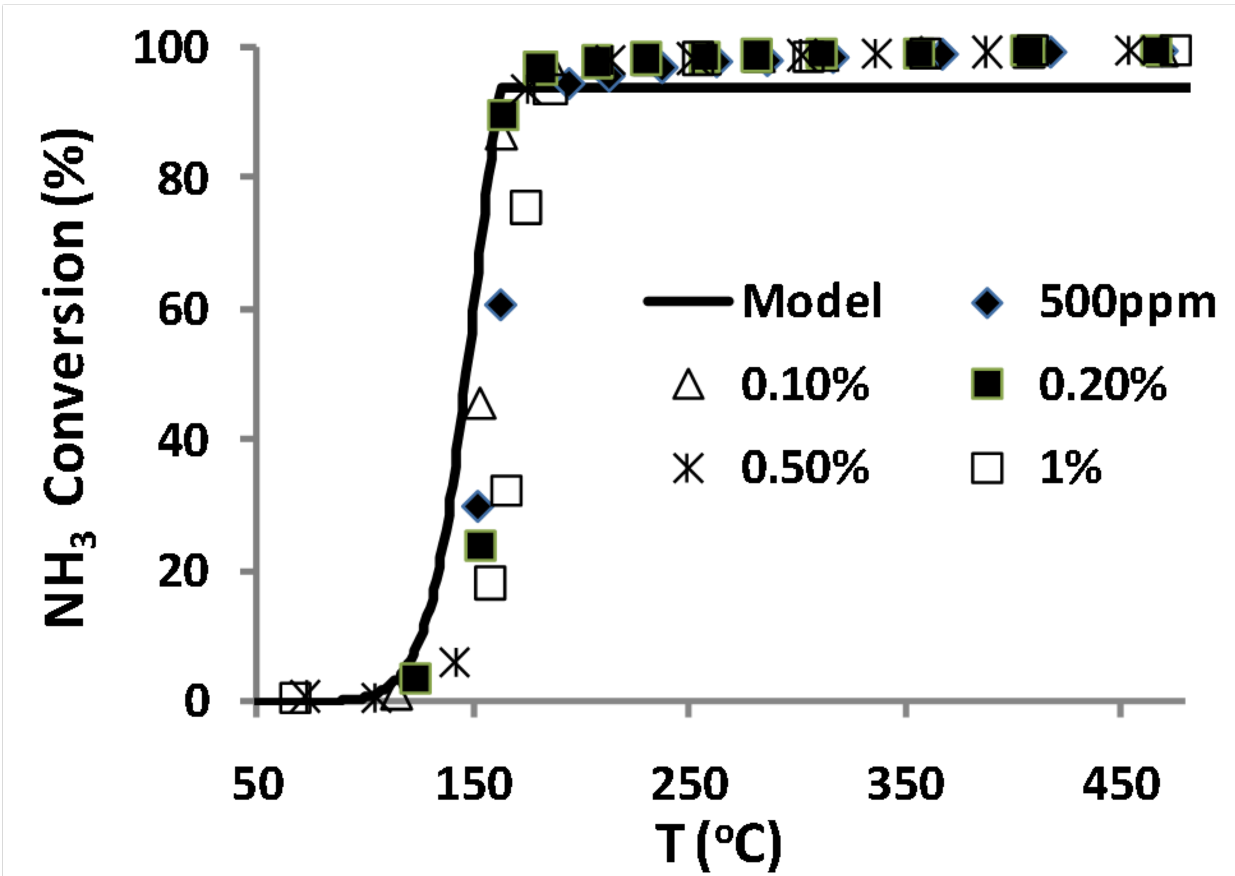
S18 $NH_3 - Pt + 3OH - Pt \rightarrow N - Pt + 3H_2O + 3Pt$

(NH_3 oxidation: S17, S18)

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

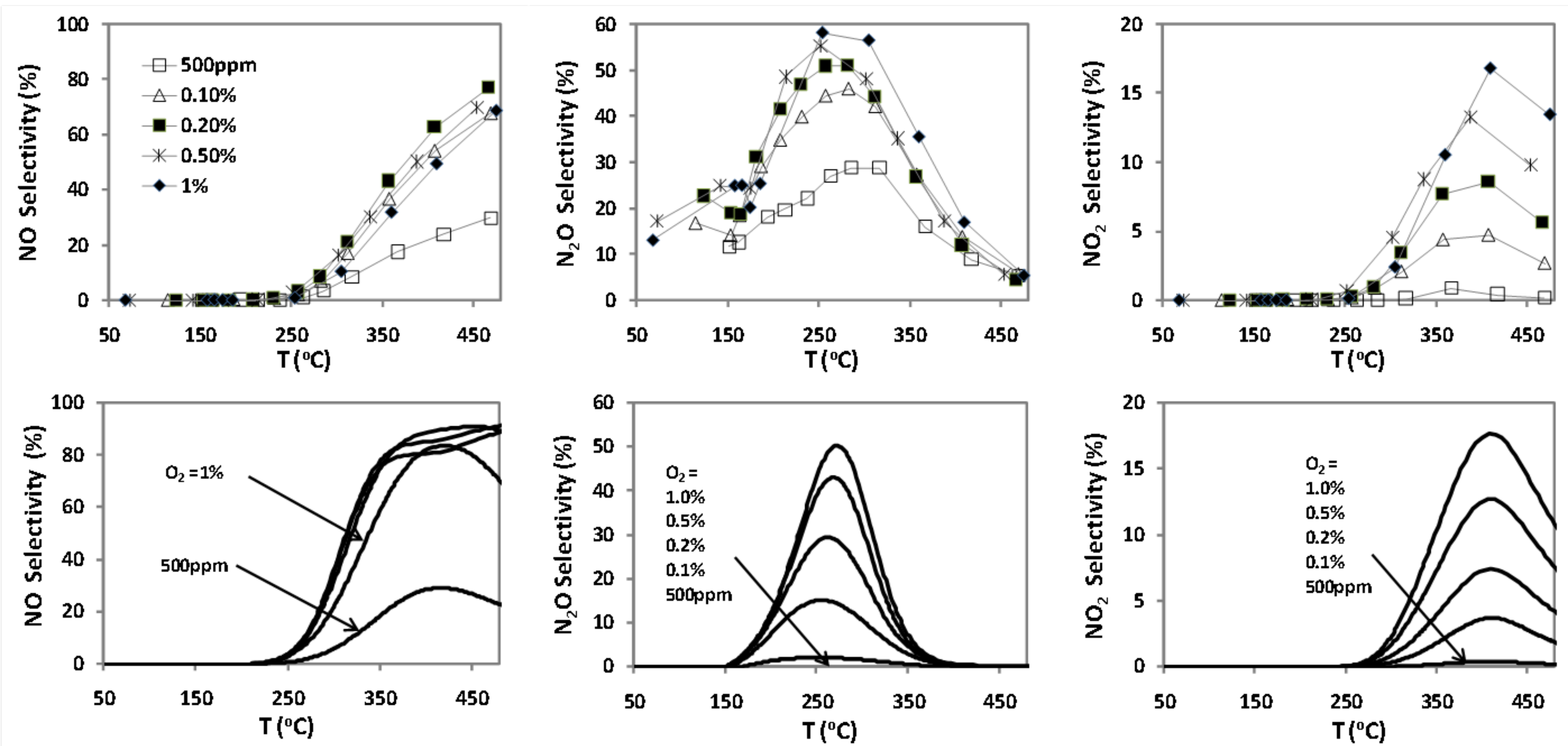
S20 $NO - Pt + 3H - Pt \leftrightarrow NH_3 - Pt + O - Pt + 2Pt$ — NH_3 formation by NO+ H_2

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



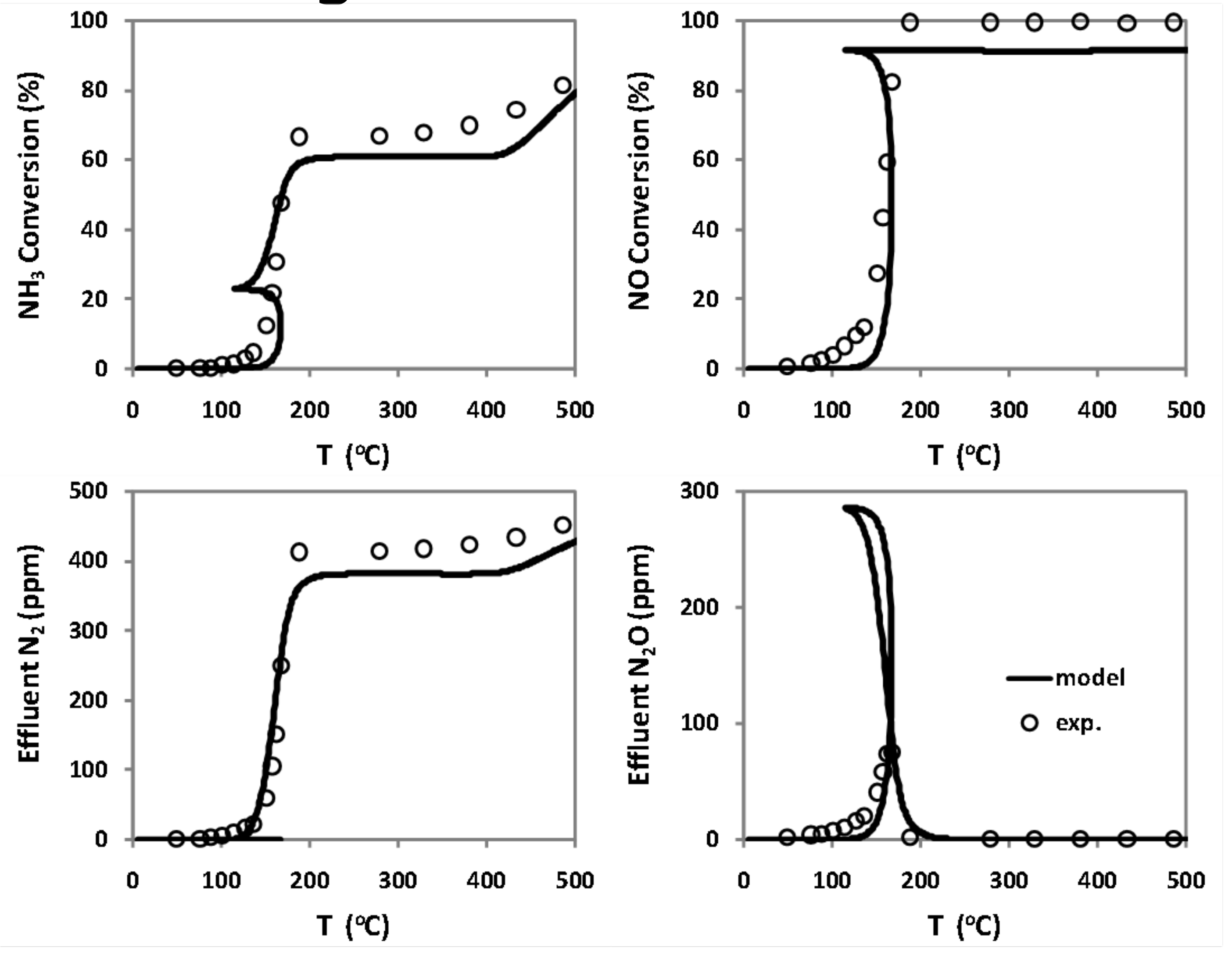
- *Model captures light-off & insensitivity to O_2 concentration*

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*

Year 4 Activities: Experiments

- Conduct bench-scale and TAP experiments on additional catalyst types
  - Complete study of Pt dispersion for Pt/BaO catalysts
  - Evaluate effect of Rh & CeO_2 with H_2 as reductant
  - Carry out isotopic studies using ^{15}NO and/or $^{18}O_2$
- Carry out evaluation of stratified monolith configurations
  - Determine if improved performance with reduced reactor volume, precious metal
- Carry out testing of selected LNTs with engine exhaust in dynamometer facility
  - Compare synthetic feed to vehicle feed

Year 4 Activities: Modeling

- Further upgrade microkinetic model through specific kinetic measurements in bench-scale & TAP reactors
- Incorporate upgraded kinetic model into integral transient LNT monolith reactor
  - Converge on simplest regeneration and storage chemistry that predicts data
- Use LNT model to investigate different NOx trap operating strategies and designs
  - Areas of focus: Maximize NH_3 production, maximize N_2 production
  - Guide experimental efforts and verification

Microkinetic Model Used for LNT Model Development

Pt Chemistry

O_2(g)+2Pt=2O-Pt
H_2(g)+2S=2H-Pt
NO(g)+Pt=NO-Pt
2N-Pt=N_2(g)+2Pt
NO_2(g)+s=NO_2-S
O-Pt+H-Pt=OH-Pt+Pt
OH-Pt+H-Pt=H_2O(g)+2Pt
NO-Pt+Pt=N-Pt+O-Pt
O-Pt+NO-Pt=NO_2-Pt+Pt
N-Pt+3H-Pt=NH_3-Pt+3Pt
NO-Pt+3H-Pt=NH_3-Pt+O-Pt+2Pt
NH_3(g)+Pt=NH_3-Pt
NO-Pt+H-Pt=N-Pt+OH-Pt
N_2O(g)+2Pt=NO-Pt+N-Pt
NH_3-Pt+3NO-Pt+3Pt=4N-Pt+3OH-Pt
NH_3-Pt+3OH-Pt=3H_2O+N-Pt+3Pt
NH_3-Pt+3O-Pt=N-Pt+3OH-Pt

Storage Chemistry

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

Spillover Chemistry at Pt/Ba Interface

NO_2-BaO+Pt=O-BaO+NO-Pt

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

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