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

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May 20, 2009

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.

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LNT Research Approach

**Experiments**
- Lean NO\textsubscript{x} Storage
- Steady-state lean NO\textsubscript{x} reduction
- NO\textsubscript{x} storage & reduction (cycling)
- Transient kinetics studies (TAP)
- Bench-scale Reactor Studies
- Vehicle Dynamometer Testing

**Modeling & Simulation**

**Kinetic Modeling**
- Microkinetics
- Global kinetics

**Reactor Modeling**
- Isothermal / short monoliths
- Non-isothermal integral monoliths

**Activities**
- Elucidation of data
- Bifurcation analysis

Implementation / Optimization of LNTs
- Develop predictive LNT models
- Optimize LNT design
- Integrate into onboard control system

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
  - Carried out detailed kinetics study of NO oxidation on Pt/Al₂O₃ & Pt/BaO/Al₂O₃
    - Identified issues of Pt deactivation & rate inhibition effects (NO, NO₂)
    - Data used to develop predictive kinetic model
  - Carried out systematic study of effect of Pt dispersion in Pt/BaO/Al₂O₃ on LNT performance
    - Compared storage, activity, and selectivity effects
    - Identified catalyst & conditions giving low or high NH₃ yield
Bench-Scale Reactor System

Feed Gas Cylinders

- MFCs
- In-line static mixer

Gas Supply System

Rich Feed Gas ➔ Lean Feed Gas

Reactors System

4 Port Valve ➔ Vent

T_f, T_c, T_e

Temperatures

Mass Spec*

* Mass spec installed 6/07

Analytical

- P
- FT-IR
- Condenser
- O_2 Analyzer
- FID
- Exhaust Vent

* 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

$H_2$ $\rightarrow$ $N_2, N_2O, NO, NOx, NH_3$ $\rightarrow$ $H_2$ $\rightarrow$ $NH_3$ $\rightarrow$ $N_2$

$NOx$ $\rightarrow$ $N_2O, N_2$ $\rightarrow$ $H_2$ $\rightarrow$ $NH_3$ $\rightarrow$ $N_2$

$Ba(NO_3)_2$, $Al_2O_3$, $PM$
Effect of Pt Dispersion

Conditions:
Lean: 500 ppm NO, 5% O₂ (60 s)
Rich: 2% H₂, 0.5% O₂, balance Ar (30 s)
Pt loading: 2.7 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 $1.3 \times 10^{-5}$ mole N
Rich: 1500 ppm H₂, balance Ar
Pt, BaO loading: 2.70 wt.%, 14.6 wt.%

High dispersion: NOx to N₂
Low dispersion: NOx to NH₃
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\textsubscript{2}, balance Ar (200 s)
Pt, BaO loading: 2.70 wt.\%, 14.6 wt.\%

- High dispersion leads to faster reduction & N\textsubscript{2}
- Low dispersion leads to slower reduction to NH\textsubscript{3}
Accomplishments in FY08, cont.

- TAP reactor studies
  - Demonstrated use of monolith catalyst in TAP reactor for first time (R9)
  - Provided performance data of Pt/BaO/Al2O3 catalysts for microkinetic models
  - Isotopic 18O2 study of NO oxidation and NOx storage
  - Isotopic 15NO decomposition and 15NO + H2 pump-probe experiments provided insight about pathways for N2, NH3 production & Pt/BaO coupling effects
Temporal Analysis of Products (TAP)

(Reference: P. Mills, DuPont)
Isotopic TAP Study: $^{15}$NO/H$_2$ Pump-Probe on Pre-nitrated Pt/BaO/Al$_2$O$_3$

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$_2$O$_3$: Instantaneous Results

T = 250 °C
H$_2$/$^{15}$NO = 4.4

$^{15}$NO/H$_2$ → $^{15}$NO/H$_2$

$^{15}$N$_2$, H$_2$O, $^{15}$NH$_3$

$^{15}$NO/H$_2$ → $^{15}$N$_2$, H$_2$O, $^{15}$NH$_3$
$^{15}$NO/H$_2$ Pump-Probe on Pre-nitrated Pt/BaO/Al$_2$O$_3$: Integral Results

$T = 250 \, ^{\circ}\text{C}$

$H_2/^{15}$NO = 4.4

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

$H$-$Pt + Ba(NO_3)_2 + ^{15}$N-Pt
Modeling Studies
Accomplishments in FY08

Modeling

- 3 papers published

Kinetic modeling

- Developed microkinetic model for H₂/NO/O₂ on Pt (R3)
- Developed micro & global kinetics for NO oxidation on Pt (R11)
- Developed micro & global kinetics for co-oxidation of H₂ & CO on Pt (R7)

NOx trap reactor modeling

- Incorporated microkinetic model into short monolith model; predicted steady-state H₂/NO/O₂ on Pt from earlier bench-scale study (R3)
- Incorporated H₂/NO/O₂ microkinetic model into LNT model with NO/O₂ 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)

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

Energy Balance

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

**Solid Phase**

Surface balances (for species j on site i)

\[
C_i \frac{\partial \theta_{ji}}{\partial t} = R_{adi}^j - R_{dei}^j - \sum \nu_j R_{rxn}
\]

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**

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

**Site Balance**

\[
\sum \theta_{ji} + \theta_{vi} = 1
\]
NO Oxidation on Pt Catalysts

- NO oxidation rate on Pt/Al\textsubscript{2}O\textsubscript{3} & Pt/BaO/Al\textsubscript{2}O\textsubscript{3}:
  - Rate inhibited by NO and NO\textsubscript{2}
  - Rate limited by kinetic (O\textsubscript{2} adsorption) and thermodynamic factors
  - Global kinetic model developed
  - Transient kinetics complicated by uptake of NO\textsubscript{2} on Al\textsubscript{2}O\textsubscript{3} & BaO and oxidation of Pt

1: \textit{NO + Pt} $\rightleftharpoons$ \textit{NO} - \textit{Pt}
2: \textit{O\textsubscript{2} + Pt} $\rightleftharpoons$ \textit{O\textsubscript{2} - Pt}
3: \textit{NO - Pt + O - Pt} $\rightleftharpoons$ \textit{NO\textsubscript{2} - Pt + Pt}
4: \textit{NO\textsubscript{2} + Pt} $\rightleftharpoons$ \textit{NO\textsubscript{2} - Pt}
5: \textit{O\textsubscript{2} - Pt + Pt} $\rightleftharpoons$ \textit{2O - Pt}

\[ R_{v,\text{NO}_{\text{ox}}} = k_f X_{O_2,s} \left[ 1 - \frac{1}{X_{O_2,s}} K_2 K_5 \left( \frac{1}{K_3} \frac{K_4 X_{\text{NO}_2,s}}{K_1 X_{\text{NO}_2,s}} \right)^2 \right] \left( \frac{1}{K_3} \frac{K_4 X_{\text{NO}_2,s}}{K_1 X_{\text{NO}_2,s}} \right) \]
Reaction System: Steady State
NO + H₂ on Pt/Al₂O₃

Model Development
Steps:
• 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 + H₂ + O₂ on Pt/Al₂O₃

- Four additional hybrid steps involving NH₃:

  S17  \[ NH₃ - Pt + 3O - Pt \rightarrow N - Pt + 3OH - Pt \]  \hspace{1cm} \text{NH₃ oxidation}

  S18  \[ NH₃ - Pt + 3OH - Pt \rightarrow N - Pt + 3H₂O + 3Pt \]

  S19  \[ NH₃ - Pt + 3NO - Pt + 3Pt \rightarrow 4N - Pt + 3OH - Pt \]  \hspace{1cm} \text{NH₃ oxidation by NO}

  S20  \[ NO - Pt + 3H - Pt \leftrightarrow NH₃ - Pt + O - Pt + 2Pt \]  \hspace{1cm} \text{NH₃ formation by NO+ H₂}
Comparison of Experiment & Model: \( \text{NH}_3 + \text{O}_2 \) on Pt: Ammonia Conversion

- Model captures light-off & insensitivity to \( \text{O}_2 \) concentration
Comparison of Experiment & Model: 
\( \text{NH}_3 + \text{O}_2 \) 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 & CeO₂ with H₂ as reductant
  - Carry out isotopic studies using ¹⁵NO and/or ¹⁸O₂
- 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