Development of Optimal Catalyst Designs and Operating Strategies for Lean NOx Reduction in Coupled LNT-SCR Systems

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May 11, 2011

ACE029

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Overview

Timeline

- Start: Oct. 1, 2010
- End: Sept. 30, 2012
- 60% complete

Budget

- Total project funding
  - DOE: $2,217,317
  - UH & partners: $687,439
- Funding received
  - FY10+FY11: $1,236,917

Barriers/Targets

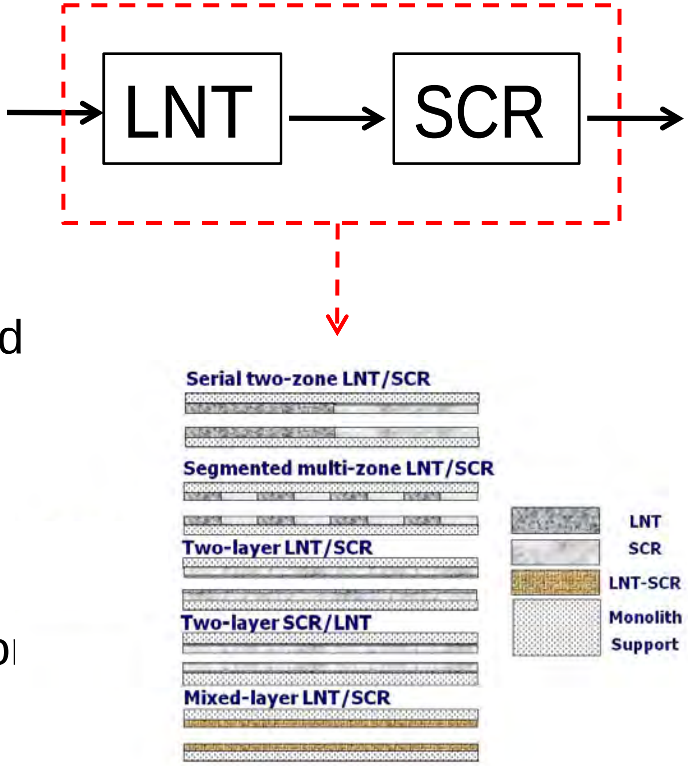
- Increase fuel efficiency of light-duty gasoline vehicles by 25% (by 2015): LNT/SCR has potential as non-urea deNOx approach for LD diesel &*lean burn gasoline vehicles*
- Reduce NOx to <0.2 g/bhp-h for heavy-duty diesel (by 2015): *LNT/SCR is promising non-urea solution*

Partners

- U. Houston (lead)
- Center for Applied Energy (U. Kentucky)
- Ford Motor Company
- BASF Catalysts LLC
- Oak Ridge National Lab

LNT / SCR Technology: Observations and Relevance

- LNT/SCR is promising non-urea deNOx technology for light- & medium duty diesel & lean burn gasoline
- Synergistic benefits of LNT/SCR have been demonstrated: Most previous studies show increased NOx conversion by adding SCR unit downstream of LNT
- Coupling between LNT & SCR not understood or characterized
- Optimal catalyst/reactor designs not yet identified; full potential not demonstrated/realized
- Understanding captured in quantitative reactor models and tuned through simulation of experiments will lead to optimal LNT/SCR designs & operating strategies
- Goals: Reduce PGM requirements, improve fuel utilization



Overall Goal & Impact of Project

Goal: Identify the NO*x* reduction mechanisms operative in LNT (Lean NOx Traps) and *in situ* SCR (Selective Catalytic Reduction) catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies.

Impact: Progress towards goal will accelerate the deployment of a non-urea NOx reduction technology for diesel vehicles.

Principal Challenges & Questions

- LNT/SCR only viable if sufficient NH_3 is generated in LNT: Identify conditions for NH_3 generation in LNT & main pathways
- Hydrocarbons present during LNT regeneration may slip past LNT: – need to understanding HC effect on SCR performance
- Possible detrimental interactions between LNT & SCR?
- LNT/SCR designs: Which is optimal?
  - Stratified, segmented, multi-layer?
  - How little precious metal can be used?
- LNT/SCR operating conditions:
  - What about low temperature operation?
  - How susceptible is performance to regeneration phase composition?

Project Deliverables

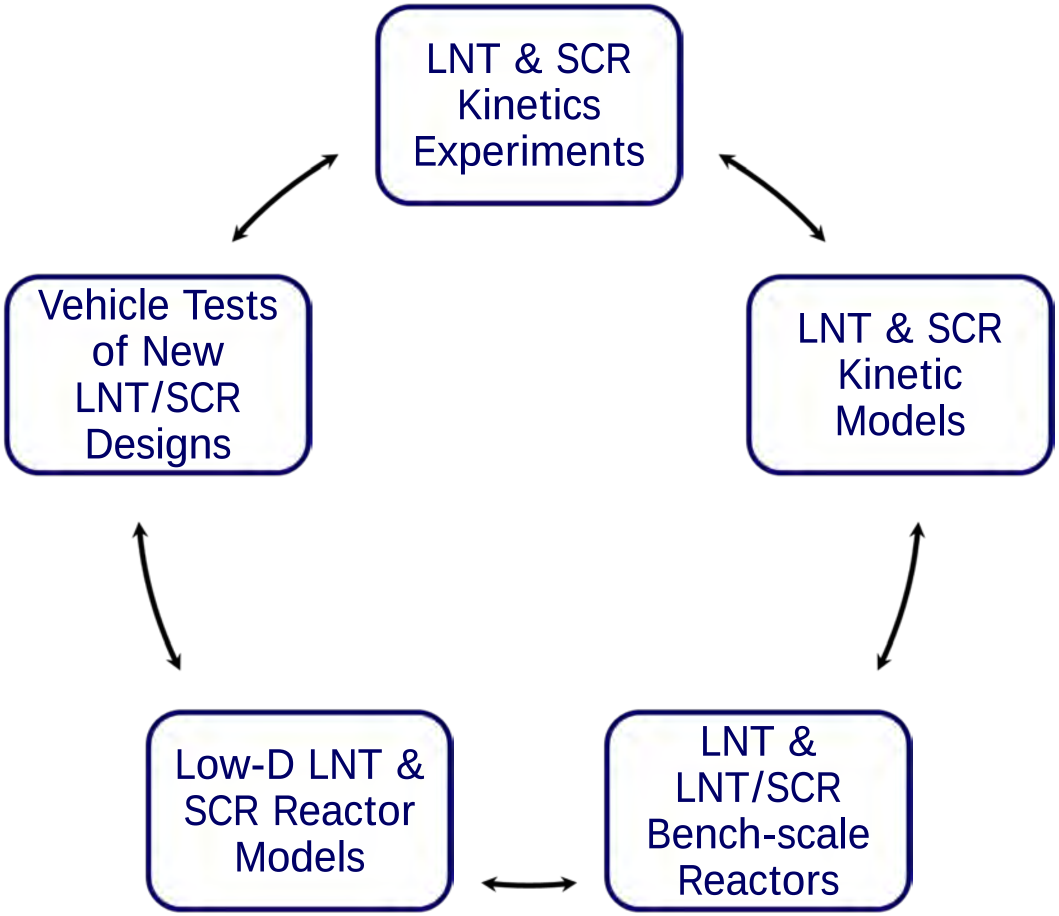
Phase 1

- Identify the main NOx conversion pathways and mechanisms in LNT-SCR systems
- Determine LNT catalyst composition effects and operating conditions for maximizing *in situ* ammonia generation, supported by model predictions
- Establish kinetics of primary reactions during NOx storage and reduction and ammonia-based SCR

Phase 2

- Develop first-principles LNT-SCR reactor model for optimization and real-time simulation
- Elucidate spatio-temporal phenomena in LNT-SCR systems with different catalyst architectures
- Demonstrate ≥20% precious metal thrifting for LNT-SCR system at equivalent NO_x reduction performance to LNT-only system

Project Approach & Tools



- Catalyst synthesis & characterization
- Bench reactors
- FTIR, QMS, CIMS
- SpaciMS
- TAP reactor
- Dynamometers

Premise: Systematic approach and state-of-art tools leads to fundamental understanding & optimized designs

Collaborative Project Team: Current Activities

- **University of Houston**
  - *Mike Harold (PI), Vemuri Balakotaiah, Dan Luss*
  - Bench-flow, TAP reactors; LNT - NH_3 generation; LNT/SCR multi-layer catalyst synthesis & reactor studies; NH_3 SCR kinetics,
- **University of Kentucky - Center for Applied Energy Research**
  - *Mark Crocker (CoPI)*
  - Bench-flow reactors, SpaciMS: LNT, HC SCR, LNT/SCR segmented reactor studies
- **Oak Ridge National Laboratory**
  - *Jae-Soon Choi*
  - Bench-flow reactor, SpaciMS: LNT, SCR spatio-temporal studies
- **BASF Catalysts LLC** (formerly Engelhard Inc.)
  - *C.Z. Wan*
  - Model catalyst synthesis & characterization; Commercial SCR catalyst
- **Ford Motor Company**
  - *Bob McCabe, Mark Dearth, Joe Theis*
  - Bench-flow reactors, SpaciMS: LNT studies – desulfation, aging
  - Vehicle testing of LNT/SCR system

Schedule of Tasks: Phase 1

Phase 1 Tasks	Year 1				Year 2			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.1: Project management & planning								
1.2: Reactor study of non-NH_3 NO_x reduction mechanism								
1.3: DRIFTS study of non-NH_3 NO_x reduction mechanism								
1.4: a. TAP study of NO_x reduction with H_2 & NH_3 on LNT								
1.4: b. TAP study of NO_x reduction with H_2 & NH_3 on LNT								
1.5: Kinetics study of NO_x storage & reduction with $H_2/CO/C_3H_6$ on LNT: 1.5.1: Steady-state kinetics of reactions on LNT 1.5.2: NO_x storage and NO oxidation on LNT								
1.6: Parametric study of LNT NO_x reduction selectivity								
1.7: Development of microkinetic models								
1.8: Development of low-dimensional models								
1.9: Phase 1 reporting								

(Red indicates in progress; indicates complete)

Schedule of Tasks: Phase 2

Phase 2 Tasks	**Year 2**				**Year 3**			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
2.1: Spatiotemporal study of LNT NO_x reduction selectivity								
2.2: Isotopic TAP study of NO_x reduction: LNT & SCR								
2.3: Transient kinetics of NO_x reduction -- LNT & SCR								
2.4: Kinetics of transient NO_x reduction w/ NH_3 on SCR								
2.5: Examine effect of PGM/ceria loading on LNT-SCR								
2.6: Prepare & evaluate double layer LNT-SCR catalysts								
2.7: Spatiotemporal study of LNT-SCR performance								
2.8: Sulfation-desulfation study of LNT-SCR system								
2.9: Modeling and simulation studies of LNT-SCR								
2.10: Phase 2 reporting								

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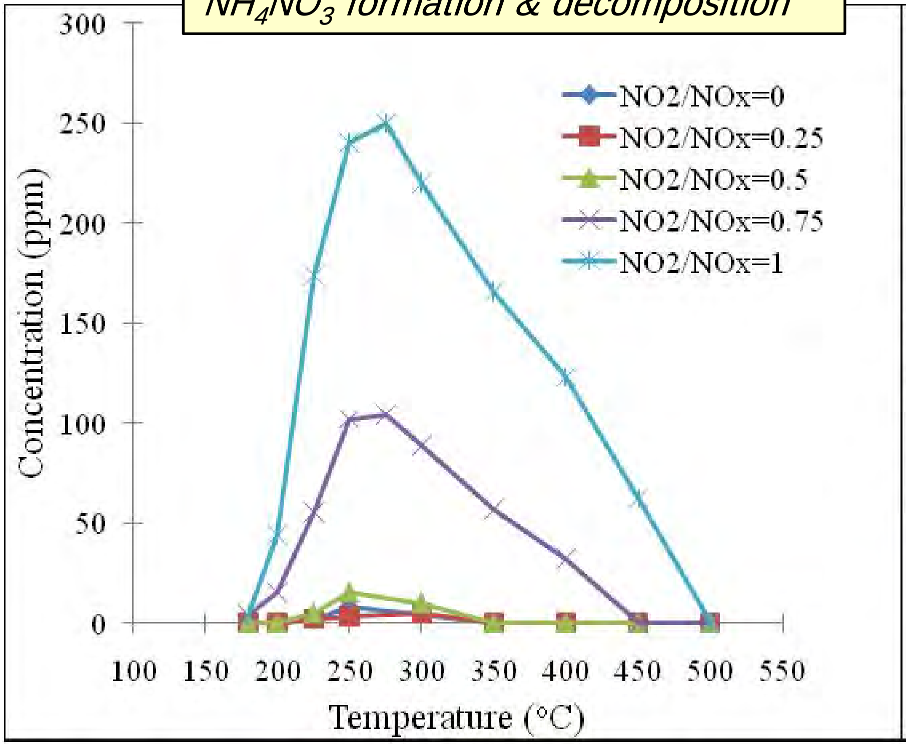
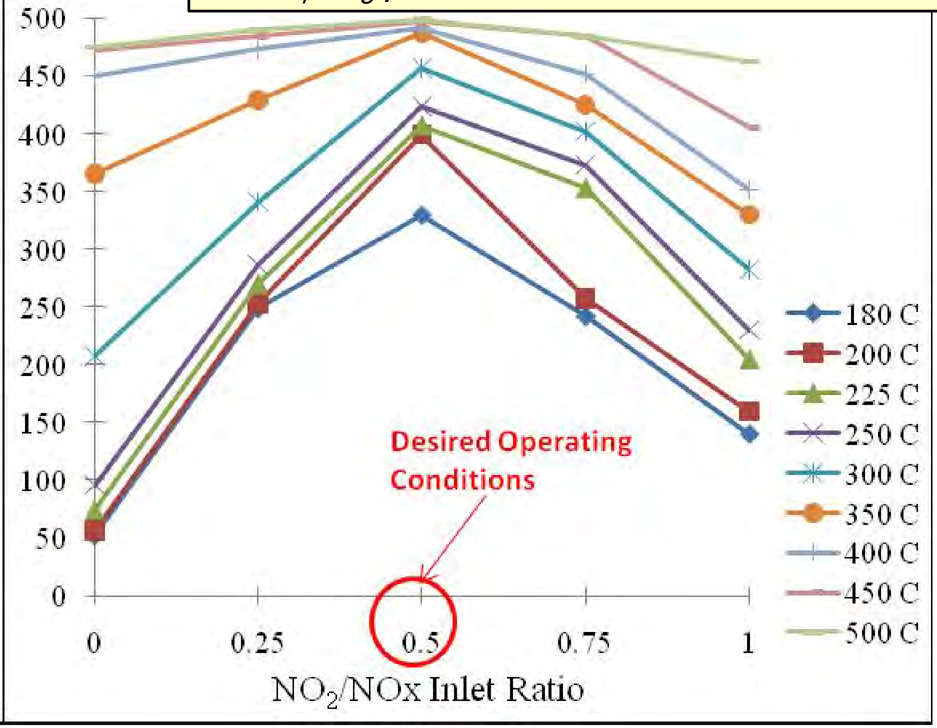
NH_3 Based SCR: Reaction Pathways & Kinetics: Fe/ZSM-5 (UH; Task 2.4)

Fast & NO_2 SCR findings:

- *Enhanced rate of NOx reduction: Washcoat diffusion limitations significant*
- *Optimal N_2 formation at NO_2/NOx = 0.5*
- *NH_4NO_3 production reduces conversion*

NO_2 increases production of N_2O via NH_4NO_3 formation & decomposition





- *Experimental kinetics study of Fe/ZSM-5 completed*
- *Similar studies underway for BASF Cu/zeolite*
- *Predictive kinetic models to be incorporated into LNT/SCR modeling effort*

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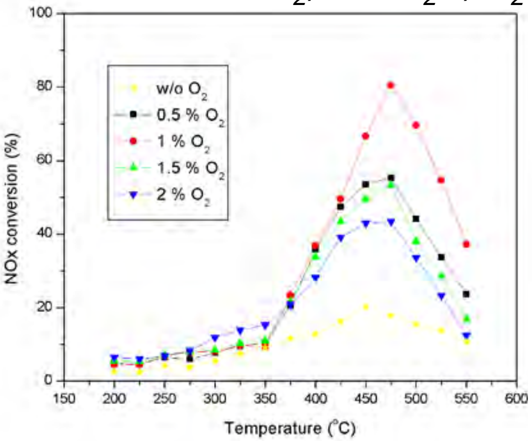
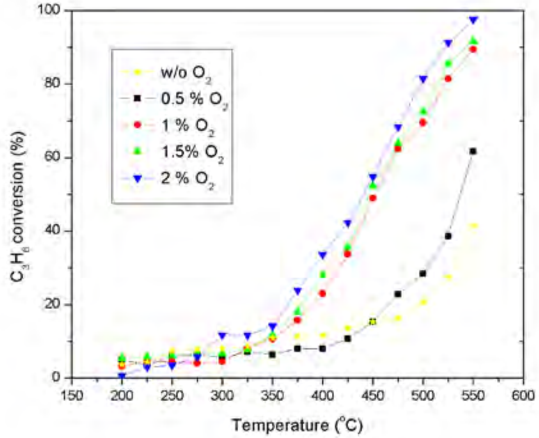
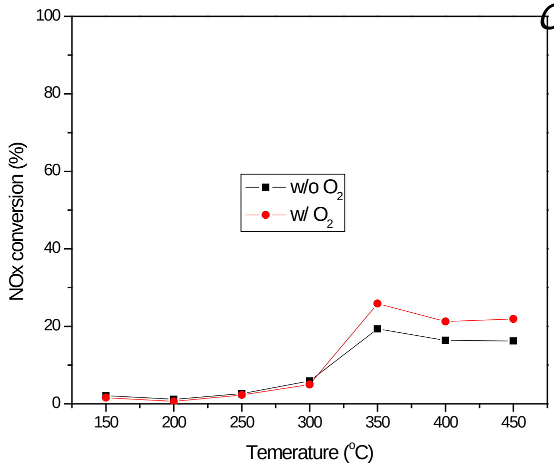
Non-NH_3 Mechanism: NOx Conversion with Propene over Commercial Cu-zeolite SCR Catalyst (UK-CAER; Task 1.2)

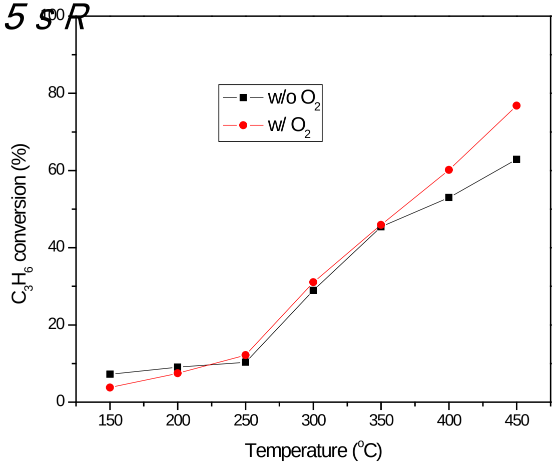
Steady-state NOx reduction: 300 ppm NO, 3333 ppm C_3H_6, 5% CO_2, 5% H_2O, N_2 balance, GHSV = 30,000 h^{-1}





Cycle-averaged NOx reduction: 300 ppm NO, 8% O_2 / 60 s L; 3333 ppm C_3H_6, 0 or 1% O_2, 5 s R



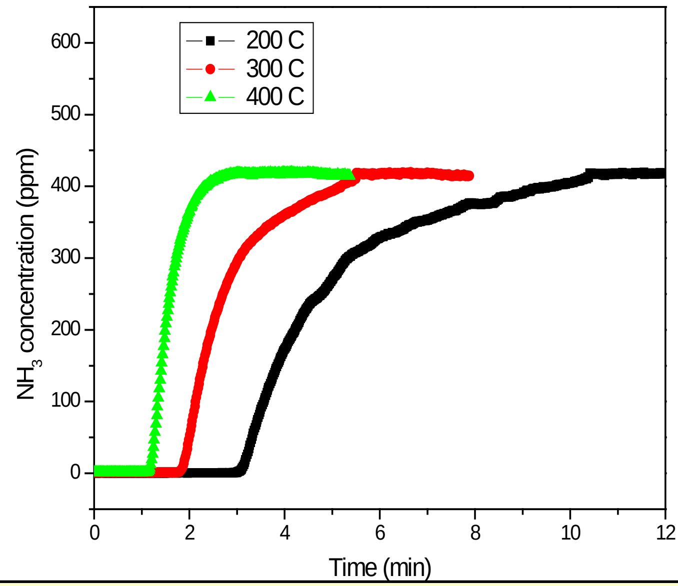


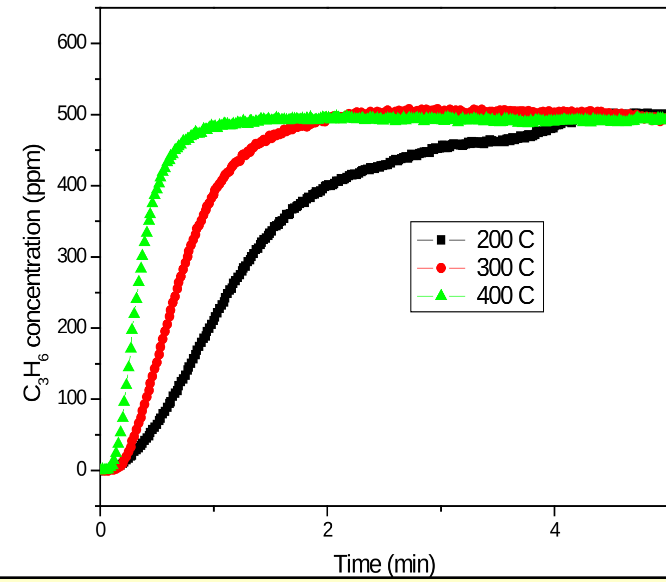
- *Propene & ethylene show moderate activity for NOx reduction over SCR catalyst under steady-state and cycling conditions*
- *Under cycling conditions, NOx is converted in rich <u>and</u> lean phases with olefins, indicating that olefin storage occurs*
- *Presence of O_2 beneficial for NOx conversion*
- *CO also shows some activity for NOx reduction, whereas H_2 does not*

Non-NH_3 Mechanism: NH_3 and Propene Adsorption on Commercial Cu-zeolite SCR Catalyst (UK-CAER; Task 1.2)

***NH_3** (left) and **propene** (right) adsorption*

Feed: 500 ppm NH_3 or C_3H_6, 5% CO_2, 5% H_2O, balance N_2, GHSV = 30,000 h^{-1}

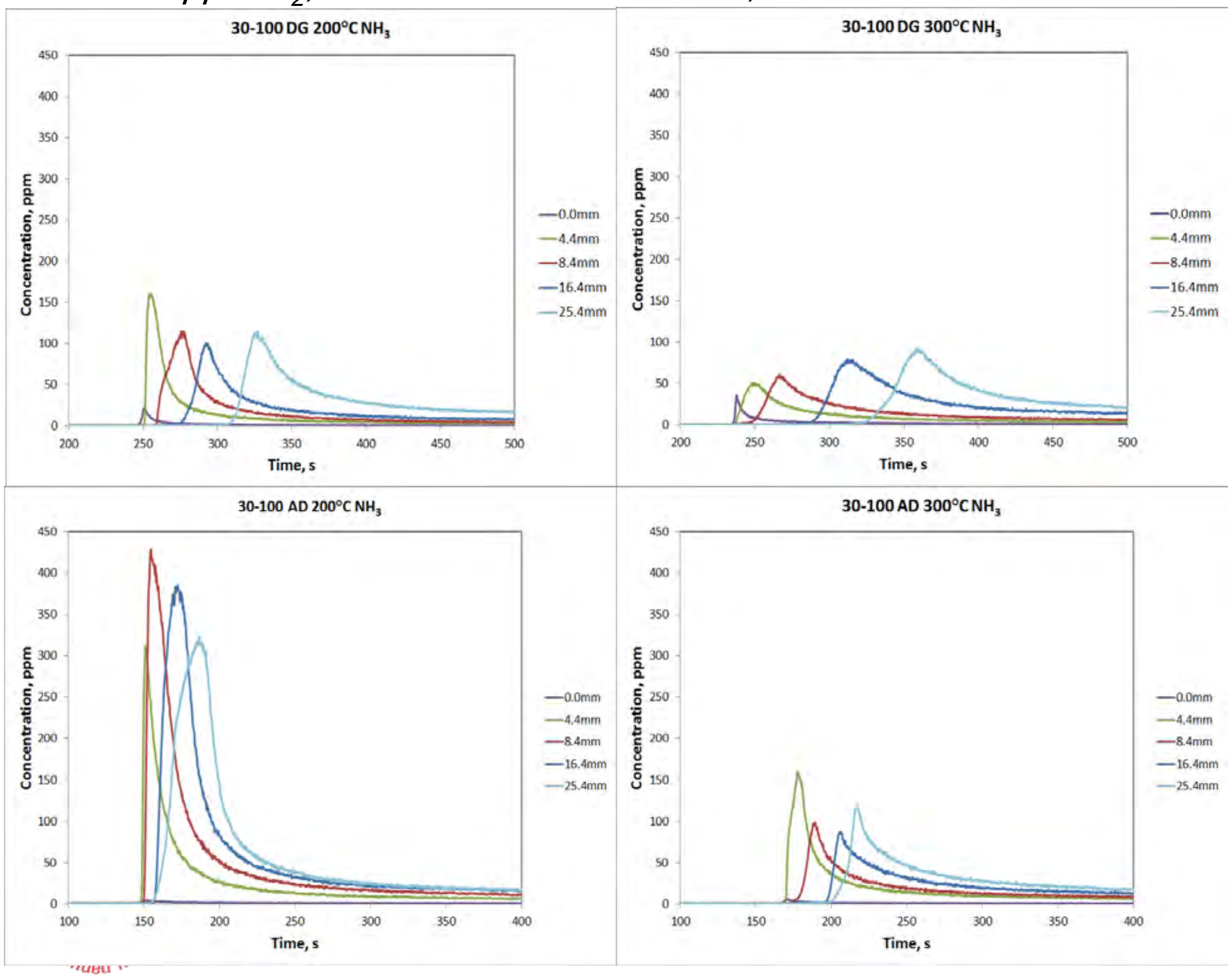




- *SCR catalyst shows significant adsorption capacity for NH_3, C_3H_6, C_2H_4 and CO*
- *NH_3 + C_3H_6 co-adsorption experiments: C_3H_6 adsorption slightly inhibited by NH_3 at 200 °C but no inhibition at 300-400 °C; NH_3 adsorption not inhibited → these results suggest that adsorption mainly occurs at different sites*
- *Olefin TPD experiments: <20% of olefin desorbed "intact", indicating conversion to other species (steam reforming, polymerization, cracking?)*

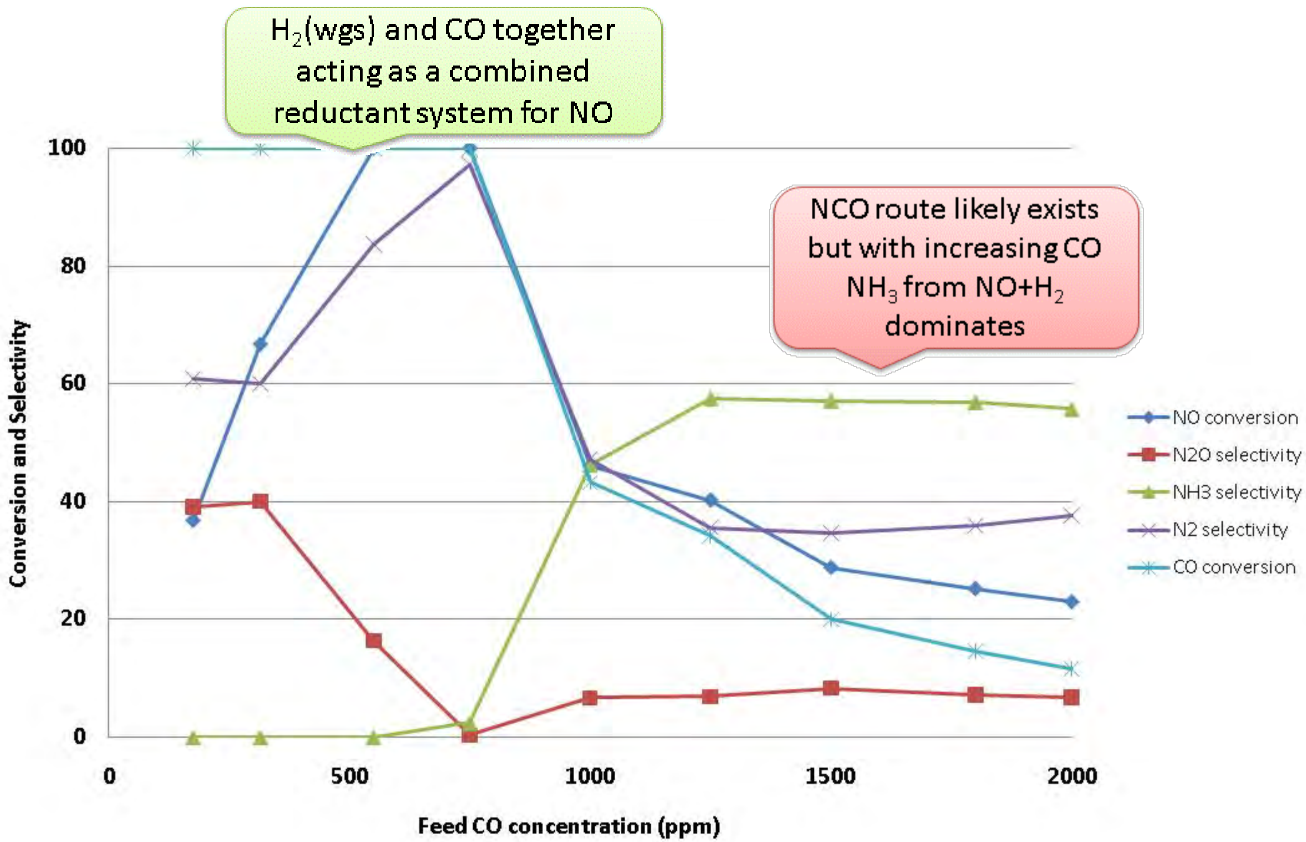
Spatio-temporal Study of LNT NOx Reduction Selectivity (UK-CAER/Ford; Tasks 1.6, 2.1)

High OSC LNT catalyst, degreened (DG) and aged (AD): fixed amount of NOx stored followed by regeneration using 1500 ppm H_2; 0 mm = front face of LNT; 25.4 mm = rear face



- *SpaciMS enables probing of transient spatial profiles of species concentrations*
- *Increase in temperature results in slower propagation of reduction front (due to more effective regeneration of storage sites and increased amount of NOx stored)*
- *Aging results in faster propagation of reduction front (due to elongation of storage zone and decreased total amount of NOx stored)*
- *Aging results in increased selectivity to NH_3*

Reactor Studies of NO/CO/H_2O on Pt/BaO Catalyst (UH; Tasks 1.5, 2.3)



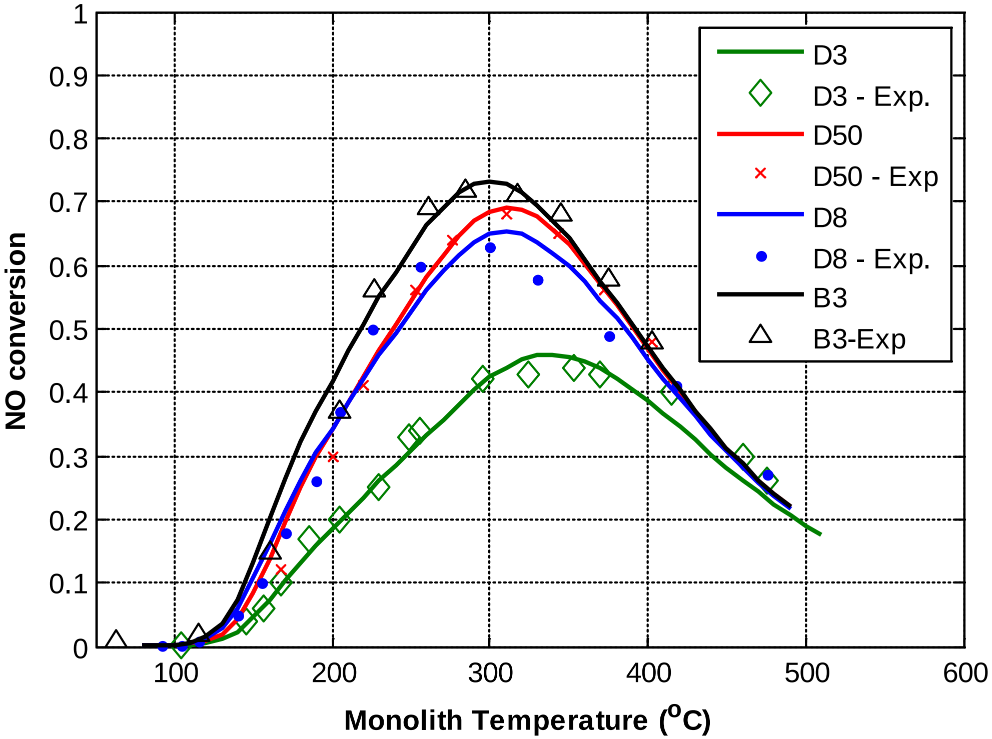
- Experiments designed to identify major NH_3 formation mechanisms:
  - $NO + CO \rightarrow NCO^-$
    $NCO^- + H_2O \rightarrow NH_3$
  - $CO + H_2O \rightarrow H_2 + CO_2$
    $NO + H_2 \rightarrow NH_3 + H_2O$
- Systematic study of NO/CO, NO/CO/H_2O, CO/H_2O, etc. reaction systems

- *Results show that NH_3 formation occurs by both isocyanate mechanism (NO + CO + H_2O) and by coupled water gas shift ($CO + H_2O \rightarrow H_2 + CO_2$) and NO+$H_2$ and chemistry*
- *Major pathway depends on conditions such as temperature and NO/CO ratio*
- *DRIFTS & isotopic labeling studies planned*

NO Oxidation on Pt/BaO: Effect of Pt Dispersion & Washcoat Diffusion (UH; Tasks 1.5, 1.8)

Steady State NO Oxidation: Comparison of Experiments & Model Predictions

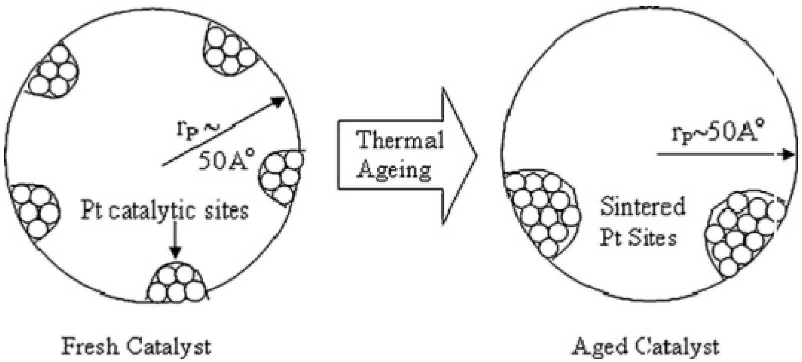
Feed: 500 ppm NO, 5% O_2 Bal Ar, 1000 sccm



Catalyst	Pt (wt.%)	BaO (wt.%)	Pt Dispersion (%)
B3	2.20	16.3	22
D3	2.48	13.0	3
D8	2.48	13.0	8
D50	2.48	13.0	50

- *NO oxidation sensitive to Pt loading, Pt dispersion and temperature*
- *Findings being incorporated into LNT & LNT/SCR modeling efforts*

NO Oxidation on Pt/BaO: Effect of Pt Dispersion & Washcoat Diffusion (UH)



Results suggest that larger Pt particles increase intrinsic activity but decrease effective diffusion coefficient due to pore blocking

$$k_i = k_{B3}\left(\frac{C_{Pt,i}}{C_{Pt,B3}}\right)\frac{1}{f}$$

$$\lambda = \frac{D_m}{D_e(r_{eff})}$$

k_i = rate constant
f = activity factor
D_m = bulk gas diffusivity
r_p = average pore size
r_c = average Pt radius

$r_{eff} \approx r_p - r_c$

<u>B3 Base Case Parameters:</u>
f=1, λ = 100, r_{eff} = 3.33 nm
D_{eNO} = 2.0x10^{-7} m^2/s
$D_{f,NO}$ = 2.0x10^{-5} m^2/s

<u>Model estimated parameters:</u>

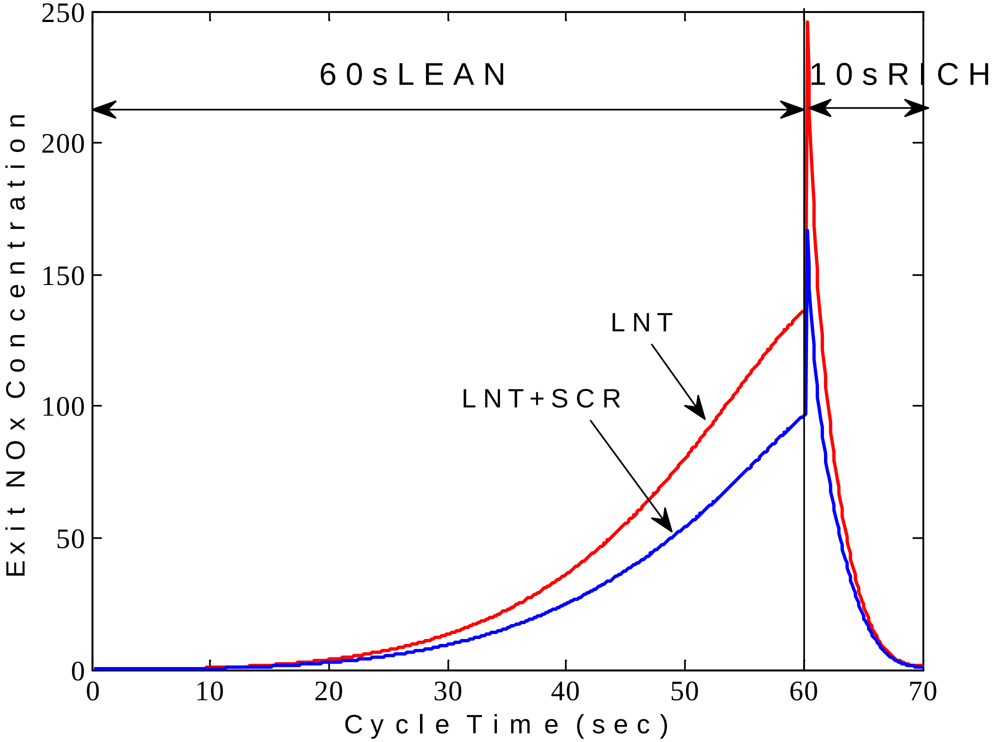
Catalyst	f	λ	De (m²/s)	r_{eff} (nm)
D3	0.52±0.28	522±360	(7.3±5.0) x 10^{-8}	1.21
D8	0.51±0.15	189±96	(1.4±0.7) x 10^{-7}	2.33
D50	4.40±1.20	90±40	(2.8±0.2) x 10^{-7}	4.66

$$\frac{1}{k_{mo}} = \frac{1}{k_{me}} + \frac{1}{k_{mi}}$$

$$k_{me}(z) = \frac{Sh_e(z)D_f}{4R_{\Omega_1}}$$

$$k_{mi}(z) = \frac{Sh_i D_e}{R_{\Omega_2}}$$

Modeling of LNT NOx Reduction Selectivity: Segmented Reactor & Global Kinetics (UH; Tasks 1.8, 2.9)

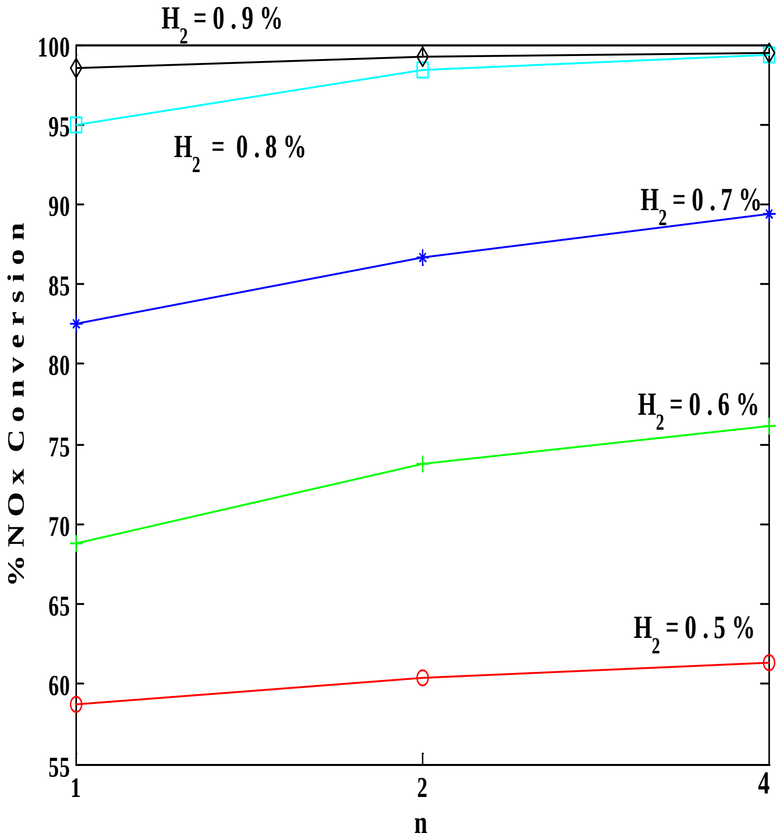


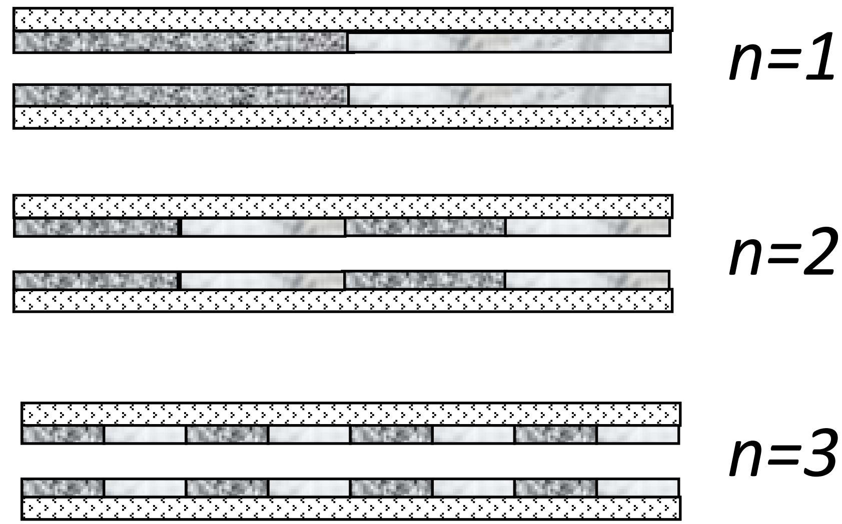
(n=1)

- *Model uses global LNT model of Bhatia et al. & global SCR model of Olsson et al.*
- *Serial design with LNT & SCR sections of equal length*
  Catalysts: Pt/BaO (LNT)
  Cu/ZSM-5 (SCR)
- *Model predicts moderate increase in cycle-averaged NOx conversion with addition of SCR section*

Length of each catalyst = 2cm;
Temperature=275 ^oC; GHSV=60,000h^{-1};
Lean inlet: NO=500ppm,O_2=5%;
Rich inlet: NO=500ppm,H_2=0.8%;

Modeling of LNT NOx Reduction Selectivity: Segmented Reactor & Global Kinetics (UH)





Arrangement of LNT(Pt/BaO/Al_2O_3) and SCR(CuZSM5) catalysts; n is the number of combined LNT+SCR units. Catalysts are divided equally in each arrangement .

Conditions: Total length = 4cm; T = 275°C ; GHSV=60,000hr^{-1};
Lean cycle (60 sec): 500ppm NO, 5% O_2;
Rich cycle (10 sec): 500ppm NO, variable H_2

- *Moderate increase in cycle-averaged NOx conversion by increasing the degree of contact of the LNT and SCR catalysts*
- *Model will be used for optimization*

Dual Layer LNT/SCR Catalysts (UH Task 2.6)

LNT

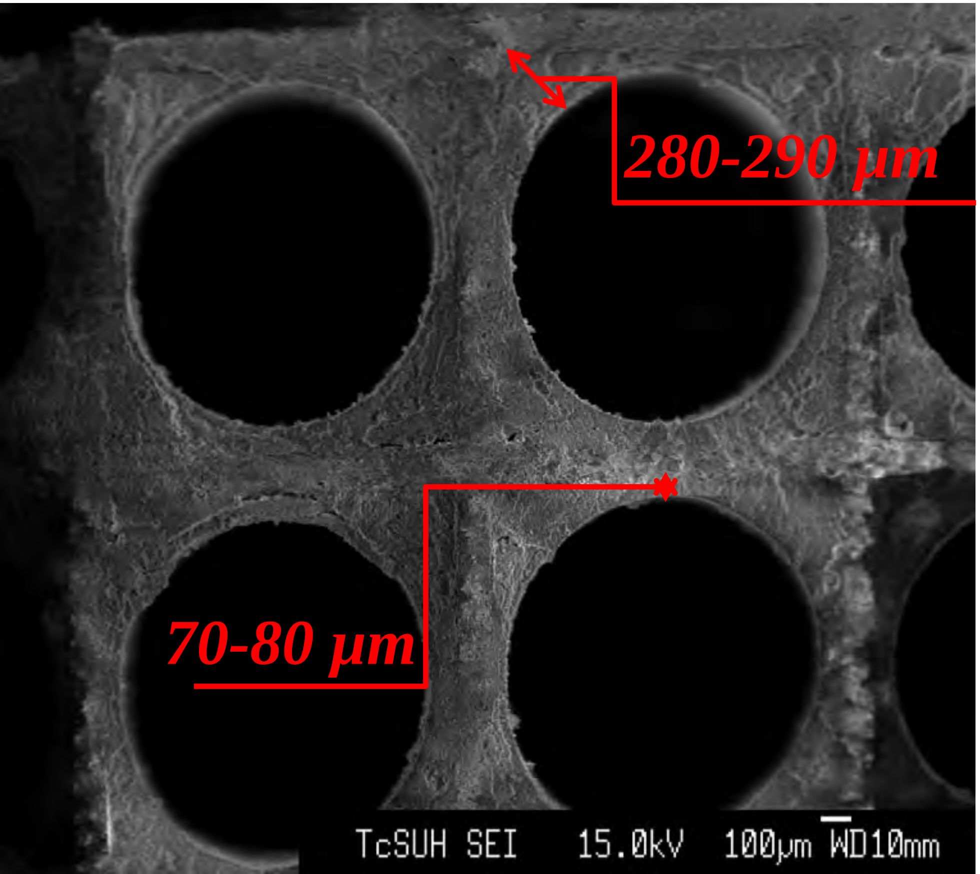
Washcoat thickness:

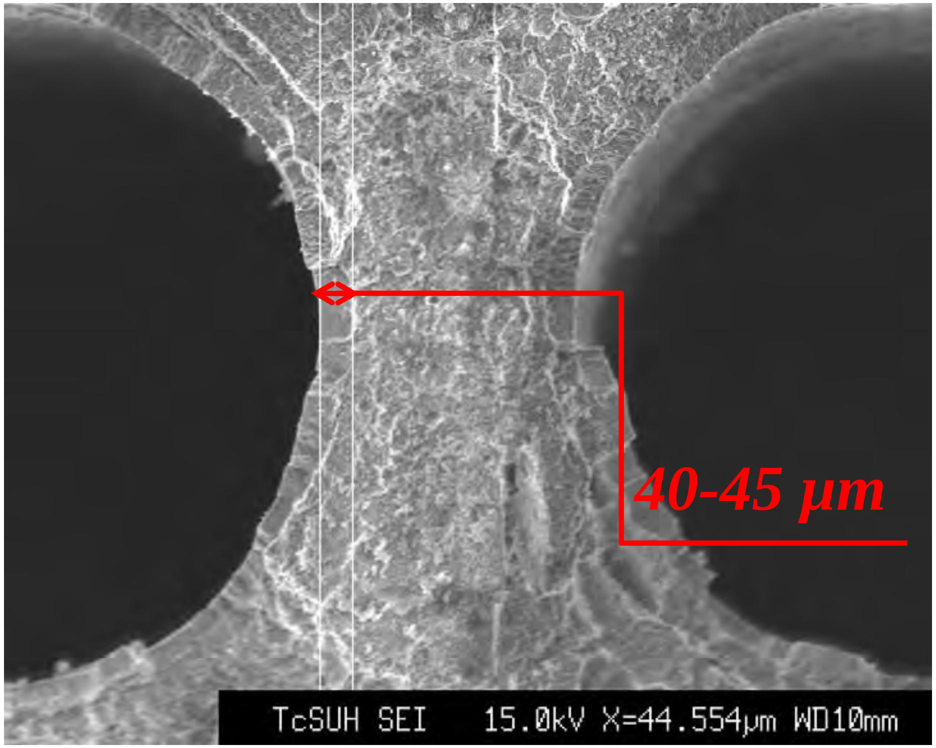
~80 μm at wall; ~290 μm at corner

LNT + SCR

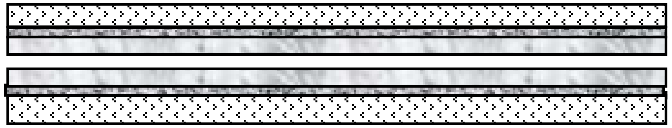
Zeolite layer thickness:

~45 μm





Dual Layer LNT/SCR Catalysts (UH; Task 2.6)

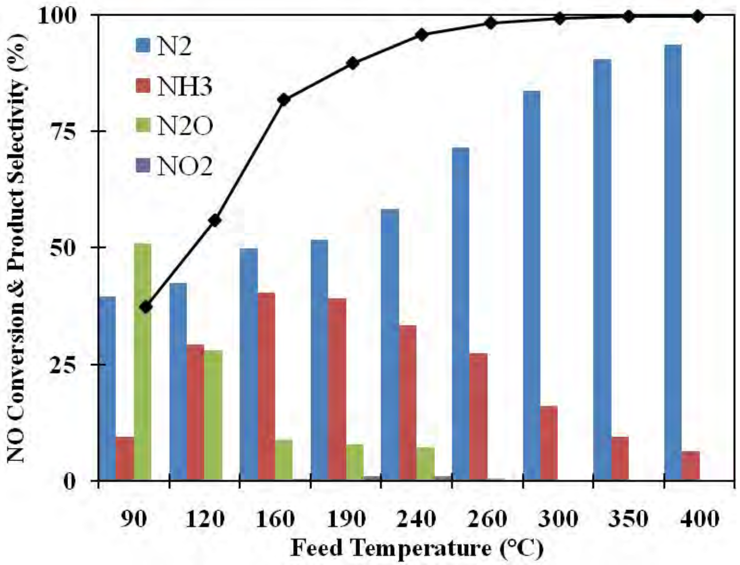


- Dual layer LNT/SCR catalyst comprises:

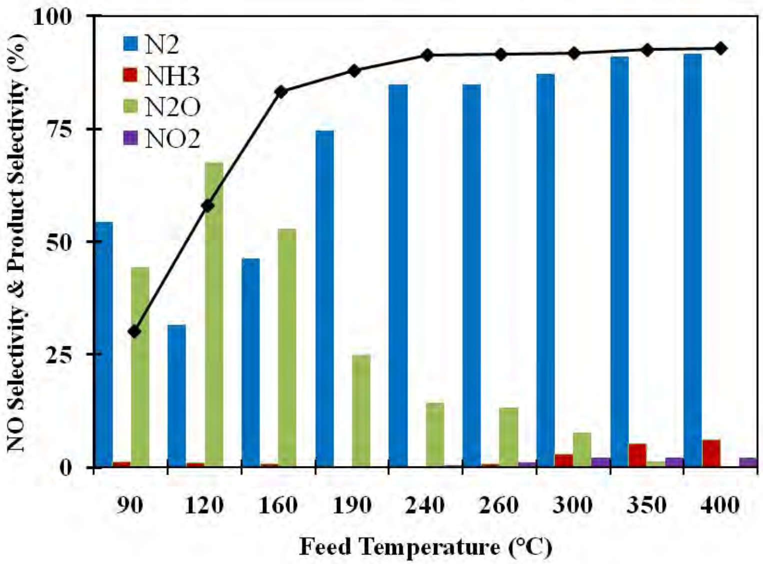
  Bottom layer: Pt/Rh/BaO/alumina; 0.7wt.%/0.07wt.%/20wt.%

  Top layer: Fe or Cu/ZSM-5/alumina 3-3.5 wt.% (10% washcoat loading)

LNT only



LNT/SCR (Fe-ZSM-5)



Initial results with dual-layer catalyst show much reduced NH_3 but increased N_2O; slight decrease in NO conversion due to undesired NO_2 trapping by SCR layer, leading to NOx slippage

Selected Activities Planned: 4QFY11, FY12 (Complete Phase 1 & most of 2; start Phase 3)

- LNT:
  - Complete SpaciMS experiments of LNT with varying ceria & Pt loading
  - Carry out model simulations of SpaciMS experiments to further elucidate NH_3 formation in $Pt/Rh/CeO_2/BaO$ monolith
  - LNT model developments
    - Extend microkinetic NSR H_2 model to H_2/CO/HC mixtures
    - Incorporate washcoat diffusion using low-dimensional approach
- SCR:
  - Complete kinetic model development for NH_3 SCR on Fe & Cu zeolites; incorporate findings into SCR models
  - Conduct *in situ* DRIFTS of SCR with HC & HC/NH_3 mixtures
- LNT/SCR:
  - Continue LNT-SCR experiments, focusing on reducing PGM content
  - Continue double-layer LNT/SCR experiments: Focus on understanding and optimization
  - Carry out vehicle studies at Ford using full-scale LNT/SCR system
  - LNT/SCR reactor modeling
    - Incorporate latest upgrades in kinetic models
    - Optimize LNT/SCR segmented architecture
    - Extend to double-layer formulations to guide experiment

Publications & Presentations

Publications – Appeared

- Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, “Determination of Kinetics and Controlling Regimes for H_2 Oxidation on Pt/Al_2O_3 Monolithic Catalyst Using High Space Velocity Experiments,” Appl. Catal. B. Environ., doi:10.1016/j.apcatb.2010.12.030 (2011).
- Kumar, A., M.P. Harold, and V. Balakotaiah, “Estimation of Stored NOx Diffusion Coefficient in NOx Storage and Reduction,” *I&EC Research*, **49**, 10334-10340 (2010).
- Kumar, A., X. Zheng, M.P. Harold, and V. Balakotaiah, “Microkinetic Modeling of the NO + H_2 System on Pt/Al_2O_3 Catalyst Using Temporal Analysis of Products ,” J. Catalysis, **279**, 12–26 (2011).

– In Press

- Ji, Y., V. Easterling, U. Graham, C. Fisk, M. Crocker, J.-S. Choi, “Effect of Aging on the NO_x Storage and Regeneration Characteristics of Fully Formulated Lean NO_x Trap Catalysts”, *Appl. Catal. B*, in press (2011).
- Liu, Y., M.P. Harold, and D. Luss, “Spatiotemporal Features of Pt/CeO_2/Al_2O_3 Catalysts During Lean/Rich Cycling,” Appl. Catal. A. General., to appear (2011).
- Metkar, P., N. Salazar, R. Muncrief, V. Balakotaiah, and M.P. Harold, “Selective Catalytic Reduction of NO with NH_3 on Iron Zeolite Monolithic Catalysts: Steady-State and Transient Kinetics ,” Appl. Catal. B. Environmental, to appear (2011).
- Wang, J., Y. Ji, V. Easterling, M. Crocker, M. Dearth, R.W. McCabe, “The Effect of Regeneration Conditions on the Selectivity of NOx Reduction in a Fully Formulated Lean NOx Trap Catalyst”, accepted for publication in *Catal. Today* (2011).
- Xu, J., M. Harold, and V. Balakotaiah, “Microkinetic Modeling of NOx Storage on Pt/BaO/Al_2O_3 Catalysts: Pt Loading Effects,” Appl. Catal. B. Environ., to appear (2011).

– In Review

- Wang, J., Y. Ji, U. Graham, C.S. Spindola de Oliveira, M. Crocker, “NOx Reduction on Fully Formulated Lean NOx Trap Catalysts Subjected to Simulated Road Aging: Insights from Steady-State Experiments”, submitted to *Chin. J. Catal.* (2011).

Presentations:

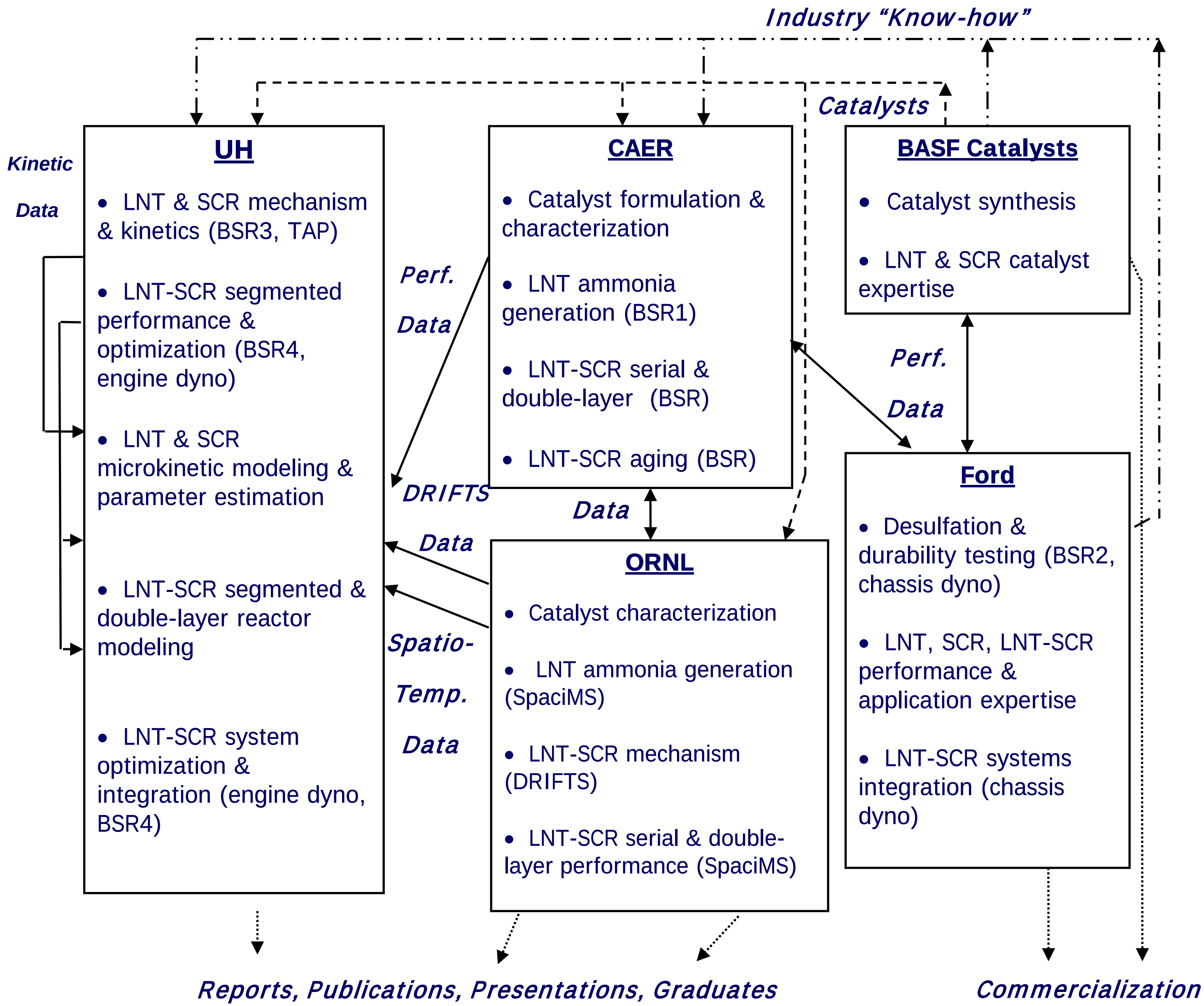
- Total: 13 oral presentations (DEER, AIChE, ACS, Inter. Conf. Envir. Catal., ISCRE, CLEERS)
  3 invited presentations (Chicago Catalysis Club, Michigan Catalysis Society)
  9 poster presentations (AIChE, DEER, ISCRE)

Summary

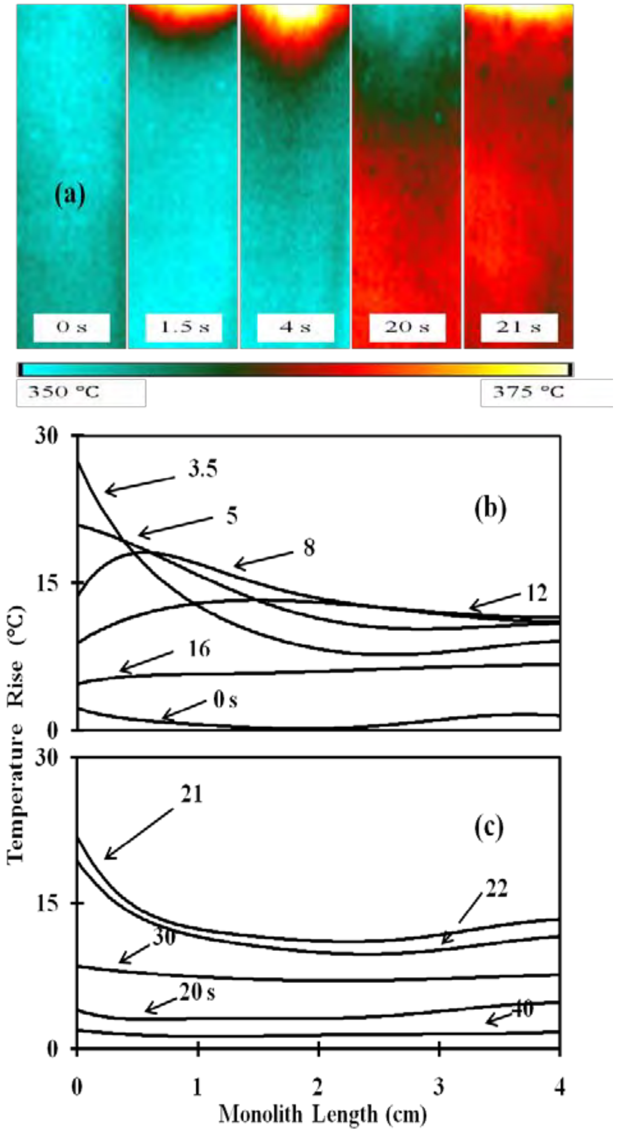
- Comprehensive program combining fundamental catalysis, reaction engineering and vehicle testing
- Good progress on Phase 1 & 2 tasks
  - Non-NH_3 SCR mechanism understood – opens up new avenues for coupled NH_3 and HC reduction
  - Conditions for NH_3 generation identified from spatio-temporal data
  - Established understanding of NH_3-based SCR kinetics for Fe- & Cu-zeolites
  - Progress on using models to understand data and to guide future experiments

Technical Backup Slides

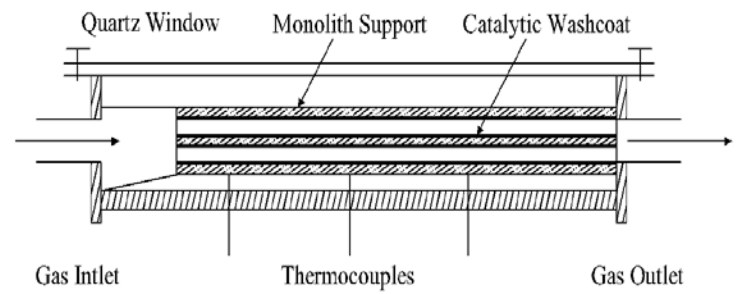
Approach: Team Participants



Periodic Oxidation of H_2 on Pt / CeO_2 (UH; Tasks 1.5, 2.3)



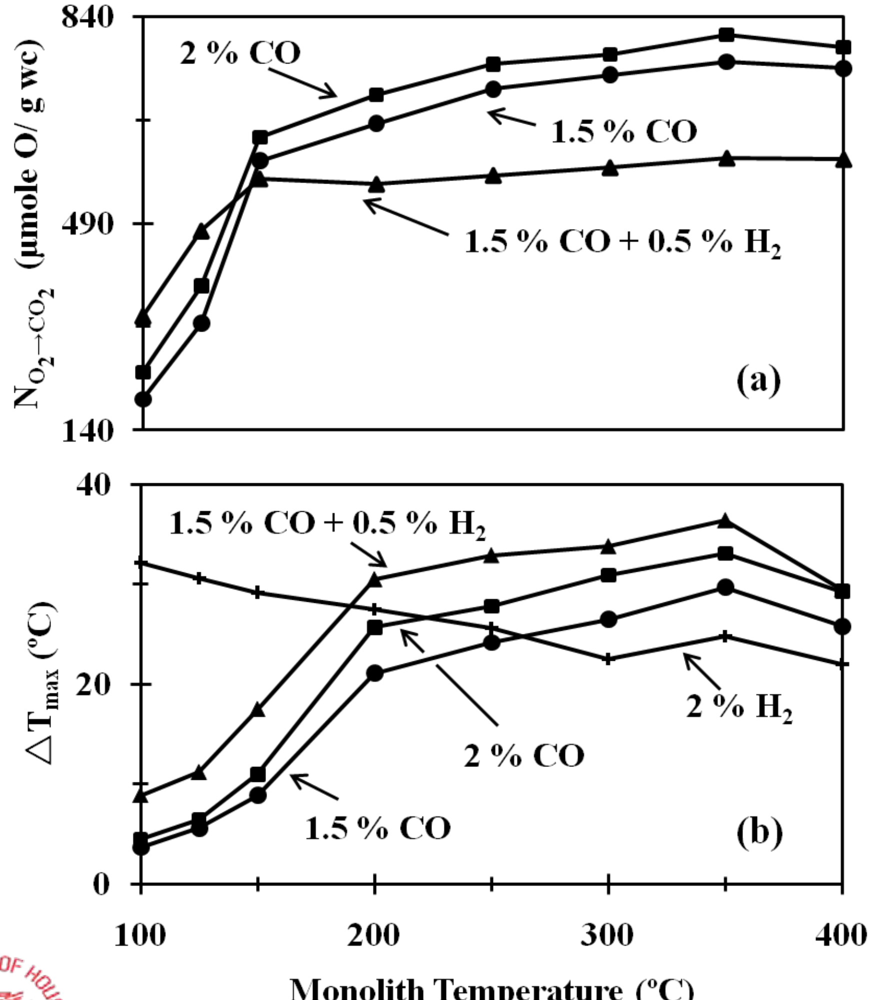
- Systematic study of transient oxidation of H_2 on $Pt/CeO_2/Al_2O_3$ monolith
- Use of infrared imaging to follow spatio-temporal distribution of temperature



Results show significant nonuniform heat effects along length of monolith

Results have bearing on rich phase of NOx storage and reduction

Periodic Co-oxidation of H_2 and CO on Pt/CeO_2 (UH; Tasks 1.5, 2.3)



- Periodic O_2/CO (lean) + H_2 (rich)

  $CO + ½ O_2 \rightarrow CO_2$

  $H_2 + ½ O_2 \rightarrow H_2O$
- Systematic study of transient co-oxidation of H_2 & CO on Pt/CeO_2/Al_2O_3 monolith

Results show significant enhancement of CO oxidation by addition of H2; suggests enhanced CO desorption and/or formation of faster pathway involving HCO intermediate

Project Objectives

<u>Phase 1 Objectives</u>:

- Elucidate the mechanism of the non-NH_3 pathway for NO*x* reduction by means of bench-scale reactor, *in situ* DRIFTS reactor, and TAP reactor studies
- Map LNT selectivity to NH_3 as a function of catalyst composition (ceria content and type) and relevant process parameters (NO*x* loading, purge duration, purge lambda and space velocity)
- Develop a microkinetic LNT model that takes into account the catalyst composition (storage component such as ceria and barium loading as well as precious metal such as Pt loading/dispersion) and H_2, CO, and C_3H_6 reductants
- Develop low-dimensional models for the LNT and the coupled LNT-SCR unit for different catalyst architectures incorporating microkinetics

Project Objectives

Phase 2 Objectives:

- Establish the chemical basis for the dependence of LNT NH_3 selectivity on ceria content
- Determine optimum ceria type and content in model LNT catalysts to achieve best net NO*x* conversion in serial LNT-SCR catalysts
- Establish the optimal operating strategy of serial and double layer catalyst systems with respect to NO*x* conversion level and fuel penalty
- Determine the level of PGM reduction possible in the serial LNT-SCR catalyst system while providing equivalent performance to the corresponding LNT-only system
- Develop microkinetic SCR model that includes non-NH_3 mechanism
- Carry out experimental optimization study of segmented LNT-SCR catalyst configurations
- Establish sulfur evolution on serial and double layer systems
- Perform simulations of the LNT and coupled LNT-SCR unit using the low-dimensional