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

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ACE029

Overview

Timeline

- Start: Oct. 1, 2010
- End: Sept. 30, 2012
- 10% complete

Barriers/Targets

- Reduce NOx to < 0.2 g/bhp-h for heavy-duty diesel by 2015
- Reduce PM to < 0.01 g/bhp-h for heavy-duty diesel by 2015
- Increase truck efficiency by 20% over current levels by 2015

Budget

- Total project funding
  - DOE: $2,217,317
  - UH & partners: $687,439
- Funding received
  - FY10: $637,728

Partners

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

LNT/SCR Research: Observations

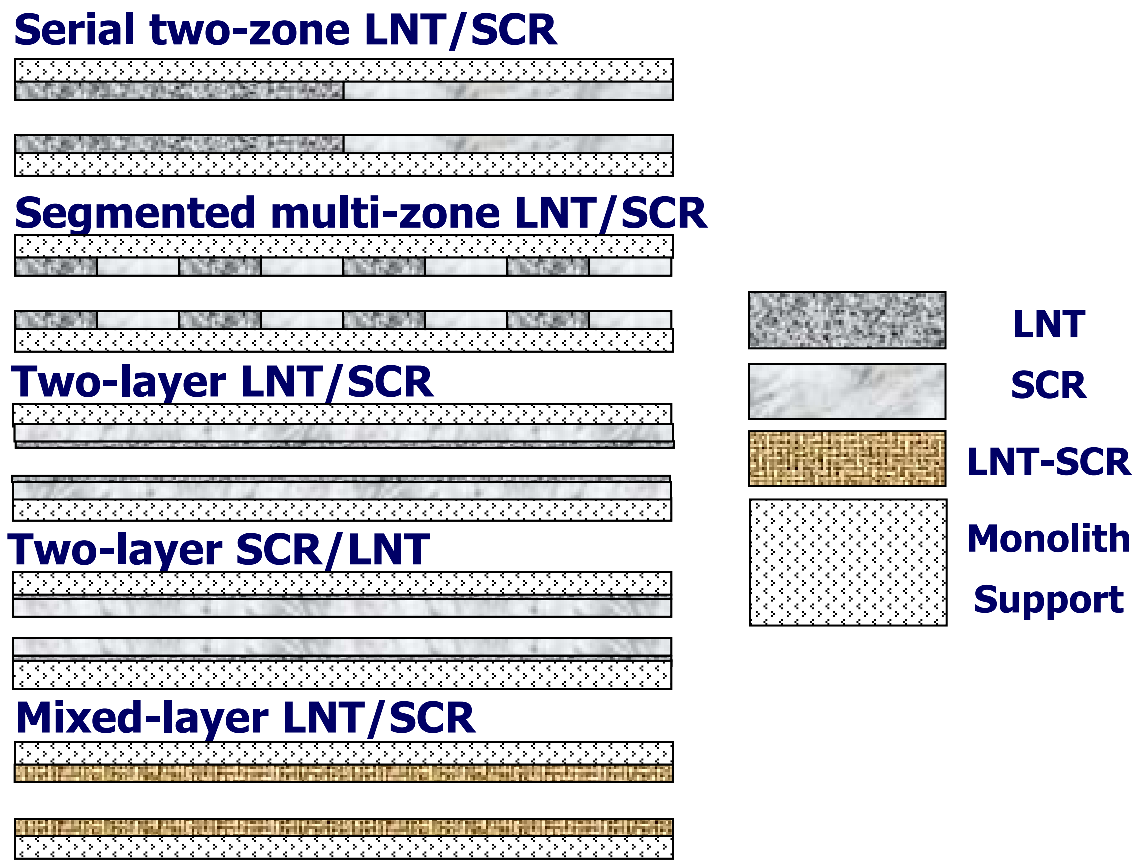
- Synergistic benefits of LNT/SCR have been demonstrated
- Most previous studies show increased NOx conversion by adding SCR unit downstream of LNT
- Mechanisms of LNT/SCR synergies not understood or characterized
- Understanding captured in quantitative models will lead to optimal LNT/SCR designs & operating strategies
  - Reduced PGM, improved fuel utilization

Overall Goal & Impact of Project

<u>Goal:</u> 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.

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

NSR/SCR Catalyst Architectures

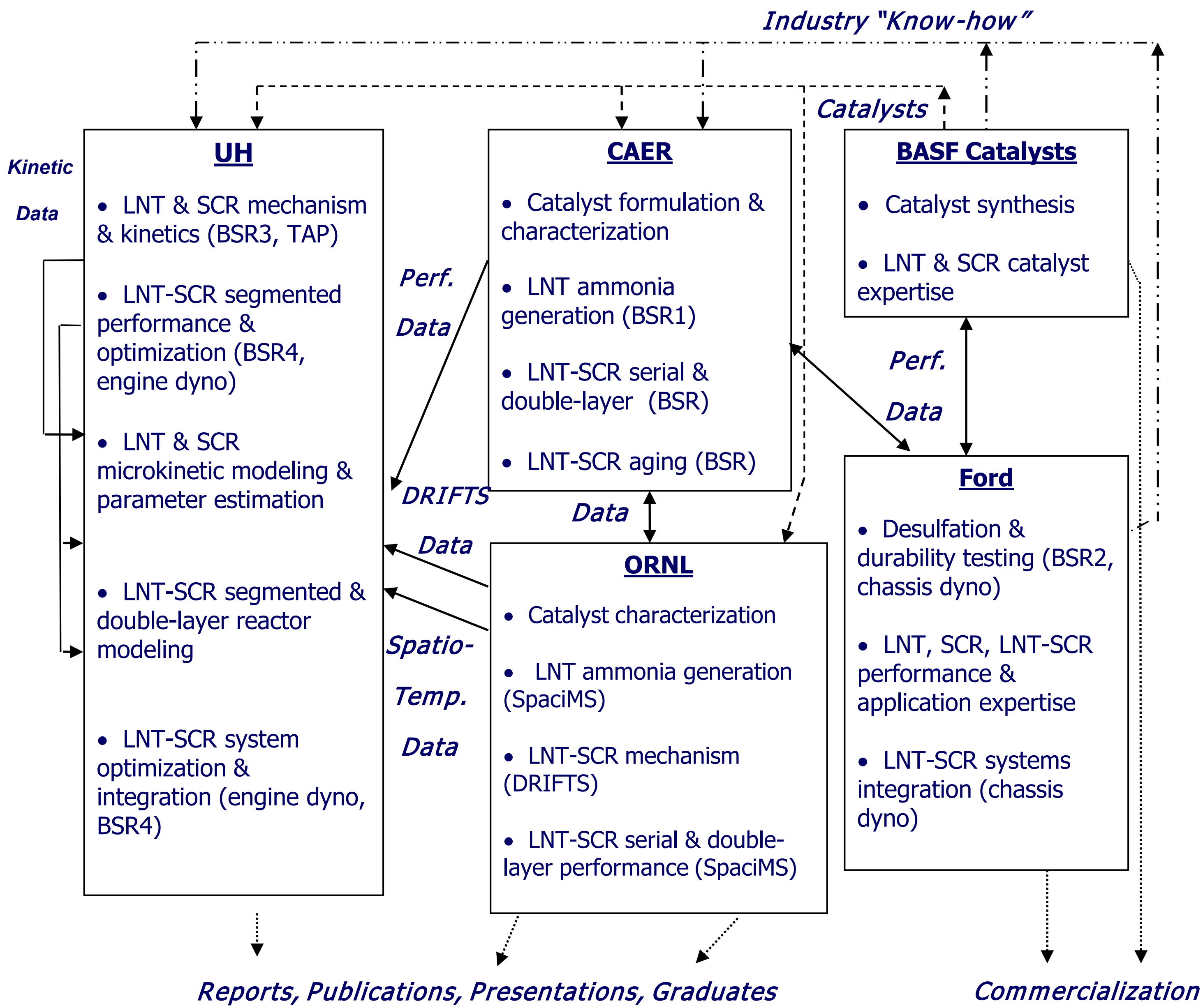


Several catalyst formulations & architectures to be evaluated in this project

Collaborative Project Team: Fundamentals to Applications

- **University of Houston**
  - Mike Harold (PI), Vemuri Balakotaiah, Dan Luss
  - Catalytic engineering; NOx storage & reduction, DPF research, Diesel emissions
- **University of Kentucky - Center for Applied Energy**
  - Mark Crocker (CoPI)
  - Catalytic materials; Lean NOx reduction & catalysis research
- **Oak Ridge National Laboratory**
  - Jae-Soon Choi
  - Extensive R&D in emission aftertreatment
- **BASF Catalysts LLC** (formerly Engelhard Inc.)
  - C.Z. Wan, Stan Roth
  - International leader in emission catalysts
  - LNT work builds off UH – BASF collaborations
- **Ford Motor Company**
  - Bob McCabe, Mark Dearth, Joe Theis
  - OEM provides path to application
  - UH & CAER/UK have had close collaborations with Ford

Approach: Team Participants



Project Deliverables: Phase 1

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

Schedule of Tasks: Phase 1

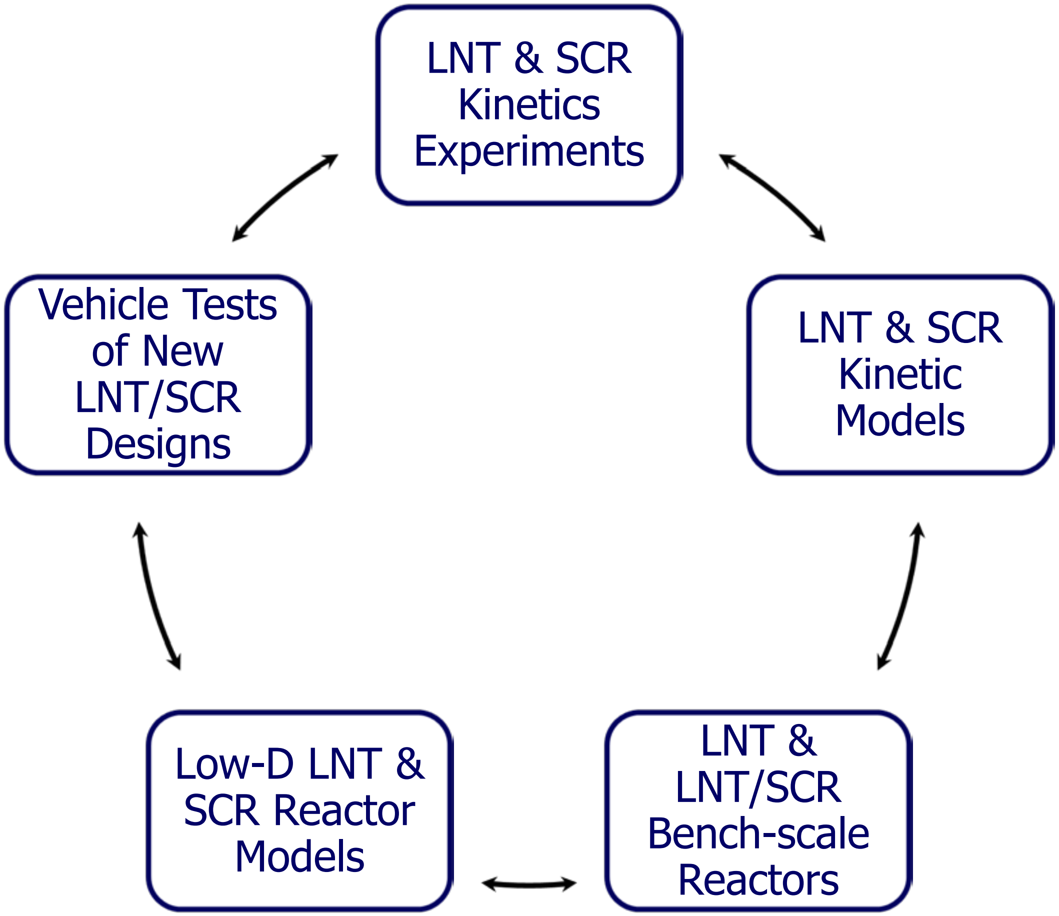
Phase 1 Tasks	Year 1				Year 2			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.1: Project management & planning								
1.2: Reactor study of non-NH_3 NO_x reduction mechanism								
1.3: DRIFTS study of non-NH_3 NO_x reduction mechanism								
1.4: TAP study of NO_x reduction with $H_2/CO/C_3H_6$ on LNT								
1.5: 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			
	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4
2.1: Spatiotemporal study of LNT NO_x reduction selectivity								
2.2: Isotopic TAP study of NO_x reduction on LNT & SCR								
2.3: Transient kinetics of NO_x reduction on 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 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								
2.10: Phase 2 reporting								

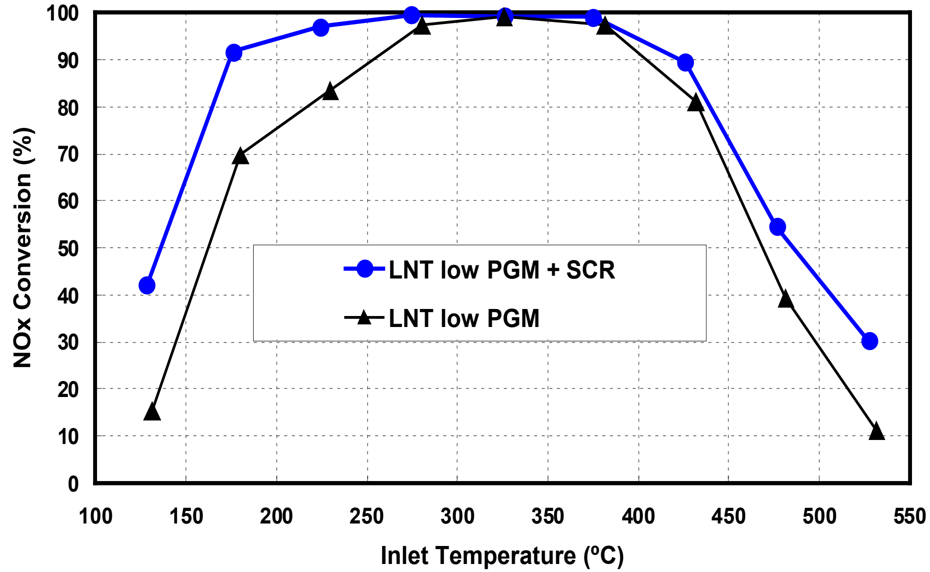
Project Approach & Tools

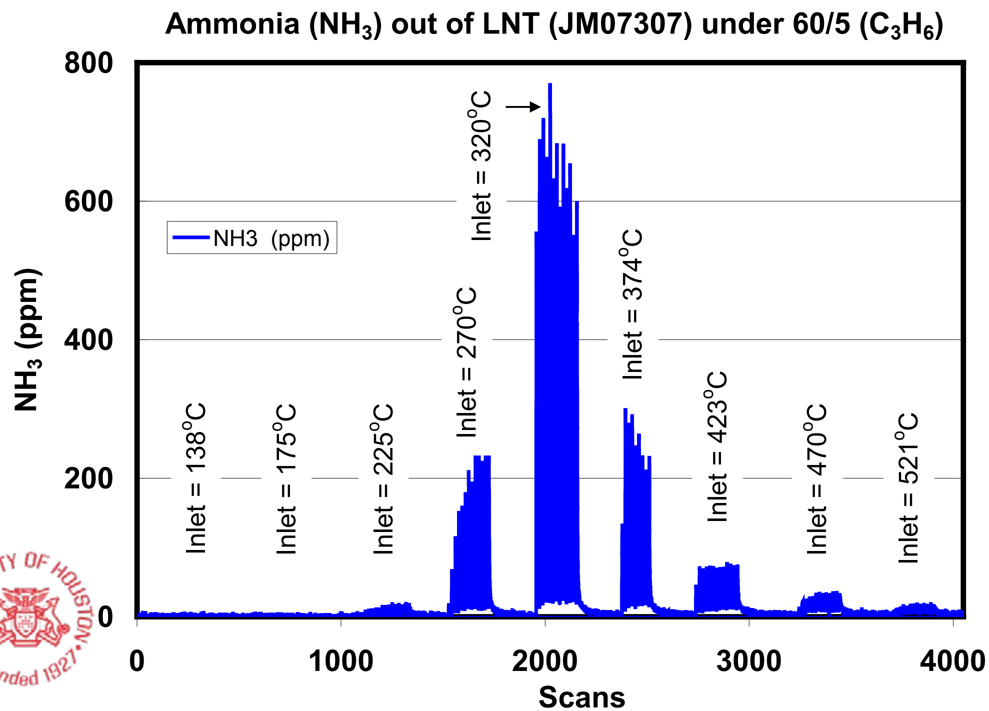


- Catalyst synthesis & characterization
- Bench reactors
- FTIR, QMS, CIMS
- SpaciMS
- TAP reactor
- Dynamometers

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

Non-Ammonia NOx Reduction Mechanism (Ford; Tasks 1.2, 2.7)



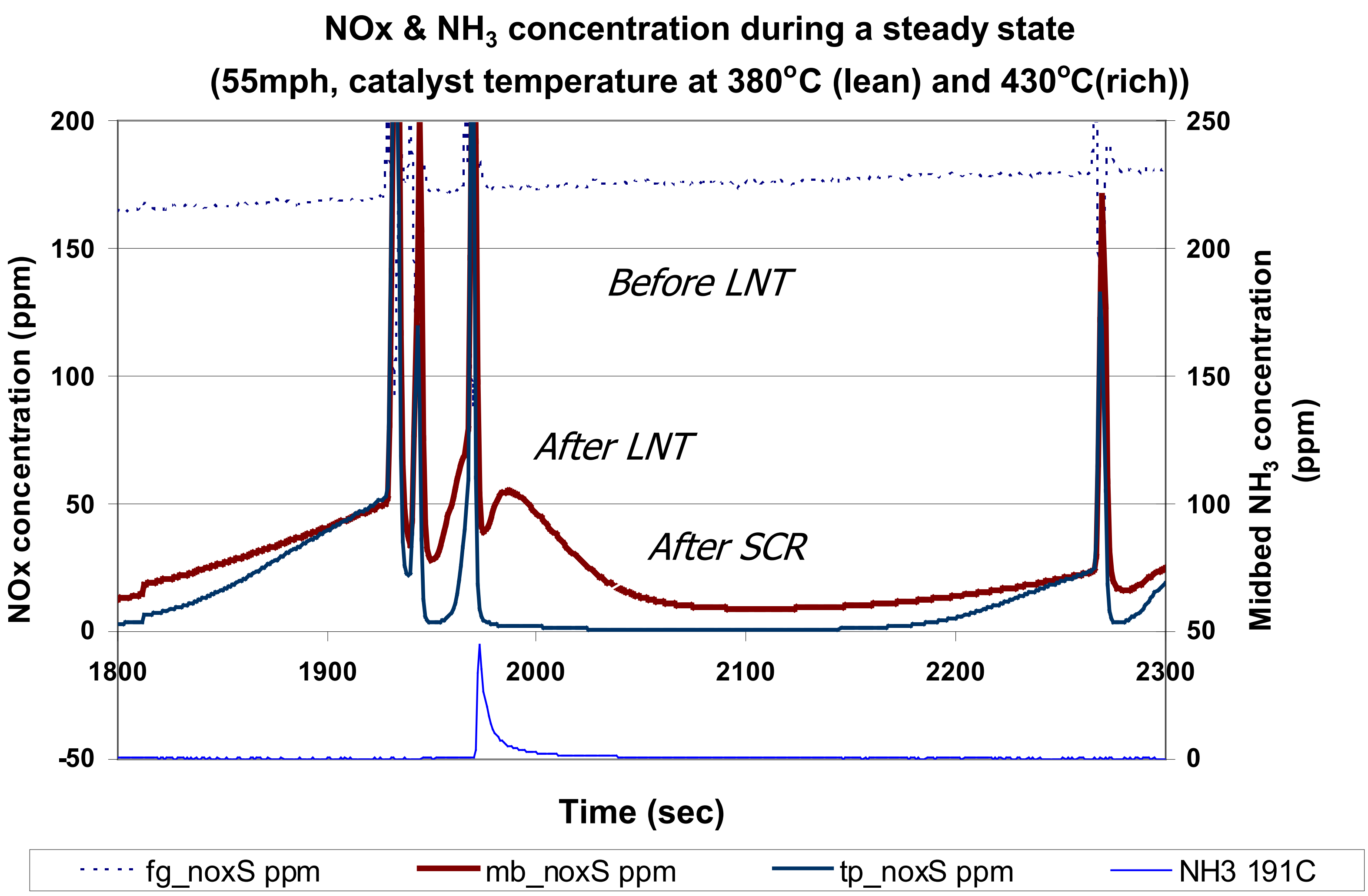


Lab reactor data suggest a non-NH_3 reduction mechanism

- *Enhanced conversion from SCR cat at temps below 225C and above 450C (where little or no NH3 is formed or expected to store on the SCR cat)*
- *Data suggest an additional non-ammonia NOx conversion mechanism over the SCR catalyst.*

Lab data: 70K simulated 3-mode Lab aging; 60sL/5sR eval. cycles

Vehicle Testing: Steady-Speed



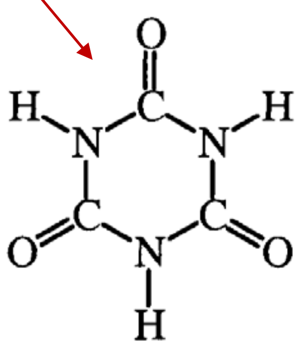
NH_3 produced cannot explain extra NOx conversion by SCR

Experimental Results (Task 1.2; Ford)

- No NH_3 observed between LNT/SCR in some cases: This rules out NH_3-SCR due to NH_3 storage (and no lean LNTNH3 production!).
- No R-NO observed between LNT/SCR: This rules out nitromethane production on the LNT and storage on the SCR.
- SCR reduces NO and NO_2 for 100-300 sec after 2-5 sec rich period: Indicates a stored or in situ reactant.
- NOx reduction over the SCR requires periodic rich purge: Reductants required to create reactive species in LNT.
- N-containing Reductant is produced on LNT, and it gives **no signal in FID and NOx analyzers**:

HCNO is likeliest possibility.

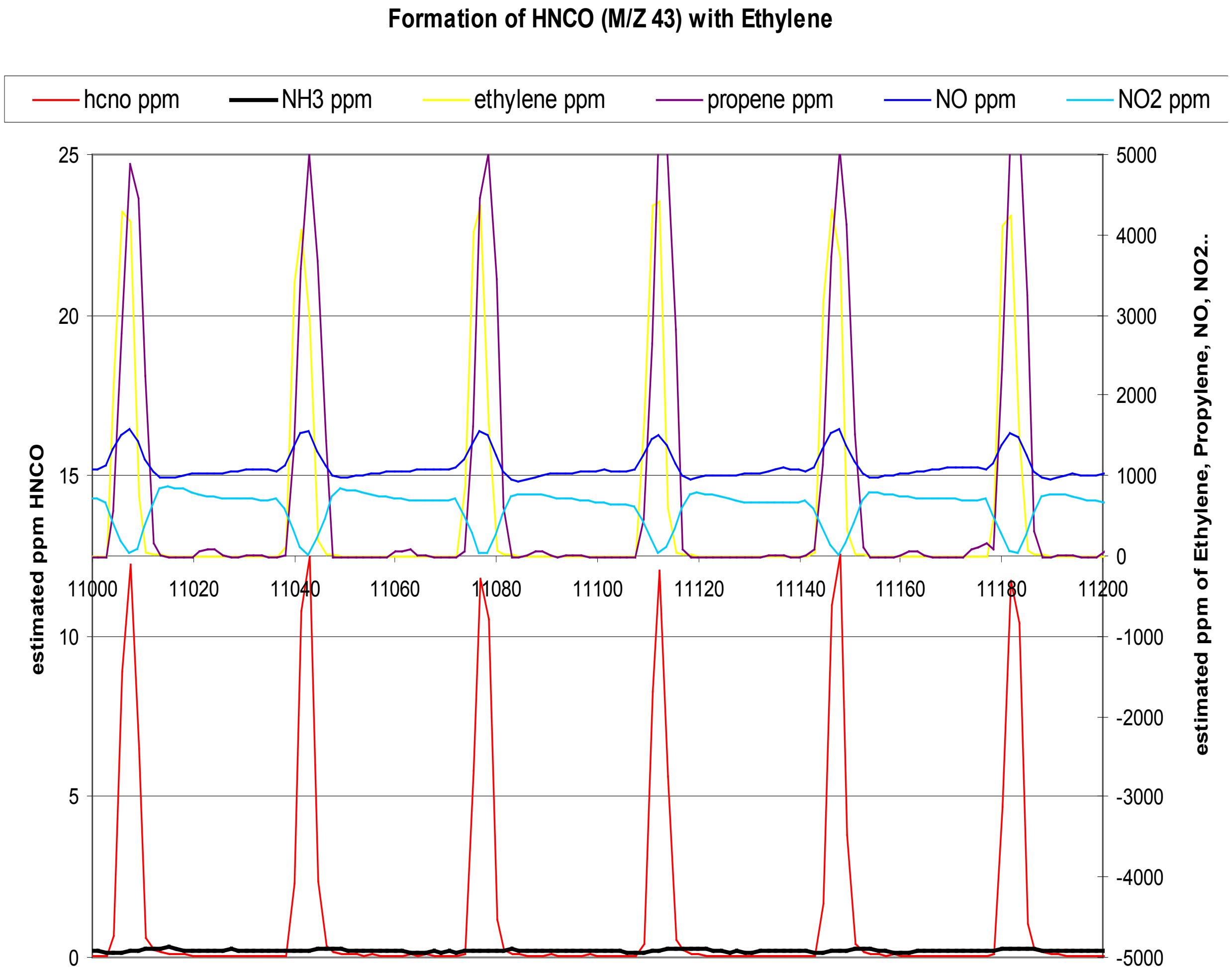
Some N-containing Species produced by LNT, as evidenced by NOx remake post LNT



cyanuric acid

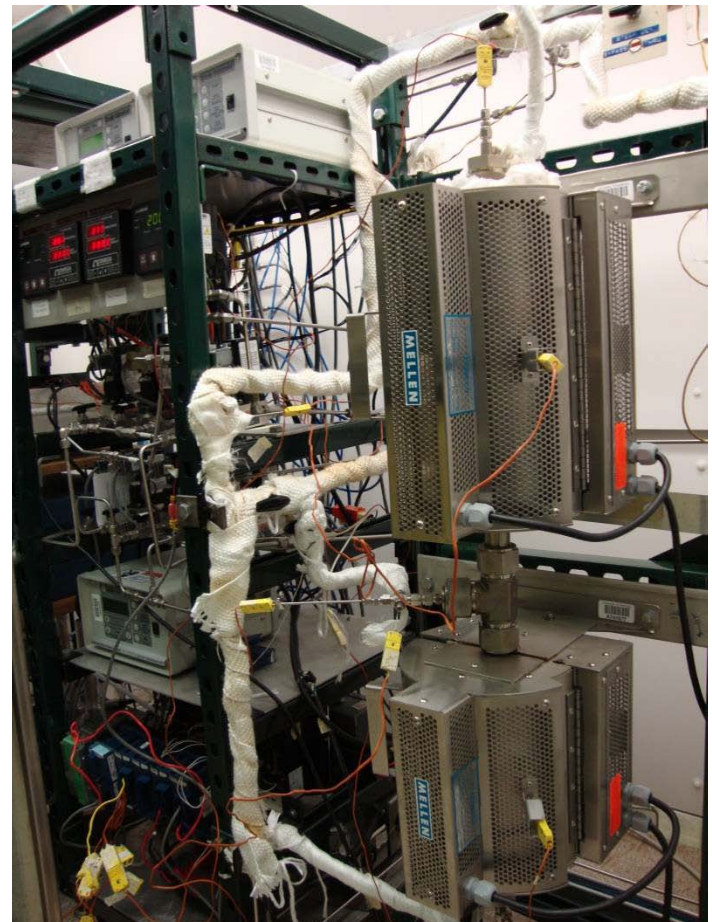
Production favored by lower temperatures and reduced oxidation/storage performance of LNT

HNCO Observed in Lab Reactor Under Lean/Rich Cycling Conditions (no H_20; CO_2)



Reactor Studies at UK CAER

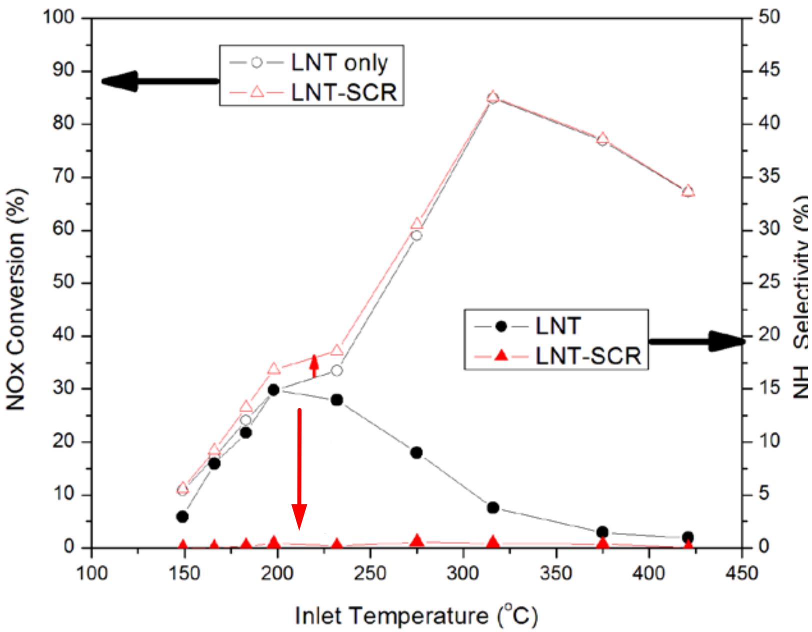
- **LNT-SCR studies:**
  - reproduce non-NH_3 NOx conversion route observed by Ford (using non-proprietary LNT catalyst)
  - identify optimal experimental conditions for subsequent *in situ* DRIFTS studies
- Low PGM-loaded LNT used, with Cu-zeolite SCR catalyst
- Gas sampling at three positions



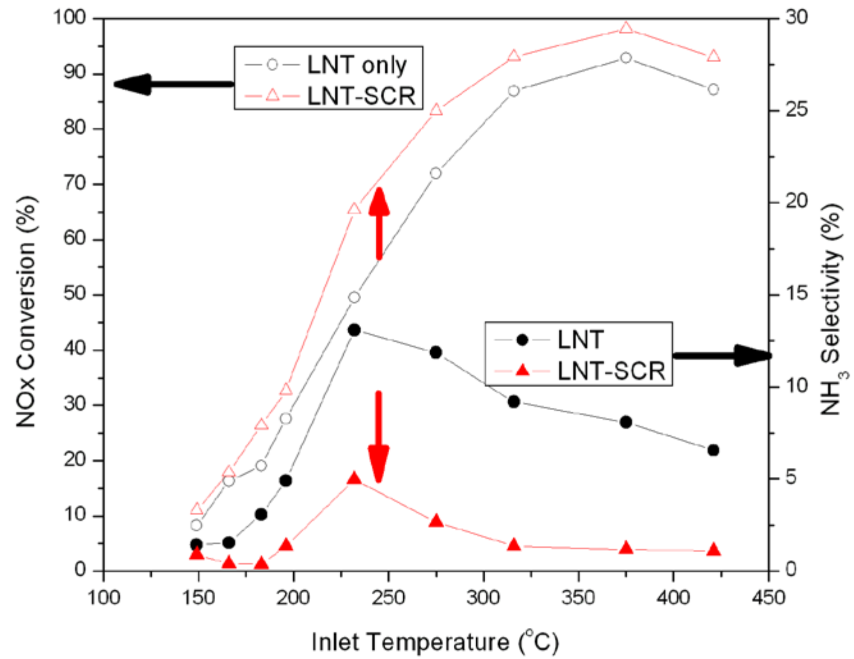
- **SpaciMS studies (Ford, ORNL):**
  - gain insights into the factors controlling NH_3 emissions from LNT catalysts: underlying chemistry, effect of process parameters, effect of catalyst composition

NOx and NH_3 Conversion in LNT-SCR System: Evidence for non-NH_3 NOx Conversion Pathway (Tasks 1.2, 1.6)

Rich phase reductant:
1% CO, 0.3% H_2



Rich phase reductant:
1% CO, 0.3% H_2, 3334 ppm C_3H_6



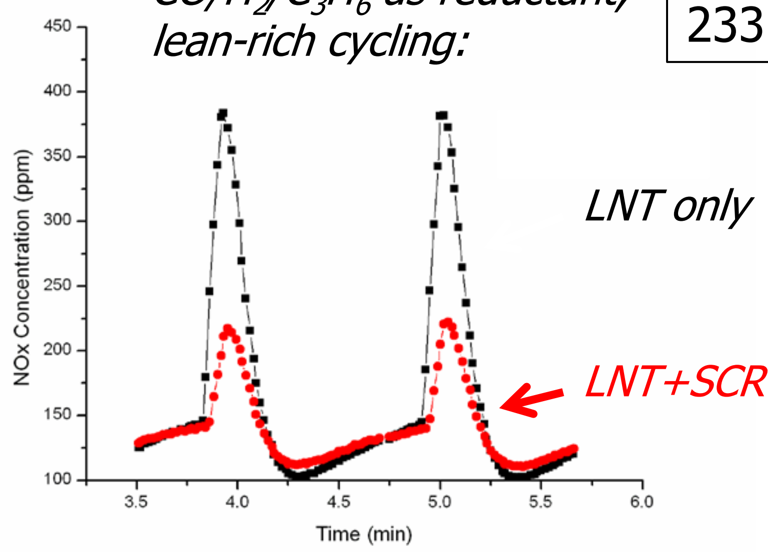
- *Observations first made by Ford confirmed at UK CAER:*
  Benefit of SCR catalyst most apparent when hydrocarbon (propene) is present
  → SCR catalyst is able to utilize propene - or a derivative thereof - as a reductant

NOx Conversion in the LNT-SCR System: Results for Different Reductants (Task 2.7)

Reductant	Total NOx conversion over SCR catalyst (%)	NOx conversion over SCR catalyst during lean phase (%)	NOx conversion over SCR catalyst during rich phase (%)
$CO/H_2/C_2H_4$	6.9	5.8	1.1
$CO/H_2/C_3H_6$	15.3	5.9	9.6
CO/H_2	3.6	3.45	0.15
C_2H_4	3.3	2.4	0.9
C_3H_6	8.0	0.8	7.2

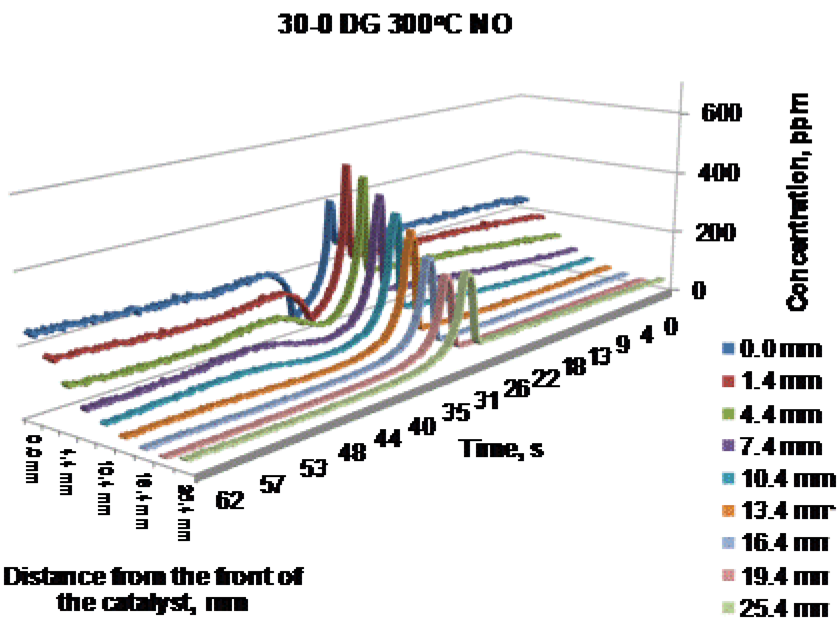
$CO/H_2/C_3H_6$ as reductant, lean-rich cycling:

233 °C



When propene is added as rich phase reductant, NOx conversion over SCR catalyst mainly occurs in rich phase (as opposed to lean phase for conventional NH_3 route)

SpaciMS Study of NH_3 Evolution in LNT Catalysts (1): <u>Degreened</u> Catalyst, Low OSC (Task 1.6)



<u>NO evolution:</u>

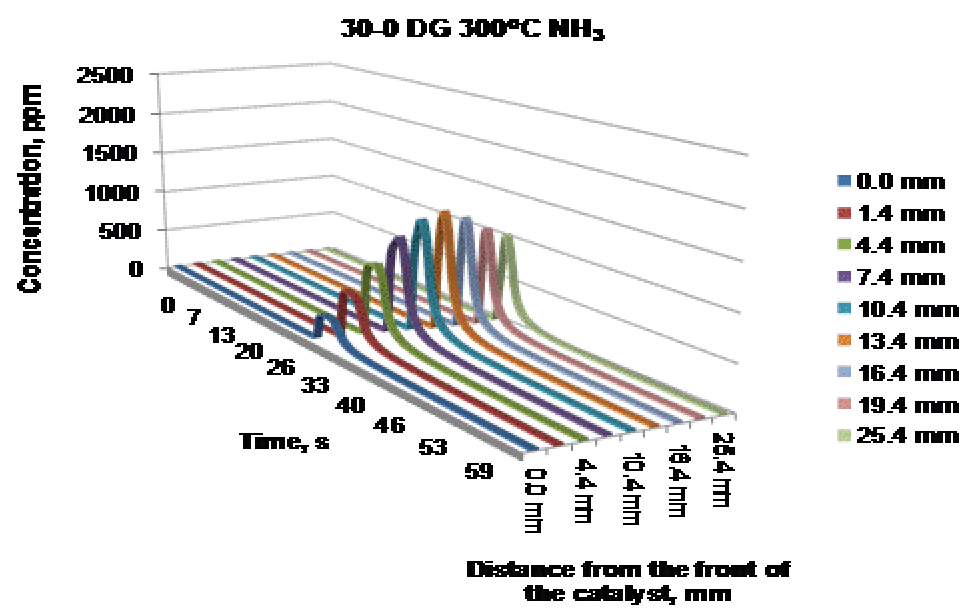
NO concentration peaks near front of catalyst:

- *NOx storage mainly in front portion*
- *NOx released to gas phase subsequently undergoes consumption (to some degree) downstream*

<u>NH_3 evolution:</u>

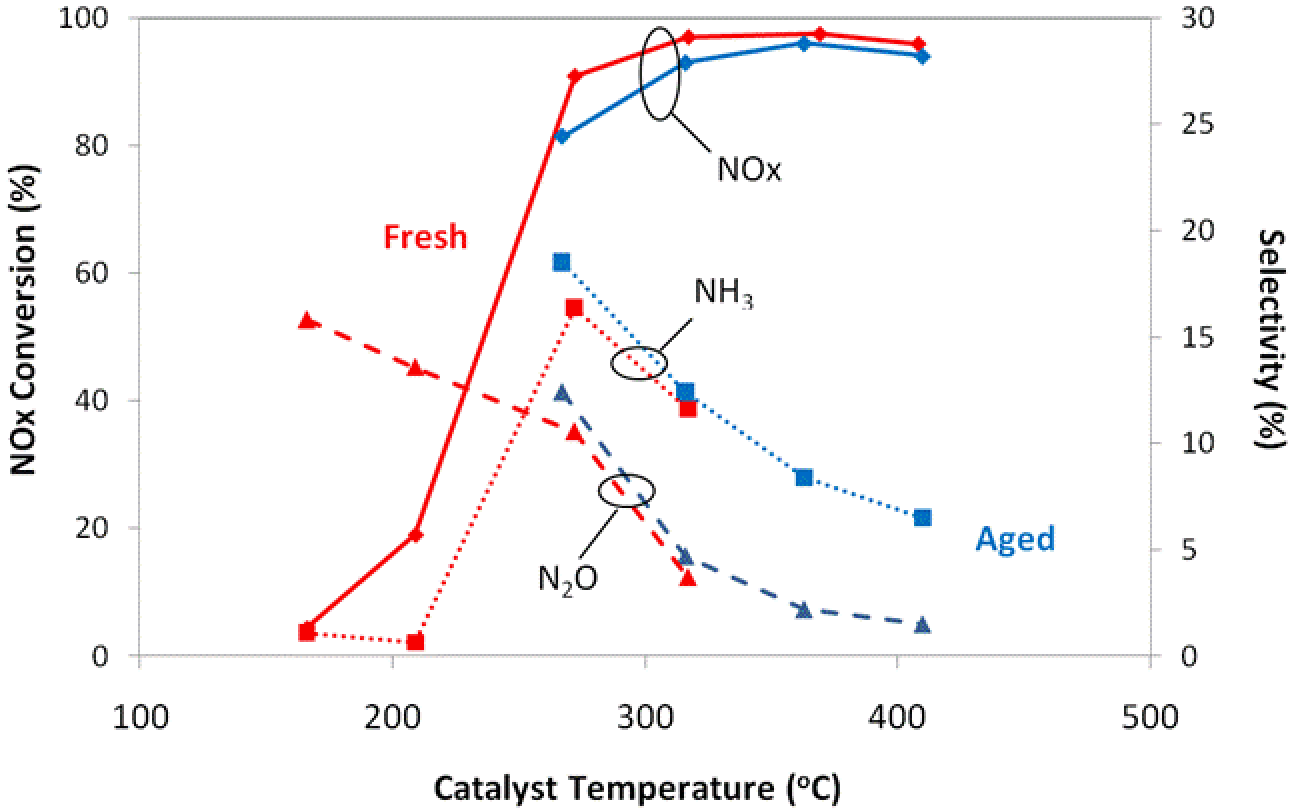
NH_3 concentration peaks near middle of catalyst:

- *possible correlation with H_2 (from prior work)*
- *NH_3 released to gas phase subsequently undergoes consumption (to some degree) downstream*



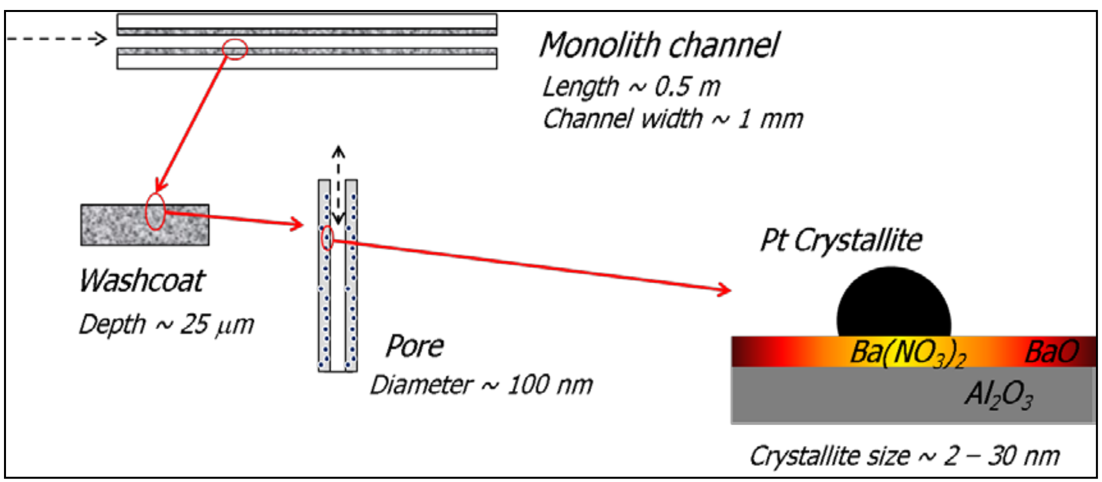
NH_3 Evolution in LNT (UH; Task 1.6)

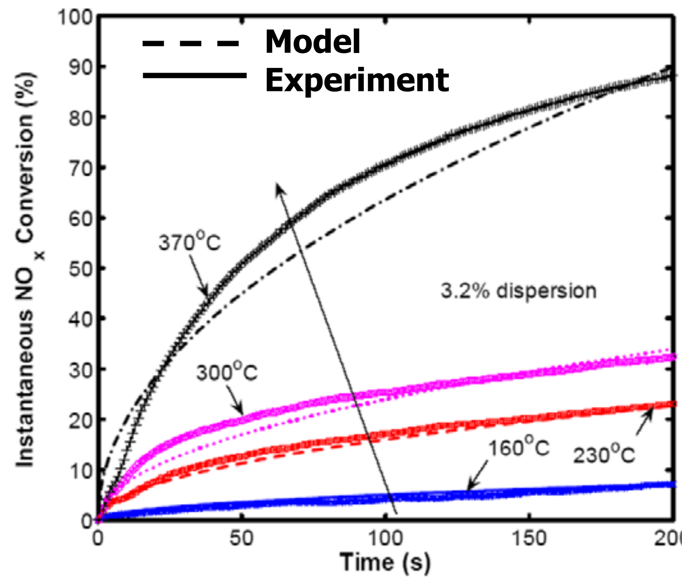
Catalyst: Pt (2.2 wt.%)/BaO (20 wt.%)
300 °C, 60 s storage; 10 s regeneration (1.5% H_2)



LNT Modeling (UH; Tasks 1.7, 1.8)

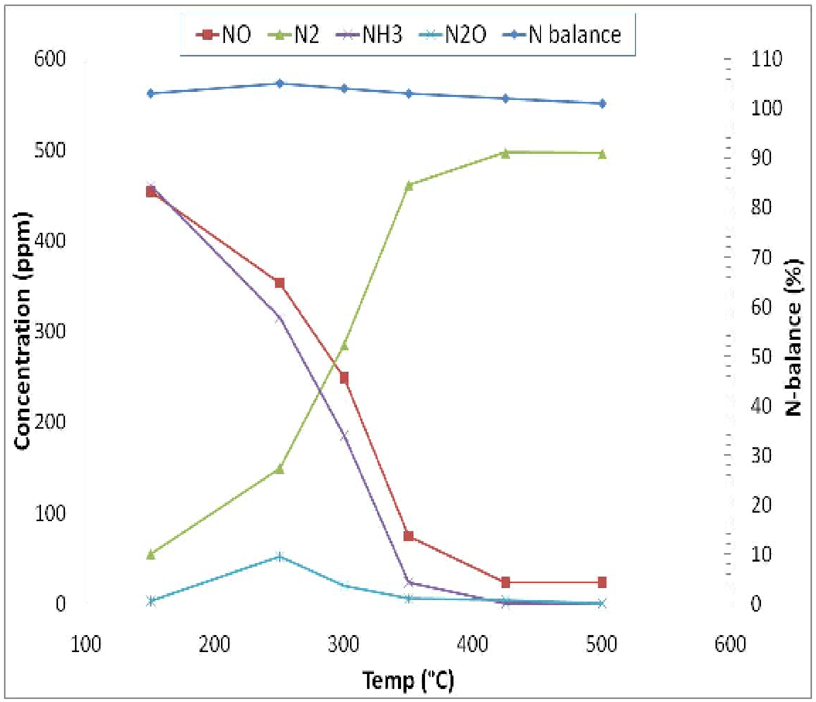
- LNT reactor models completed for Pt/BaO, H_2 as reductant
  - Microkinetic formulation: storage & reduction
  - Global kinetic model formulation accounts for particle size effects, $NH_3/N_2O/N_2$ selectivity

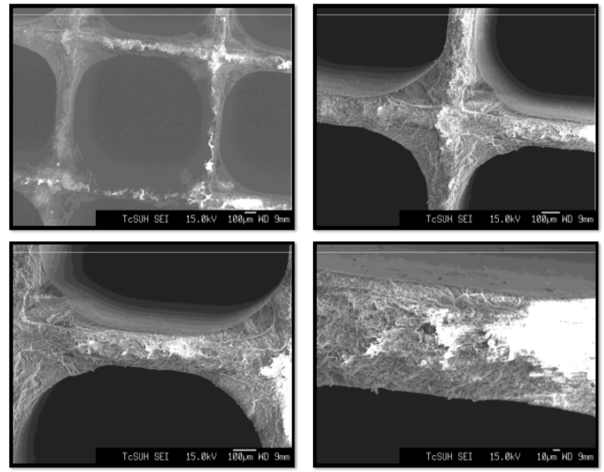




NH_3 SCR on Fe-Zeolite (UH; Task 2.4)

500 ppm NO, 500 ppm NH_3, 5% O_2





Washcoat:

50µm

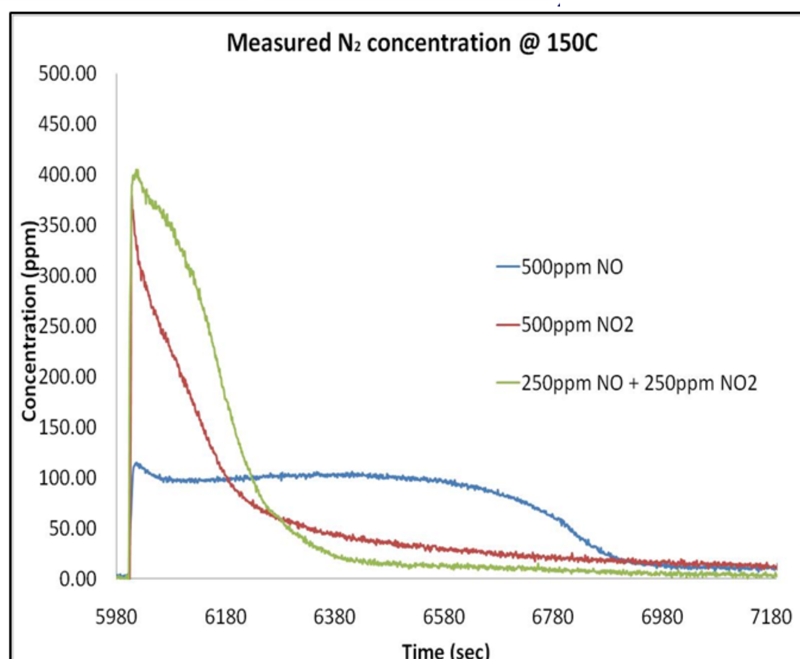
Fe 4 wt.%

Ti: 1.5% wt.%

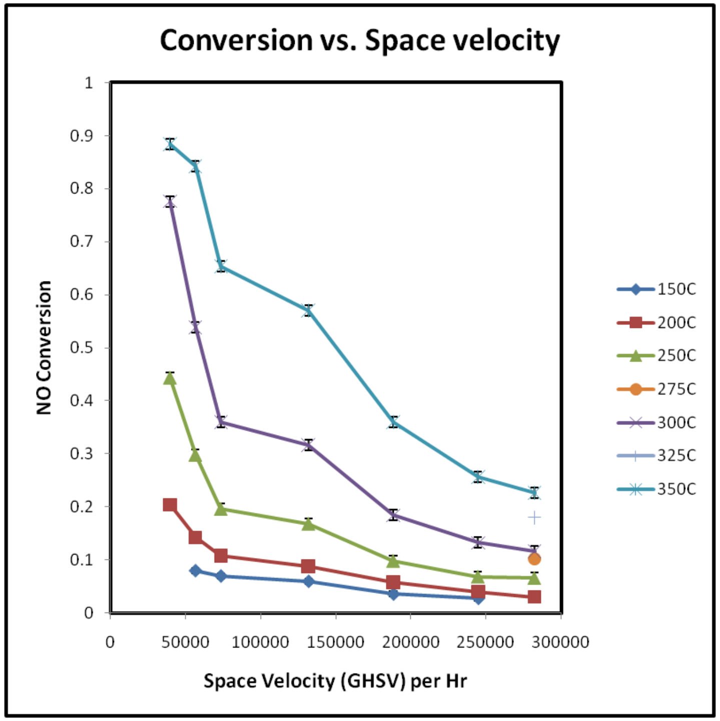
Al: 4.5% wt.%

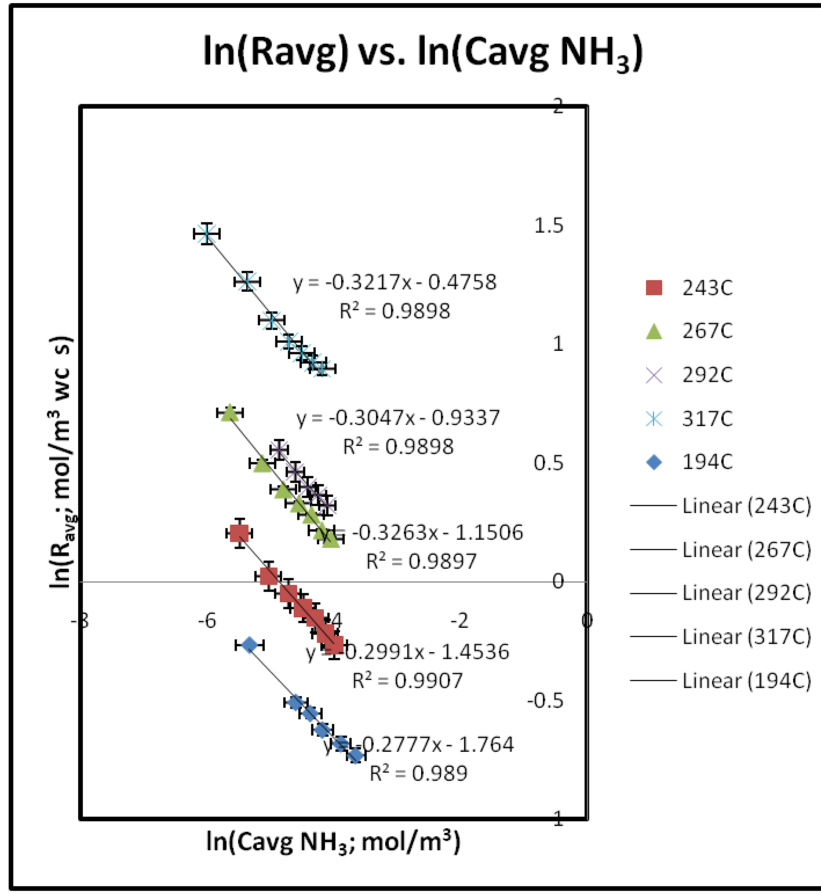
Si: 38% wt.%

- Steady-state & transient tests & intrinsic kinetics
- Fe- & Cu-zeolite catalysts: provided & synthesized



NH_3 SCR Kinetics on Fe-Zeolite





<u>Standard SCR:</u>

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

<u>Kinetic Rate form:</u>

$$-R_{NO} = Ae^{-E/RT} * [NO]^1\ [NH_3]^{-0.3}\ [O_2]^{0.56}$$

$E \sim 42$ kJ/mol

SCR rate: positive order in NO & O_2, inhibited by NH_3

Activities Planned: 4QFY10, FY11

- Spatio-temporal LNT data to be collected for comparison to global model with focus on NH_3
- TAP study of SCR, NSR with H_2 & CO
- In situ DRIFTS study at ORNL: identification of possible $C_aH_bN_cO_d$ species formed on LNT/SCR catalysts
- Complete LNT-SCR reactor studies, including parametric study of NH_3 formation over model LNT catalysts varying in ceria content
- Isotopic ^{15}NO bench & TAP reactor experiments
- Development of kinetic & reactor models
  - SCR microkinetic model & SCR reactor with comparison to data
  - Integration of LNT & SCR global kinetic based reactor models

Summary

- Good progress on several fronts
  - Non-NH_3 SCR mechanism important
  - Conditions for NH_3 generation identified from spatio-temporal data
  - SCR kinetics for Fe-zeolite
  - LNT micro & global kinetics & reactor models
- Next steps to focus on LNT/SCR data & modeling, DRIFTS & TAP studies