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

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ACE029

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Overview

Timeline

- Start: Oct. 1, 2010
- End: Sept. 30, 2012
- 75% complete

Budget

- Total project funding
  - DOE: $2,217,317
  - UH & partners: $687,439
- Funding received
  - FY10-FY12: $2,103,496

Barriers/Targets

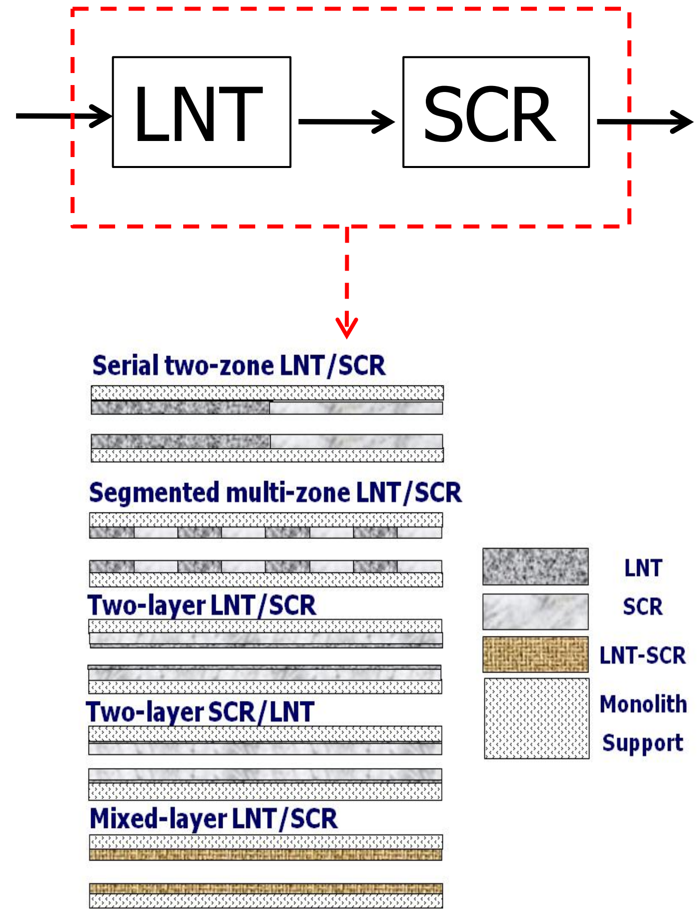
- Increase fuel efficiency of light-duty gasoline vehicles by 25% (by 2015): LNT/SCR has potential as non-urea deNOx approach for LD diesel &*lean burn gasoline vehicles*
- Reduce NOx to <0.2 g/bhp-h for heavy-duty diesel (by 2015): *LNT/SCR is promising non-urea solution*

Partners

- U. Houston (lead)
- Center for Applied Energy Research (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
- Need to reduce PGM requirements & minimize fuel utilization in meeting NOx reduction targets



Overall Goal, Impact & Approach 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.

Premise of Approach: Focused experiments complemented by predictive reactor models tuned through simulation of experiments can be used to identify optimal LNT/SCR designs & operating strategies

Principal Challenges & Questions

- LNT/SCR only viable if sufficient NH_3 generated in LNT: Need to identify conditions for NH_3 generation in LNT & main pathways
- Hydrocarbons present during LNT regeneration may slip past LNT: Need to understand and quantify HC role as supplemental reductant in SCR
- LNT/SCR configurations and operating conditions: Which is optimal?
  - Stratified, segmented, multi-layer?
  - How little precious metal can be used to meet NOx reduction targets?
- LNT/SCR operating conditions:
  - What can be done about low temperature limitations?
  - How susceptible is performance to regeneration phase composition?

Collaborative Project Team: Current Activities

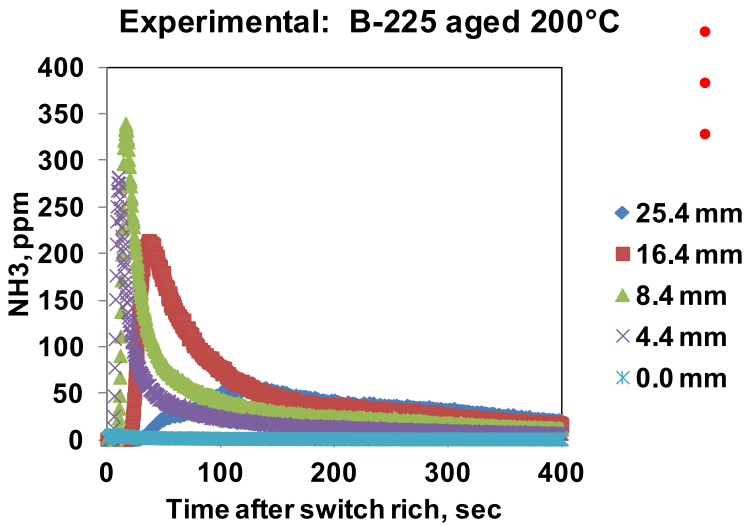
- **University of Houston**
  - *Mike Harold (PI), Vemuri Balakotaiah, Dan Luss*
  - Bench-flow, TAP reactors; LNT - NH_3 generation; LNT/SCR multi-layer catalyst synthesis & reactor studies; NH_3 SCR kinetics on Fe and Cu zeolite catalysts
- **University of Kentucky - Center for Applied Energy Research**
  - *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

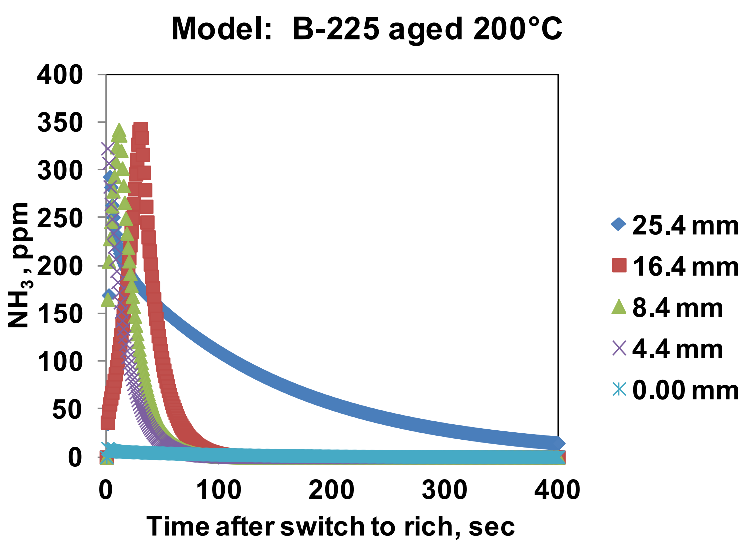
Activity Highlights from this Period

- Since project inception: 22 peer-reviewed publications, 20 presentations, 4 invited lectures & 1 keynote
- LNT
  - DRIFTS study shows involvement of isocyanate pathway during regeneration
  - SpaciMS regeneration data features predicted by LNT regeneration model
  - Predictive crystallite LNT model predicts lean-rich cycling data & identifies optimal conditions for NH_3 formation
- SCR
  - Comprehensive kinetics and modeling completed for Fe/ZSM-5 & Cu/chabazite catalysts
  - New dual-layer Fe/Cu SCR catalyst shows significant extension of temperature window resulting in high NOx conversion
  - SpaciMS experiments provide compelling evidence for olefin trapping and reduction as supplement to NH_3
- LNT-SCR
  - N_2O emissions from LNT mitigated by downstream Cu/chabazite
  - First LNT/SCR dual-layer catalyst experimentally demonstrated
  - Predictive LNT/SCR model quantifies segmented configuration performance

LNT

LNT Regeneration Modeling of SpaciMS Data (Tasks 2.1, 2.7, 2.9, 3.5; UK, Ford, UH)



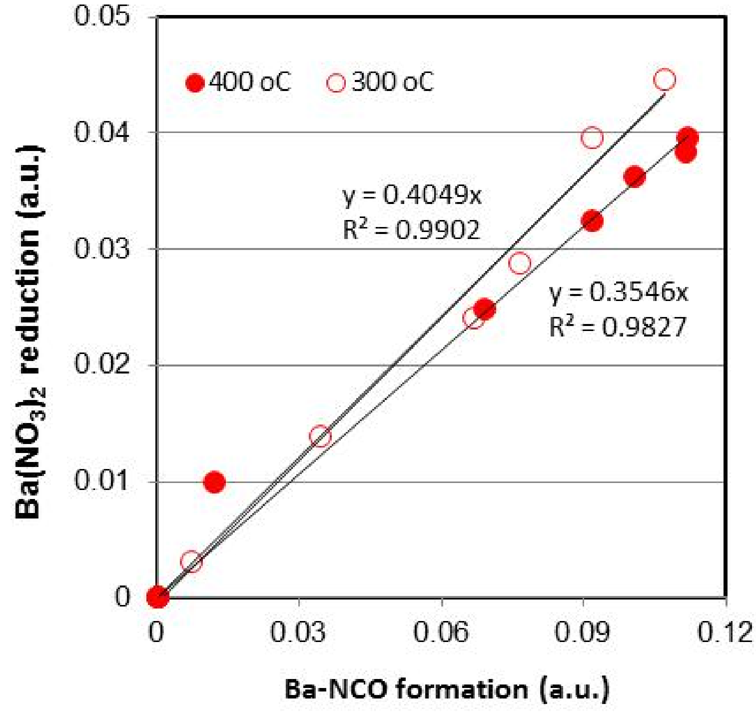


- *Pt/Rh/BaO/Al_2O_3 aged catalyst (225 g washcoat/L)*
- *Regeneration using H_2*
- *Data fitted to UH model of Pt/BaO/Al_2O_3 catalyst*

- *First fit – no optimization of kinetic parameters!*
- *Aged catalyst:*
  - *decrease in Pt site density*
  - *decrease in Pt and BaO site proximity*
- *Peak broadening present in the experimental data (e.g., 16.4 mm position) probably due to the NH_3 delay in the capillary due to the polar nature of NH_3*
- *Tuning underway to fully capture trends*

DRIFTS Study of NOx Reduction with CO on LNT Catalysts (Task 3.1; UK)

- UK-ORNL DRIFTS study employing $Pt/BaO/Al_2O_3$ catalyst
- Lean–rich cycling performed in absence of H_2O
- Strong isocyanate bands observed during rich purging
- Isocyanate reactivity: $H_2O > NO+O_2, O_2 > NO$

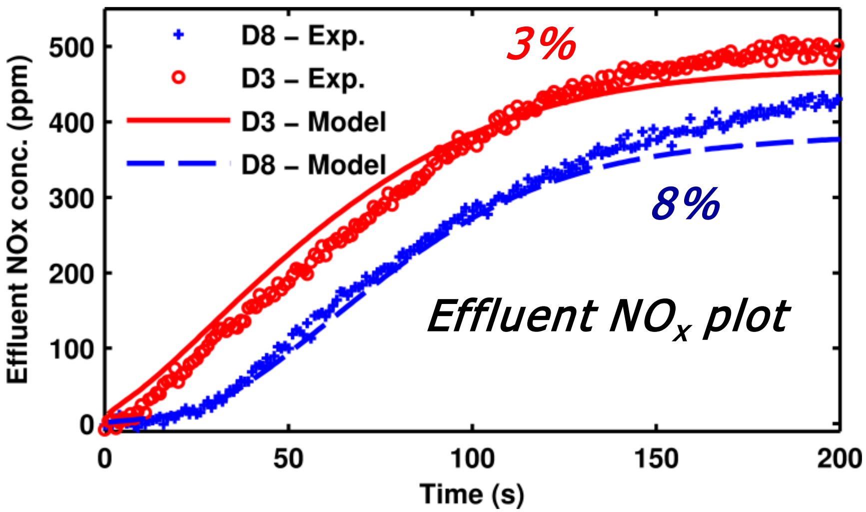


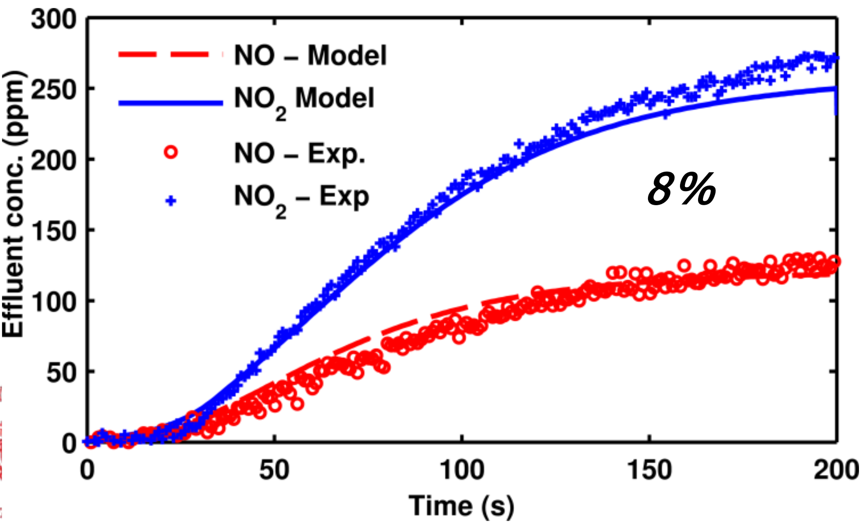
- *Linear relationship between Ba-NCO formation (2162 cm^{-1}) and Ba-nitrate reduction (1320 cm^{-1}) implies that Ba-NCO is a direct intermediate in nitrate reduction*
- *At >100 °C, kinetics of Ba-NCO hydrolysis (to NH_3) are very fast*

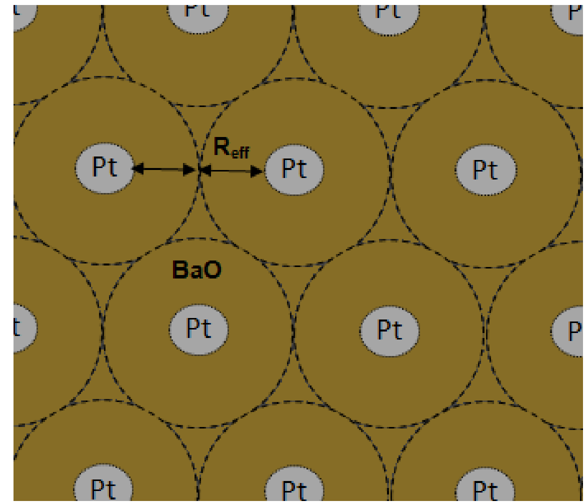
Crystallite-Scale Model of NO_x Storage & Reduction on Pt/BaO: Storage (Tasks 2.1, 2.7, 2.9; UH)

Effect of Pt Dispersion

Feed: *500 ppm NO, 5% O_2 Bal Ar, GHSV: 60,000 hr^{-1}*







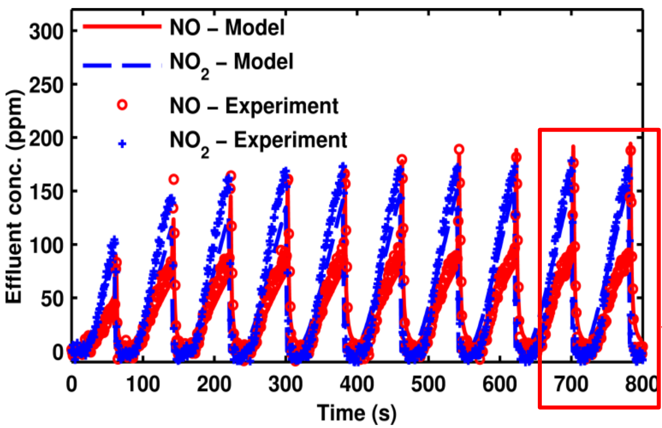
Loading (wt. %):
Pt = 2.48
BaO = 13

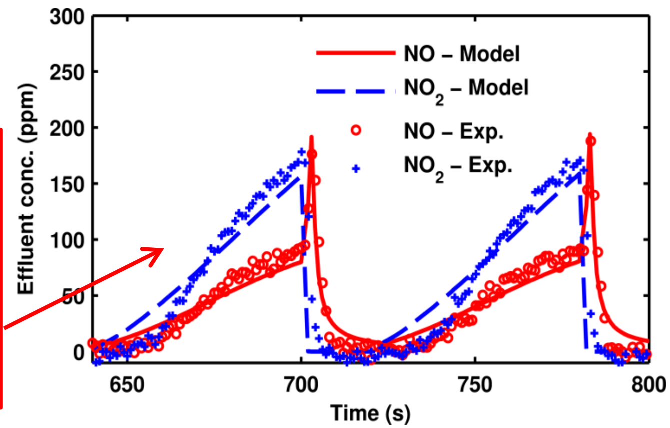
Catalyst	Pt radius, R_c (nm)	Effective Storage Radius, R_{eff} (nm)	Pt Dispersion (%)
D3	15.0	440	3
D8	6.3	120	8

- *Model predicts effect of Pt dispersion on NOx breakthrough (fixed Pt loading)*

Crystallite-Scale Model of NO_x Storage and Reduction on Pt/BaO: Cycling Results (UH)

Feed: ***Lean:*** *500 ppm NO, 5% O_2, 60s;* ***Rich:*** *5000 ppm H_2, 5-30s, Bal Ar GHSV: 60,000 hr^{-1}*

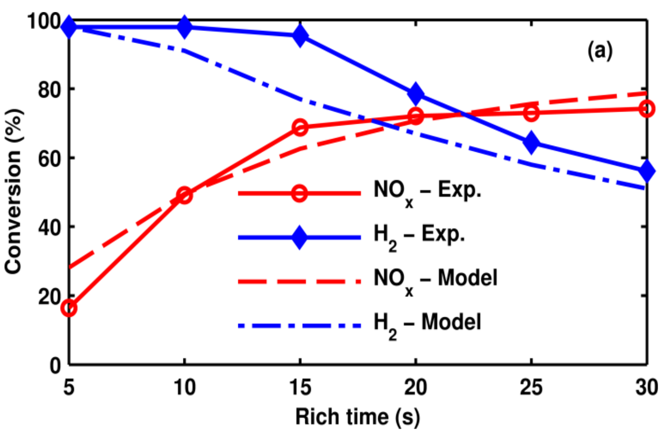




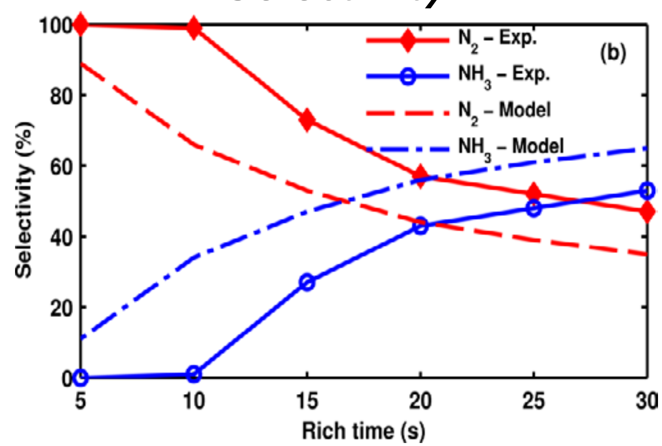
- *Model captures both initial and cyclic steady-state NO_x profiles*

Catalyst D8 (8%)

Conversion



Selectivity



- *Good agreement between model & experiments for different rich time*

- *Key finding: Enhanced diffusion in the storage phase during the regeneration, indicative of H_2 spillover and diffusion*

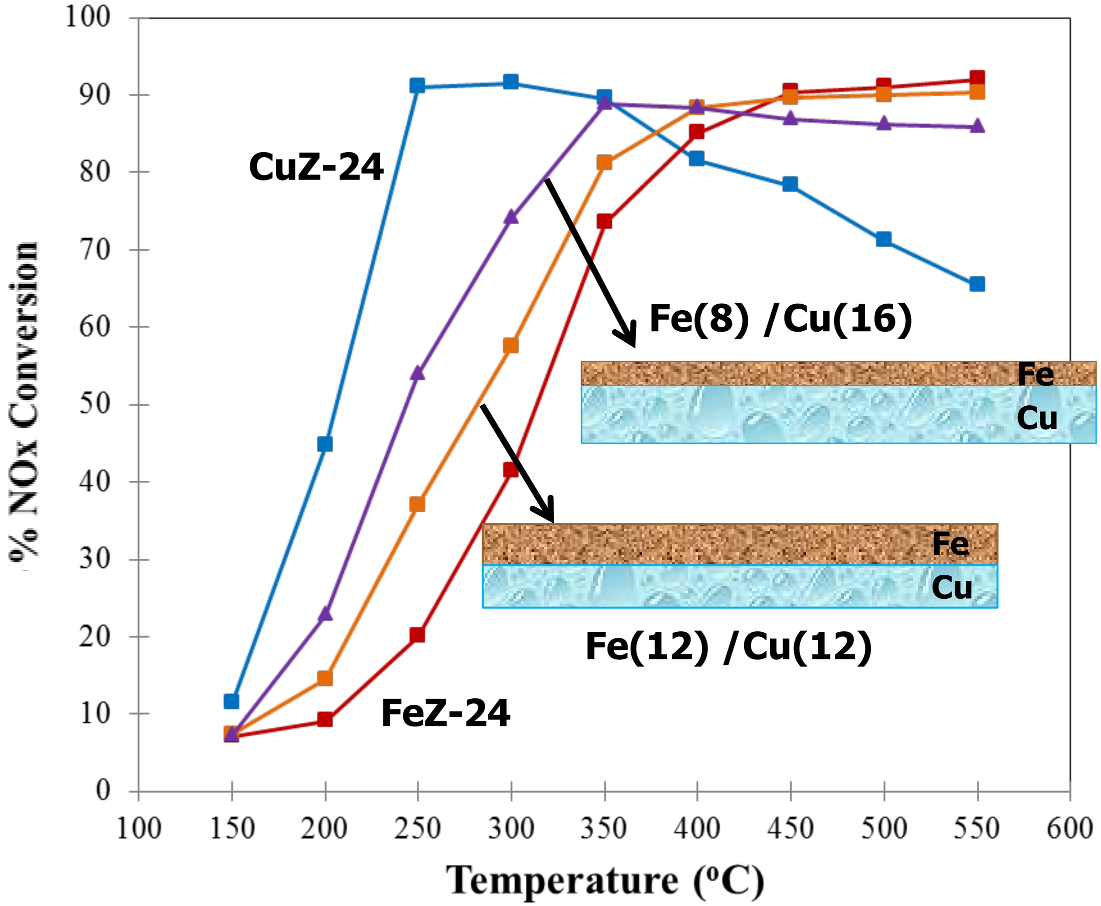
SCR

SCR Kinetics: Fe/ZSM-5 & Cu/chabazite (Tasks 2.1, 2.4, 2.9, 3.4; UH)

- Systematic kinetic model developed from compartmental approach
  - NO oxidation — differential kinetics +
  - Standard SCR — ammonia uptake +
  - NO_2 SCR — integral kinetics +
  - Fast SCR
- Incorporation into SCR monolith model to simulate single-, dual-layer, dual-zone catalysts
  - Include HC as reductant (ongoing)

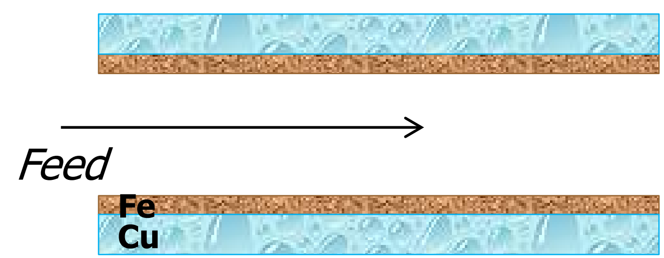
University of Houston · Founded 1927

Combination of Fe- and Cu-zeolite: Dual-layer Catalyst System (UH)



Total washcoat loading:
24% (by wt)

Top layer: **Fe-zeolite (33%)**
Bottom layer: **Cu-zeolite (67%)**



Lab-synthesized catalysts

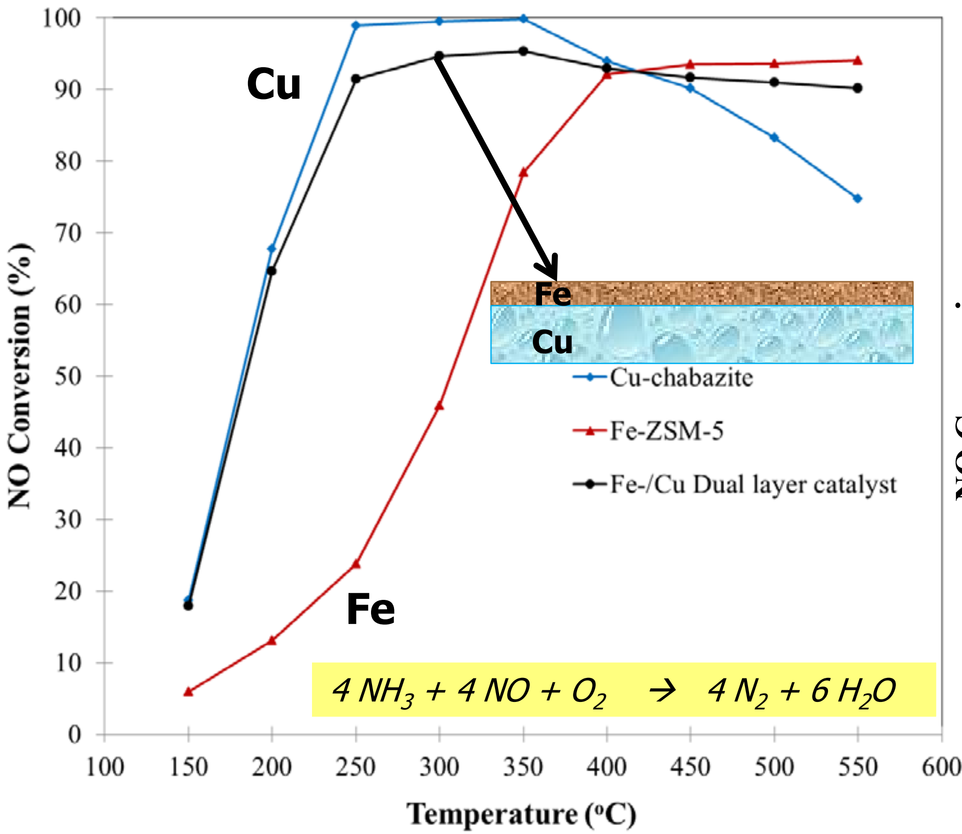
Dual layer catalyst the NO_x reduction efficiency over a wide temperature range

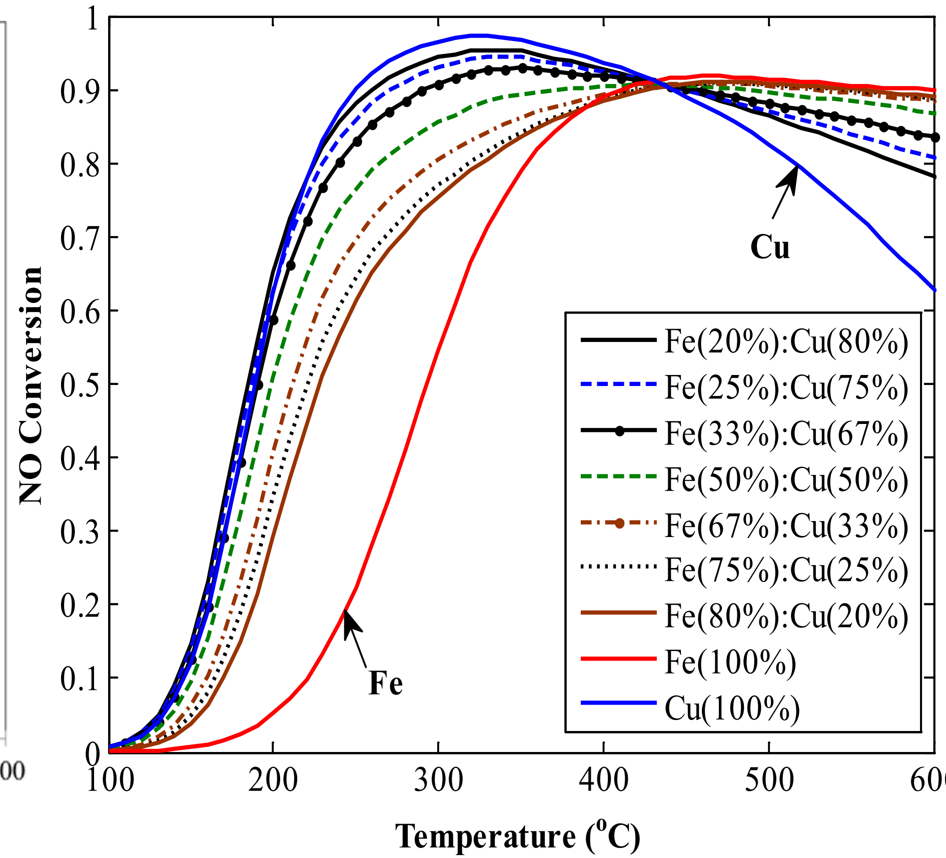
UNIVERSITY OF HOUSTON · Founded 1927 ·

Harold & Metkar, Patent Pending (2011)

Dual-Layer Catalyst System (UH)

Experiments vs Simulations





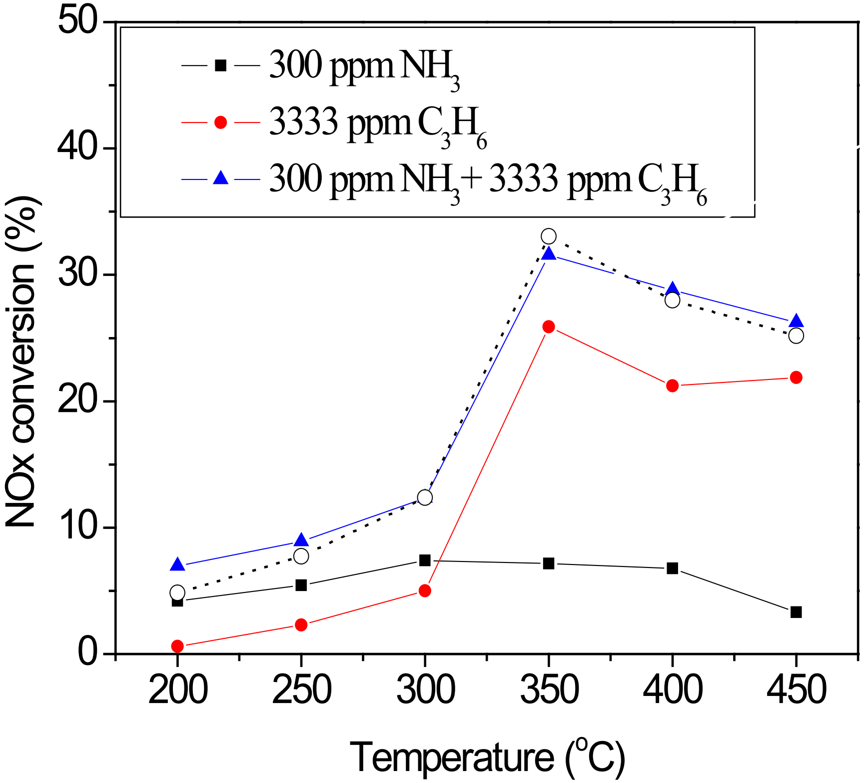
Model accurately captures the experimental trends for single layer and dual-layer Fe-/Cu-zeolite catalysts

Non-NH_3 NOx Reduction Pathway in LNT-SCR: NOx Conversion with Olefins over Cu-zeolite SCR Catalyst (Tasks 2.4, 2.7; UK)

<u>Lean-rich cycling using SCR catalyst (w/o upstream LNT):</u>

Lean (60 s): 300 ppm NO, 8% O_2, 5% CO_2, 5% H_2O, bal. N_2;

Rich (5s): 300 ppm NO, 3333 ppm C_3H_6 and/or 300 ppm NH_3, 5% CO_2, 5% H_2O, bal. N_2

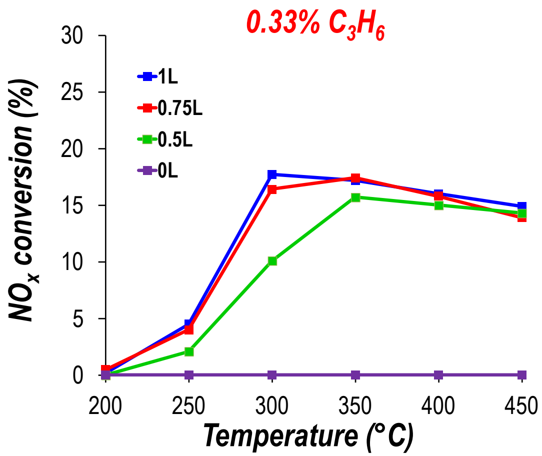


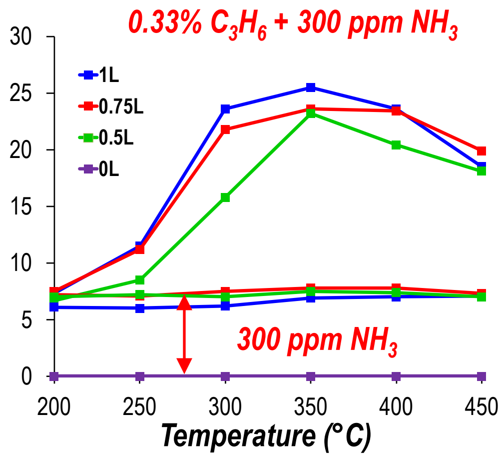
Dotted line = sum of individual NOx conversions obtained separately using NH_3 and C_3H_6 as reductants

- ***Effects of NH_3 and C_3H_6 on NOx reduction over the SCR catalyst are additive***
- ***Under cycling conditions, NOx reduction with olefins occurs in the rich phase <u>and</u> in the beginning of the lean phase, indicating that olefin storage occurs***
- ***Rich phase NOx storage in SCR catalyst decreases HC slip (HC can be stored until it is oxidized in the lean phase)***
- ***HC-SCR pathway to be captured in LNT-SCR model (on-going work at UH)***

SCR Performance Determined by Spatiotemporal Distribution of Regeneration Chemistry (Task 2.7; ORNL, UK)

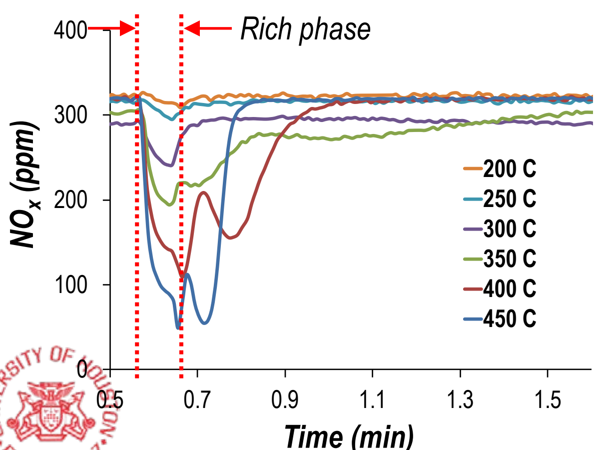
Lean/rich cycling *Cu-chabazite (base gas: 5% H_2O, 5% CO_2, N_2 balance)*
Lean (60 s): 300 ppm NO, 8% O_2 Rich (5 s): 300 ppm NO, 1% O_2, reductant

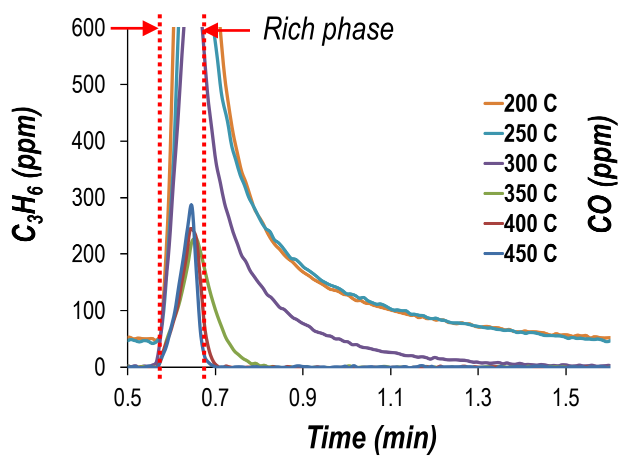


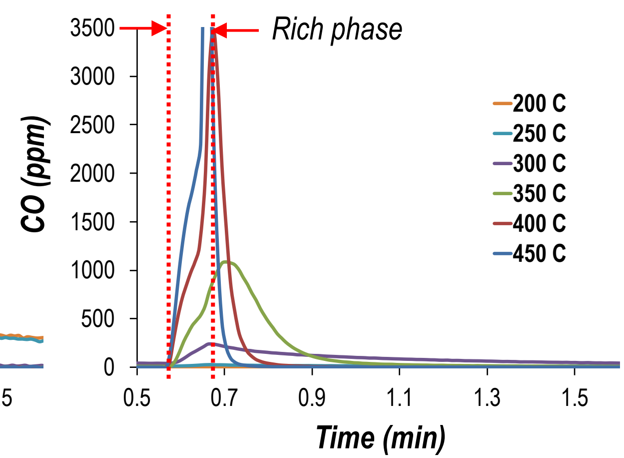


- *HC-SCR effective above 250 °C*
- *NH_3-SCR highly effective at all temps.*
- *NH_3 & C_3H_6 effects additive*
- *Near max NO_x reduction by 0.5L at 350 °C and above*
- *Optimal spatiotemporal distribution of storage, conversion & release of C_3H_6 & reductant products at 300-350 °C*

0.33% C_3H_6, 0.5L catalyst location

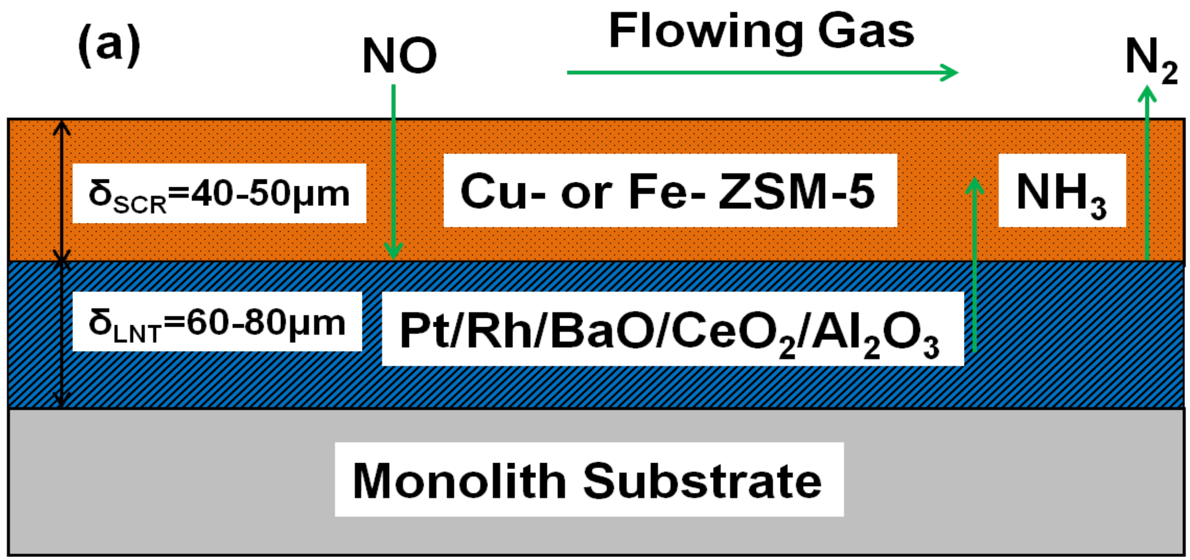


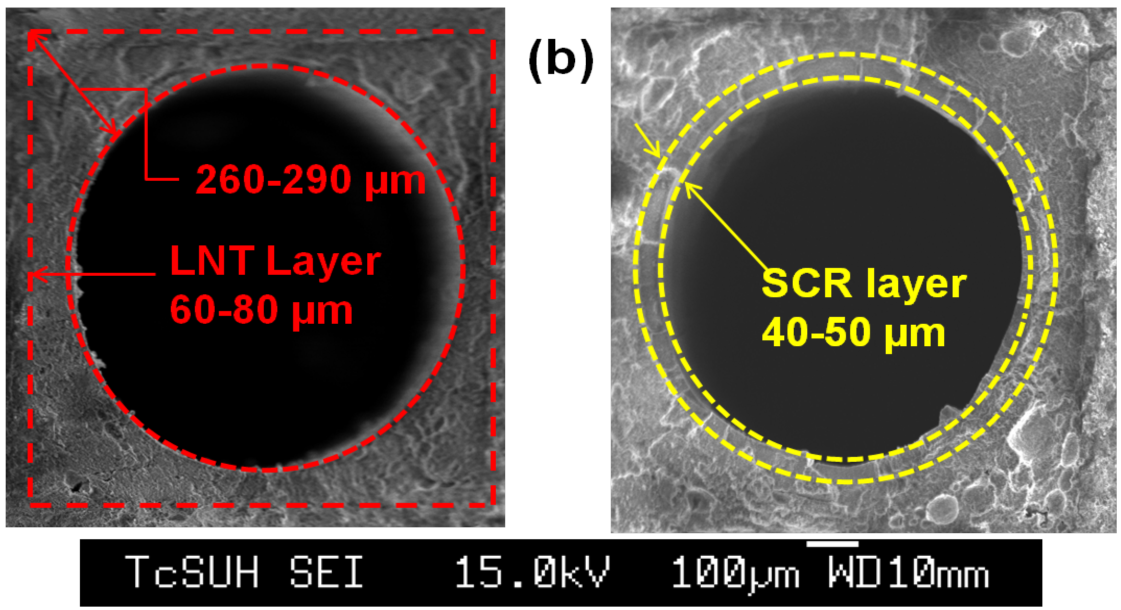




LNT-SCR

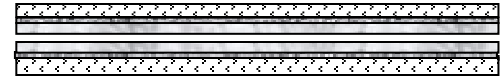
Dual Layer LNT/SCR Catalysts (Task 2.6; UH)





LNT before washcoating LNT after washcoating

Dual Layer LNT/SCR Catalysts

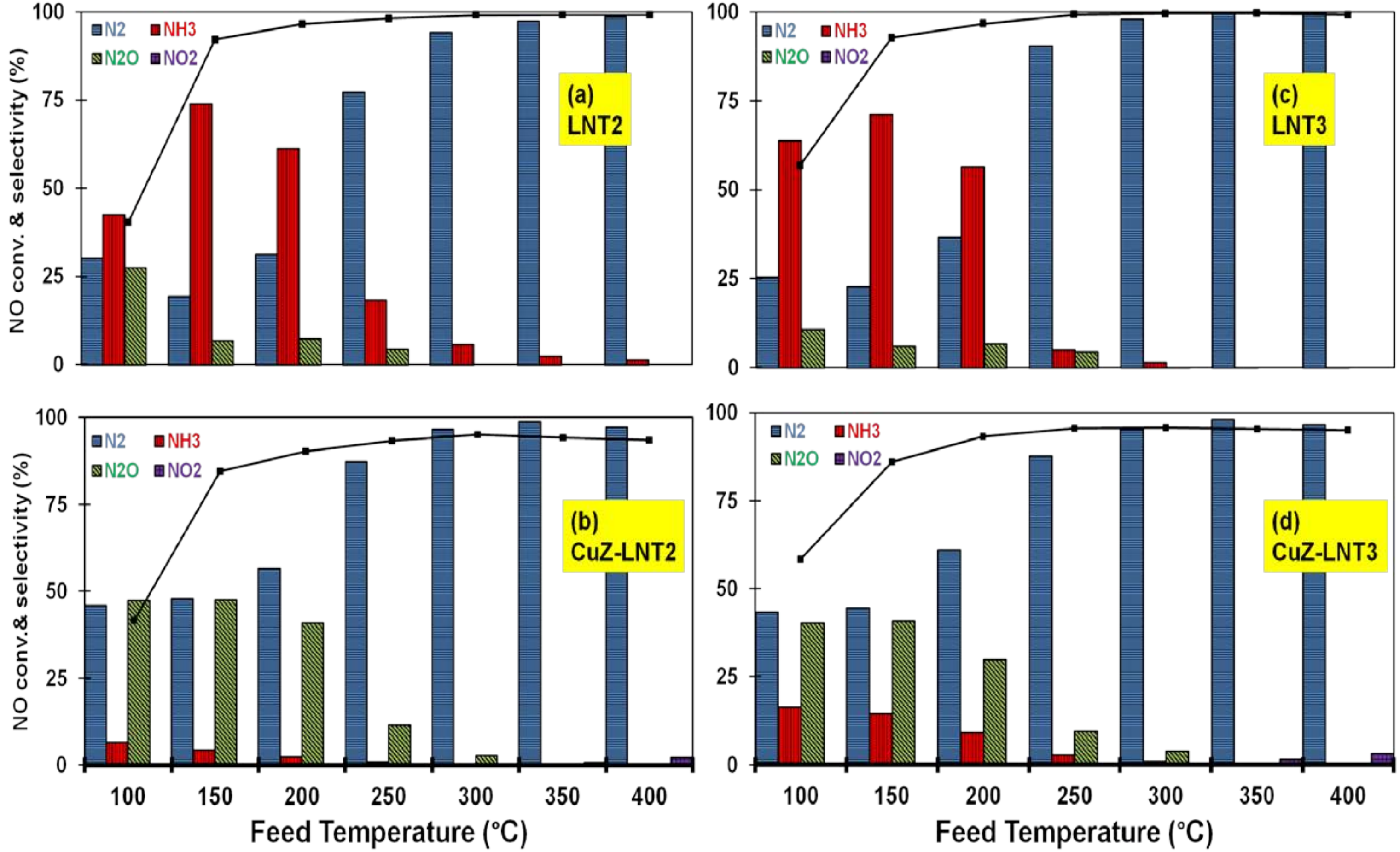


Lean/rich cycling

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

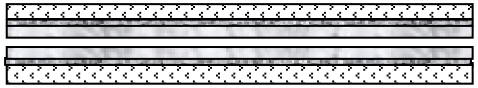
Rich (5 s): 2.5% H_2, balance Ar

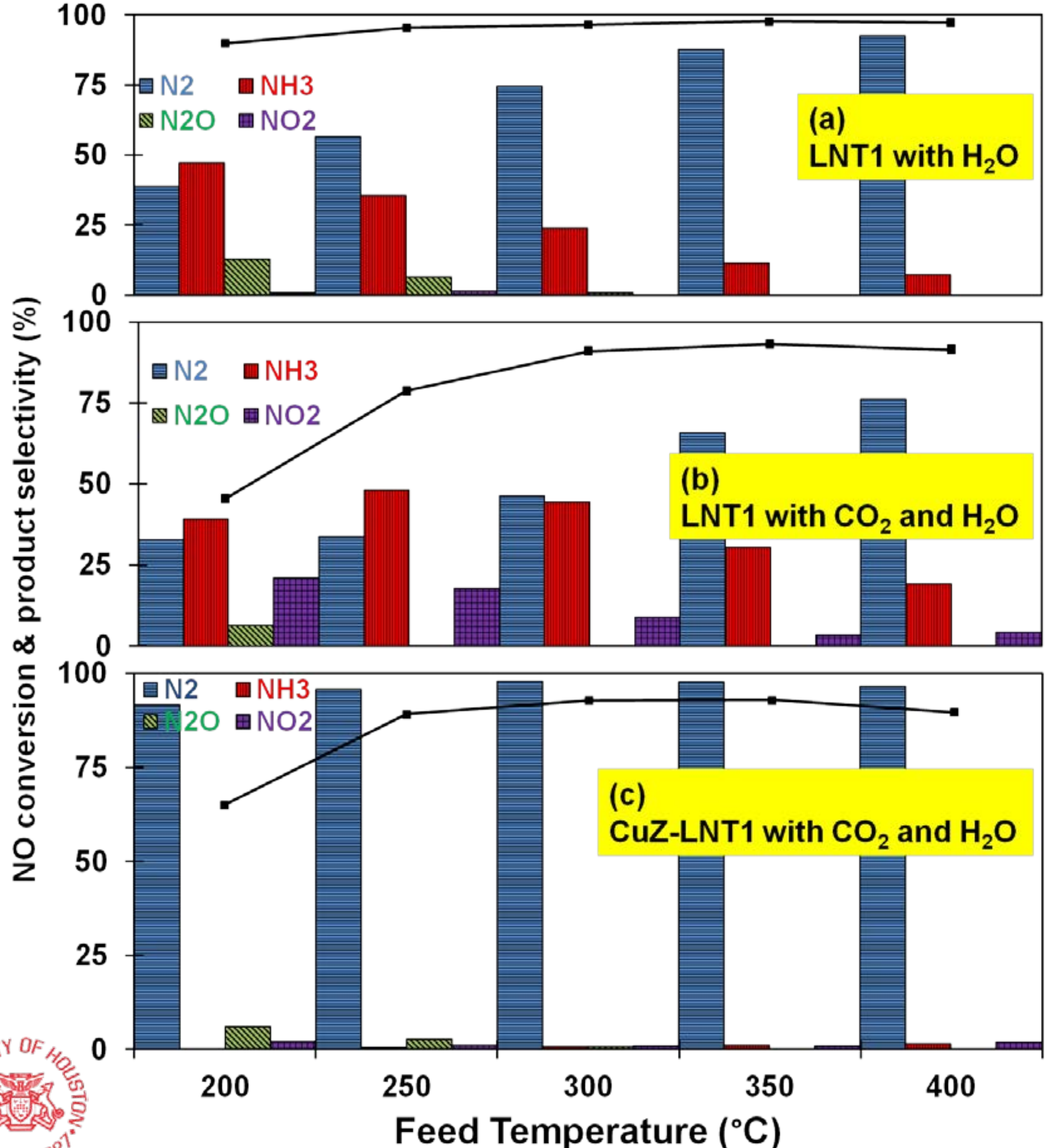
	Pt/Rh (g/ft^3)	BaO (wt%)	CeO_2 (wt%)
LNT1	90	14	0
LNT2	90	14	17
LNT3	90	14	34



- *Addition of SCR layer on LNT layer results in utilization of NH_3 with some increase in N_2O production while maintaining high conversion*

Dual Layer LNT/SCR Catalysts





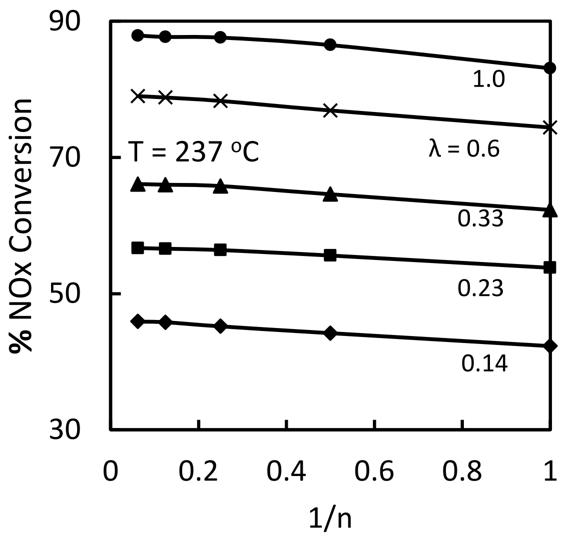
Lean/rich cycling

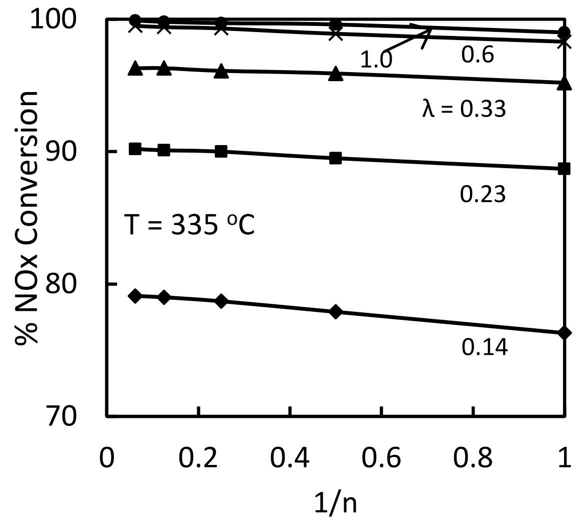
Lean (60 s): 500 ppm NO, 5% O_2, 2.0% CO_2, 2.5% H_2O, balance Ar

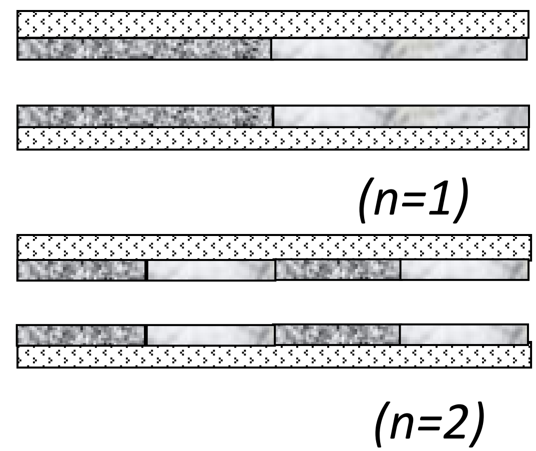
Rich (5 s): 2.5% H_2, 2.0% CO_2, 2.5% H_2O, balance Ar

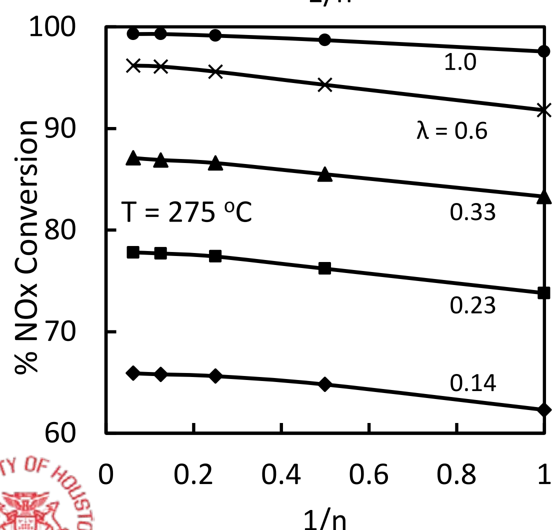
- *Improved performance in presence of CO_2 & H_2O*
- *Elimination of NH_3 and very low N_2O*
- *Good low temperature performance*

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









Serial design with LNT & SCR sections of equal length

Catalysts: Pt/BaO (LNT) Cu/ZSM-5 (SCR)

Length of each catalyst = 2cm; GHSV=60,000 h^{-1};

Lean inlet: NO=500ppm,O_2=5%;

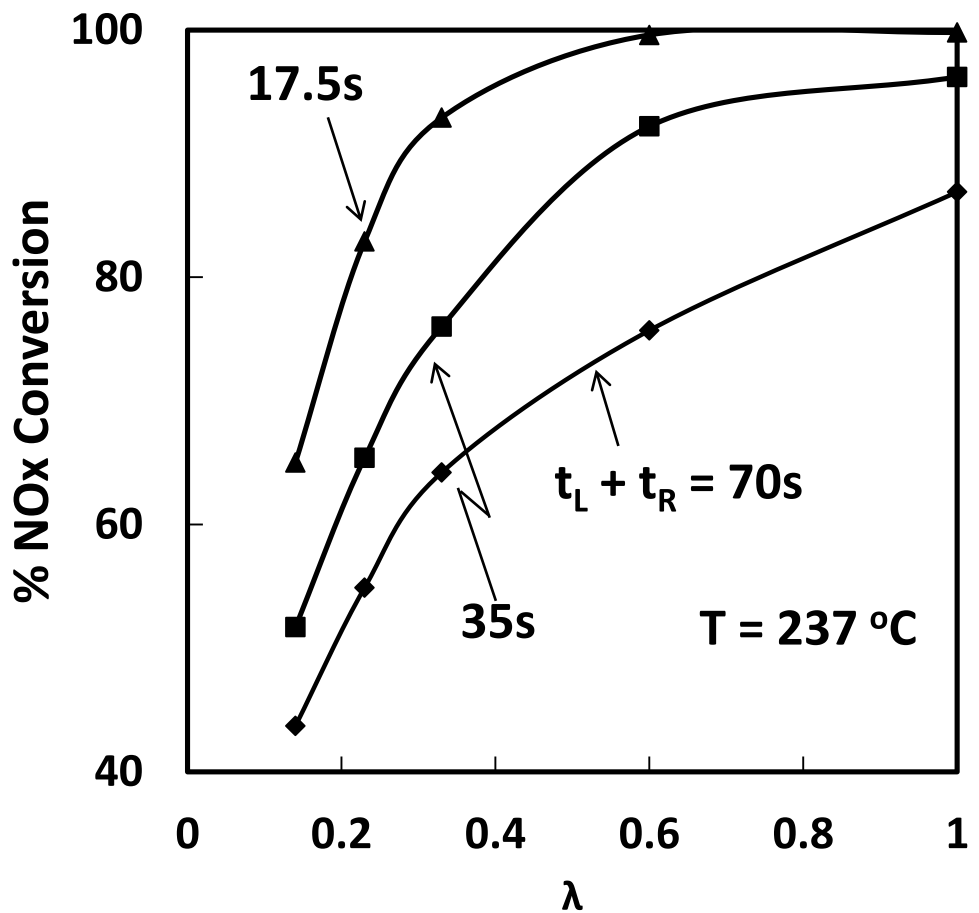
Rich inlet: NO=500ppm,H_2=0.875%;

λ = Total LNT length/Total SCR length

n = number of LNT-SCR bricks

- ***Low temperature operation is major constraint in optimizing the catalyst sequence***

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



(n=2)

Length of each catalyst = 2cm;
GHSV=60,000h^{-1};
Lean inlet: NO=500ppm,O_2=5% ;
Rich inlet: NO=500ppm,H_2=0.875% ;
λ = Total LNT length/ Total SCR length
$t_L = 6t_R$

- *Cycle time has significant impact on LNT-SCR performance (NOx conversion)*

Selected Activities Planned: 3Q-4QFY12 (Complete Phase 2 & 3)

- LNT:
  - Carry out model simulations of cyclic 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 study of for $NH_3 + C_3H_6$ SCR on Cu/chabazite
  - Carry out isotopic (^{15}NO) TAP study of $NH_3 + C_3H_6$ SCR on Cu/chabazite
- LNT/SCR:
  - Continue double-layer LNT/SCR experiments: Focus on reducing PGM content
  - LNT/SCR reactor modeling
    - Combine crystallite-scale LNT model and Cu/chabazite SCR models
    - Simulate LNT/SCR segmented architecture
    - Simulate LNT/SCR double-layer architecture

Publications & Presentations

Publications – Appeared Since Project Inception

- 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).
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- 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).
- 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," Applied Catalysis B: Environmental, **102**, 484–495 (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 ," Applied Catalysis B: Environmental, **104**, 110–126 (2011).
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- Ji, Y., V. Easterling, U. Graham, C. Fisk, M. Crocker, J,-S. Choi, "Effect of aging on the NO_x storage and reduction characteristics of fully formulated lean NO_x trap catalysts", Appl. Catal. B 103 (2011) 413.
- Liu, Y., M.P. Harold, and D. Luss, "Spatiotemporal Features of $Pt/CeO_2/Al_2O_3$ Catalysts During Lean/Rich Cycling," Applied Catalysis A, General, **397**, 35-45 (2011).*
- Ren, Y., and M.P. Harold, "NOx Storage and Reduction with H_2 on $Pt/Rh/BaO/CeO_2$: Effects of Rh and CeO_2 in the Absence and Presence of CO_2 and H_2O," ACS Catalysis, 1, 969-988 (2011).
- Metkar, P., V. Balakotaiah, and M.P. Harold, "Experimental Study of Mass Transfer Limitations in Fe- and Cu-Zeolite Based NH_3 -SCR Monolithic Catalysts," Chem. Eng. Sci., **66**, 5192–5203 (2011).
- J. Wang, Y. Ji, Z. He, M. Crocker, M. Dearth, R.W. McCabe, "A non-NH_3 pathway for NO_x conversion in coupled LNT-SCR systems", Appl. Catal. B **111-112** (2012) 562.

Publications & Presentations, cont.

Publications – Appeared Since Project Inception, cont.

- Metkar, P., V. Balakotaiah, and M.P. Harold, "Experimental Study of Selective Catalytic Reduction of NO_x on a Combined System of Fe and Cu-based Zeolite Monolithic Catalysts," Applied Catalysis B: Environmental, **111– 112**, 67– 80 (2012).

– Accepted and In Press

- Joshi, Joshi, S., Y. Ren, M.P. Harold, and V. Balakotaiah, "Determination of Kinetics and Controlling Regimes for Propylene and Methane Oxidation on Pt/Al_2O_3 Monolithic Catalyst Using High Space Velocity Experiments," Ind. Eng. Chem. Res., in press (2012).
- Kota, A., D. Luss and V. Balakotaiah, "Modeling and Optimization Studies of Combined LNT-SCR Catalyst Systems", Ind. Engng. Chem. Res., in press (January, 2012).
- Metkar, P., M.P. Harold, and V. Balakotaiah, "Experimental and Kinetic Modeling Study of NO Oxidation: Comparison between Fe and Cu-zeolite Catalysts," Catalysis Today, in press (December, 2011).
- Dasari, P., R. Muncrief,, and M.P. Harold, "Elucidating NH_3 Formation During NO_χ Reduction by CO on $Pt\text{-}BaO/Al_2O_3$ in Excess Water," Catalysis Today, in press (December, 2011).
- Shakya, B., M.P. Harold, and V. Balakotaiah, "Modeling the Effects of Pt Dispersion During NO_x Storage and Reduction on $Pt/BaO/Al_2O_3$," Catalysis Today, in press (February, 2012).
- Harold, M.P., "NOx Storage and Reduction in Lean Burn Vehicle Emission Control: A Catalytic Engineer's Playground", Current Opinion in Chemical Engineering, in press (February, 2012).
- Liu, Y., M.P. Harold, and D. Luss, "NOx Storage and Reduction in Dual Layer Pt/BaO/Cu/ZSM5 Monolith Catalyst," Appl. Catal. B. Environmental, under review (January, 2012).

Patents Since Project Inception

- Harold, M.P., and P. Metkar, US Provisional Patent Application, "Multi-Component and Layered Formulations for Enhanced Selective Catalytic Reduction Activity," June 6, 2011**.**

Presentations – Since Nov. 2010:

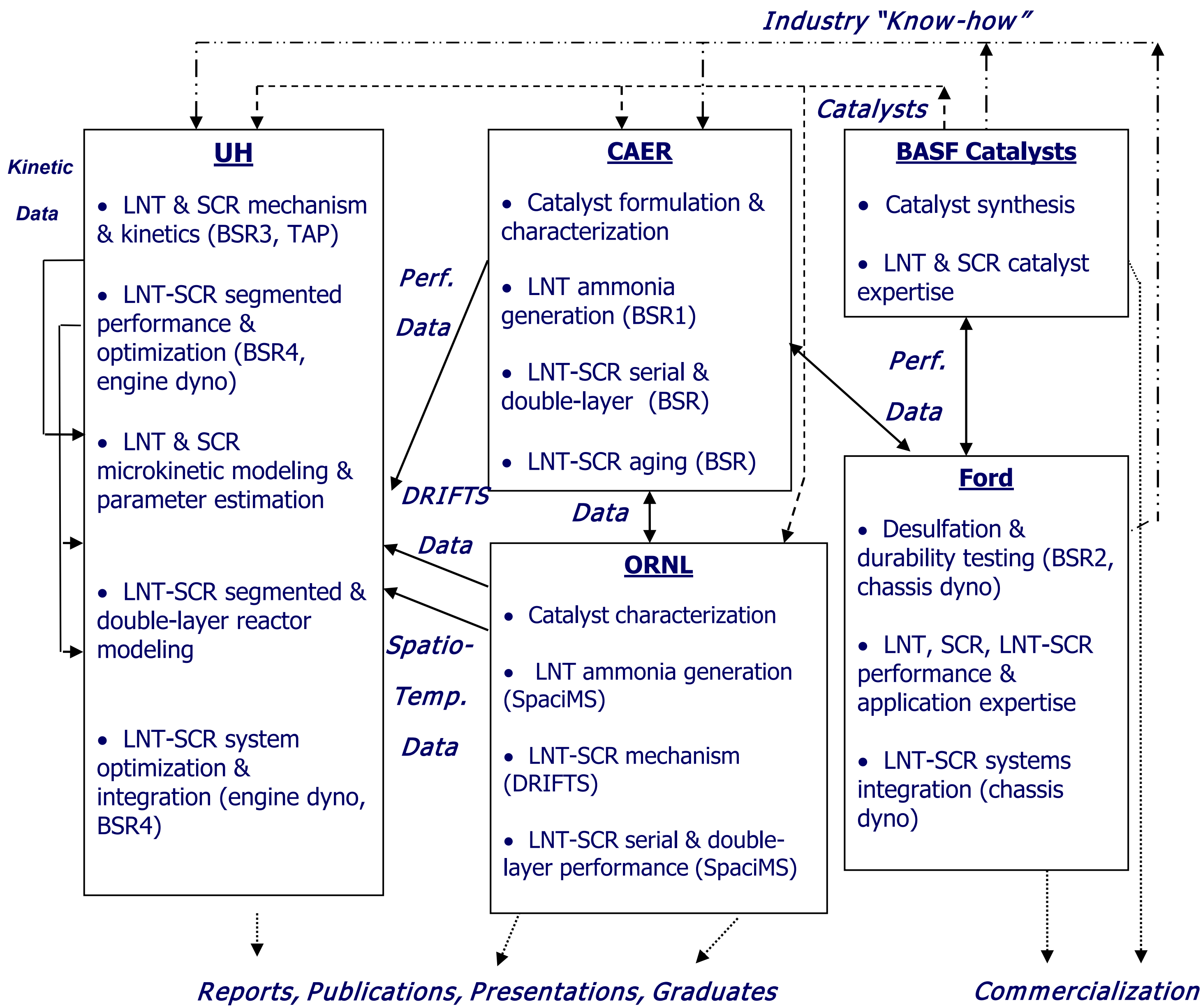
- Total: ~21 oral presentations (AIChE, NAM, CLEERS, ACS, etc.)
  5 invited presentations (NAM Keynote, ACS National Meeting, Philadelphia Catalysis Society, Michigan Catalysis Society, Chicago Catalysis Club, etc.)

Summary

- Comprehensive program combining fundamental catalysis, reaction engineering and vehicle testing
- Very good progress on Phase 2 & 3 tasks
  - SpaciMS LNT measured temporal profiles predicted by LNT regeneration model
  - Predictive crystallite LNT model identifies optimal conditions for NH_3 formation
  - Definitive evidence for olefin trapping and role as NOx reductant
  - New dual-component SCR catalyst
  - First LNT/SCR dual-layer catalyst
  - Predictive LNT/SCR model quantifies segmented configuration performance
- Final efforts to close loop on identifying optimal LNT-SCR configurations with reduced PGM content

Technical Backup Slides

Approach: Team Participants



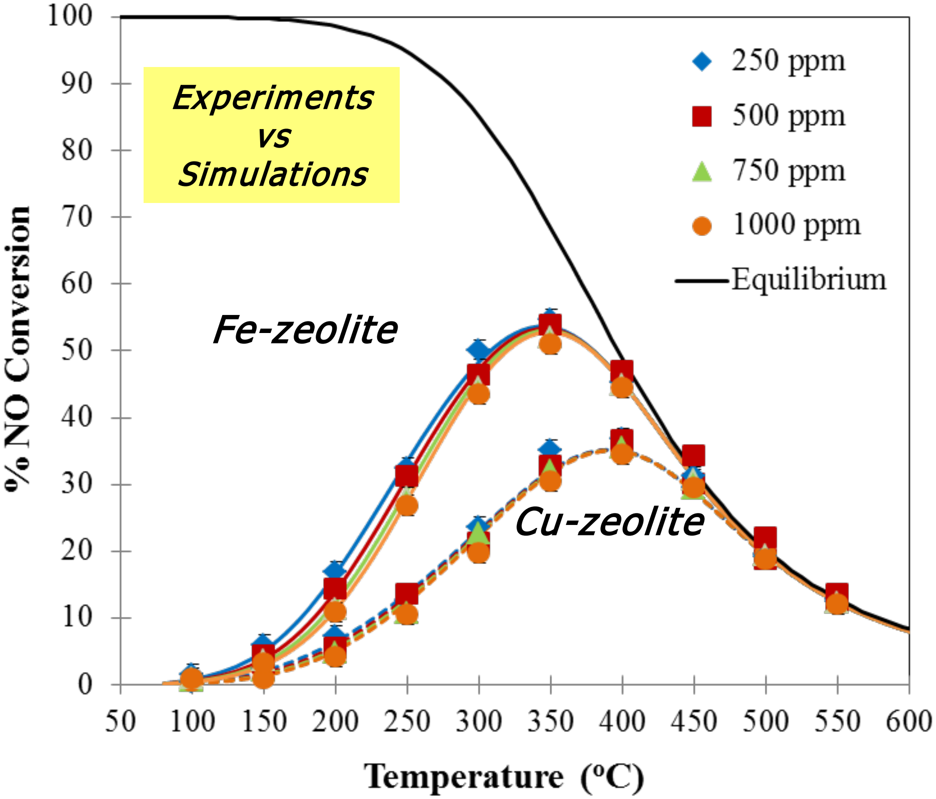
Schedule of Tasks: Phases 2 & 3

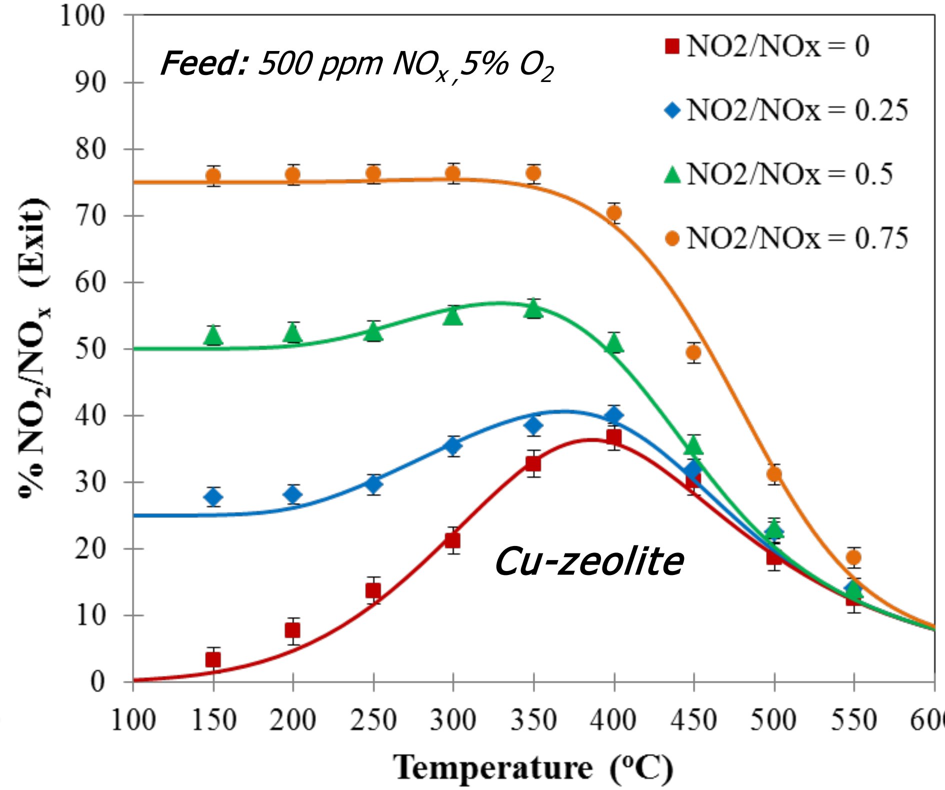
Phase 2 Tasks	Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
2.1: Spatiotemporal study of LNT NO_x reduction selectivity								
2.2: Isotopic TAP study of NO_x reduction on LNT & SCR								
2.3: Transient kinetics of NO_x reduction on LNT & SCR								
2.4: Kinetics of transient NO_x reduction w/ NH_3 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								

Phase 3 Tasks	Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
3.1: In situ DRIFTS study on double layer LNT-SCR								
3.2: Age LNT-SCR systems on bench reactor								
3.3: Comparison study of segmented LNT-SCR systems								
3.4: Completion of microkinetic model for LNT and SCR								
3.5: Optimization/simulations of LNT-SCR system								
3.6: Identification of optimal segmented LNT-SCR config.								
3.7: Reactor studies on aged LNT-SCR systems								
3.8: Physico-chemical analysis of aged LNT-SCR systems								
3.9: Vehicle tests on aged LNT-SCR system								

NO Oxidation on Cu/chabazite: Experiments vs. Simulations (UH)

$NO + \frac{1}{2} O_2 \leftrightarrow NO_2$



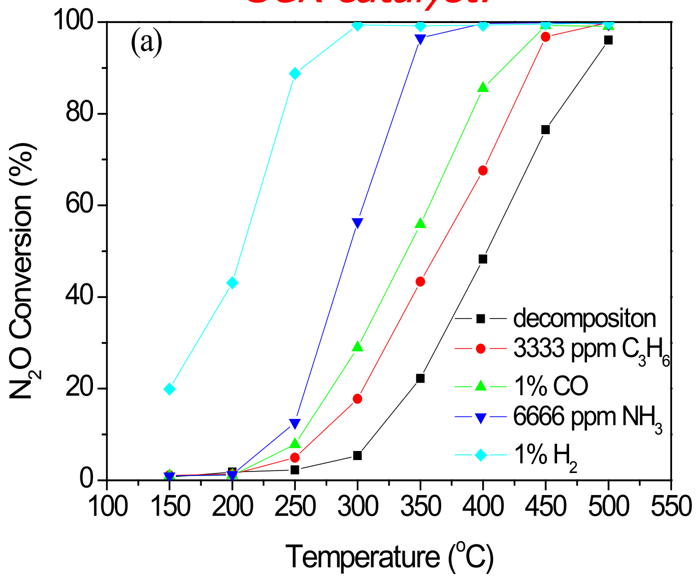


- *Model accurately predicts the experimental data for different feeds and temperatures*
- *Effect of NO_2 inhibition on the NO oxidation is well captured by the model*

N_2O Reduction Over Cu-chabazite SCR Catalyst (Tasks 2.4, 2.7; UK)

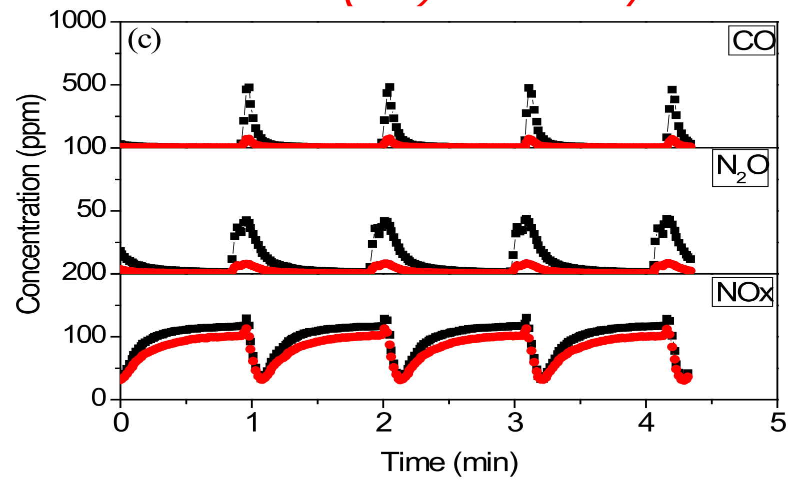
Under lean-rich cycling conditions, SCR catalyst helps to mitigate N_2O emissions from upstream LNT catalyst

Steady state (continuous flow); SCR catalyst:



Feed: 100 ppm N_2O, 5% H_2O, 5% CO_2, reductant as shown, bal. N_2; GHSV = 30,000 h^{-1}

Lean-rich cycling, LNT-SCR, 275 °C; concentration profiles before (black) and after (red) SCR catalyst:



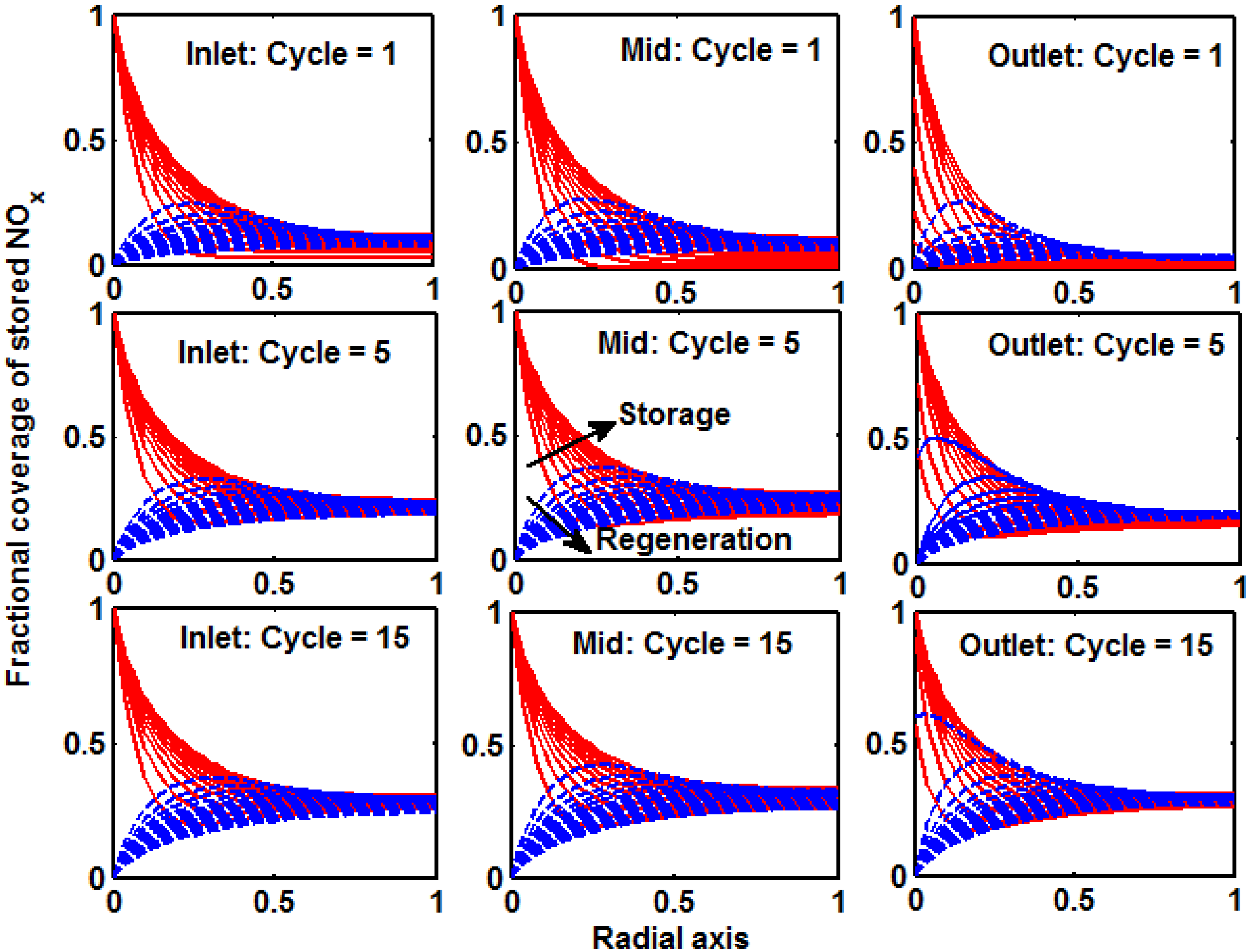
60 s L - 5 s R; L: 300 ppm NO, 8% O_2, 5% H_2O, 5% CO_2, bal. N_2; R: 1% H_2, 5% H_2O, 5% CO_2, bal. N_2. GHSV = 30,000 h^{-1}

- ***H_2 best reductant, followed by NH_3***

- ***N_2O conversions can reach 80% under favorable conditions***

Crystallite-Scale Model of NO_x Storage and Reduction on Pt/BaO: Cycling Results (UH)

Feed: ***Lean:*** *500 ppm NO, 5% O_2, 60s;* ***Rich:*** *5000 ppm H_2, 10s, Bal Ar GHSV: 60,000 hr^{-1}*



- *Model predicts nonuniform storage and reduction at crystallite scale and along reactor length*