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

Mike Harold, PI

University of Houston

May 15, 2013

ACE029

Overview

Timeline

- Start: Oct. 1, 2009
- End: Sept. 30, 2013
- 90% complete

Budget

- Total project funding
  - DOE: $2,217,317
  - UH & partner match: $687,439
- Funding received
  - FY10-present: $2,217,317
  - No-cost extension through 8/31/13

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

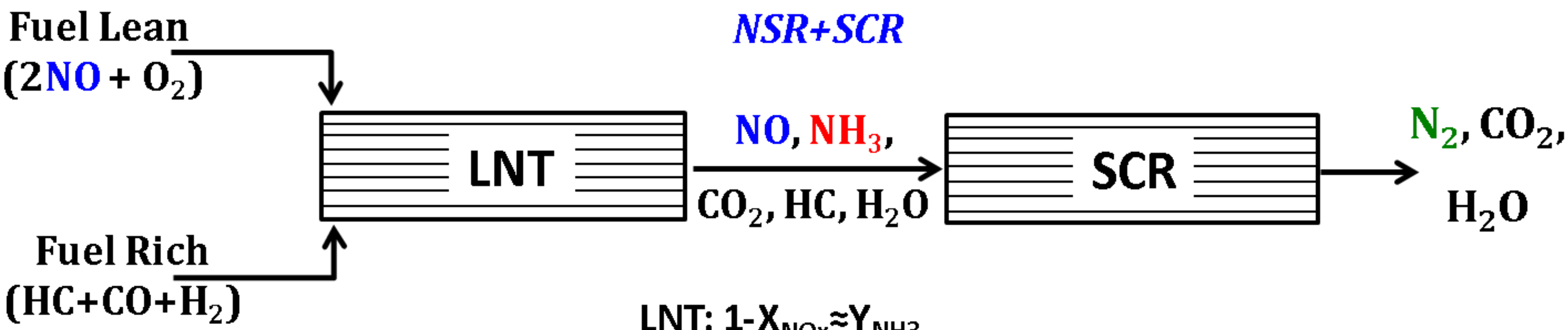
Overall Goal, Impact & Approach of Project

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

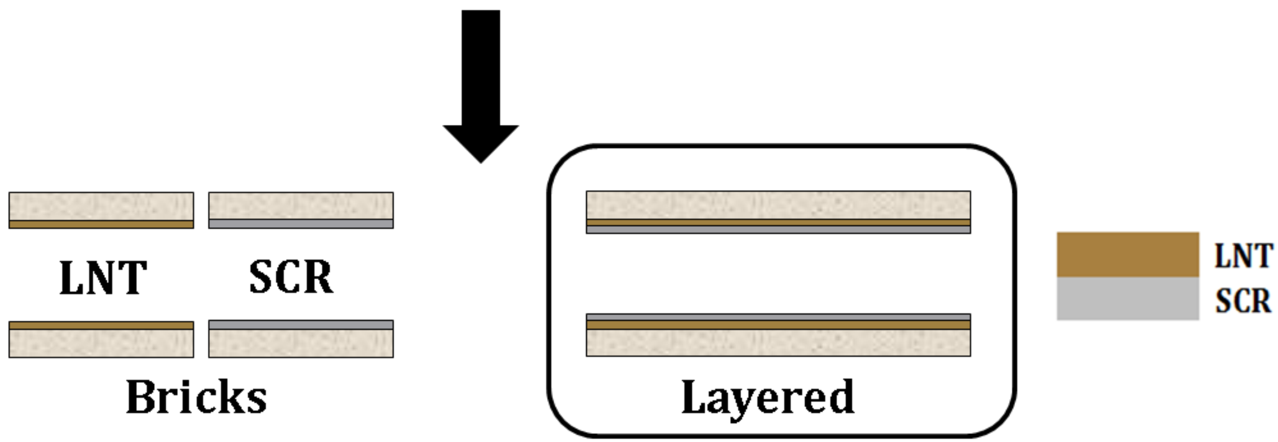
LNT/SCR Technology Concept



LNT: $1-X_{NOx} \approx Y_{NH3}$

$X_{NOx}=0.5$
$S_{NH3}=1$ →

$$\begin{array}{llllll}
\text{LNT:} & NO + 4H_2 & + 0.75O_2 & \rightarrow & NH_3 & + 2.5H_2O \\
\text{SCR:} & NO + NH_3 & + 0.25O_2 & \rightarrow & N_2 & + 1.5H_2O \\
\hline
\text{OVERALL:} & 2NO + 4H_2 & + O_2 & \rightarrow & N_2 & + 4H_2O
\end{array}$$



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 designs?
  - For multi-layer, how thick should LNT and SCR layers be?
  - How little precious metal can be used to meet NOx reduction targets?
- LNT/SCR operating conditions:
  - How susceptible is performance to regeneration phase composition & make-up?
  - What is more desirable: Prolonged regeneration with low reductant concentration or short regeneration with high reductant concentration?
  - What can be done about low temperature limitations?

Activity Highlights from this Period

- Comprehensive program combining fundamental catalysis, reaction engineering and vehicle testing
- Collaboration between academic, national lab, and industrial researchers
- Very good progress on Phase 2 & 3 tasks
- Since project inception: 25 peer-reviewed publications, 27 presentations, 1 book chapter, 5 invited lectures & 3 keynotes
- LNT (UK, UH, ORNL, Ford, BASF)
  - Use of isotopic labeling facilitated detailed study of isocyanate (NCO) reactivity
  - Predictive crystallite LNT model predicts lean-rich cycling data & identifies optimal conditions for NH_3 formation as function of catalyst variables like PGM loading & dispersion (and indirectly age)
- SCR (UK, UH, BASF)
  - Monolith reactor model for Fe/ZSM-5 & Cu/chabazite predicts performance over wide range of conditions, including for dual layer Fe/Cu catalyst
  - Mechanism of HC-SCR (propene) on Cu-CHA elucidated through systematic bench flow reactor and DRIFTS experiments
  - Study of N_2O mitigation by Cu-CHA quantifies this important pathway for N_2O mitigation
- LNT-SCR (UK, UH, BASF)
  - Synergy of LNT and SCR catalysts demonstrated for aged system
  - Addition of ceria to LNT/SCR dual-layer catalyst shown to improve low temperature performance
  - Axial zoning of ceria on dual-layer catalyst shown to be superior to uniform loading
  - Predictive (& tuned) LNT/SCR dual layer model developed which predicts the effect of LNT and SCR loading on overall performance

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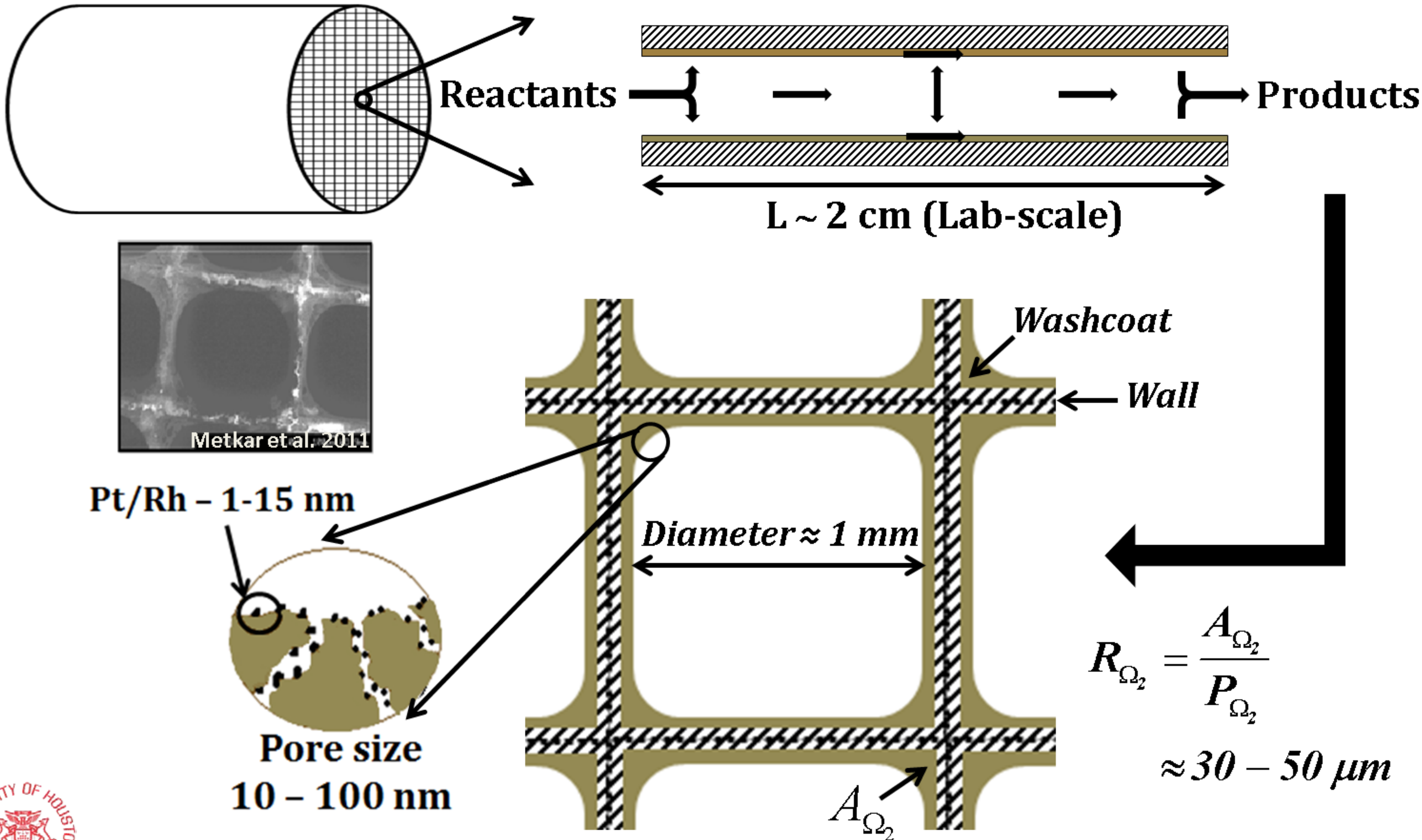
LNT

Modeling Spans Many Scales

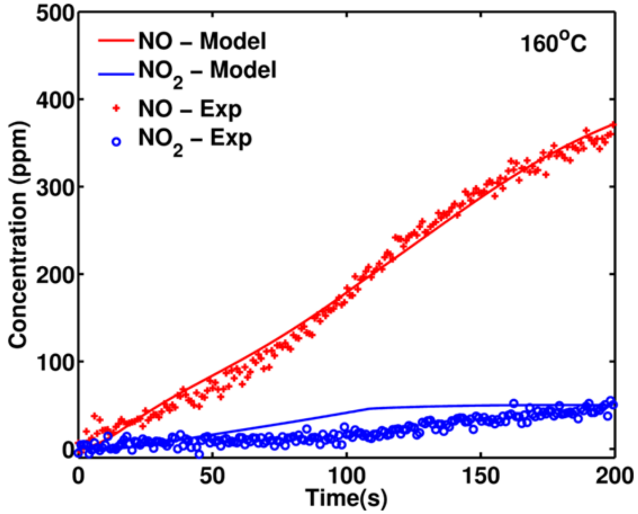


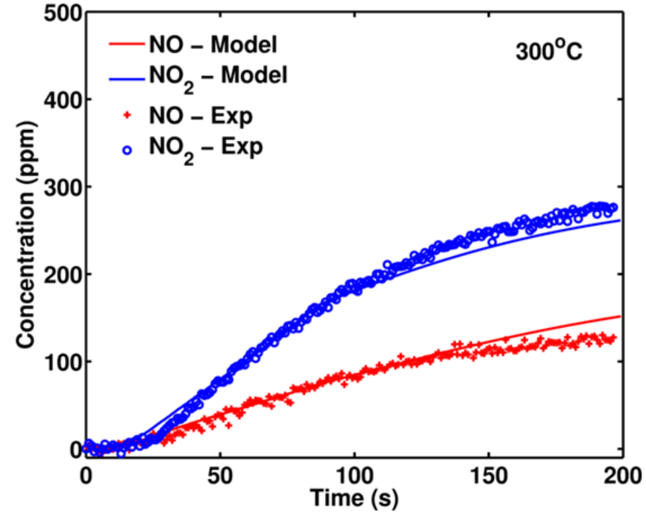
LNT Reaction Model

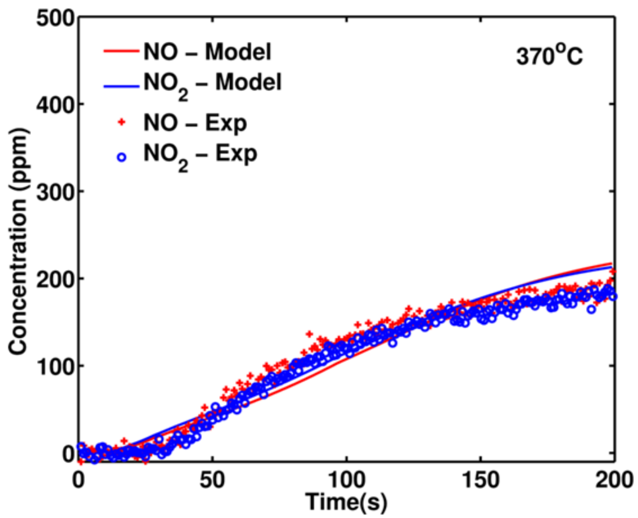
NO oxidation	1.	$NO + 0.5\ O_2 \leftrightarrow NO_2$
NO storage in the presence of O_2	2. 3.	$2\ NO + 1.5\ O_2 + BaO_{(f)} \leftrightarrow Ba(NO_3)_{2\ (f)}$ $2\ NO + 1.5\ O_2 + BaO_{(S)} \leftrightarrow Ba(NO_3)_{2\ (S)}$
NO_2 Storage	4. 5.	$2\ NO_2 + 0.5\ O_2 + BaO_{(f)} \rightarrow Ba(NO_3)_{2\ (f)}$ $3\ NO_2 + BaO_{(s)} \rightarrow Ba(NO_3)_{2\ (s)} + NO$
Nitrate reduction by H_2	6. 7.	$Ba(NO_3)_{2(f)} + 3\ H_2 \rightarrow BaO_{(f)} + 2\ NO + 3\ H_2O$ $Ba(NO_3)_{2(s)} + 3\ H_2 \rightarrow BaO_{(s)} + 2\ NO + 3\ H_2O$
Nitrate reduction by NH_3	8. 9.	$Ba(NO_3)_{2(f)} + 10/3\ NH_3 \rightarrow BaO_{(f)} + 8/3\ N_2 + 5\ H_2O$ $Ba(NO_3)_{2(s)} + 10/3\ NH_3 \rightarrow BaO_{(s)} + 8/3\ N_2 + 5\ H_2O$
Pt catalyzed NO reduction	10. 11. 12.	$2\ NO + H_2 \rightarrow N_2O + H_2O$ $NO + 5/2\ H_2 \rightarrow NH_3 + H_2O$ $3/2\ NO + NH_3 \rightarrow 5/4\ N_2 + 3/2\ H_2O$
NH_3 adsorption and consumption	13. 14.	$NH_3 + X \leftrightarrow NH_3\text{-}X$ $NH_3\text{-}X + 3/4\ O_2 \rightarrow 1/2\ N_2 + 3/2\ H_2O + X$

Sample	Pt (%)	Pt dispersion%	BaO (%)
$Pt/BaO/Al_2O_3$	2.48	8	13.0

NOx Storage: Model vs. Experiment







Conditions:

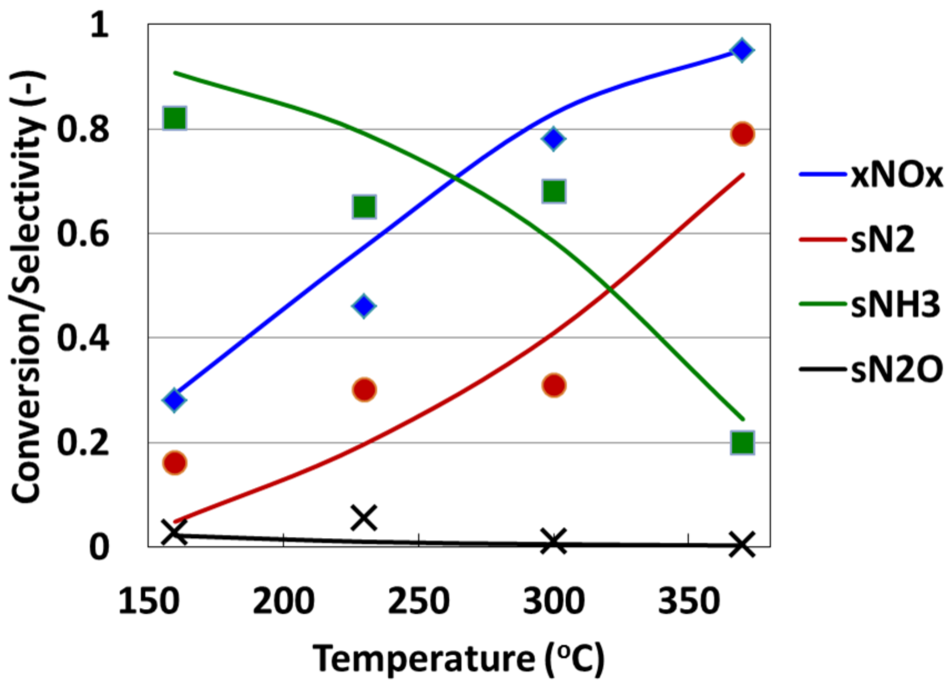
Lean inlet: 500 ppm NO + 5% O_2
GHSV: 60,000 hr^{-1} (based on monolith volume) (20 ms @ 300°C)

Catalyst:

2 cm long; 28 channels
400 cpsi; 30 μm washcoat

‡ R.D. Clayton PhD Dissertation University of Houston 2008

LNT Regeneration: Model vs. Experiments

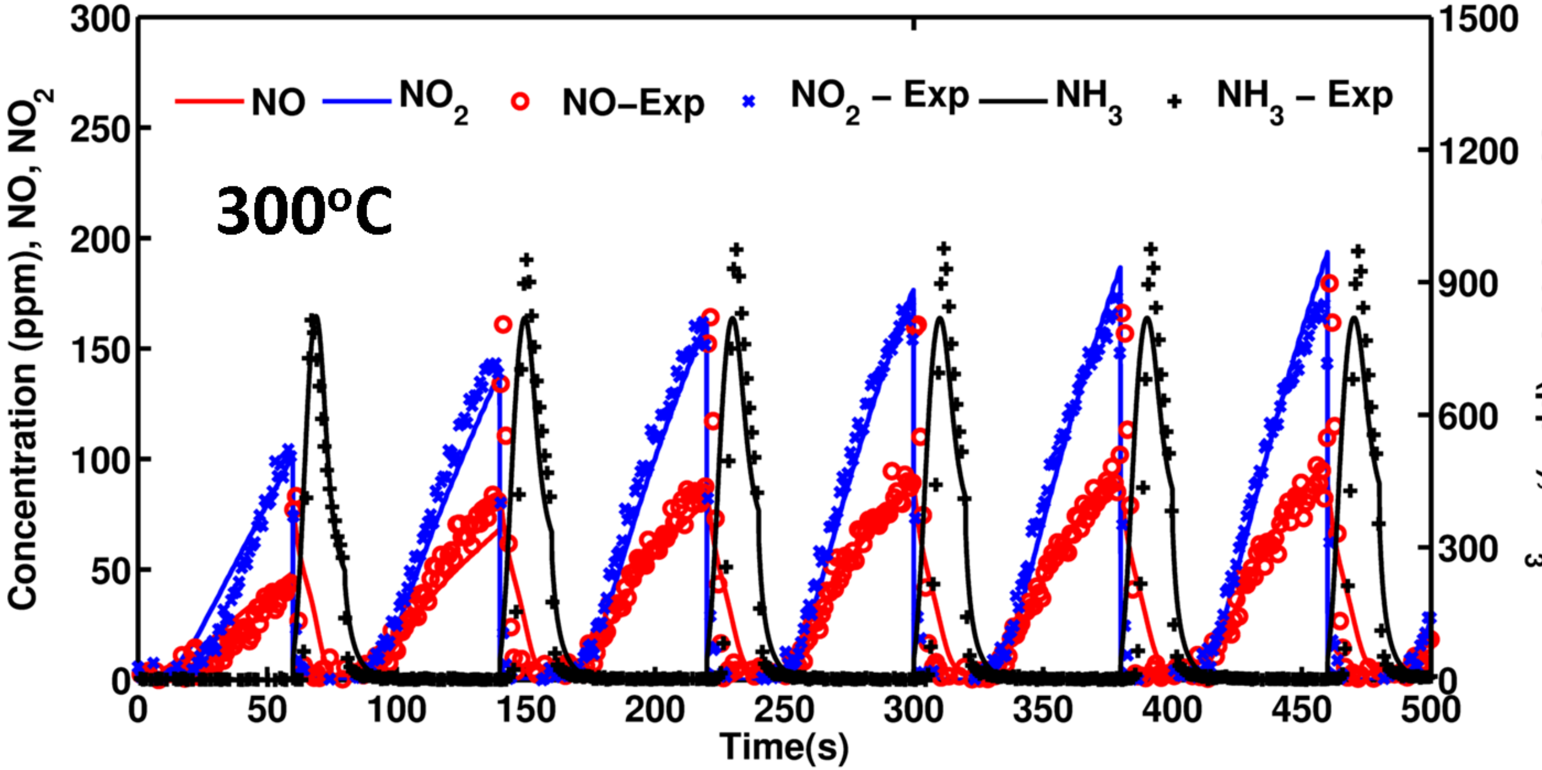


Conditions:
NOx stored: *1.5×10^{-5} moles*
Rich inlet: 1500 ppm H_2 – 200s
GHSV: 60,000 hr^{-1} (based on monolith volume)

Catalyst:
2 cm long; 28 channels
400 cpsi; 30 µm washcoat

‡ R.D. Clayton PhD Dissertation University of Houston 2008

LNT Cycling: Model vs. Experiment



Conditions:

Lean inlet: 500 ppm NO + 5% O_2 in bal Ar / Duration: 60s

Rich inlet: 5000 ppm H_2 in bal Ar / Duration: 20s

Temperature: 300°C

GHSV: 60,000 hr^{-1} (based on monolith volume)

Catalyst:

2 cm long

28 channels

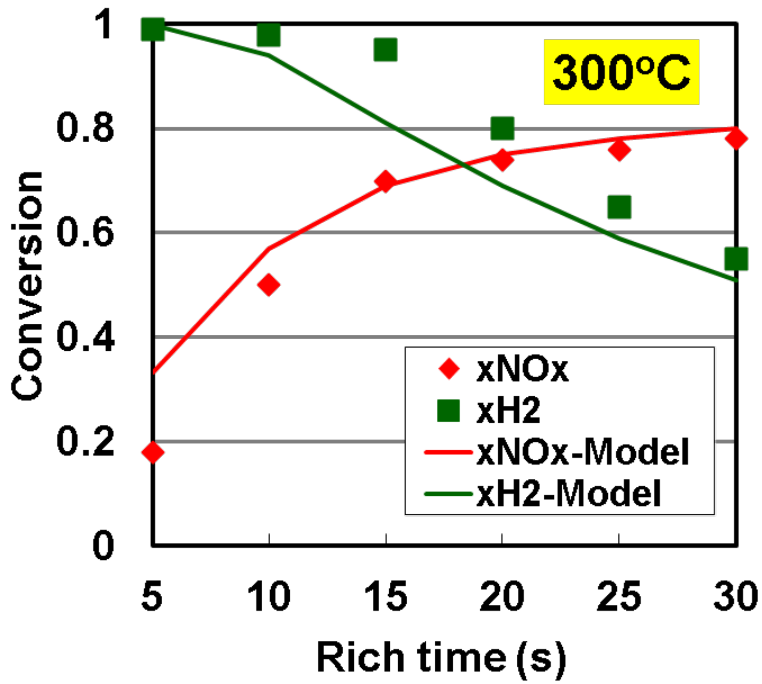
400 cpsi

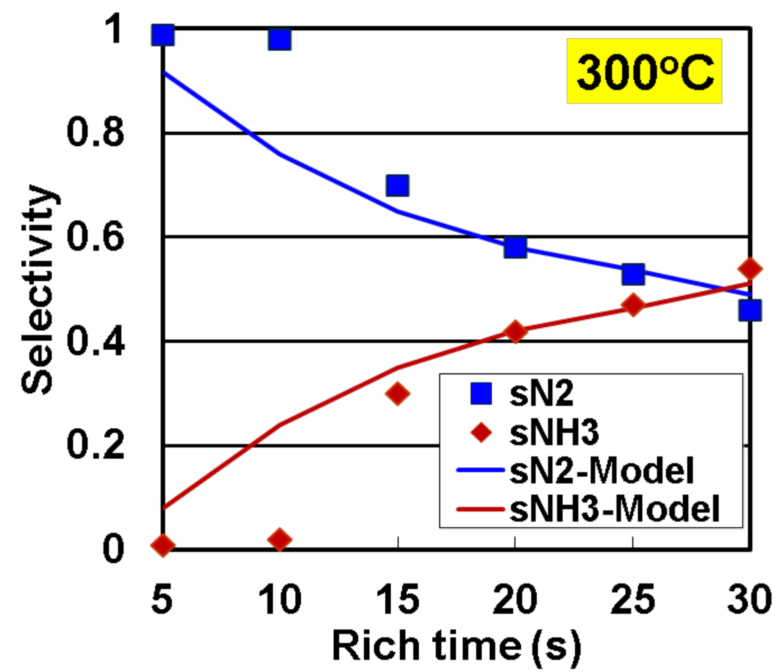
30 µm washcoat

‡Shakya et al. / Catalysis Today 184 (2012) 27-42

Effect of Rich Time: Model vs. Experiment

Effect of Rich phase duration





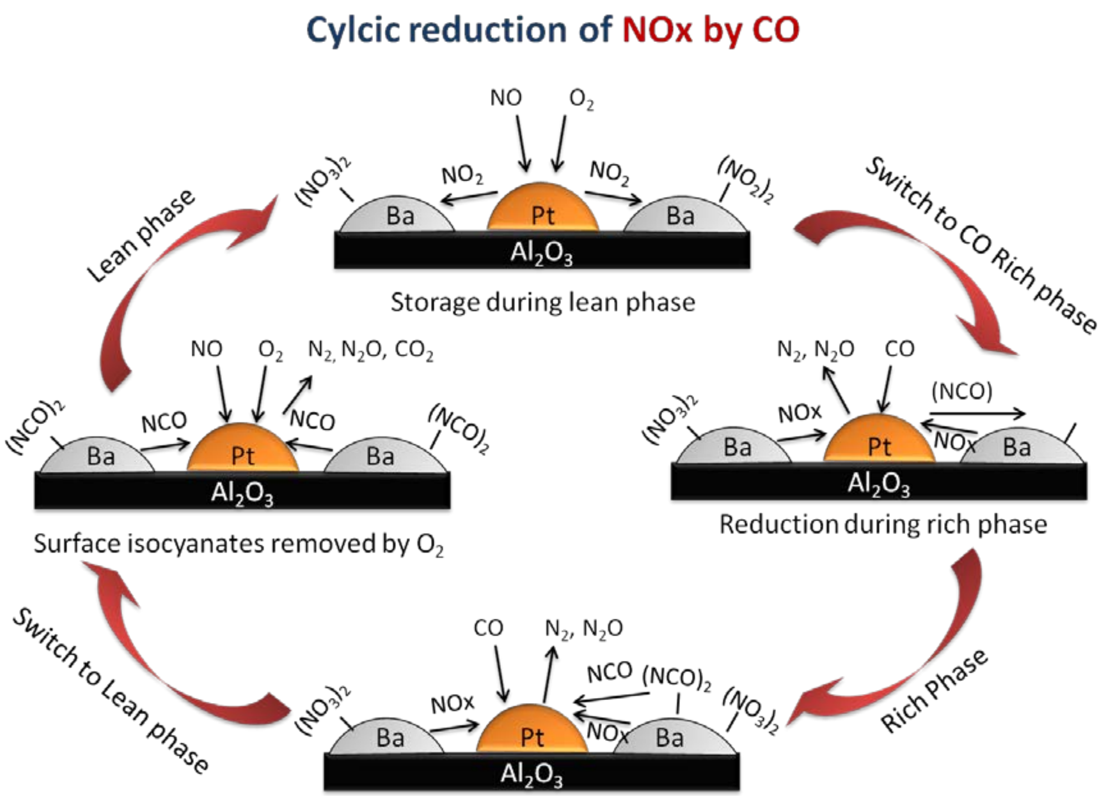
Model accurately predicts the effect of rich phase duration on conversion and selectivity

Conditions: Lean inlet: 500 ppm NO + 5% O_2 in bal Ar / Duration: 60s

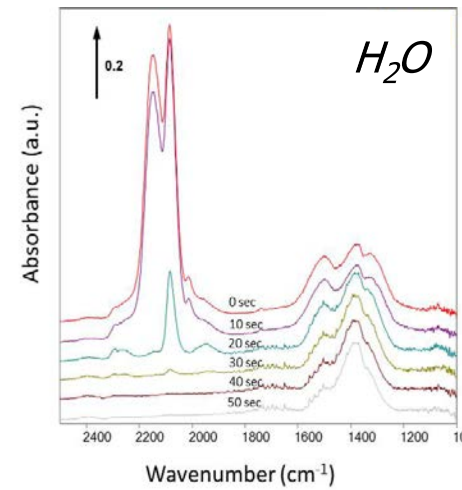
Rich inlet: 5000 ppm H_2 in bal Ar / Duration: 5-30s

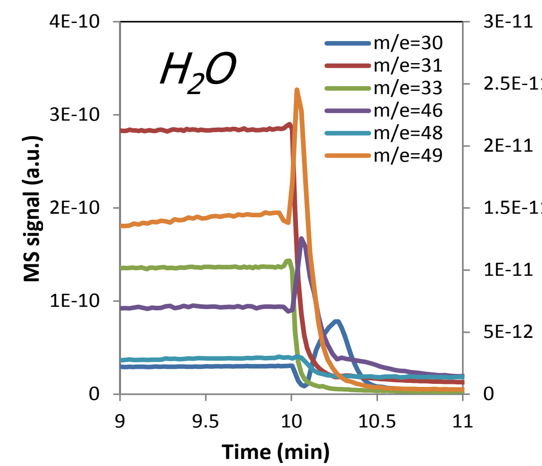
ǂ Shakya et al. / Catalysis Today 184 (2012) 27-42

NOx Reduction with CO on LNT Catalysts



Evolution of DRIFTS and MS spectra during isothermal reaction of isocyanate ($^{15}N^{13}CO$) at 350 °C under different conditions: O_2, $^{15}N^{18}O$, & H_2O



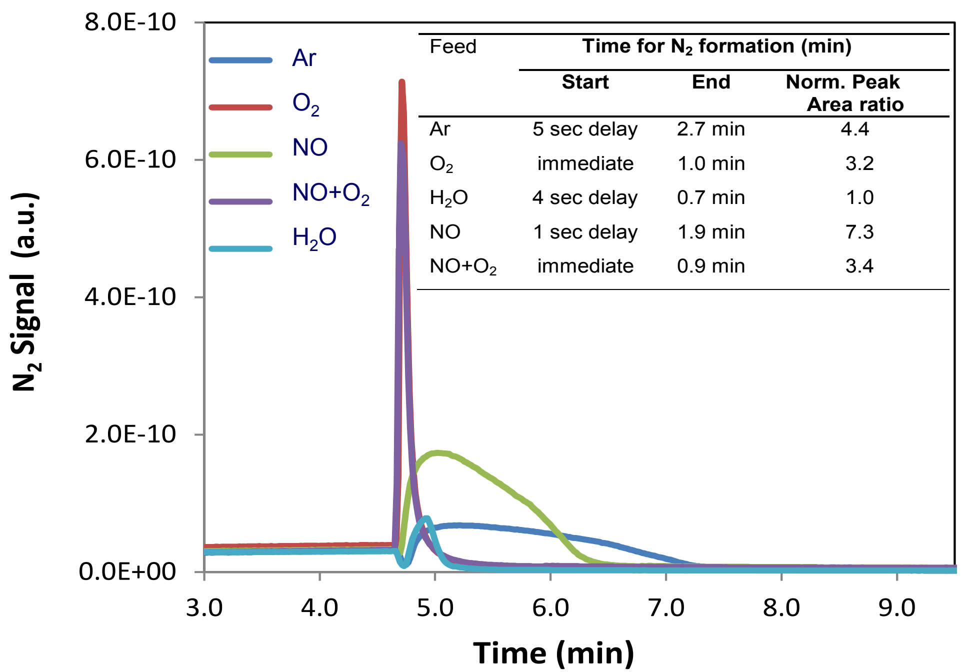


- *Reactivity towards isocyanate: H_2O >> O_2 > NO*
- *H_2O produces NH_3 (which reacts with nitrate to produce N_2); reaction with O_2 gives mainly N_2 and NO_2*

DRIFTS Study of NOx Reduction with CO on LNT Catalysts

Isocyanate formation and reactivity studied using DRIFTS/MS, coupled with use of $^{15}N^{18}O$ and ^{13}CO (to differentiate between CO and N_2)

Time dependence of N_2 formation during isothermal reactions of isocyanate at 350 °C:



Feed	Time for N_2 formation (min)		
	Start	End	Norm. Peak Area ratio
Ar	5 sec delay	2.7 min	4.4
O_2	immediate	1.0 min	3.2
H_2O	4 sec delay	0.7 min	1.0
NO	1 sec delay	1.9 min	7.3
$NO+O_2$	immediate	0.9 min	3.4

Main findings:

- *Under dry cycling conditions with CO as reductant, N_2 is mainly formed via NCO reaction with $NO+O_2$ after the L to R switch, rather than being formed during the rich phase*
- *H_2O is the most reactive species with respect to isocyanate of those tested (H_2O, O_2, NO, NO/O_2)*
- *In the case of H_2O, N_2 originates from a secondary reaction of the initial product, NH_3, with residual nitrate*

SCR

SCR Kinetics: Fe/ZSM-5 & Cu/chabazite

- Systematic kinetic model developed from compartmental approach
  - NO oxidation
  - Standard SCR
  - NO_2 SCR
  - Fast SCR

  differential kinetics +
  ammonia uptake +
  integral kinetics +

- Incorporation into SCR monolith model to simulate single-, dual-layer, dual-zone catalysts
  - Include HC as reductant (ongoing)

SCR Reaction Model

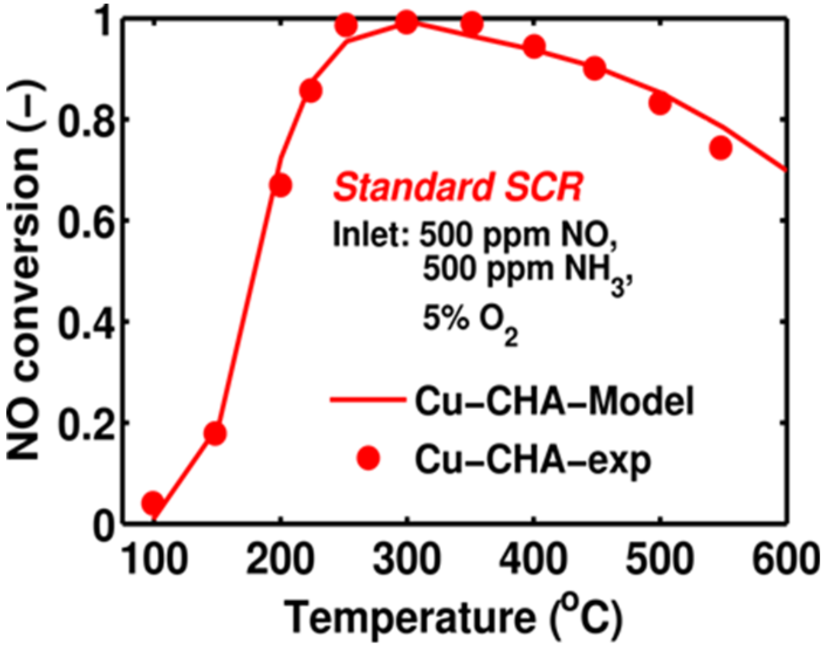
NH_3 adsorption / desorption	1.	$NH_3 + S$	$\leftrightarrow$	$NH_3\text{-}S$
NH_3 oxidation	2.	$2NH_3\text{-}S + 1.5O_2$	$\rightarrow$	$N_2 + 3H_2O + 2S$
NO oxidation	3.	$NO + \frac{1}{2}\,O_2$	$\leftrightarrow$	NO_2
Standard SCR	4.	$4NH_3\text{-}S + 4NO + O_2$	$\rightarrow$	$4N_2 + 6H_2O + 4S$
Fast SCR	5.	$2NH_3\text{-}S + NO + NO_2$	$\rightarrow$	$2N_2 + 3H_2O + 2S$
NO_2-SCR	6.	$4NH_3\text{-}S + 3NO_2$	$\rightarrow$	$3.5N_2 + 6H_2O + 4S$
Ammonium nitrate formation	7.	$2NH_3\text{-}S + 2NO_2$	$\rightarrow$	$N_2 + NH_4NO_3 + H_2O + 2S$
Ammonium nitrate decomposition	8.	NH_4NO_3	$\rightarrow$	$N_2O + 2H_2O$

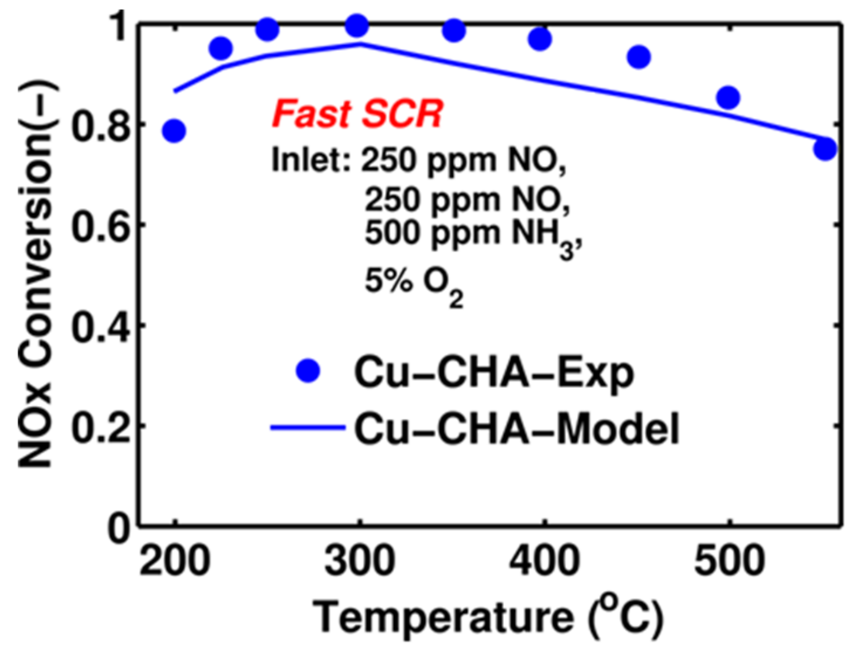
Sample	Cu (%)
Cu-Chabazite	2.48

SCR global reaction model comprises major stoichiometric reactions

‡ Metkar et. al. 2012 / Chem. Eng. Sci. / doi: http://dx.doi.org/10.1016/j.ces.2012.09.008

Steady-State SCR on Cu-Chabazite & Fe-ZSM-5: Model vs. Experiment





"Standard" SCR

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

"Fast" SCR

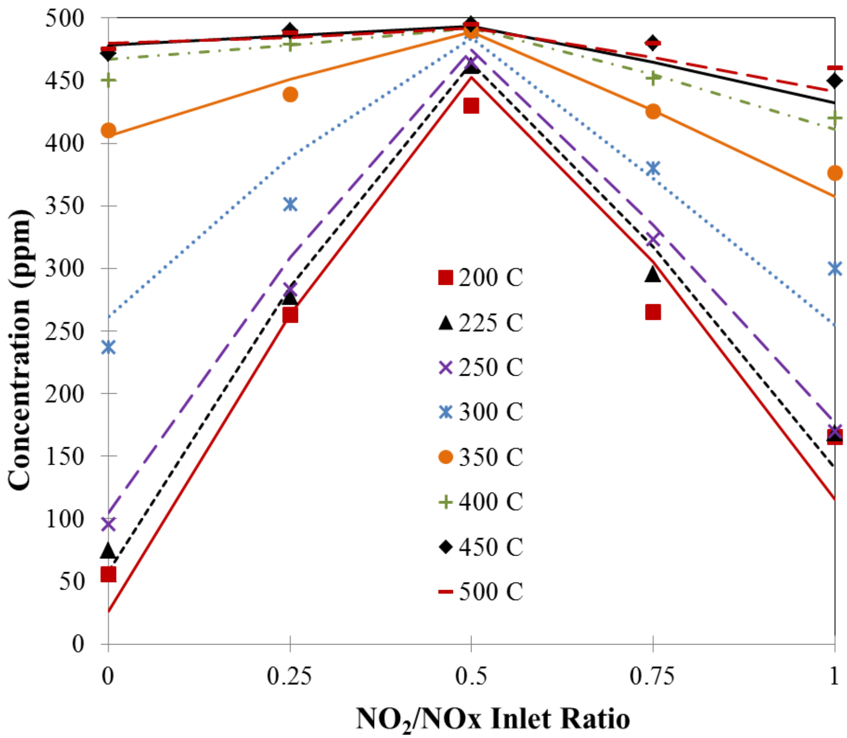
$$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$$

Cu-Chabazite gives high NO_x conversion activity over wide range of operating temperature and feed composition

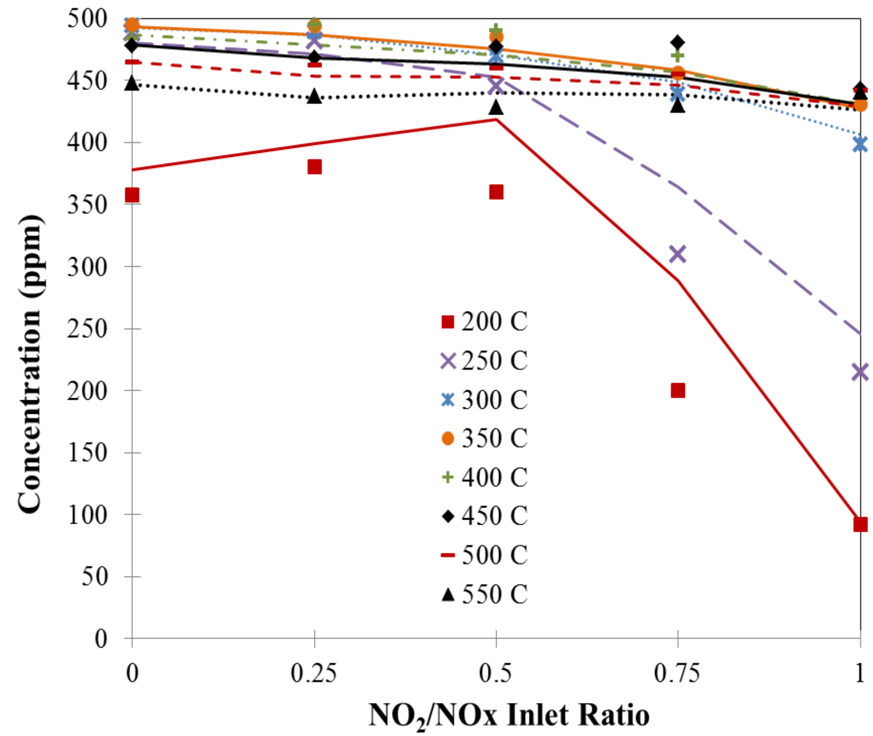
‡ Metkar et. al. 2012 / Chem. Eng. Sci. / doi: http://dx.doi.org/10.1016/j.ces.2012.09.008

Effect of NO_2/NOx on Cu/CHA & Fe-ZSM-5: Model vs. Experiment

Feed: 500 ppm NH_3, 500 ppm NOx, 5% O_2, 2% H_2O



Fe/ZSM-5

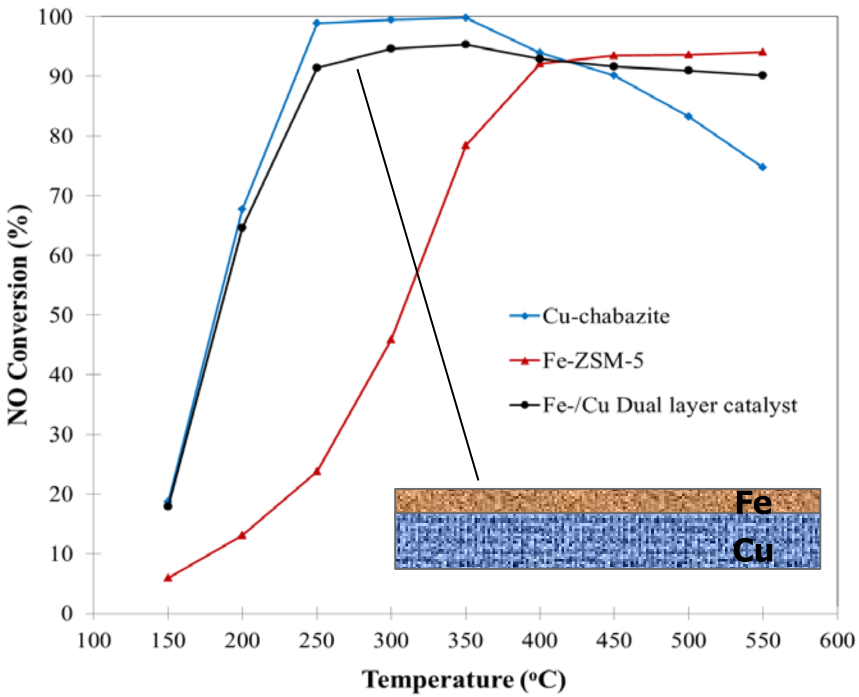


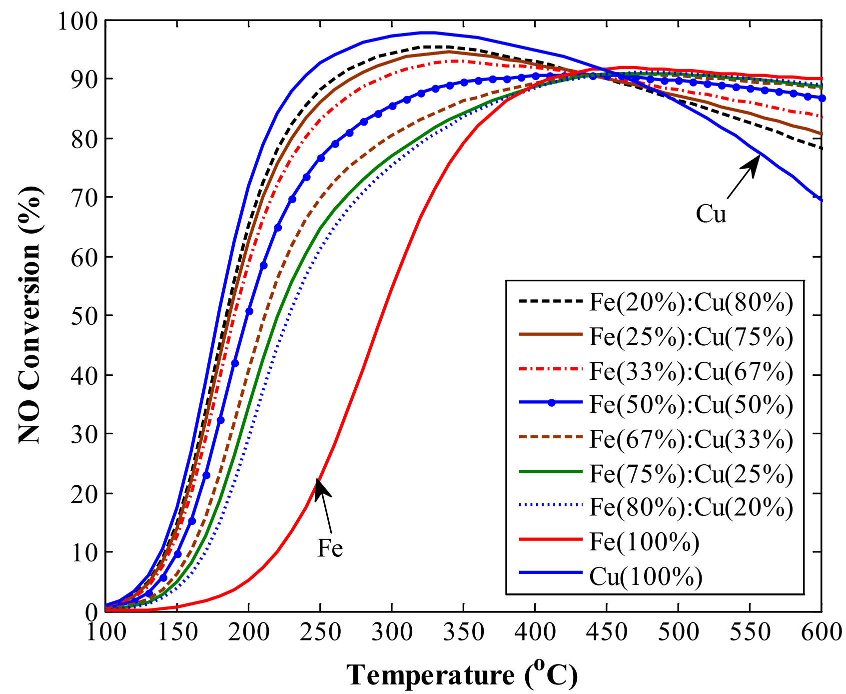
Cu/CHA

Model captures large differences between the two catalysts

Dual Layer Cu/CHA+Fe/ZSM-5: Model vs. Experiment

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



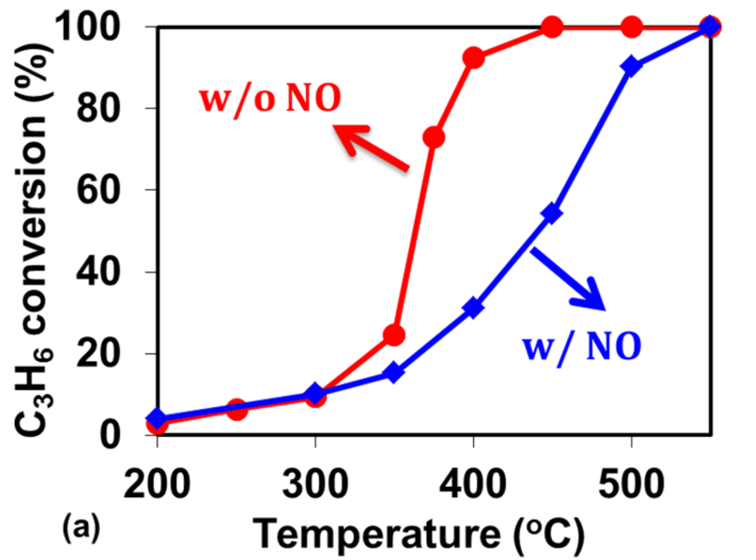


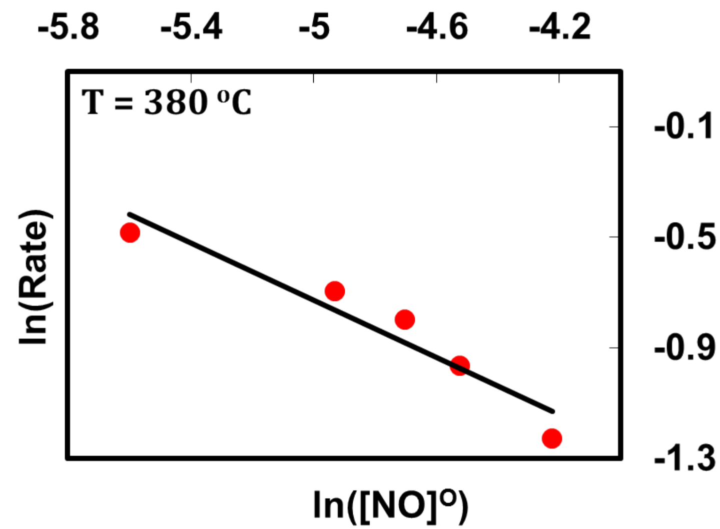
Experiment **Model**

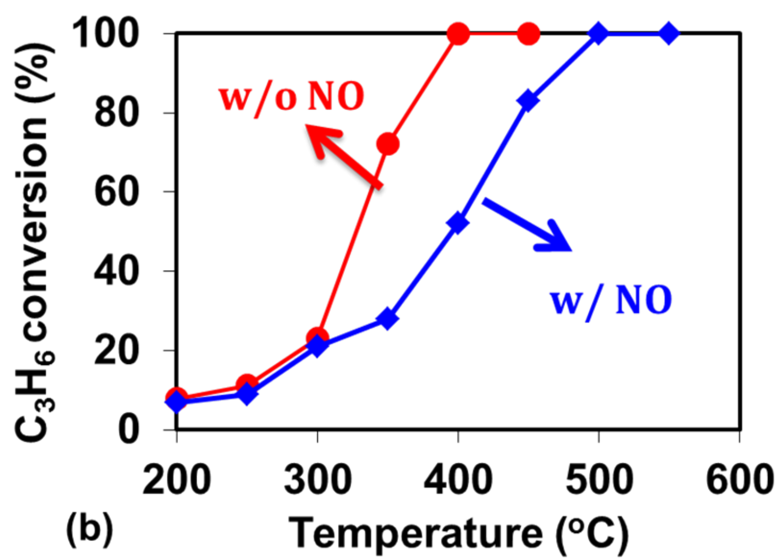
Model captures all of the main trends in dual layer data

Harold & Metkar, Patent Pending (2011)

Lean NOx Reduction With Propylene on Cu/CHA

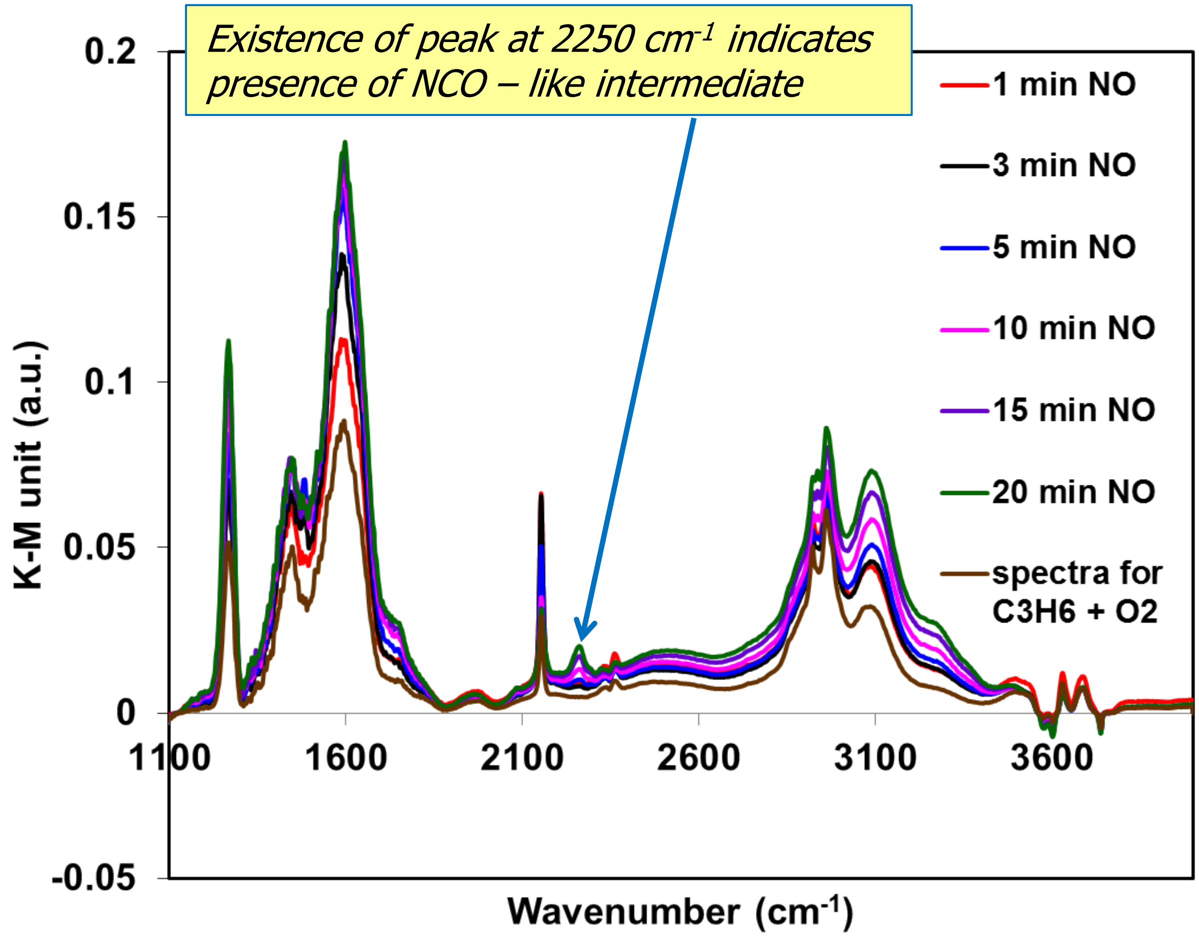






- *Evidence for inhibition of propene oxidation by NO confirmed by negative reaction order*
- *Indicated complex surface chemistry during lean NOx reduction with propylene*

DRIFTS Measurements for $C_3H_6+NO+O_2$ on Cu/CHA

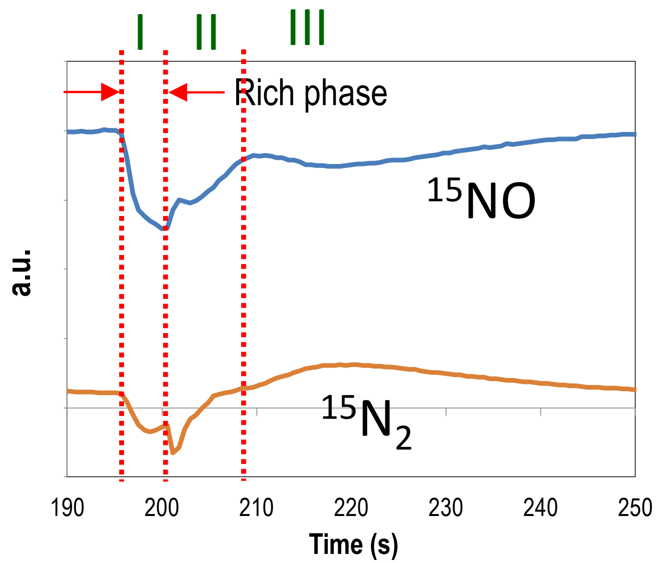


Hydrocarbon NO_x reduction pathway on Cu-chabazite clarified: NH_3 intermediate (1)

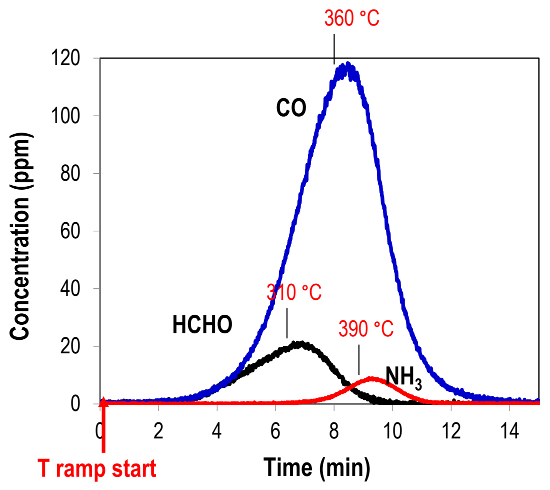
Lean/rich cycling *(base gas: 5% H_2O, 5% CO_2, N_2 balance)*

– Lean (60 s): 600 ppm $^{15}N^{18}O$, 8% O_2 – Rich (5 s): 600 ppm $^{15}N^{18}O$, 1% O_2, 3333 ppm C_3H_6

- ***Rich-phase (regime I)***
  - *$^{15}N^{18}O + C_3H_6$ (gas) → $^{15}NH_3$ or its precursors*
  - *Storage of $^{15}NH_3$ or its precursors*
- ***Lean-phase, early (regime II)***
  - *$^{15}N^{18}O + C_3H_6$ (stored) → $^{15}NH_3$ or its precursors*
  - *Storage of $^{15}NH_3$ or its precursors*
- ***Lean-phase, late (regime III)***
  - *$^{15}N^{18}O$ + stored $^{15}NH_3$ (or precursors) → $^{15}N_2$*
  - ➡ ***NO reduction via NH_3 intermediate***
  - *Initiated when C_3H_6 (gas, stored) is depleted*



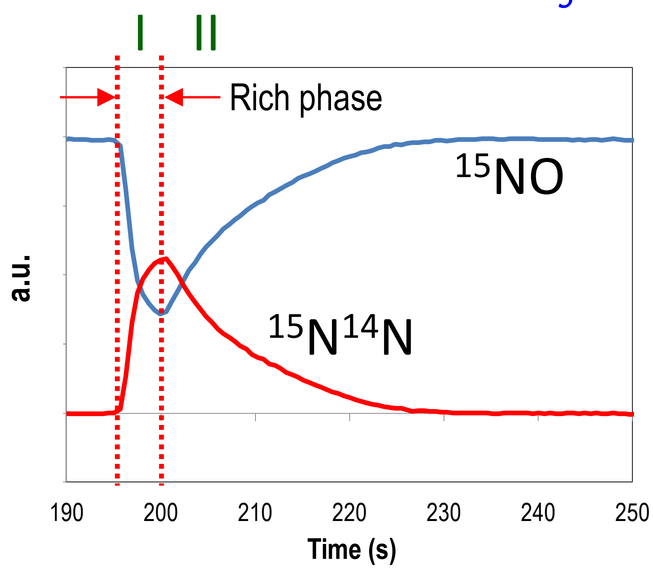
- ***Post-cycling temperature-programmed desorption confirmed stored NH_3 or NH_3 precursors***



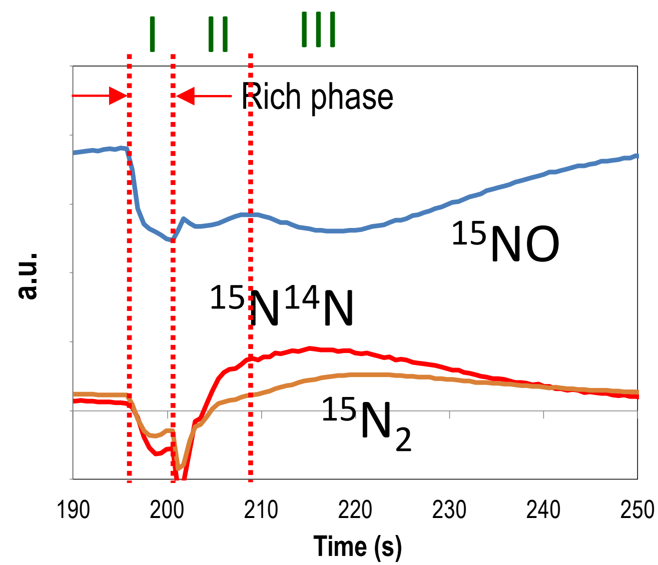
Hydrocarbon NO_x reduction pathway on Cu-chabazite clarified:

HC inhibition of NH_3 utilization (2)

Reductant: NH_3



Reductant: NH_3 + C_3H_6



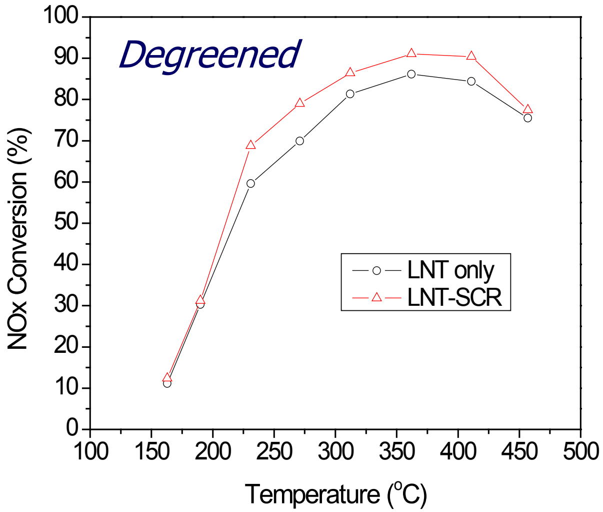
- ***Rich-phase (regime I)***
  - $^{15}N^{18}O + {}^{14}NH_3$ (gas) $\rightarrow {}^{15}N^{14}N$
  - Storage of $^{14}NH_3$
- ***Lean-phase, early (regime II)***
  - $^{15}N^{18}O + {}^{14}NH_3$ (stored) $\rightarrow {}^{15}N^{14}N$

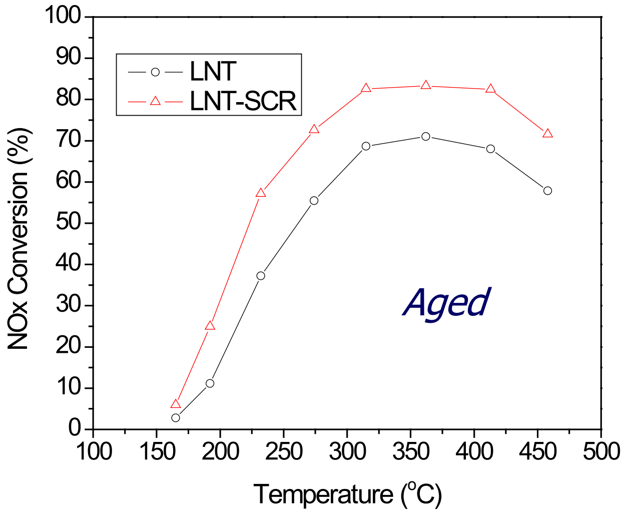
- ***Rich-phase (regime I)***
  - Storage of $^{14}NH_3$ (gas)
  - Formation/storage of $^{15}NH_3$ or its precursors
- ***Lean-phase, early (regime II)***
  - Formation/storage of $^{15}NH_3$ or its precursors
- ***Lean-phase, late (regime III)***
  - $^{15}N^{18}O$ + stored $^{14}NH_3$ and $^{15}NH_3$ (or precursors) $\rightarrow {}^{15}N^{14}N$ and $^{15}N_2$

C_3H_6 inhibition of NO + NH_3 reactions

LNT-SCR

LNT/SCR Dual Brick: Effect of Age





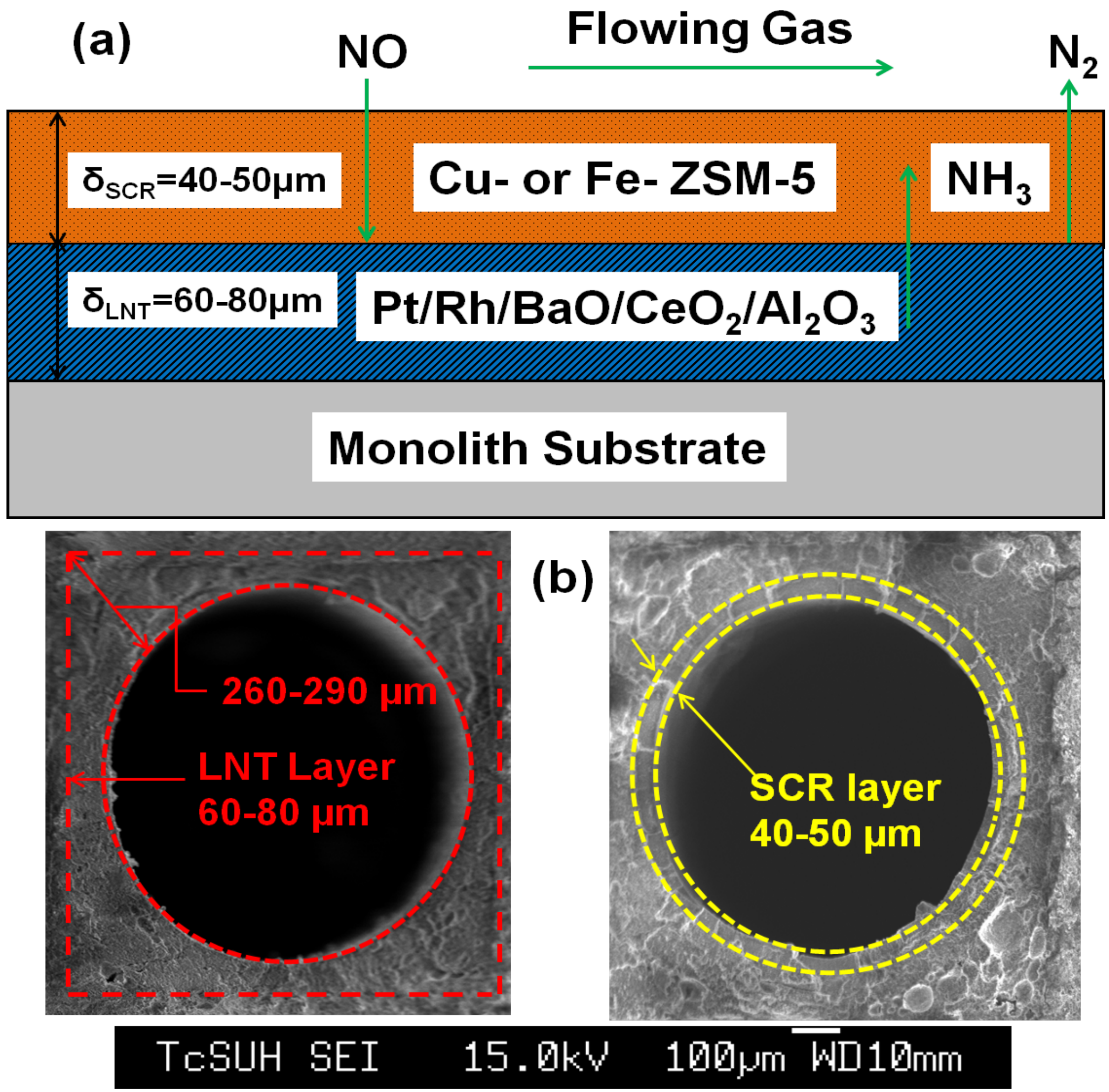
LNT-SCR system aged on bench reactor according to Ford accelerated aging protocol (ca. 75,000 miles)

Cycle-averaged NOx conversion for BASF LNT and LNT-SCR systems

Feed: lean (60 s): 500 ppm NO, 8% O_2, 5% CO_2, 5% H_2O, balance N_2; rich (5 s): 2.5% CO, 5% CO_2, 5% H_2O, balance N_2. GHSV = 60,000 h^{-1}.

- *After aging, deterioration in LNT NOx conversion is observed; based on analytical data, this can be attributed to accumulation of residual sulfate in washcoat and Pt-Ba phase segregation (→ decreased NOx storage capacity)*
- *After aging, NOx conversion over SCR catalyst is increased, due to increased LNT selectivity to NH_3 and increased NOx slip available for reaction*
- *Hence, SCR catalyst helps to compensate for deterioration in LNT NOx conversion*

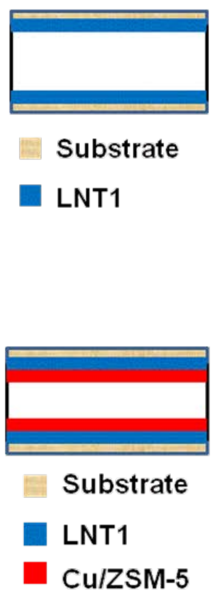
Dual Layer LNT/SCR Catalysts

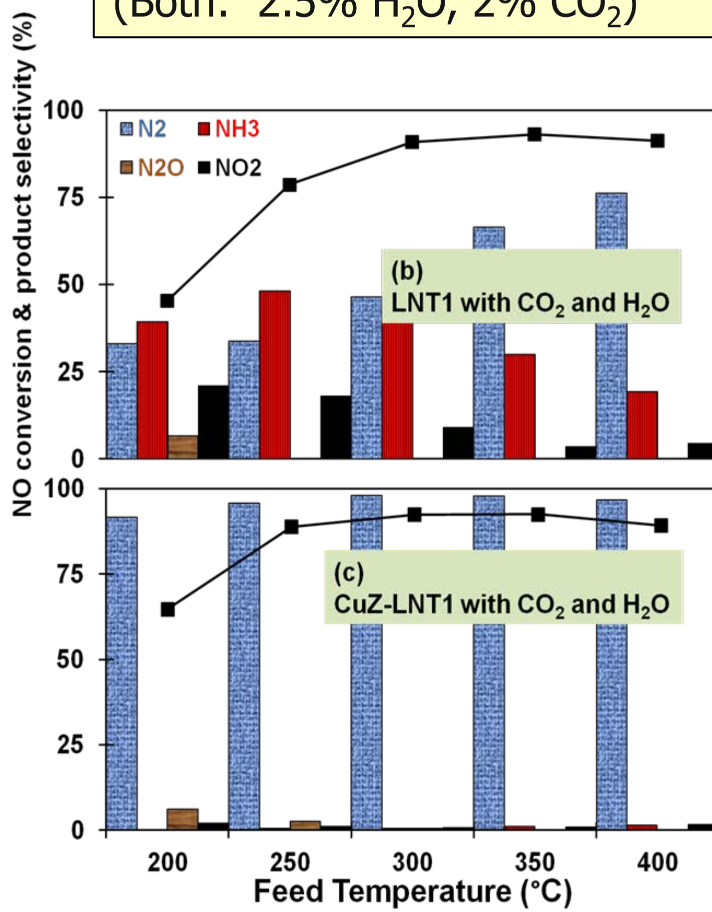


LNT before washcoating LNT after washcoating

LNT/SCR Dual Layer Synergy

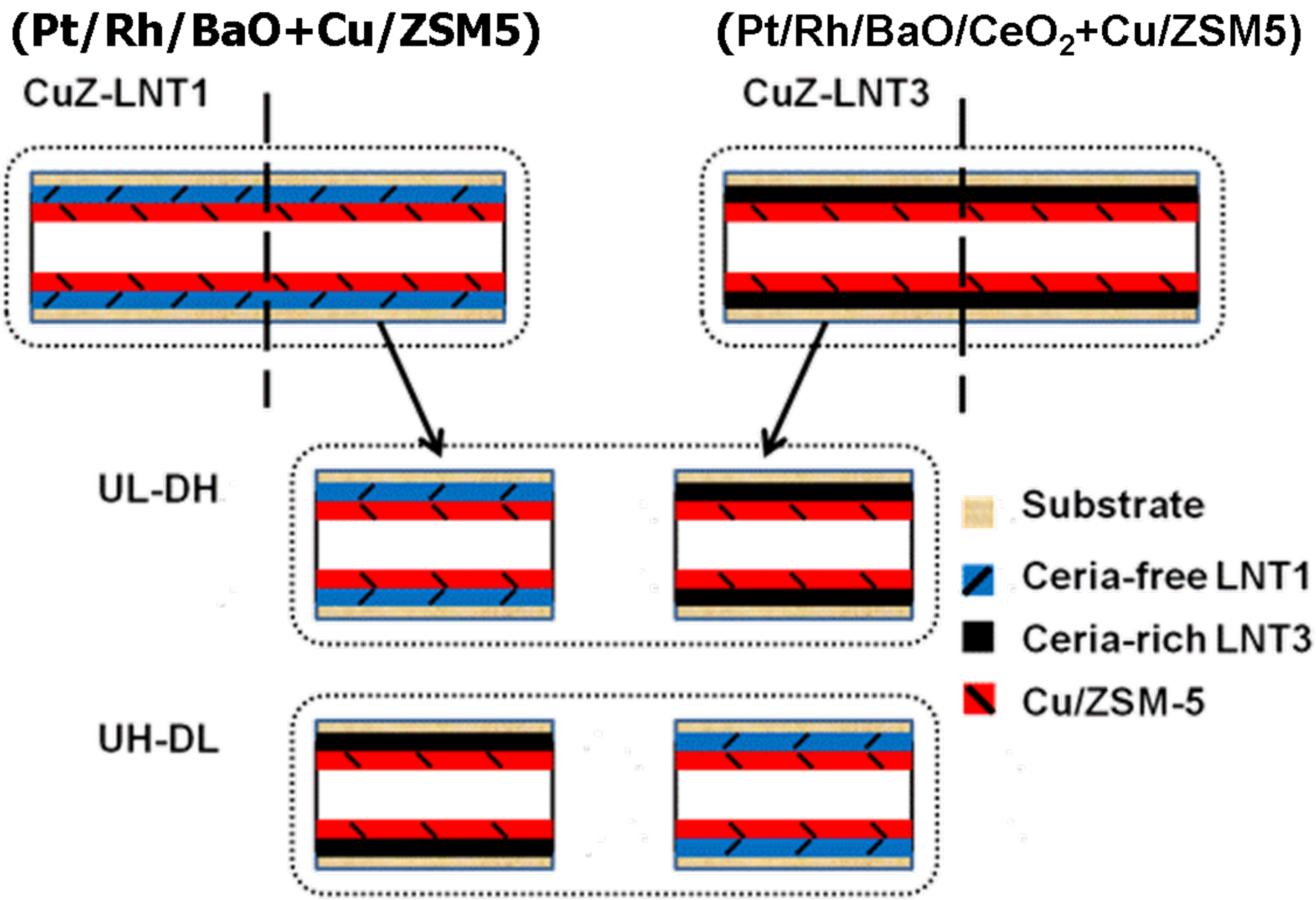
<u>Conditions:</u>
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
(Both: 2.5% H_2O, 2% CO_2)





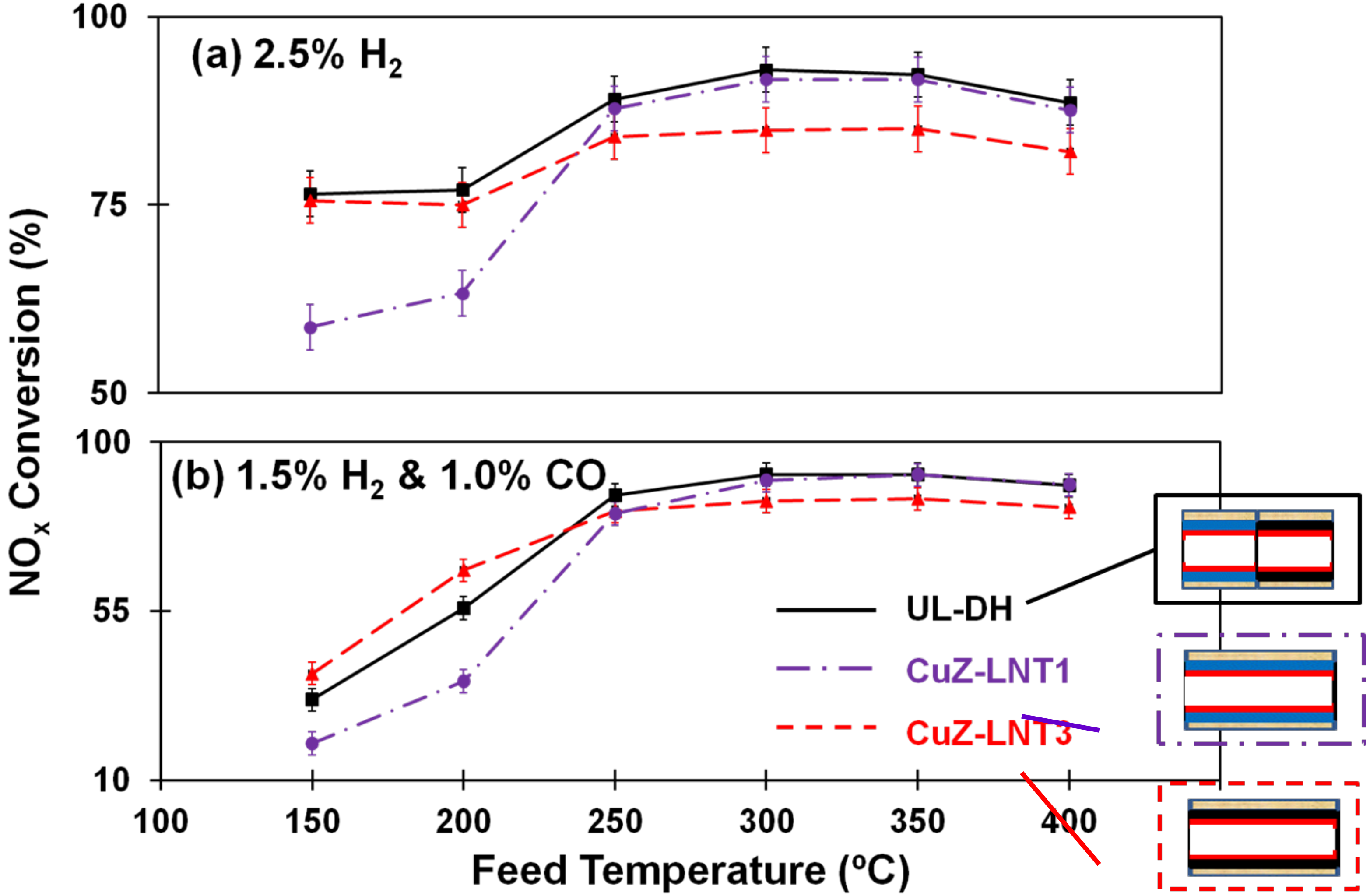
- *LNT produces product containing NH_3, NO, & unreacted NO*
- *Addition of SCR layer leads to increase in NO conversion & elimination of NH_3 & NO_2*

LNT/SCR Dual-Layer: CeO_2 Axial Zoning



LNT/SCR: Ceria Zoning

Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
or 2.5% H_2, 1.0% CO
(with 2.5% H_2O, 2% CO_2)

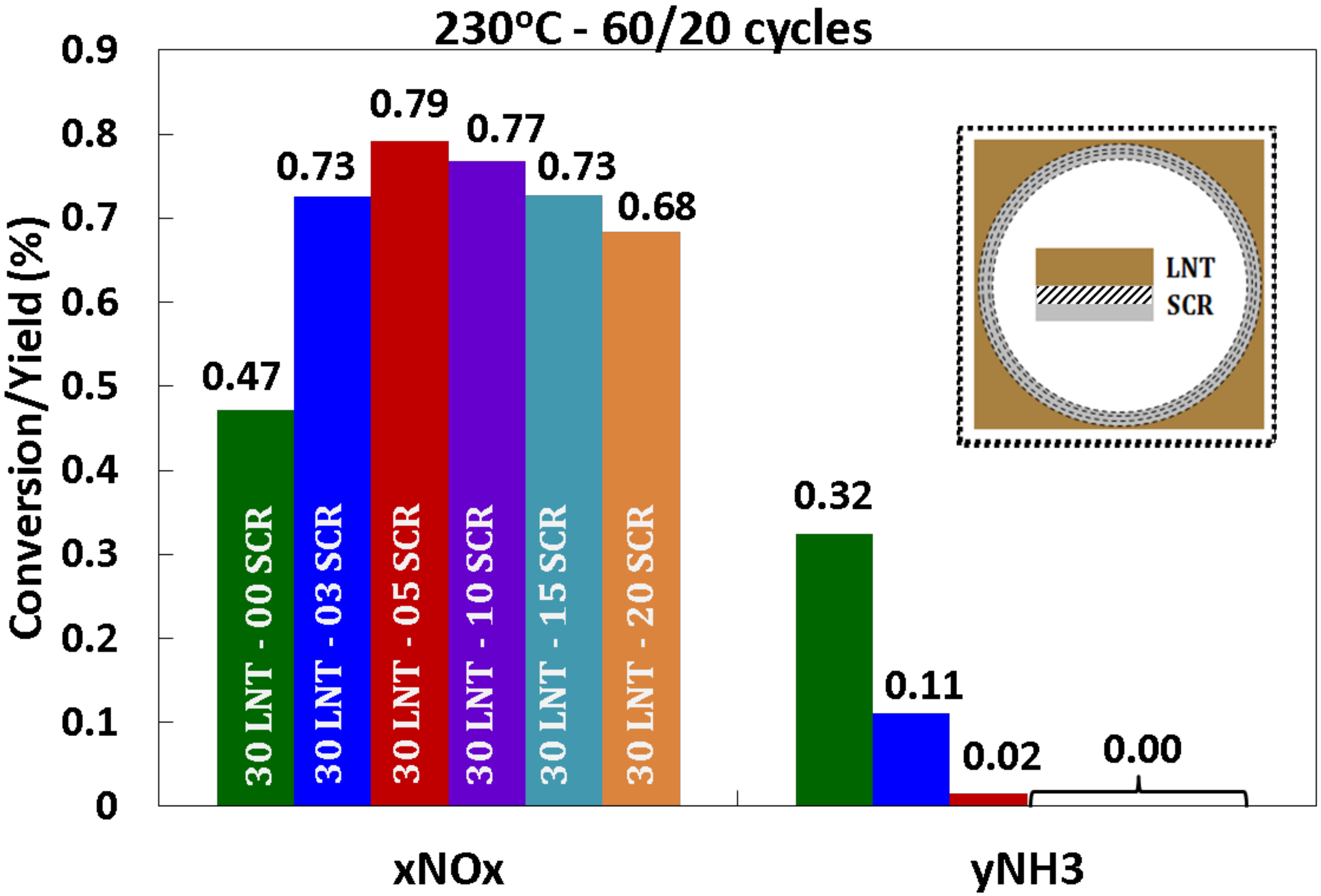


Zoning of ceria leads achieves balance of higher NOx conversion at low & high temperatures

Effect of SCR Washcoat Loading

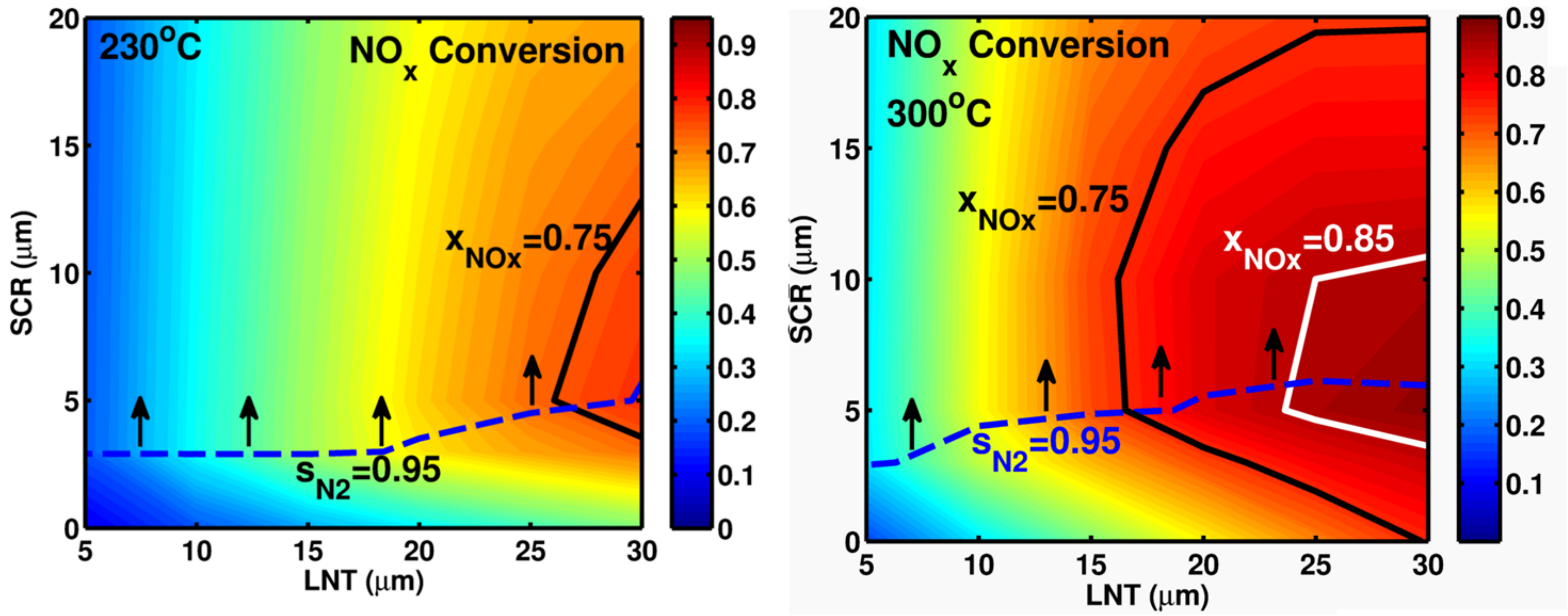
Conditions:
Lean: 60s
500 ppm NO
5% O_2
Rich: 20s
5000 ppm H_2
230°C

Washcoat Thickness:
LNT = 30 μm
SCR = 0-20μm



Excessive SCR loading leads to lower NOx conversion because of undesired diffusion limitation

Effect of LNT/SCR Washcoat Loadings



Several combinations of LNT/SCR loadings are possible to achieve the same conversion

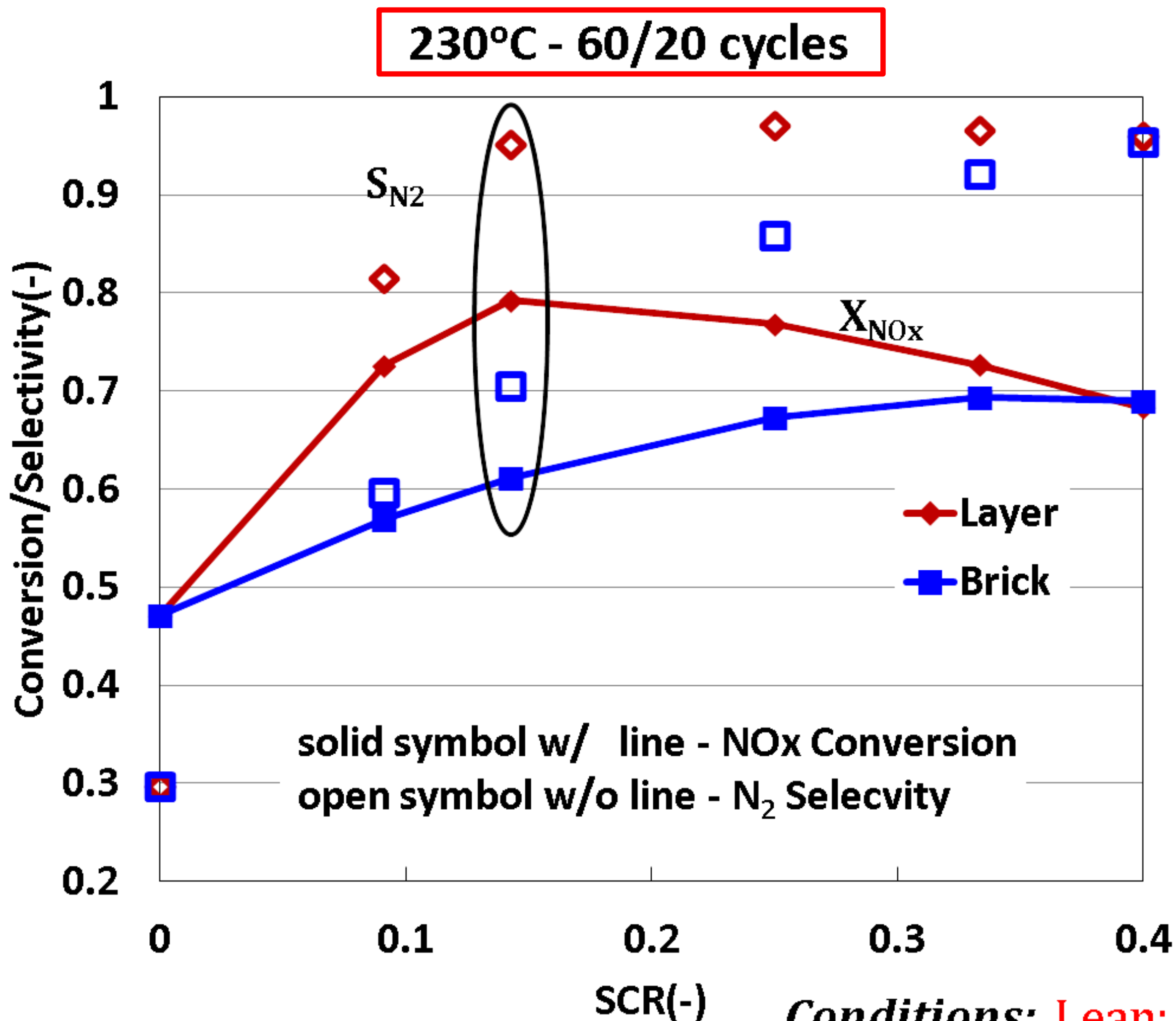
Conditions:

Lean inlet: 500 ppm NO + 5% O_2 in bal Ar / Duration: 60s

Rich inlet: 5000 ppm H_2 in bal Ar / Duration: 20s

Temperature: 230°C ***GHSV:*** 60,000 hr^{-1} (based on monolith volume)

LNT/SCR: Dual Layer vs. Dual Brick



L = 2cm

LNT = 30 μm

SCR (%)	Layer (μm)	Brick (cm)	R_{Ω_2} (μm)
0.00	0	0.00	30
0.09	3	0.18	33
0.14	5	0.28	35
0.25	10	0.50	40
0.33	15	0.66	45
0.40	20	0.80	50

Conditions: Lean: 60s 500 ppm NO + 5% O_2
Rich: 20s 5000 ppm H_2

Selected Activities Planned: 3Q-4QFY13 (Complete Phase 3)

- LNT:
  - Carry out SpaciMS study of propylene regenerated LNT under nonisothermal conditions
  - Apply crystallite-scale model to combined CO + H_2 reductant mixture

- SCR:
  - Complete experimental study of reactivity of NH_3 + C_3H_6 + NO on Cu/chabazite
  - Complete kinetic and modeling study of C_3H_6 SCR on Cu/chabazite
  - Complete optimization study of dual layer Cu/Chabazite + Fe/ZSM-5 SCR catalyst

- LNT/SCR:
  - LNT/SCR experiments
    - Complete SpaciMS study of serial LNT/SCR dual brick
  - LNT/SCR reactor modeling
    - Complete modeling study and optimization of LNT/SCR dual layer catalyst
    - Complete modeling study of sequential segmented LNT/SCR for nonisothermal operation

Summary

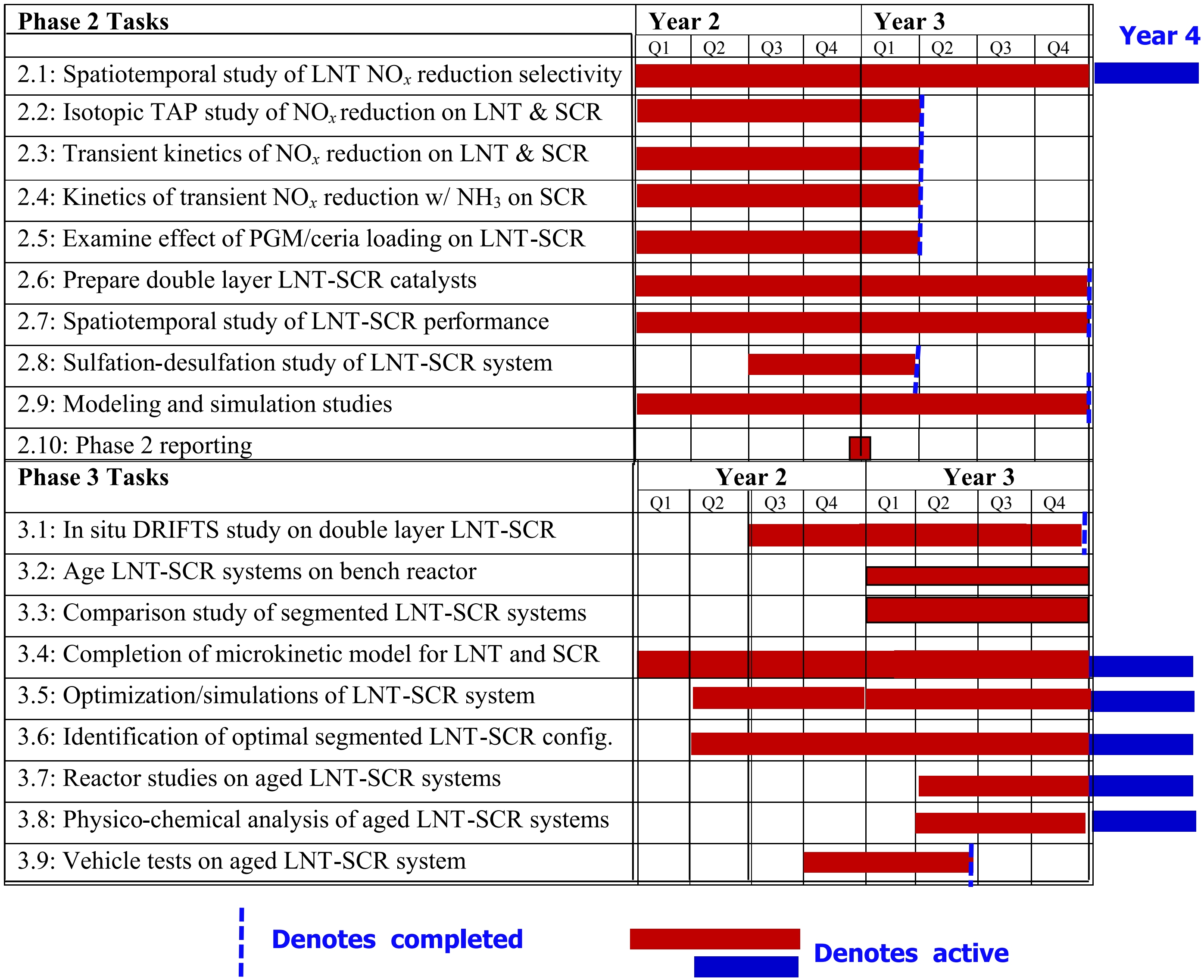
- Comprehensive program combining fundamental catalysis, reaction engineering and vehicle testing
- In past year, very good progress on Phase 2 & 3 tasks
- No-cost extension period will enable completion of active tasks
- Project has generated considerable pioneering results and understanding of LNT/SCR technology, including 25^+ peer-reviewed publications and several invited lectures
- Specific technical accomplishments include:
  - Comprehensive isotopic kinetics and reactor performance studies elucidate NO + CO + H_2O on LNT system
  - Demonstration of dual layer LNT/SCR catalyst
  - Prediction that dual layer LNT/SCR catalyst can out-perform dual-brick catalyst under certain conditions
  - Novel use of ceria to achieve enhanced performance over wide temperature range
  - Demonstration that aged LNT/SCR is viable
  - Predictive reactor models developed for LNT, SCR, & LNT/SCR for data analysis & optimization

Technical Backup Slides

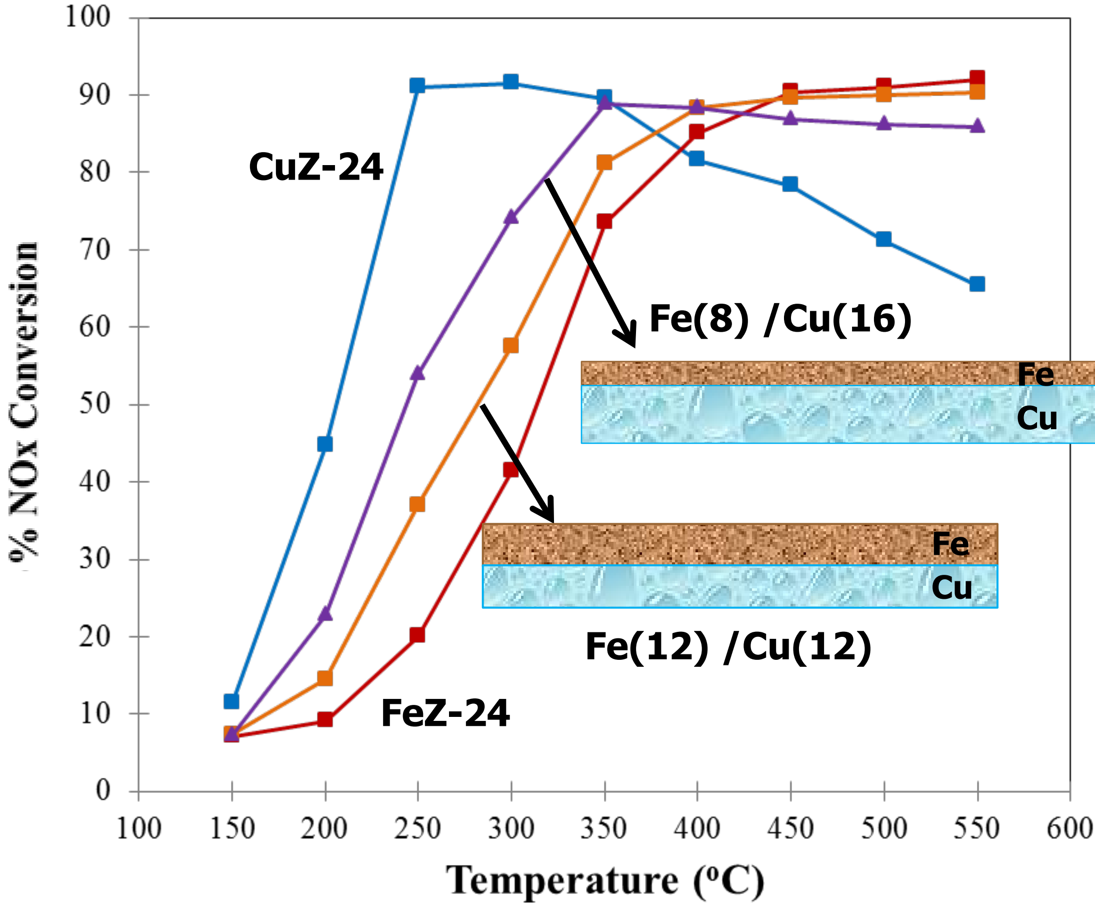
Collaborative Project Team: Current Activities

- **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.)
  - Model catalyst synthesis & characterization; Commercial SCR catalyst
- **Ford Motor Company** (until Aug. 2011)
  - *Bob McCabe, Mark Dearth, Joe Theis*
  - Bench-flow reactors, SpaciMS
  - Vehicle testing of LNT/SCR system

Schedule of Tasks: Phases 2 & 3

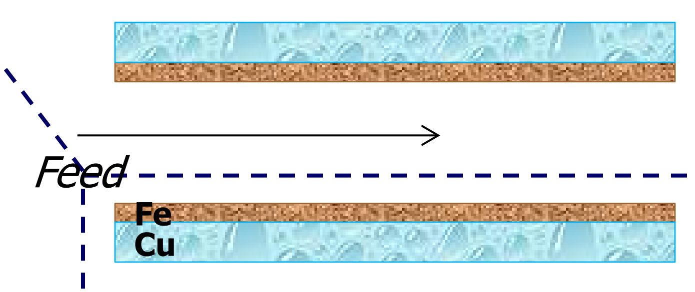


Combination of Fe- and Cu-zeolite: Dual-layer Catalyst System (UH)



Total washcoat loading:
24% (by wt)

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

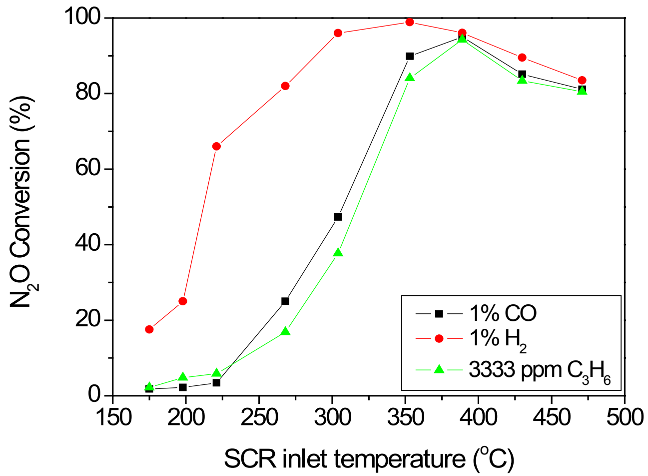


Lab-synthesized catalysts

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

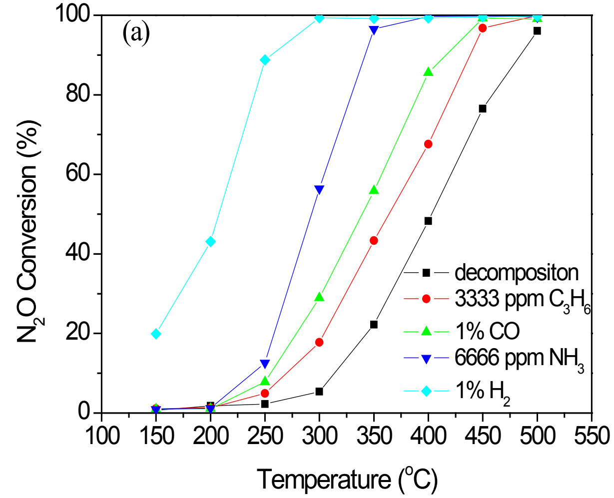
Harold & Metkar, Patent Pending (2011)

N_2O Reduction Over Cu-Chabazite SCR Catalyst



Cycle-averaged N_2O conversion over SCR catalyst in LNT-SCR system during 60 s lean/5 s rich cycling

Lean: 300 ppm NO, 8% O_2; Rich: 300 ppm NO, 1% H_2 or 1% CO or 3333 ppm C_3H_6 as reductant; 5% CO_2, 5% H_2O, N_2 as bal. in L and R phases; GHSV = 30,000 h^{-1}



N_2O conversion over Cu-CHA under steady state, continuous flow conditions

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

- *Under L/R cycling, N_2O formed over LNT catalyst is converted to significant degree over Cu-CHA SCR catalyst; H_2 is best reductant*
- *Other data show that N_2O decomposition is weakly promoted by NO, e.g.: $N_2O + NO \rightarrow N_2 + NO_2$*

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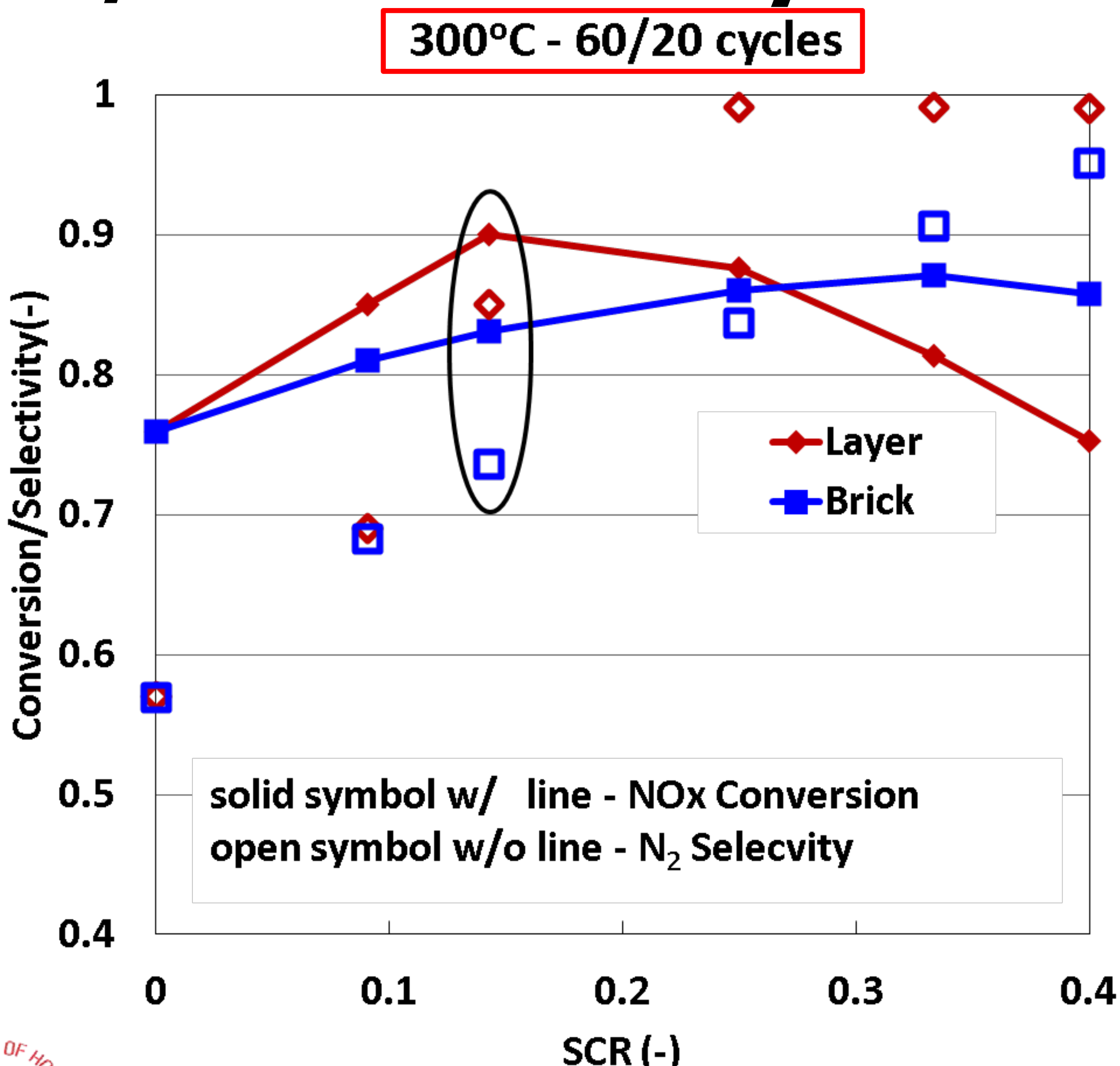
LNT/SCR: Dual Layer vs. Dual Brick



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