Lean NOx Reduction With Dual Layer LNT/SCR Catalysts

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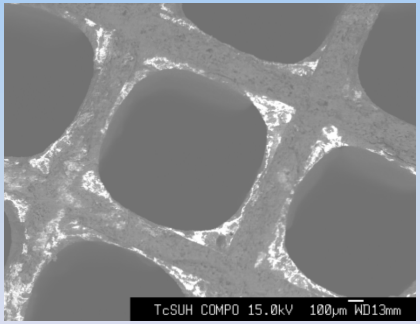


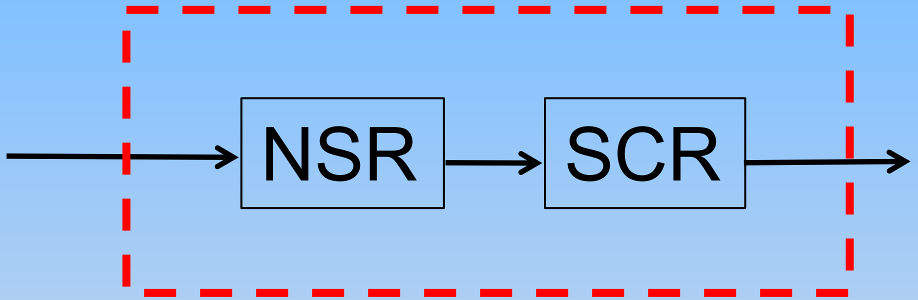
Presentation at DEER 2012

October 2012

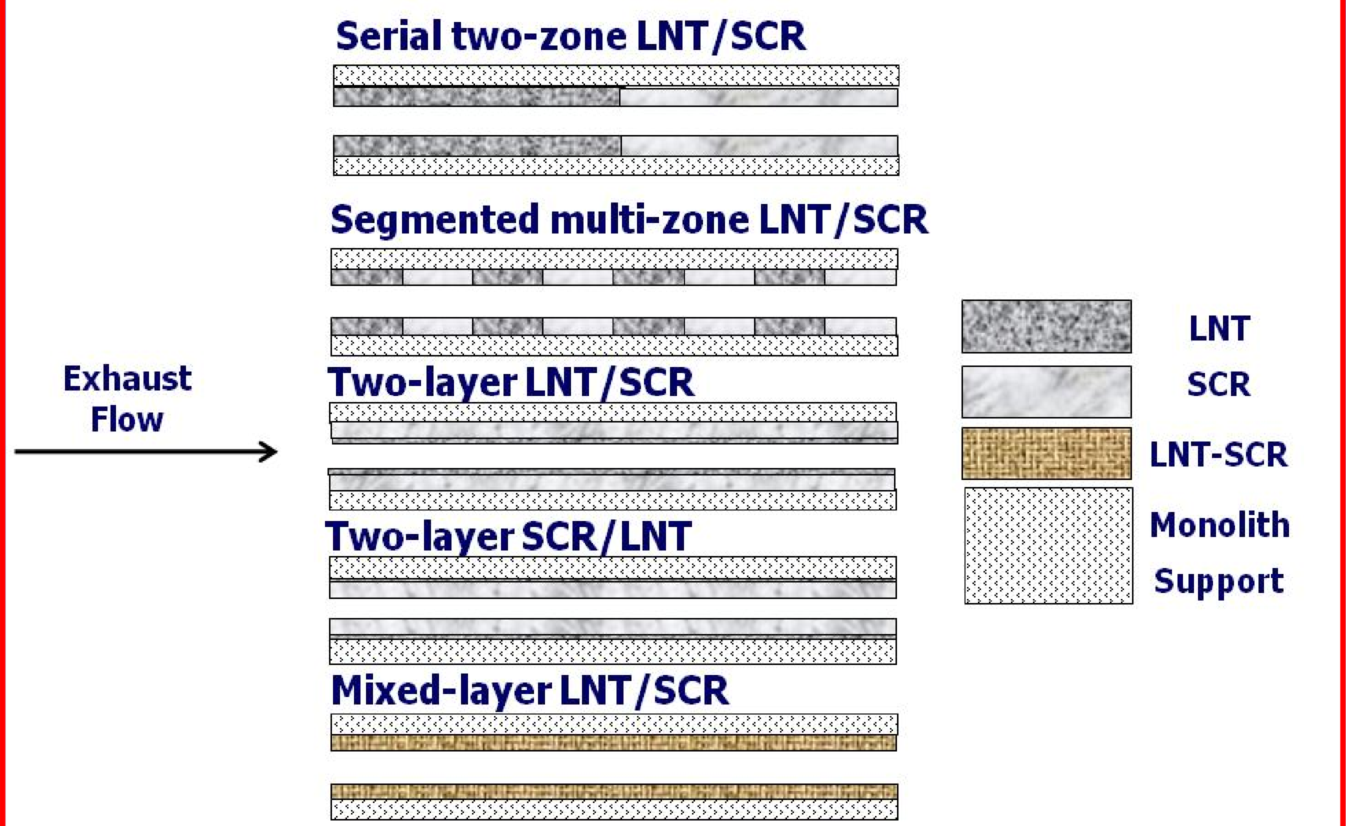
Acknowledgements:
DOE-EERE – Office of Vehicle Technologies, BASF, Ford, U. Kentucky, ORNL

NSR/SCR Technology

- Promising non-urea deNOx technology for light- & medium-duty diesel & lean burn gasoline
- Synergistic benefits demonstrated: Increased NOx conversion by adding SCR unit downstream
- Understanding of the coupling between LNT & SCR series-brick configuration is emerging



NSR/SCR Technology



(adapted from Gandhi et al., US Patent, 2007)

Goal: Reduce PGM & minimize fuel penalty in meeting NOx emission targets

Fundamental Issues for Dual Layer

- LNT – SCR proximity: Dual layer vs. physical mixture
- LNT composition, structure & loading
- SCR composition & loading
- Thermal durability
- Dual layer vs. sequential monolith configuration
- etc.

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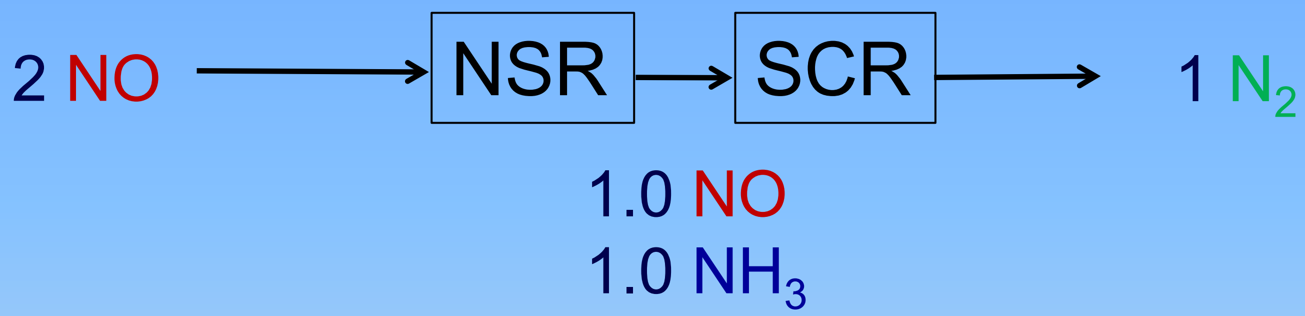
- etc.

our aim is to resolve some of these issues…

NSR/SCR: A Different Role for the LNT



- LNT Ideal Target: 50% NOx conversion &100% NH_3 selectivity:

$$\text{LNT:}\quad NO + 4\,H_2 + 0.75\,O_2 \rightarrow NH_3 + 2.5\,H_2O$$

$$\text{SCR:}\quad NO + NH_3 + 0.25\,O_2 \rightarrow N_2 + 1.5\,H_2O$$

$$\text{Overall:}\quad 2\,NO + 4\,H_2 + O_2 \rightarrow N_2 + 4\,H_2O$$

LNT does not have to be highly effective NSR catalyst in the combined NSR/SCR application

LNT/SCR Catalyst Synthesis

- LNT layer monolith (from BASF)

	LNT1	LNT2	LNT3
PGM (g/ft^3)* **(Pt:Rh = 7)**	90	90	90
Ba (wt%)	14	14	14
Ce (wt%)	0	17	34

*~4.6 g/in^3 washcoat loading; 1.1wt.% PGM in γ-Al_2O_3

- SCR top-layer contains Fe/ZSM5 or Cu/ZSM5
  ~0.9 g/in^3 washcoat loading (unless otherwise stated)

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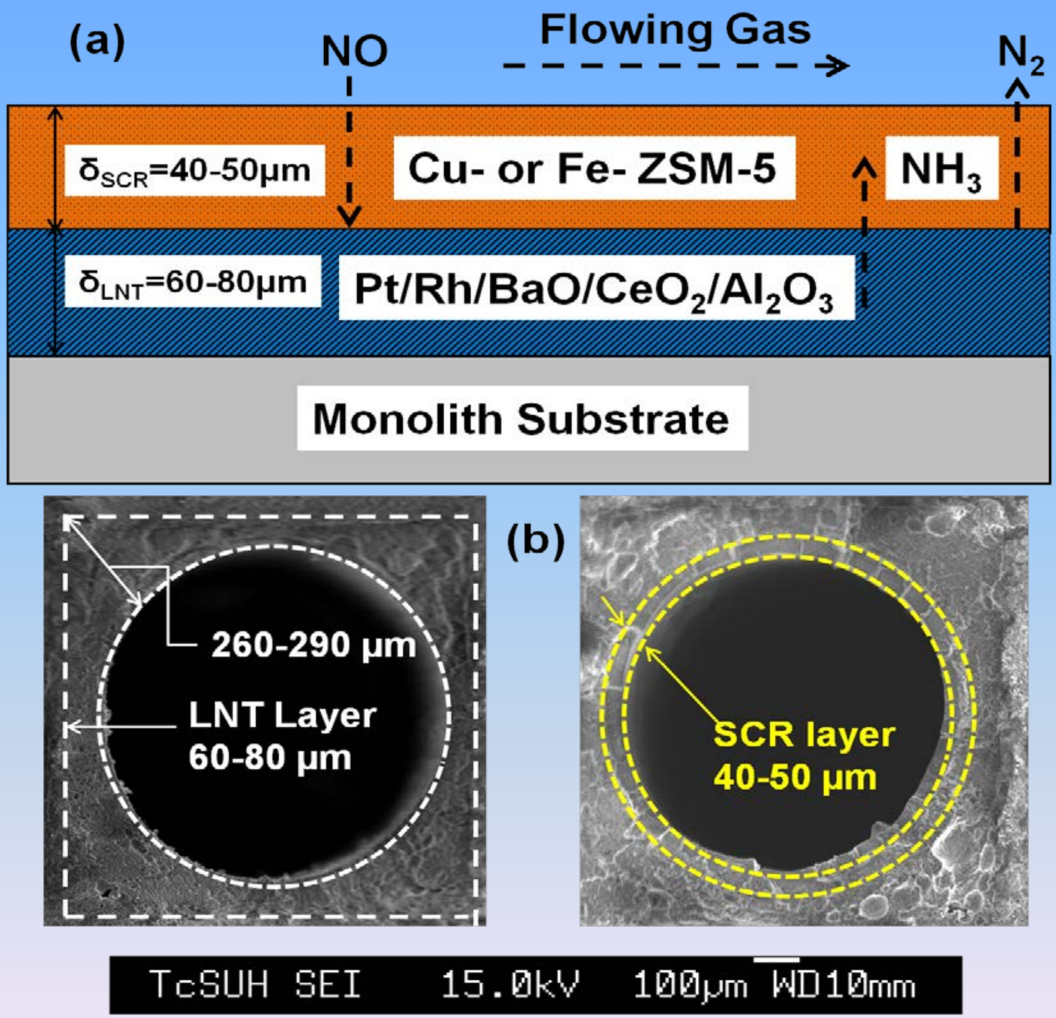
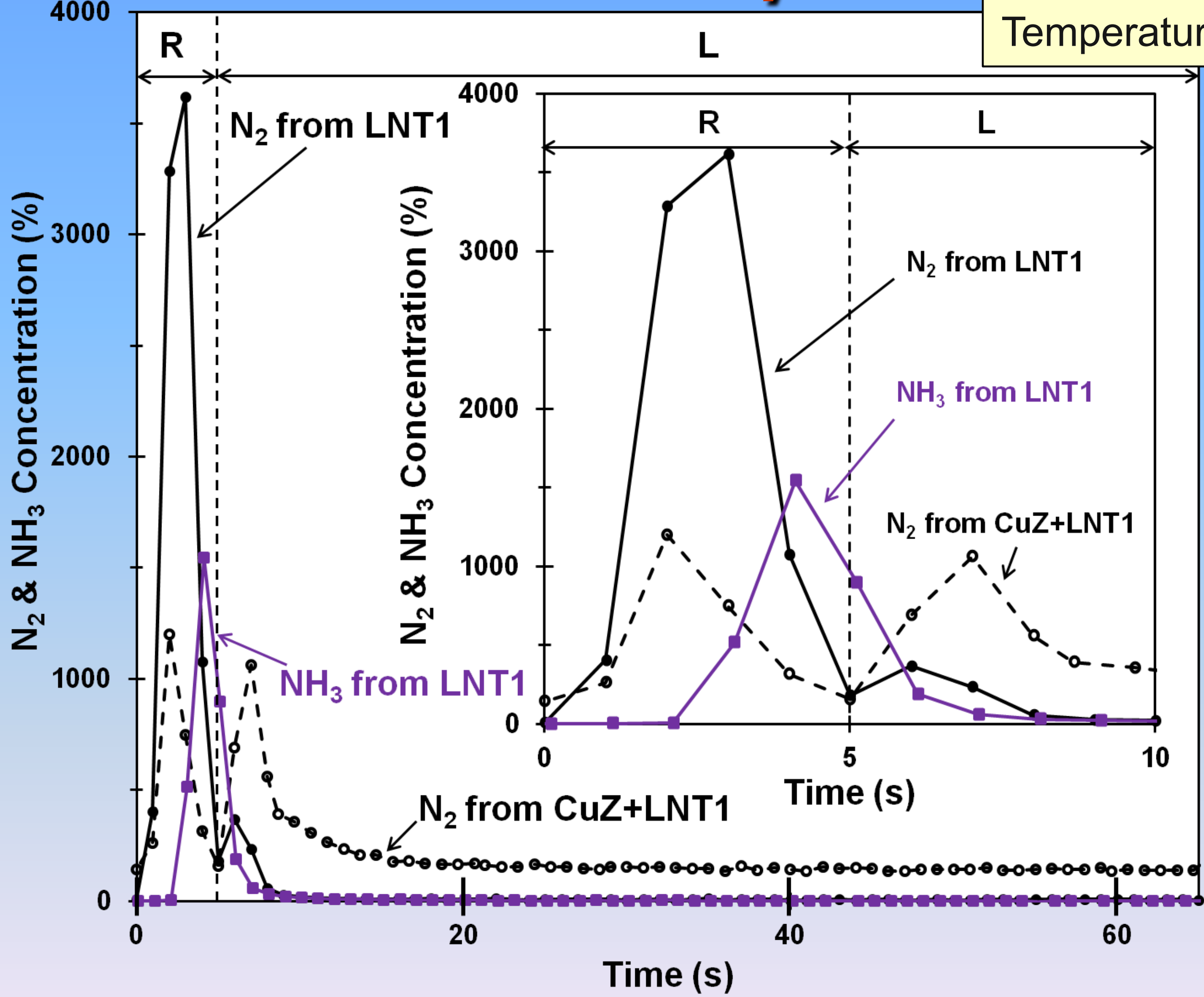
Dual-Layer Catalyst Structure



LNT before washcoating LNT after washcoating

Comparison of LNT & LNT/SCR Lean-Rich Cycle

Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
Temperature: 300°C



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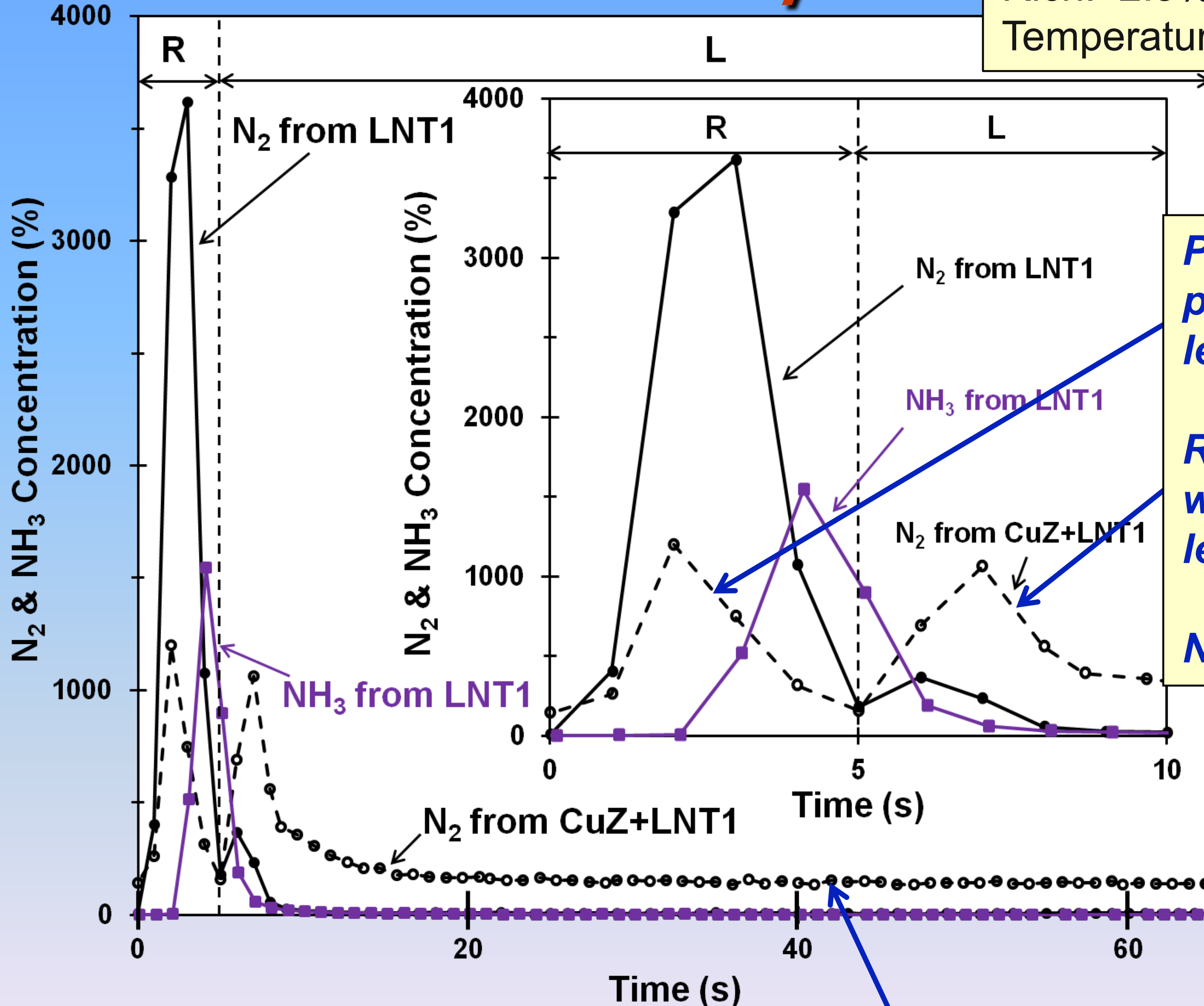

Prominent dual N_2 peaks during rich & lean

Rcn. of stored NH_3 with O_2 & NOx during lean phase

No NH_3 for CuZ+LNT

Sustained N_2 production for entire lean period; due to slow NH_3 release from Cu-Z & reduction

Summary of Results w/o CO_2 & H_2O*

- Dual layer concept works
- LNT/SCR has slightly lower NO conversion than LNT only
- Low temperatures (< 225 °C): Undesired oxidation of NH_3 on Pt (to N_2O) occurs due to trapped NH_3 migrating to LNT layer
- Higher temperatures (> 250 °C): Undesired oxidation of NH_3 on Pt (to NO) occurs
- LNT/SCR dual layer out-performs LNT+SCR single layer
- Aged LNT/SCR can lead to improved performance

*Liu, Y., M.P. Harold, and D. Luss, *Appl. Catal. B. Environ.* 121-122 (2012) 239-251

LNT/SCR: H_2 Reductant in Presence of CO_2 & H_2O

Conditions:
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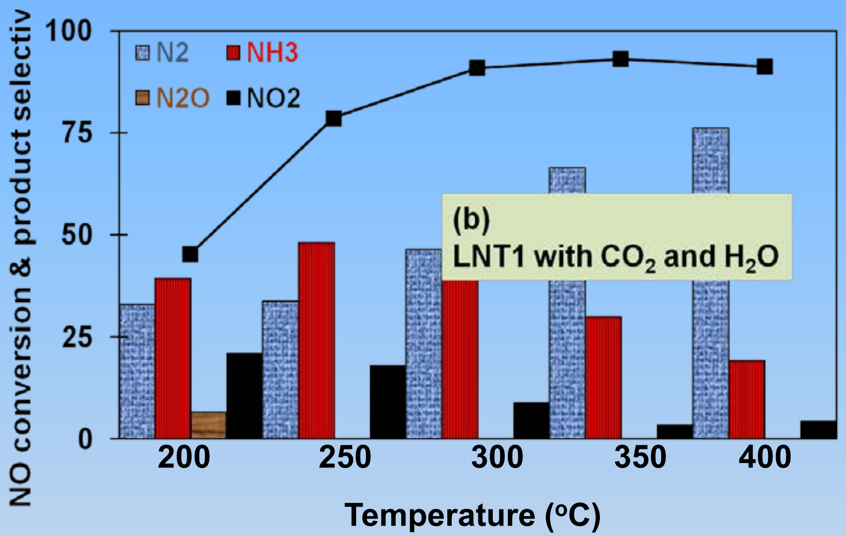
(Both: 2.5% H_2O, 2% CO_2)



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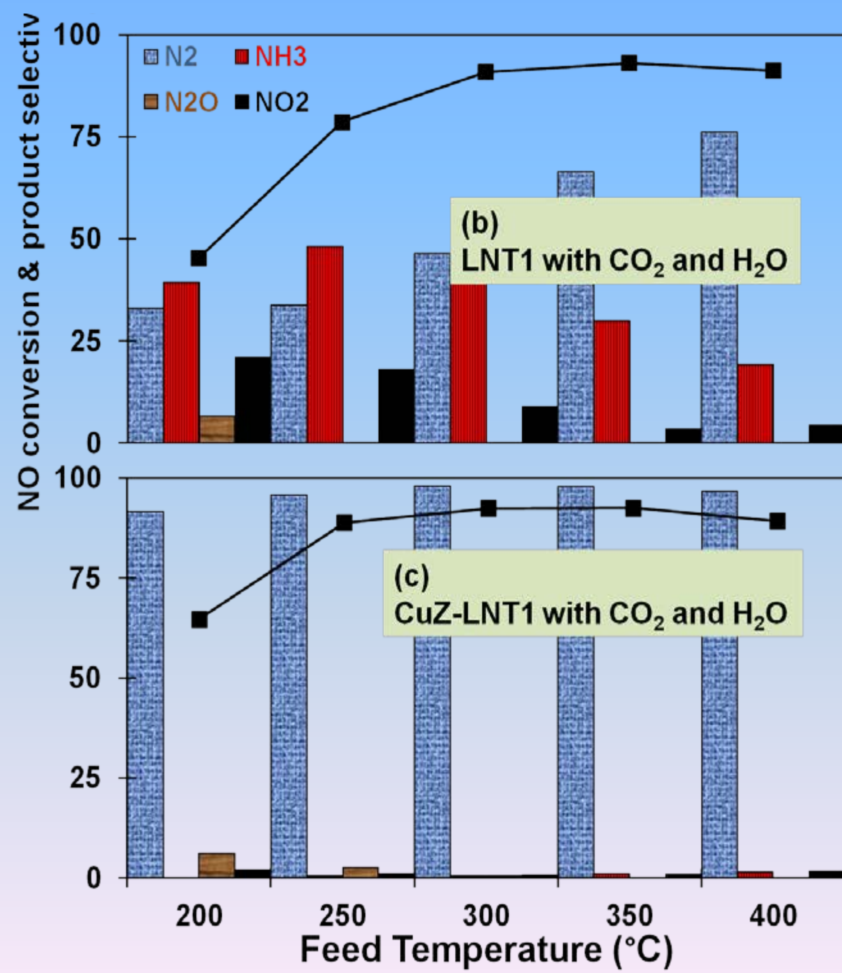

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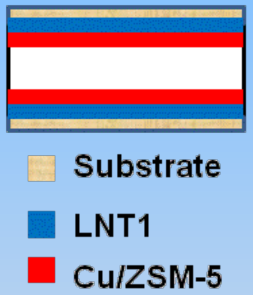
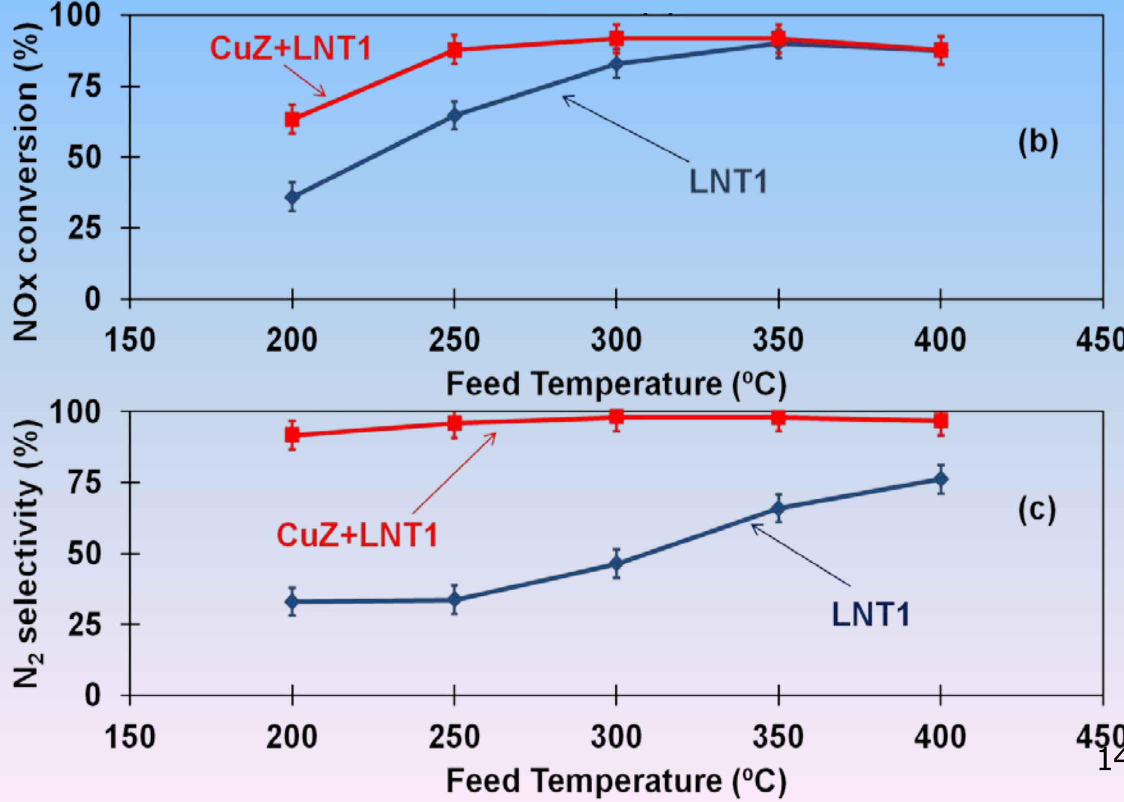
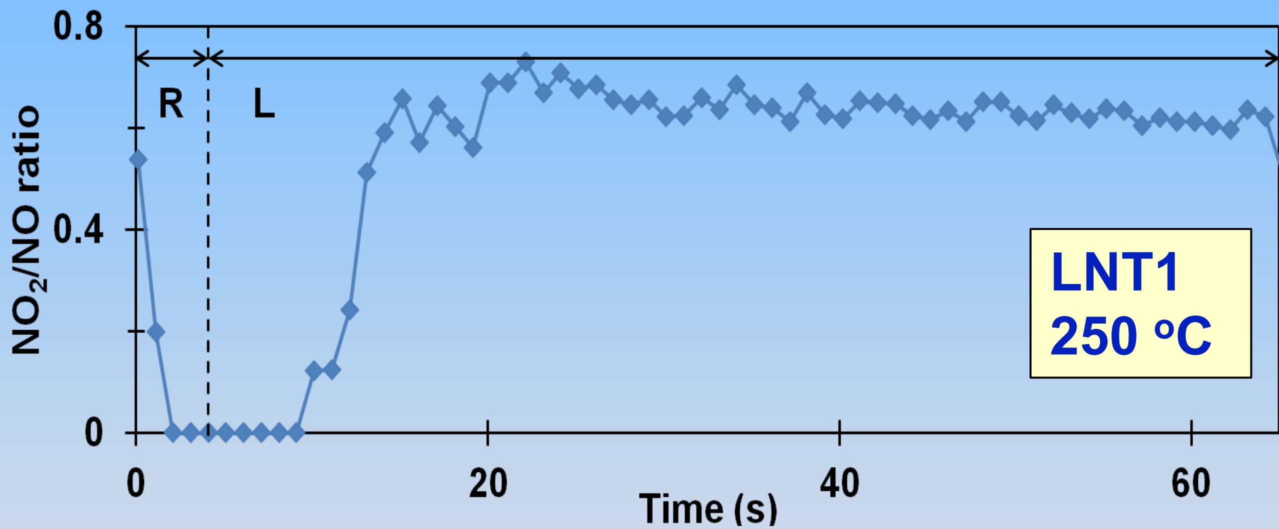




LNT/SCR: Enhanced NOx conversion & N_2 selectivity over wide temperature range

LNT/SCR Performance in Presence of CO_2 & H_2O



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

Fast SCR

LNT: Serves as NO_2 generator during lean phase & NH_3 generator during rich phase

LNT/SCR: SCR stores NH_3 during rich and reacts with NO/NO_2 during lean

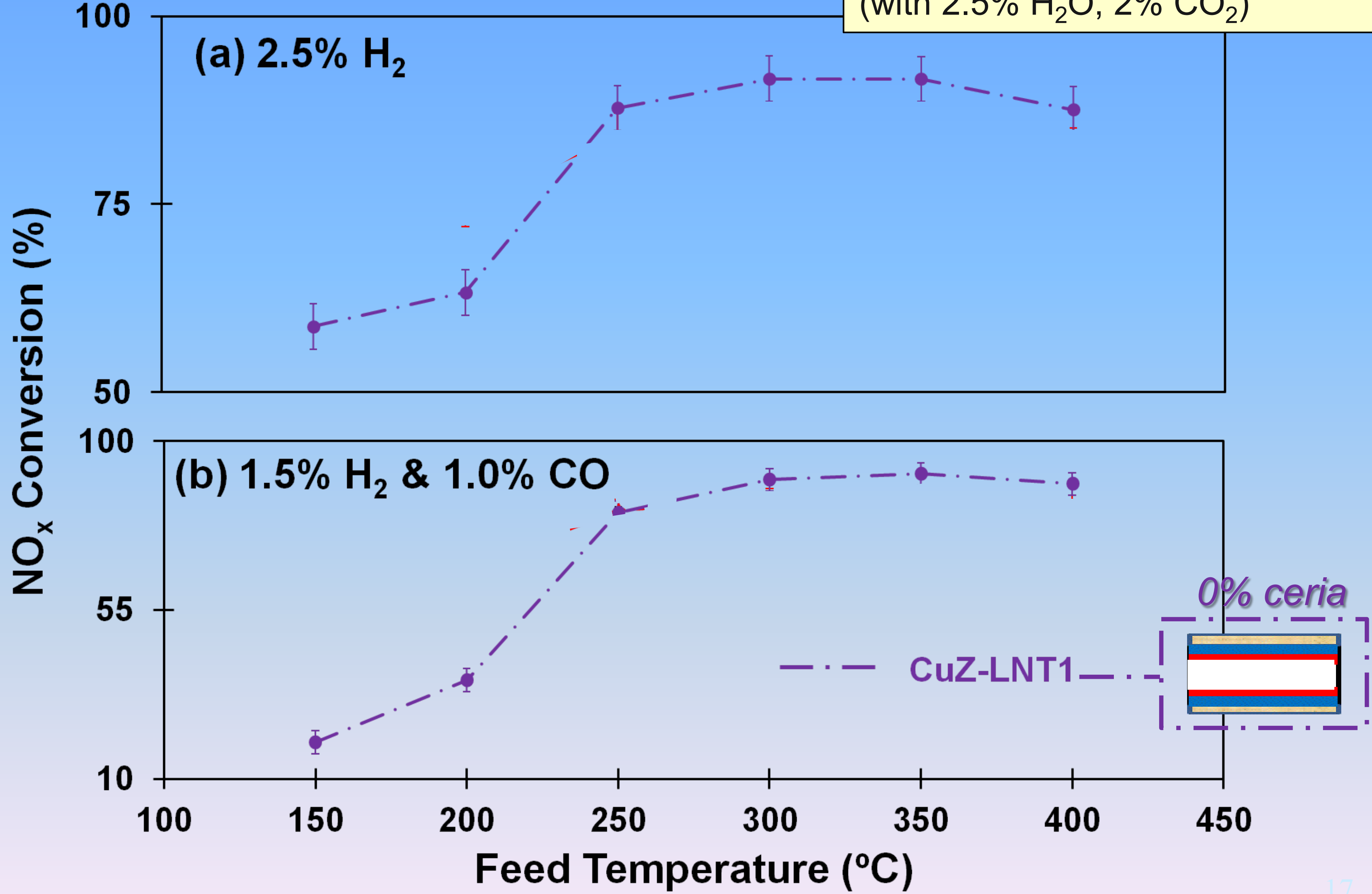
Ceria Addition

	LNT1	LNT2	LNT3
PGM (g/ft^3)	90	90	90
Ba (wt%)	14	14	14
Ce (wt%)	0	17	34

- Ceria effects:
  - Improved low T performance
  - Mitigation of CO poisoning at low T
  - Promotes WGS reaction ($CO + H_2O \leftarrow\rightarrow CO_2 + H_2$)
  - Stabilization of Pt
  - Increased NH_3 oxidation at high T

Ceria Loading Effect

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)



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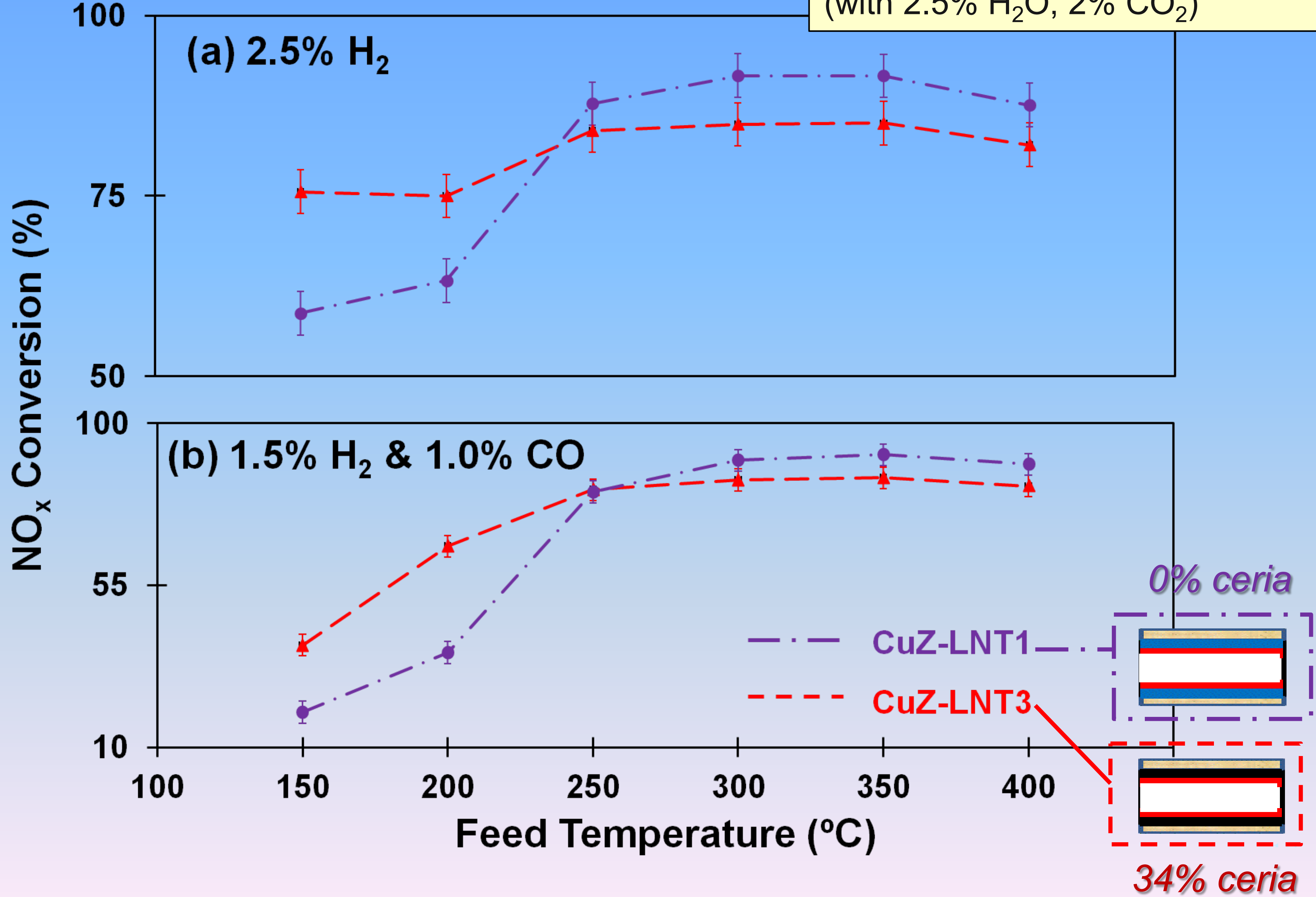

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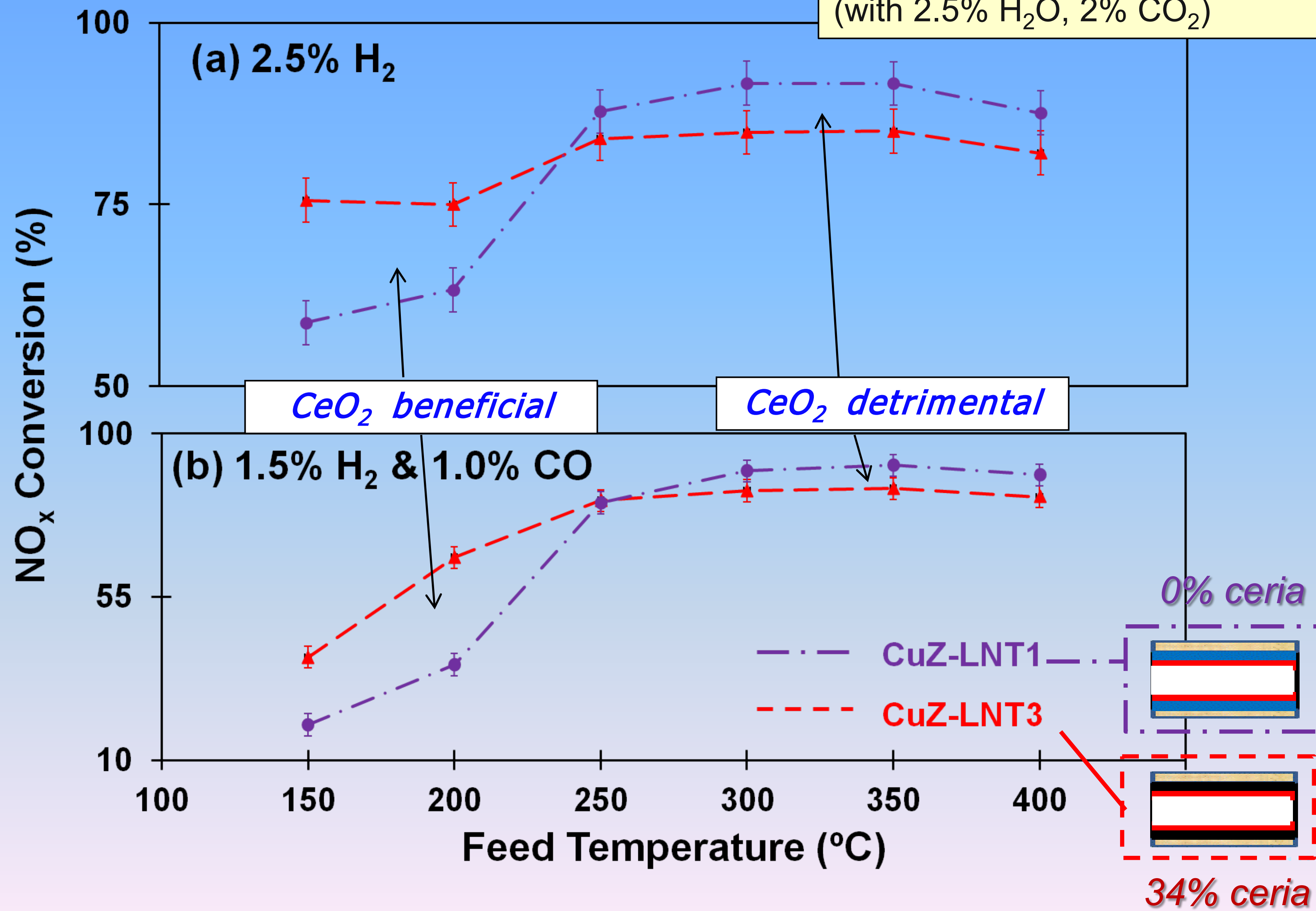
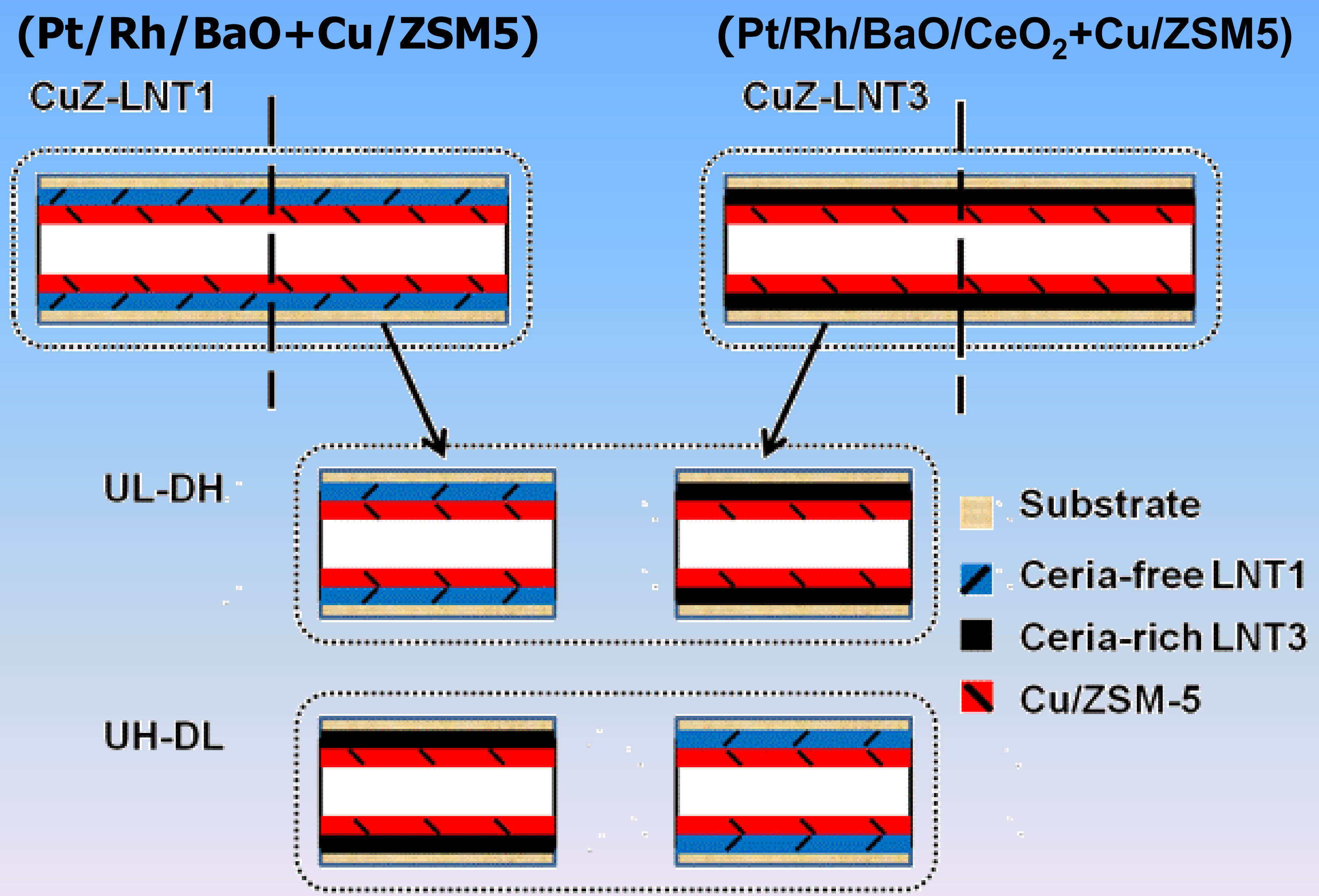


LNT/SCR Dual-Layer: CeO_2 Axial Zoning



Liu, Y., Y. Zheng, M.P. Harold, and D. Luss, Appl. Catal. B. under review (2012).

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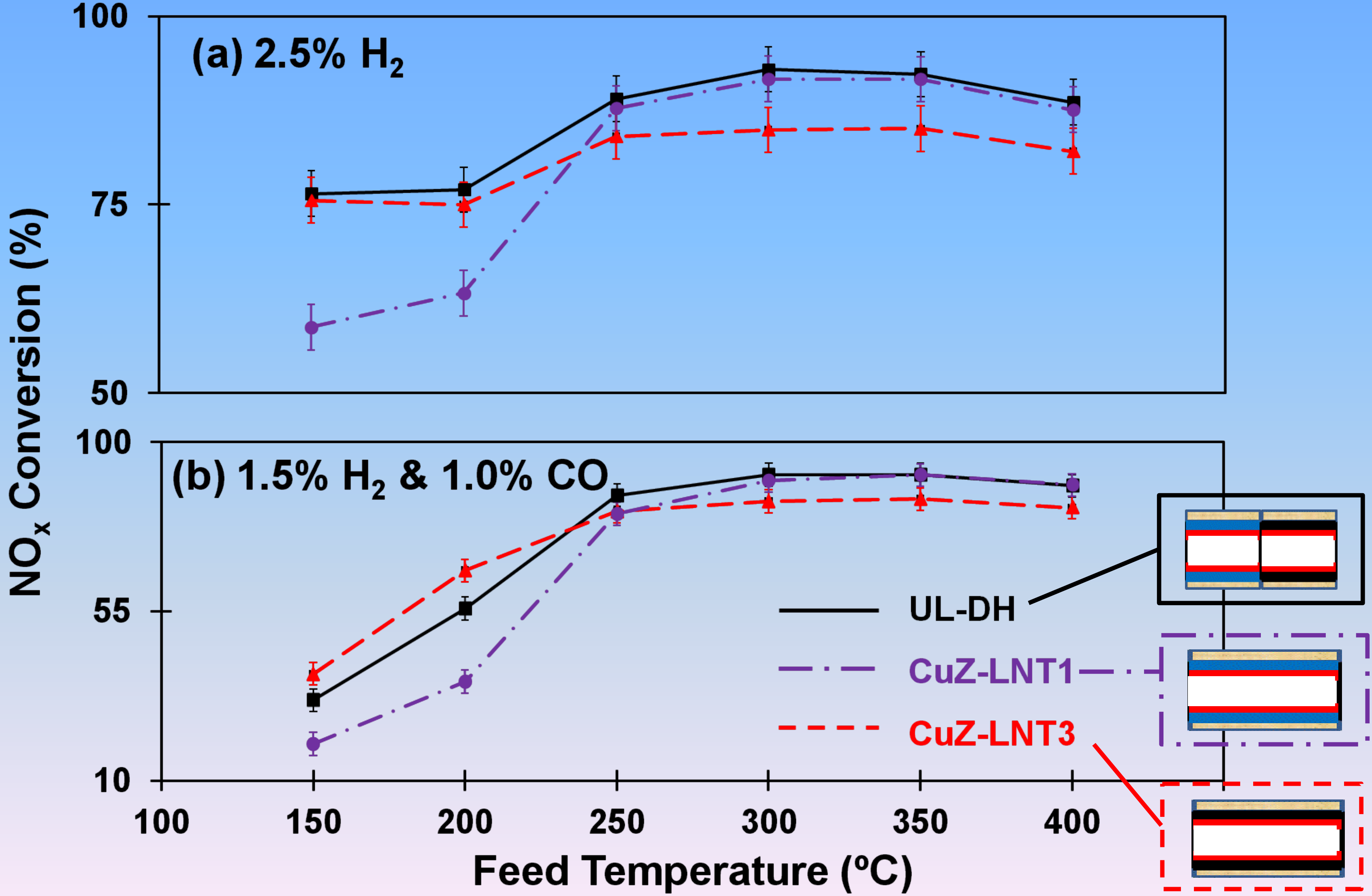
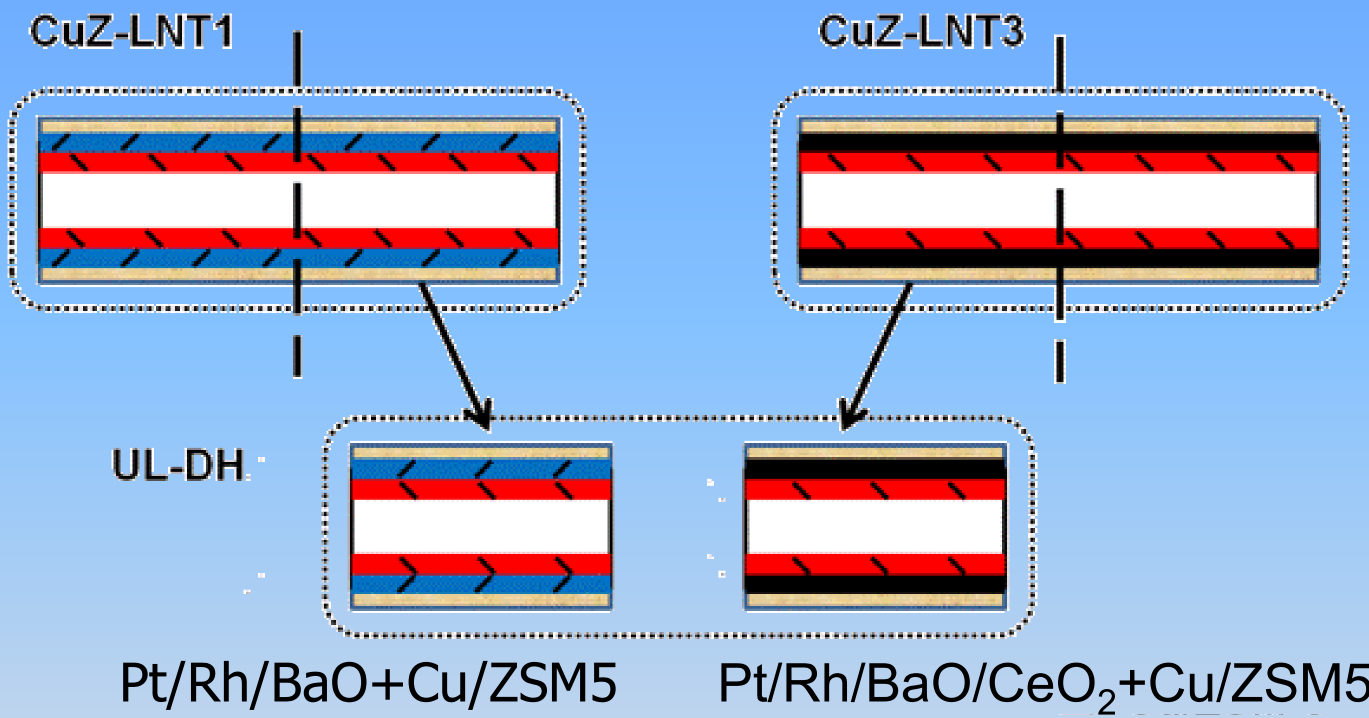
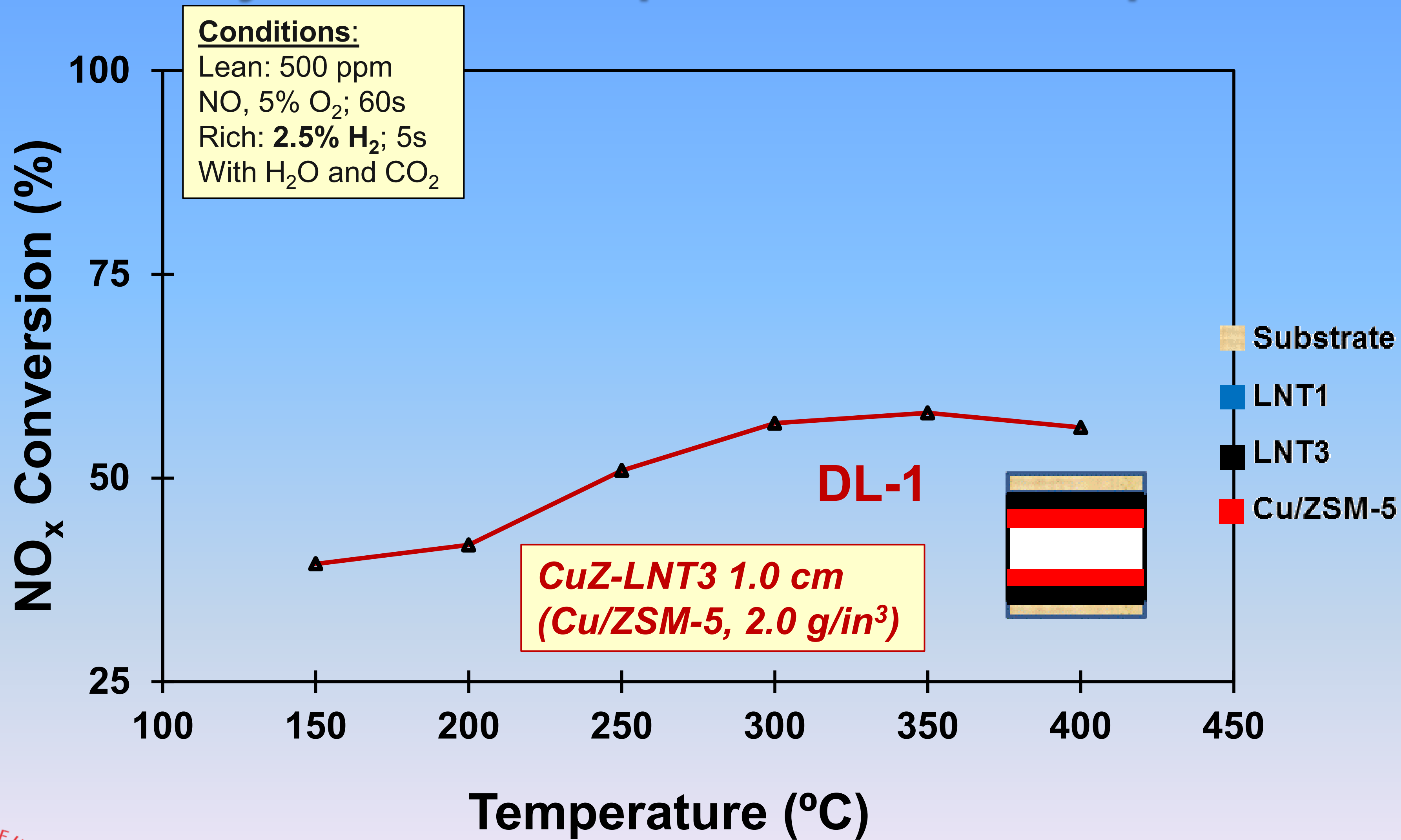


"Dual-Layer/Dual-Zone" Catalyst



- *Ceria zoning: achieves low temperature activity enhancement & minimized high temperature oxid. of NH_3*
- *Aged LNT upstream + Higher SCR loading beneficial*
  - *Lower PGM dispersion benefits NH_3 selectivity*
  - *Higher loading of SCR sustains high NOx conversion*
- *Further improvements with cycle timing*

Dual Layer vs. Sequential: Comparison



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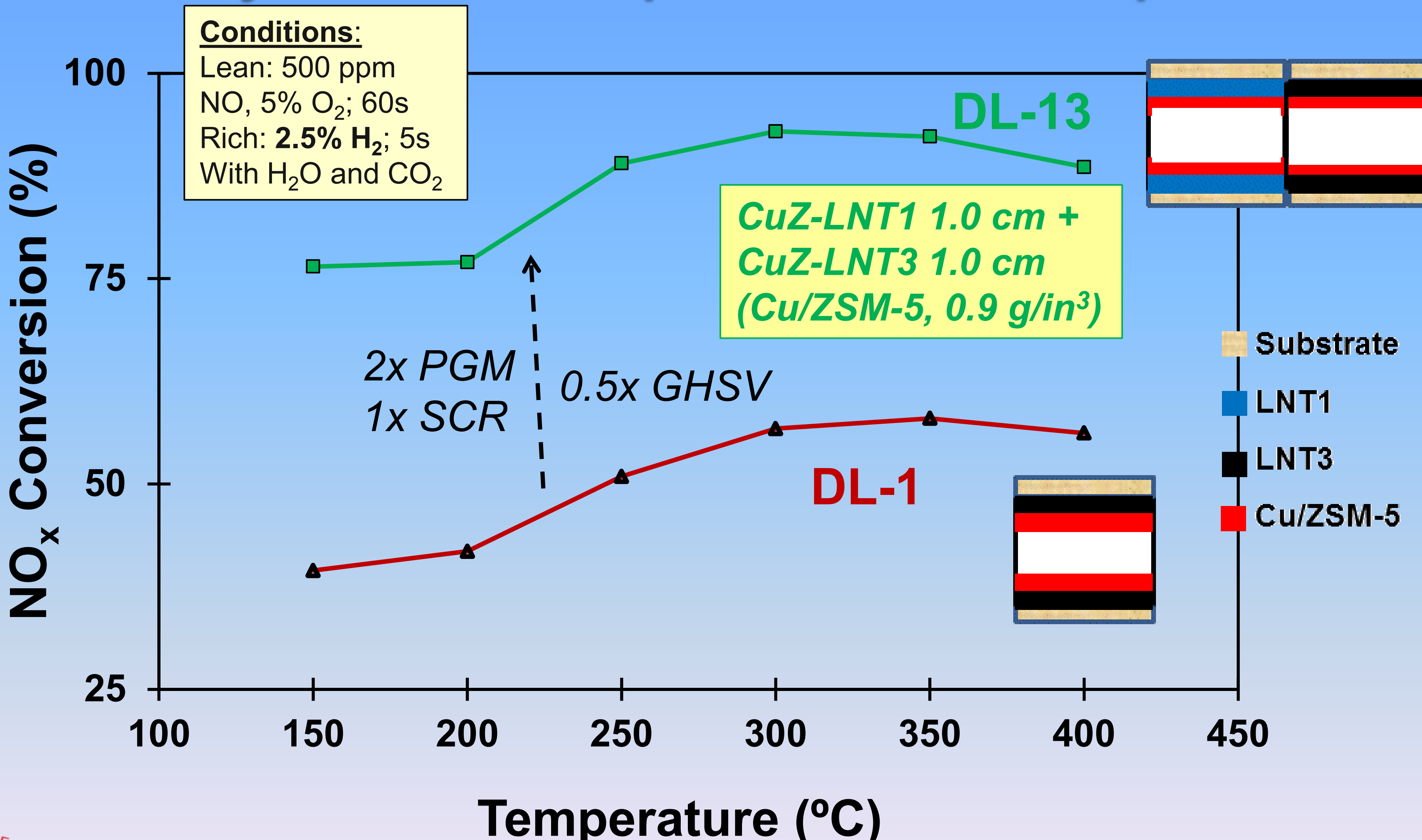

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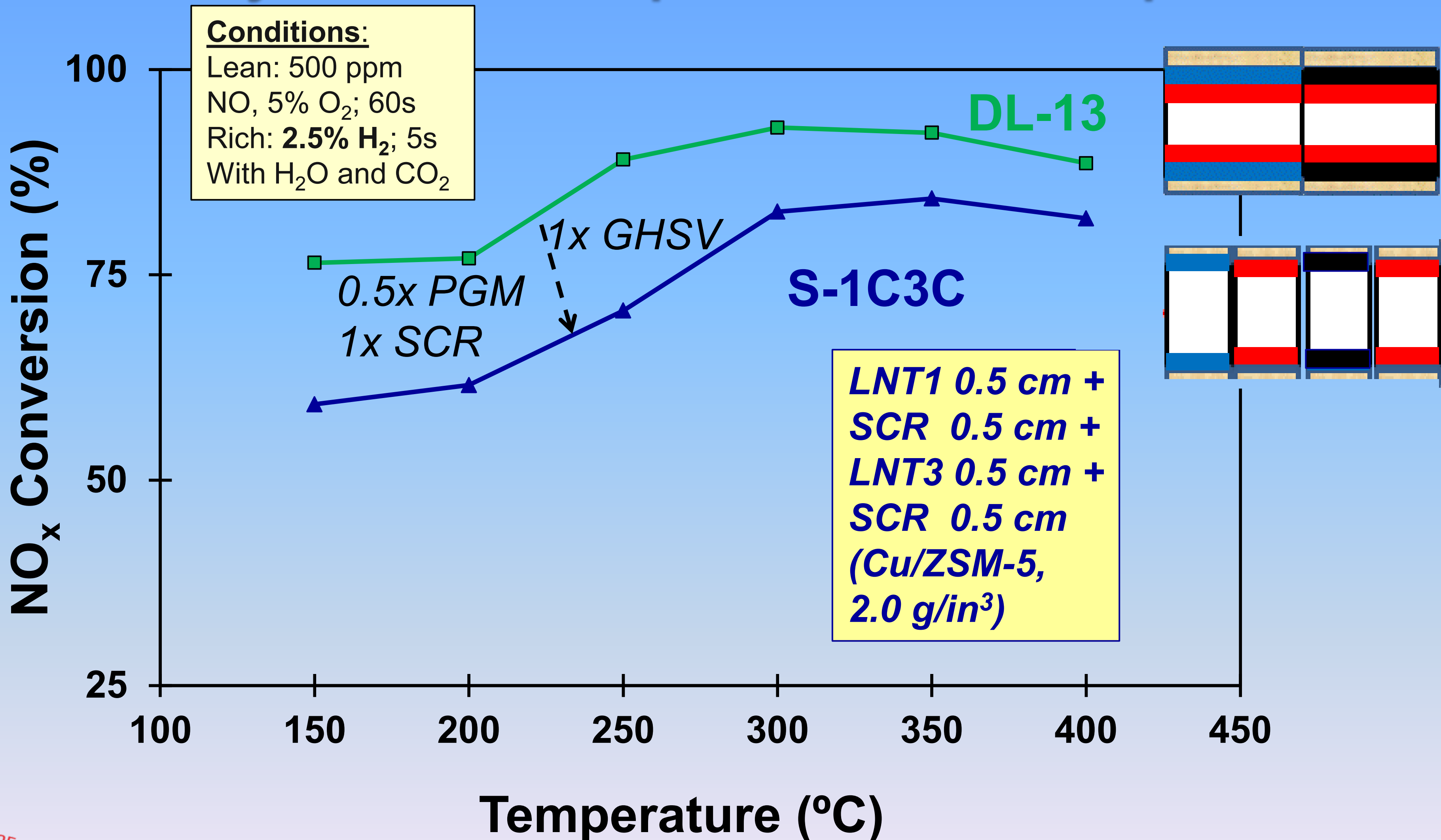

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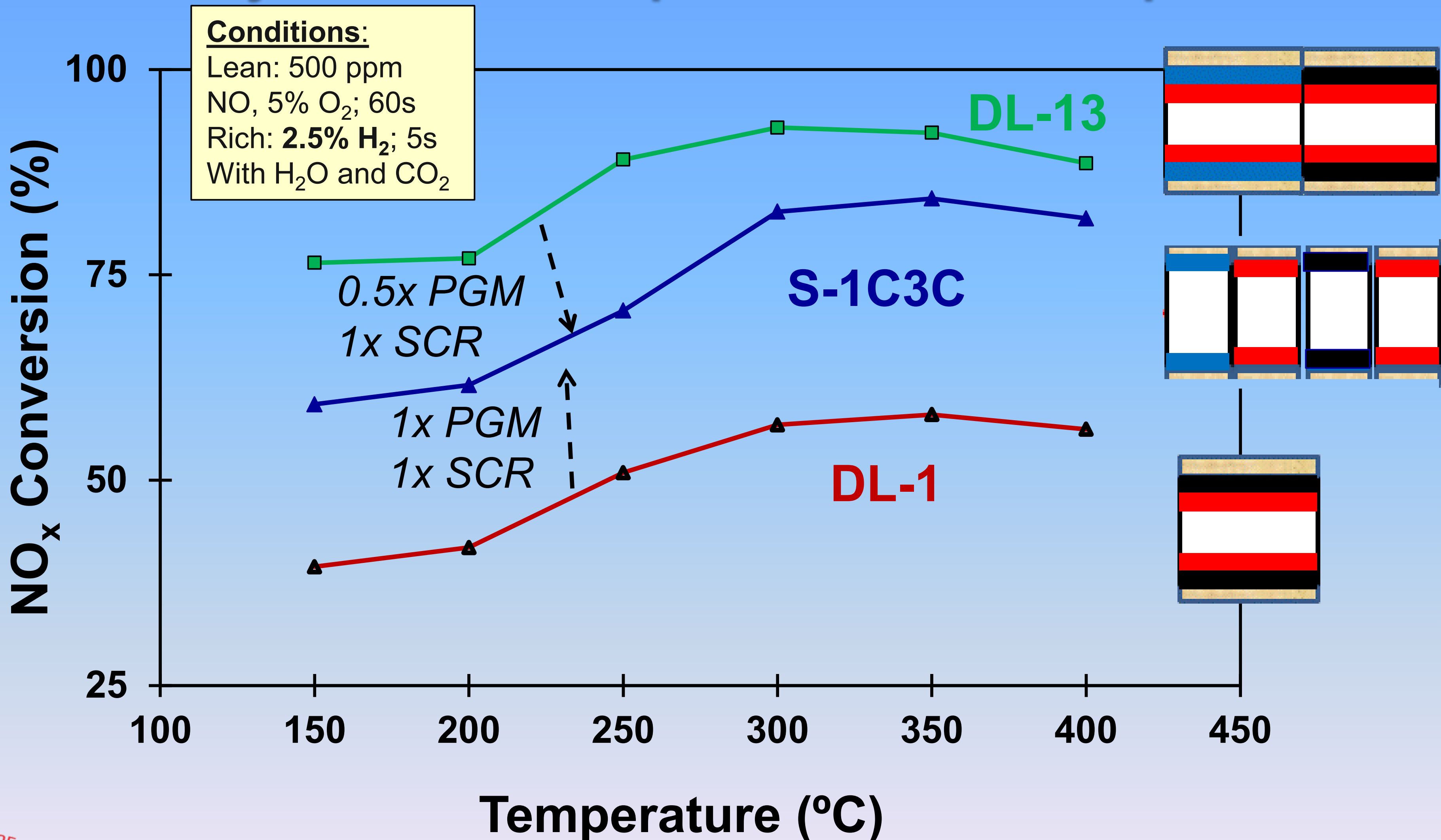

Dual Layer vs. Sequential: Factors

- LNT vs. SCR proximity:

More NH_3 oxidation on dual layer catalysts due to closer proximity of NH_3 storage and Pt sites

- Diffusion limitations:

Dual layer catalyst has more extensive diffusion limitations; SCR top layer inhibits transport to LNT bottom layer

Conclusions

- Dual-layer LNT/SCR works
  - Increased N_2 yield, decreased NH_3 yield
  - NOx conversion: depends on conditions & catalys
  - Close proximity of LNT and SCR functions important but segregated layers needed
- Ceria addition to LNT helps on many fronts
  - Low temperature conversion
  - Lessens effects of CO inhibition
  - Mitigates effects of thermal degradation
- Axial profiling & customized cycle timing hold promise
- Further opportunities for optimization

THANKS!

Introduction

Storage & Reaction on Multi-Functional Catalysts in Exhaust Aftertreatment

Method	Application	Reaction	Catalyst	Stored Species
TWC	Spark-ignited gasoline	H_2/CO/HC + O_2	Pt/Pd/Rh/CeO_2/Al_2O_3	O_2
DOC	Diesel	CO/HC + O_2	Pt/Pd/zeolite-β/Al_2O_3	High MW HC
DPF	Diesel	C + O_2/NO_2	Pt/cordierite	PM
NSR	Lean burn, Diesel	H_2/CO/HC + NOx	Pt/Rh/BaO/CeO_2/Al_2O_3	NOx
SCR	Diesel	NH_3 + NO +NO_2	Cu or Fe/zeolite	NH_3
NSR + SCR	Lean burn, Diesel	H_2/CO/HC + NOx NH_3 + NO +NO_2	Pt/Rh/BaO/CeO_2/Al_2O_3 Cu or Fe/zeolite	NH_3, NOx, HC
ASC	Diesel	NH_3 + O_2	Cu/zeolite + Pt/Al_2O_3	NH_3

M. Harold, Current Opinion in Chem. Eng., 1, 1-9 (2012)

Storage & Reaction on Multi-Functional Catalysts in Exhaust Aftertreatment

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DPF	Diesel	C + O_2/NO_2	Pt/cordierite	PM
NSR	Lean burn, Diesel	H_2/CO/HC + NOx	Pt/Rh/BaO/CeO_2/Al_2O_3	NOx
SCR	Diesel	NH_3 + NO +NO_2	Cu or Fe/zeolite	NH_3
NSR + SCR	Lean burn, Diesel	H_2/CO/HC + NOx NH_3 + NO +NO_2	Pt/Rh/BaO/CeO_2/Al_2O_3 Cu or Fe/zeolite	NH_3, NOx, HC
ASC	Diesel	NH_3 + O_2	Cu/zeolite + Pt/Al_2O_3	NH_3

M. Harold, Current Opinion in Chem. Eng., 1, 1-9 (2012)

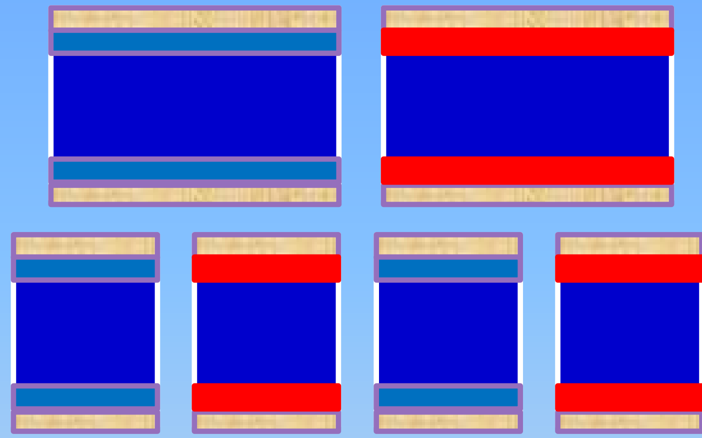
Collaborative Project Team

- **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

Different LNT-SCR Architectures

LNT-SCR series configuration

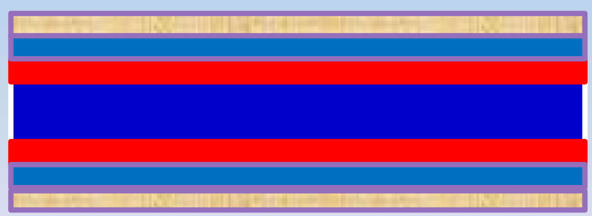
- Substrate
- LNT
- SCR



- Daimler
- Ford

LNT-SCR layered configuration

- Substrate
- LNT
- SCR

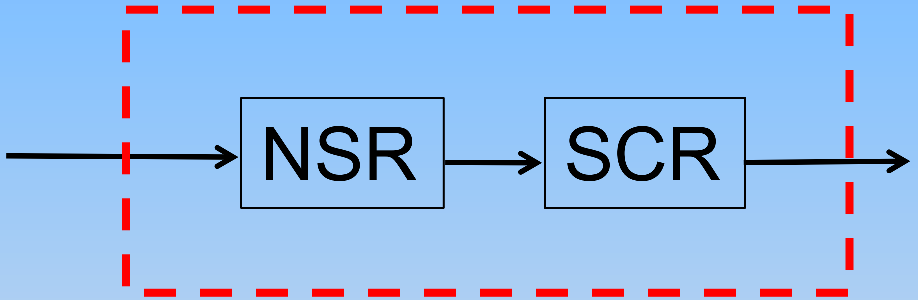


- Honda

Several architectures under investigation in DOE project

NSR/SCR Technology

- LNT/SCR is promising non-urea deNOx technology for light- & medium-duty diesel & lean burn gasoline
- Synergistic benefits of LNT/SCR have been demonstrated: Previous studies show increased NOx conversion by adding SCR unit downstream of LNT
- Understanding of the coupling between LNT & SCR series-brick configuration is emerging



NSR/SCR: A Different Role for the LNT

2 NO → **NSR** → 1.0 N_2

- NSR Target: 100% NOx conversion with 100% N_2 selectivity

LNT: $2\,NO + 4\,H_2 + O_2 \rightarrow N_2 + 4\,H_2O$

Objectives

- Gain understanding of impact of LNT-SCR multilayer architecture
- Determine impact of multilayer catalyst design variables and operating strategies
- Provide data to develop LNT-SCR models for design and optimization

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Learning. Leading.

Fundamental Issues/Questions

- What should be proximity between LNT and SCR functions?
- Does SCR layer always increase the overall NOx conversion or could it reduce it (e.g. serve as diffusion barrier)?
- What are the optimal thicknesses and compositions of the LNT and SCR layers? Pt dispersion? Ceria? Fe- or Cu-zeolite?
- What about thermal durability? What about migration of Pt from LNT layer to SCR layer?
- How does the dual layer compare to sequential monolith configuration?

our goal is to answer some of these questions…

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Summary of Results w/o CO_2 & H_2O*

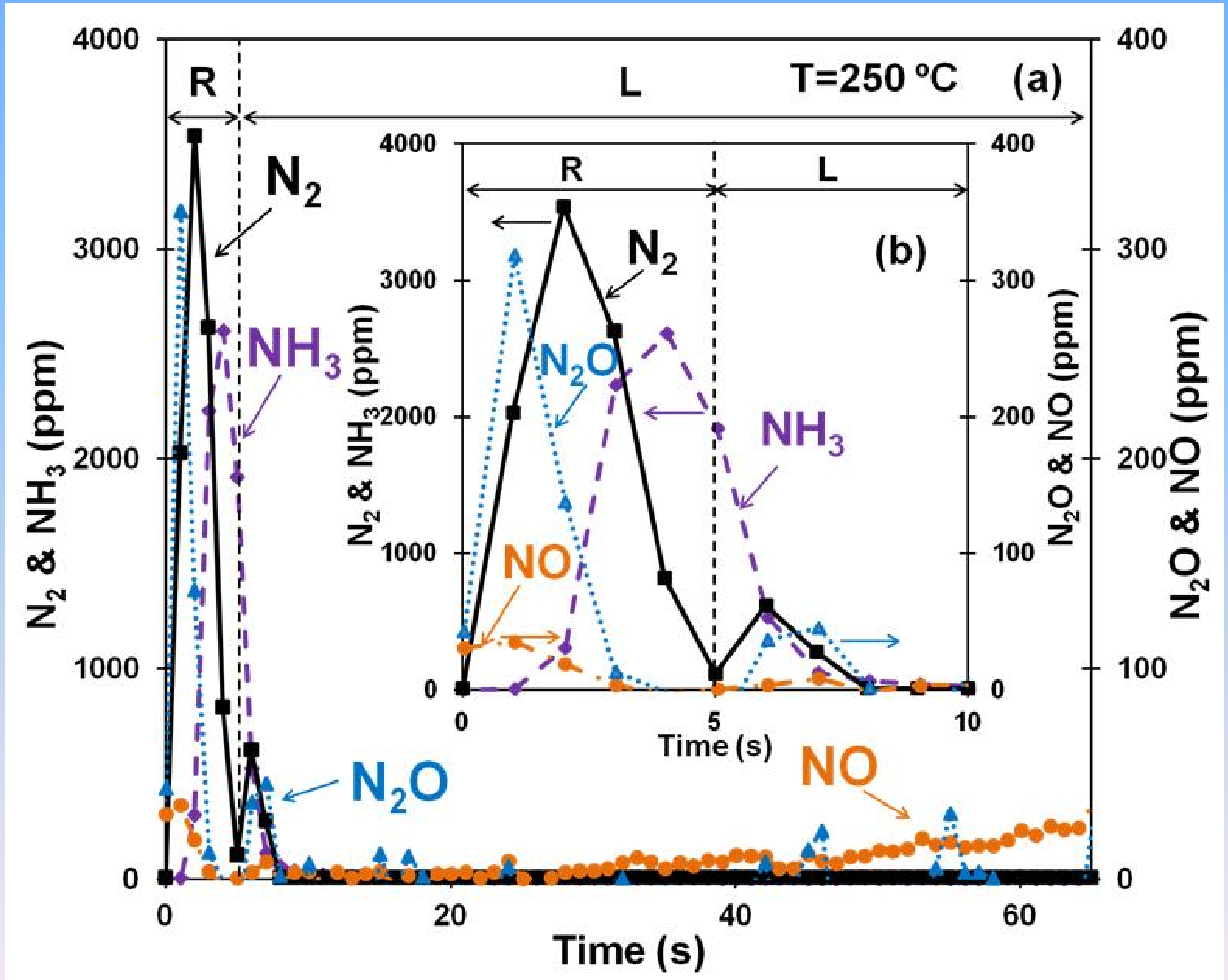
- Without H_2O & CO_2 in feed, LNT/SCR has slightly lower NO conversion than LNT only
- At low temperatures (< 225 ^oC) most reaction occurs in LNT layer with generated NH_3 effectively trapped by Cu-zeolite; trapped NH_3 desorbs to Pt layer & is oxidized to N_2O
- At higher temperatures (> 250 ^oC) undesired oxidation of NH_3 on Pt (to N_2O & NO) occurs

*Reference: Liu, Y., M.P. Harold, and D. Luss, Appl. Catal. B. Environ. 121-122 (2012) 239-251

Results w/o CO_2 & H_2O

Typical Lean-Rich Cycle for PGM/BaO (LNT1)

Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
Temperature: 250°C

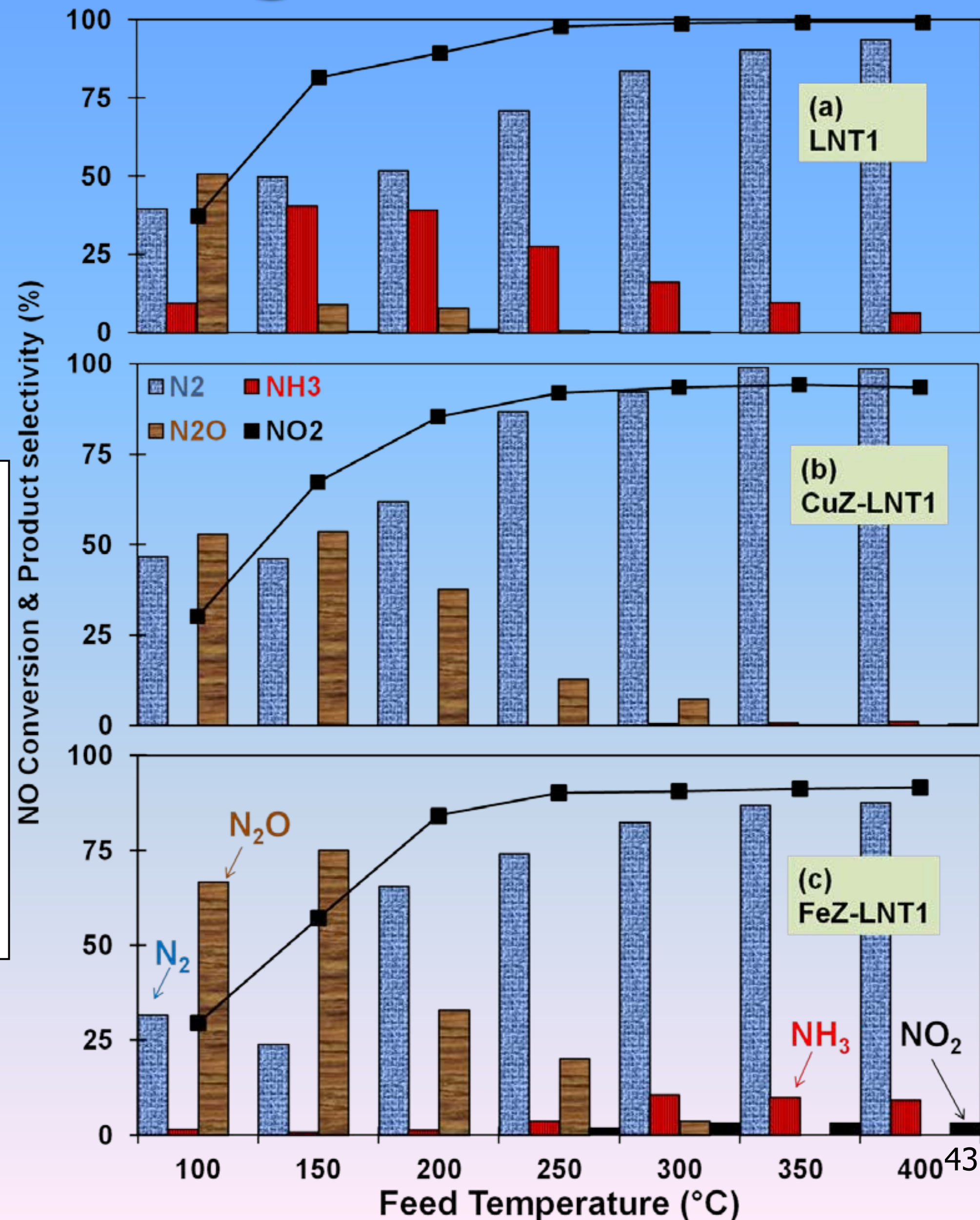


LNT vs. LNT/SCR: Integral Results

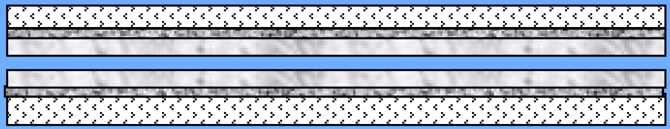
<u>Conditions:</u>
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
No CO_2 or H_2O in feed

LNT1 + CuZ:

- ***Slight decrease in NOx conversion***
- ***Consumption of NH_3***
- ***Some increase in N_2O***
- ***Better catalyst than LNT1 + FeZ***



Dual Layer LNT/SCR Catalysts

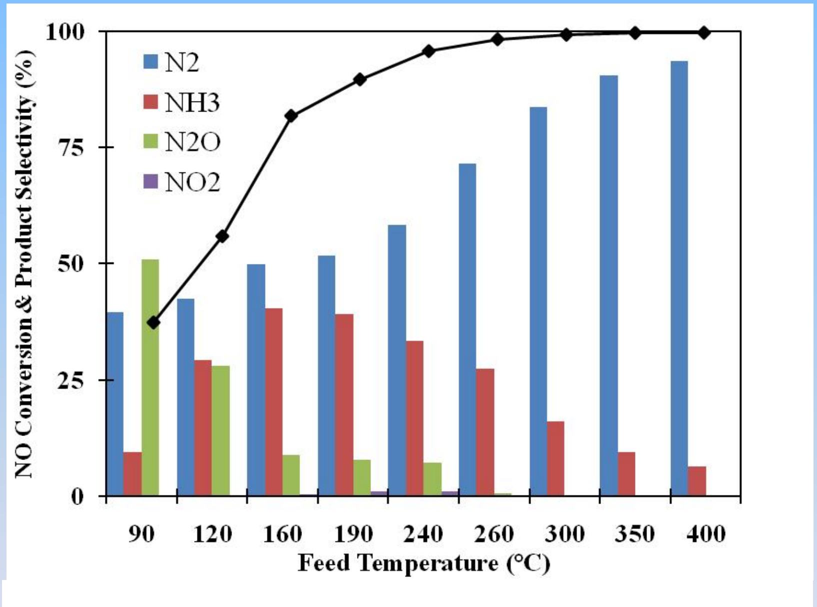


- Dual layer LNT/SCR catalyst comprises:

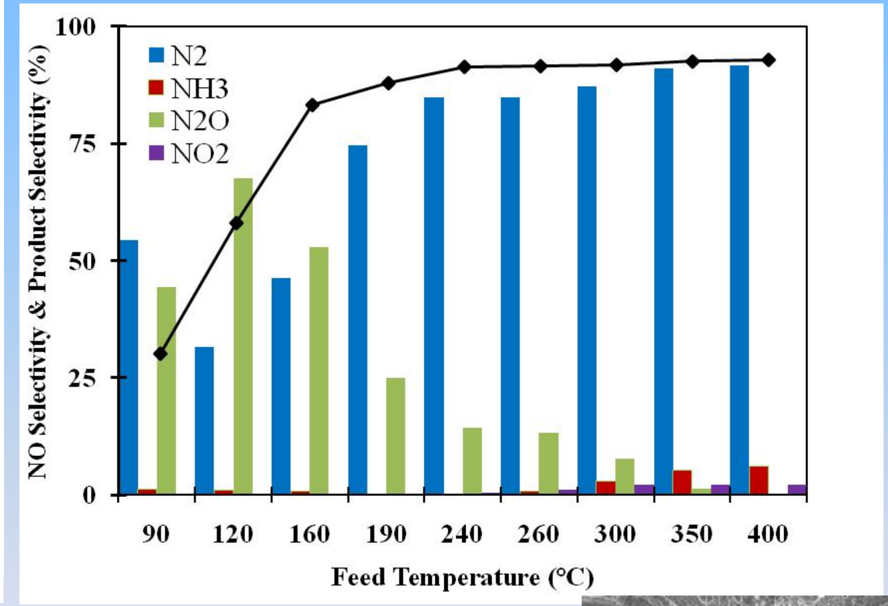
  Bottom layer: Pt/Rh/BaO/alumina — 0.7wt.%/0.07wt.%/20wt.%

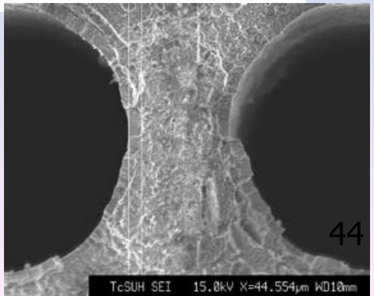
  Top layer: Fe-ZSM-5/alumina — 3-3.5 wt.% (10% washcoat loading)

LNT only



LNT/SCR (Fe-ZSM-5)





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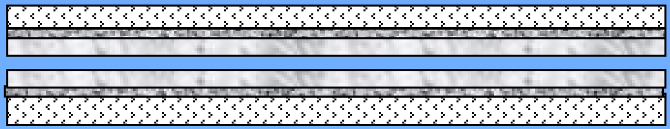
Dual Layer LNT/SCR Catalysts



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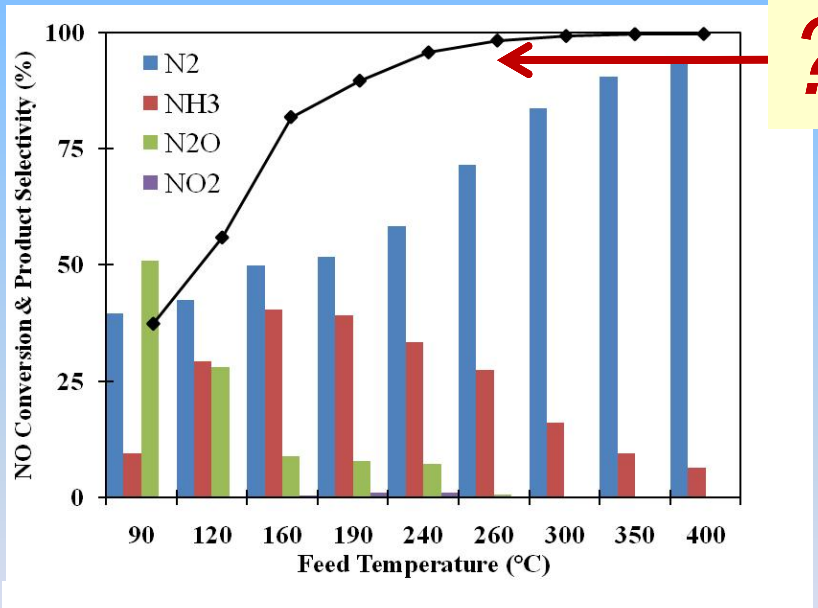
LNT only



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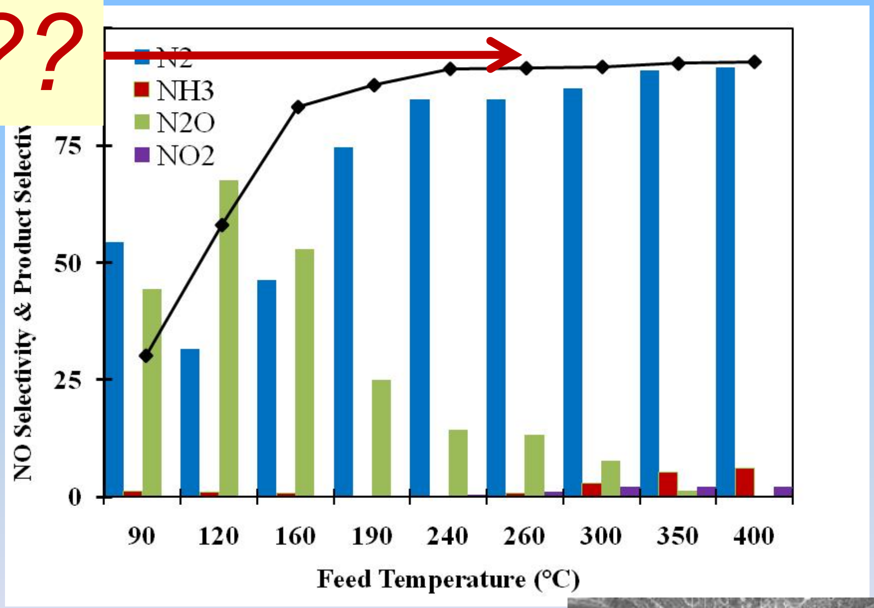
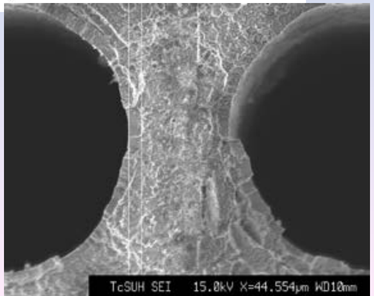
LNT/SCR (Fe-ZSM-5)



Dual-layer catalyst: reduced NH_3, increased N_2O, but a small reduction in NOx conversion!



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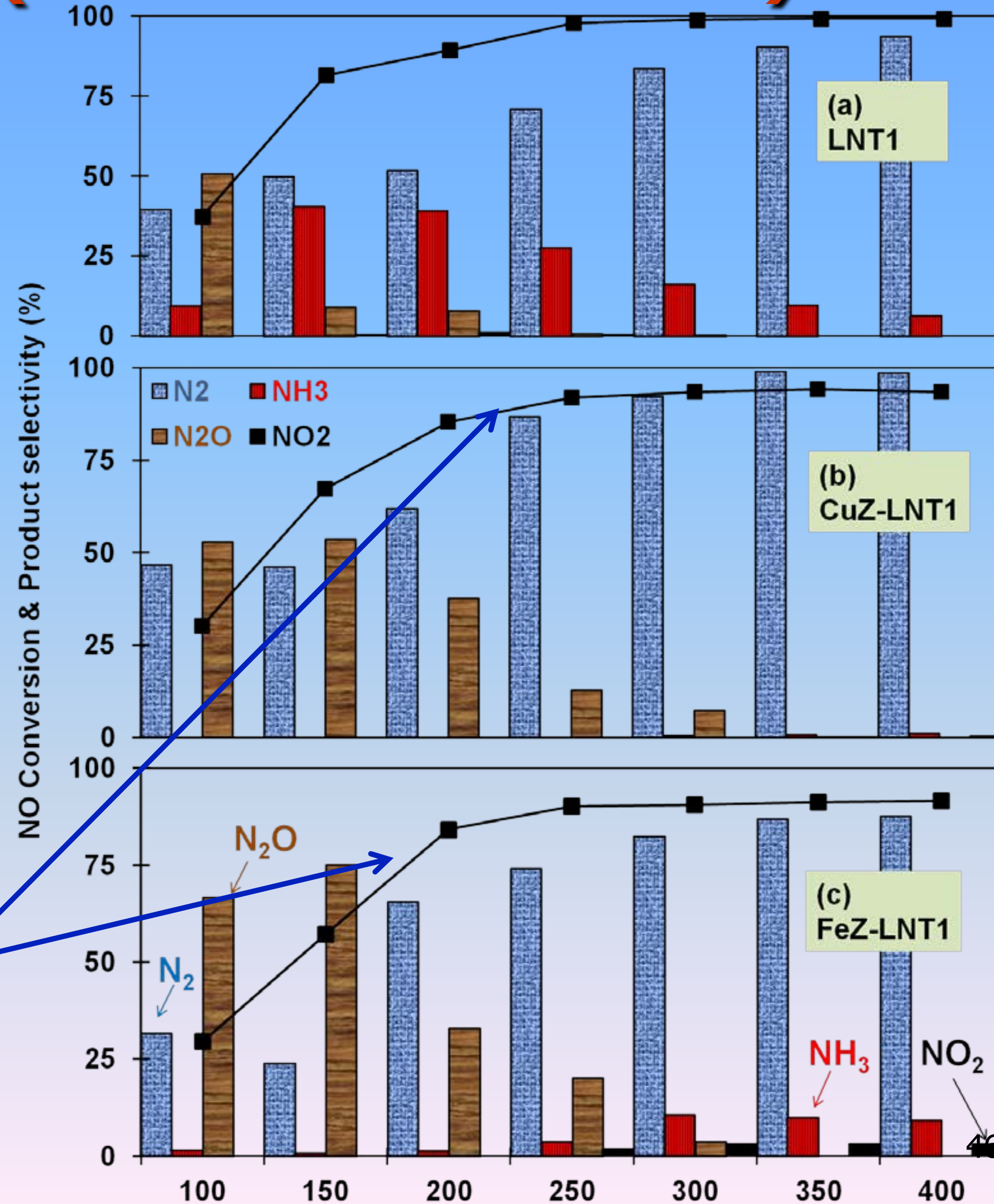
Comparison: LNT vs. LNT/SCR (Fe- or Cu-ZSM5)

<u>Conditions:</u>
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
No CO_2 or H_2O in feed

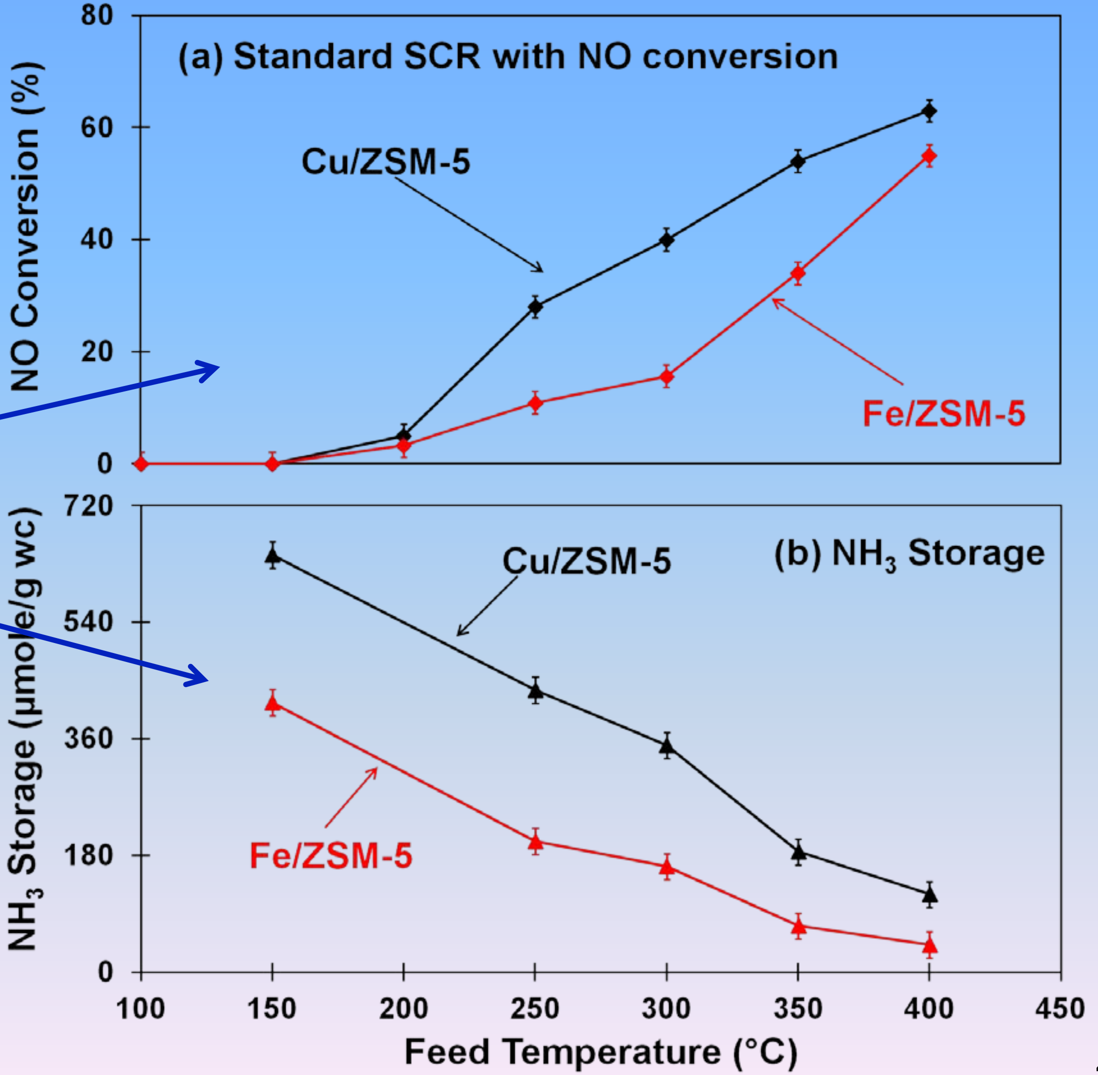
Cu/ZSM5 out-performs Fe/ZSM5 under identical conditions



Comparison of Fe/ZSM5 and Cu/ZSM5

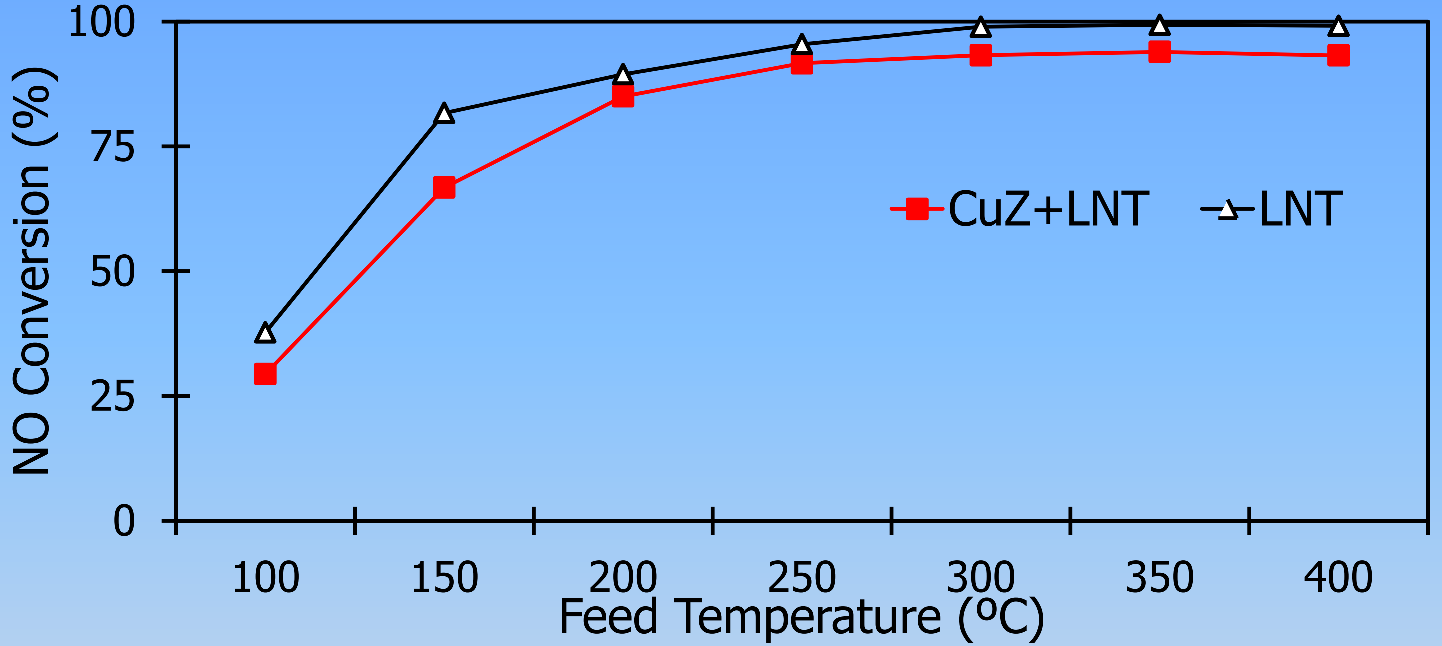
Conditions:
500 ppm NO, 5% O_2
500 ppm NH3

Fe/ZSM-5 has lower standard SCR activity & NH_3 storage capacity

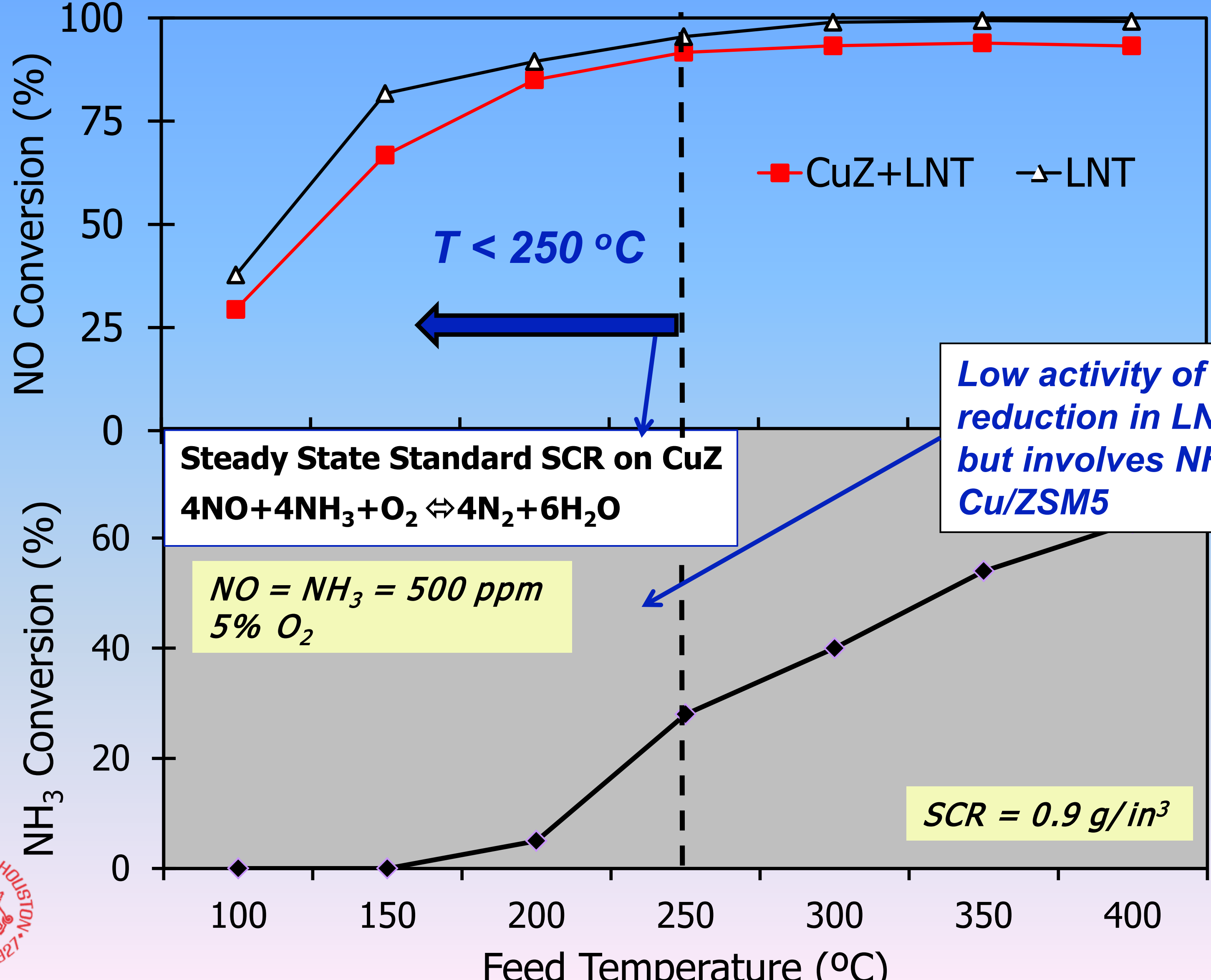


Conditions:
500 ppm NH_3
20 minute storage

Low Temperature LNT/SCR Behavior

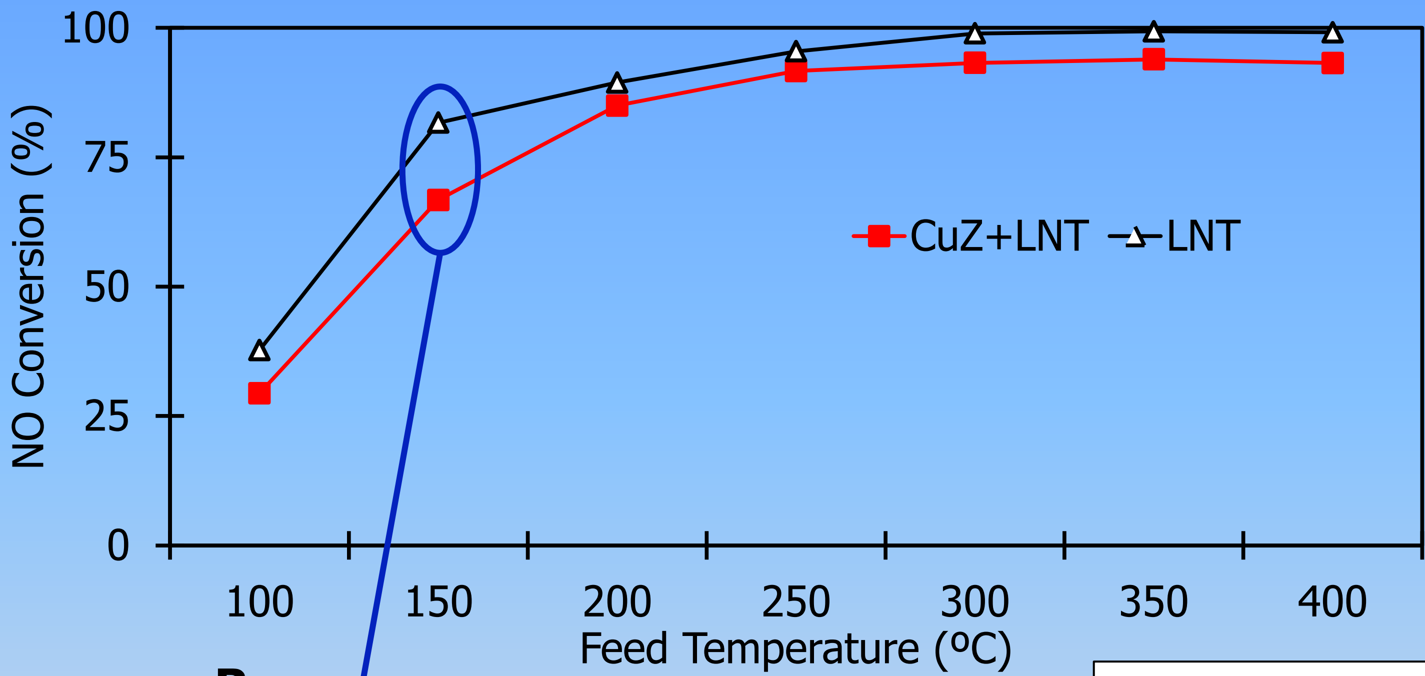


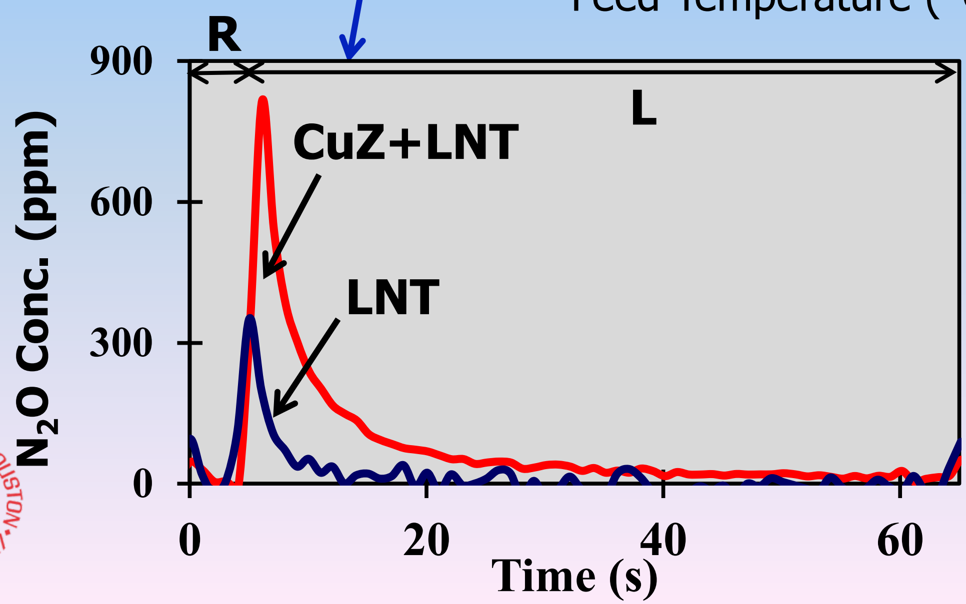
Low Temperature LNT/SCR Behavior



Low activity of CuZ …. NOx reduction in LNT layer mostly but involves NH_3 trapped in Cu/ZSM5

N_2O Formation at Low Temperature





__Pathway:__

NH_3 trapped on zeolite

⇩

NH_3 migration to LNT

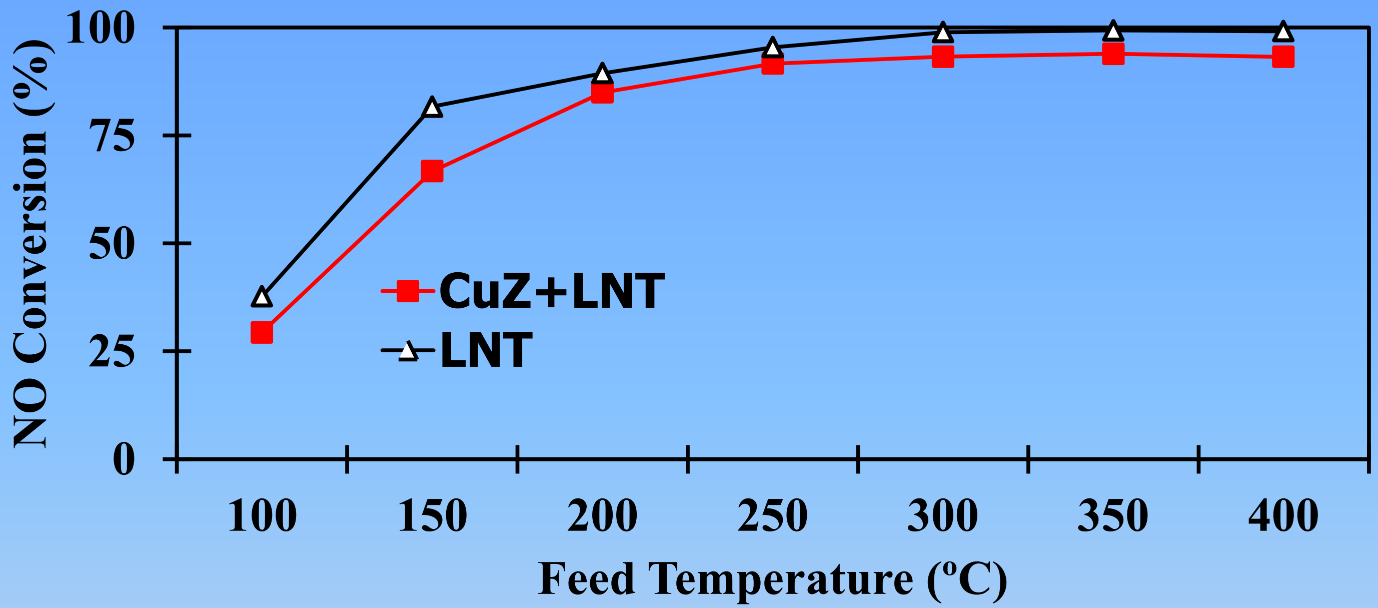
⇩

$NH_3 + O_2$ & NO on LNT

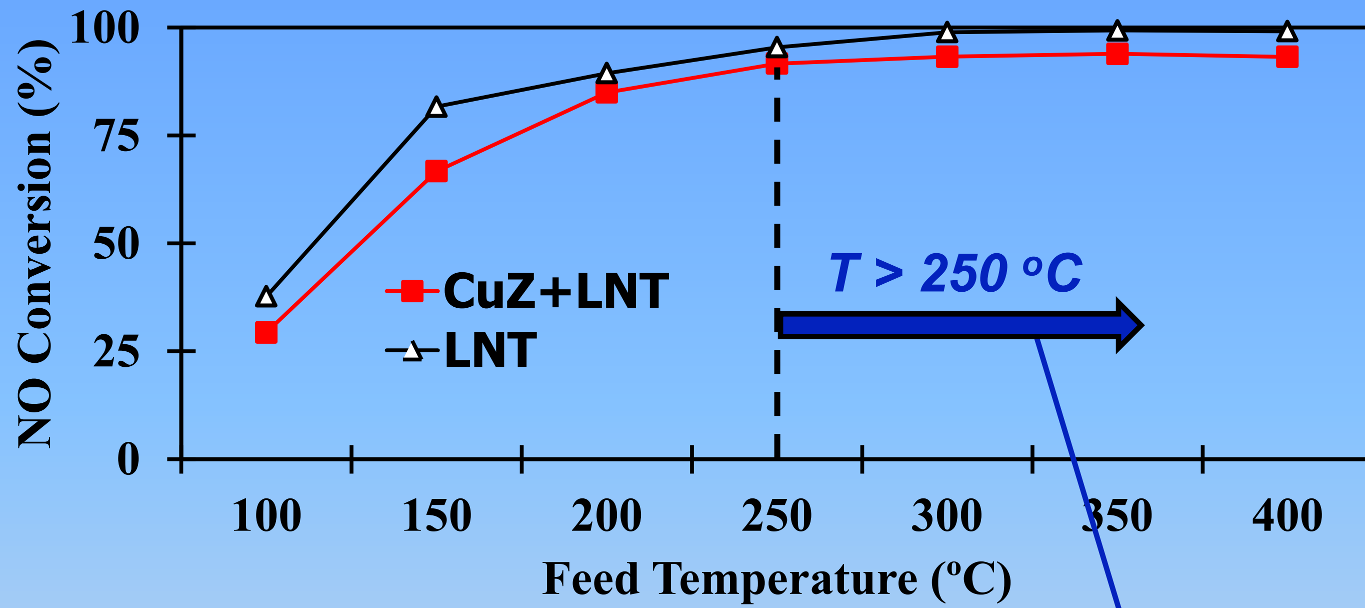
⇩

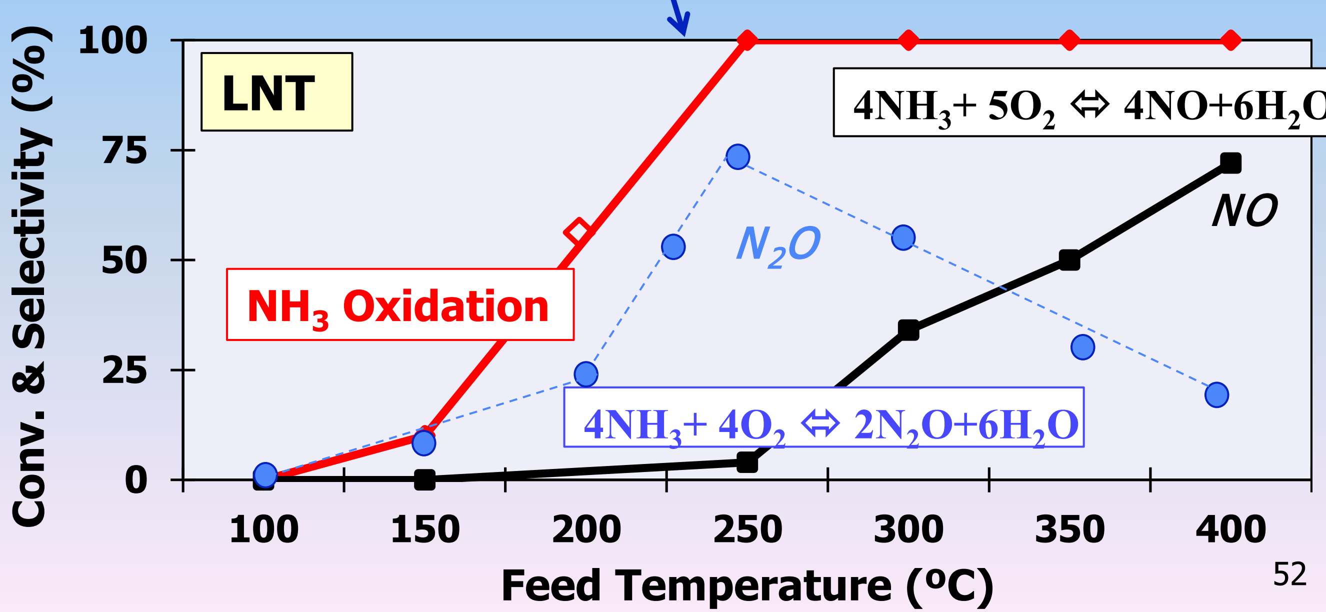
N_2O & N_2

NH_3 Oxidation to NOx at High Temp.



NH_3 Oxidation to NOx at High Temp.





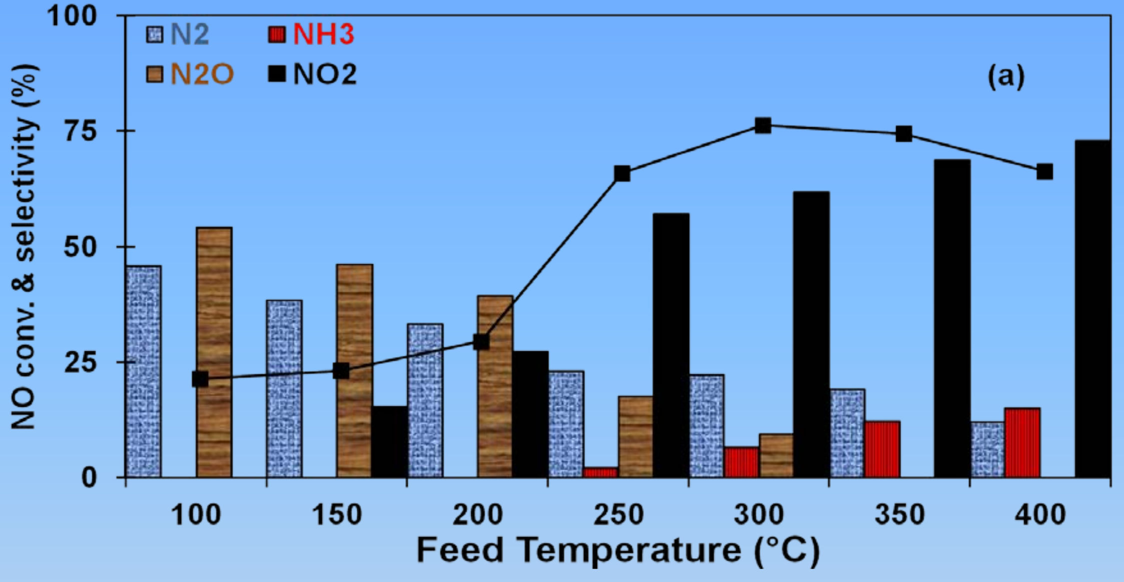
NH_3 oxidation in LNT layer involving NH_3 trapped by CuZ

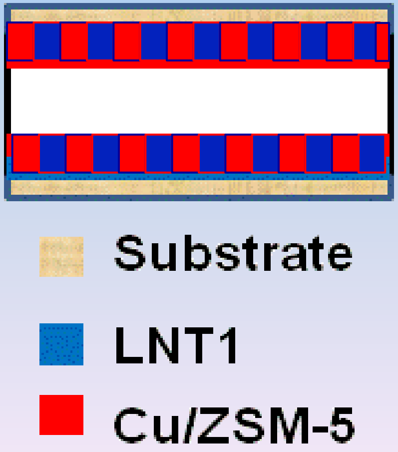
Mixed Washcoat Results

Mixed Washcoat Performance

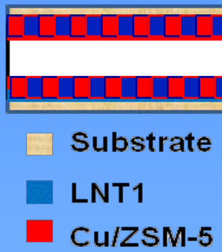
<u>Conditions:</u>
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
Temperature: 250°C

<u>Washcoat:</u>
Physical mixture of LNT1 & CuZ
2.1 g/in³ LNT1, 0.9 g/in³ CuZ





Mixed Washcoat Performance

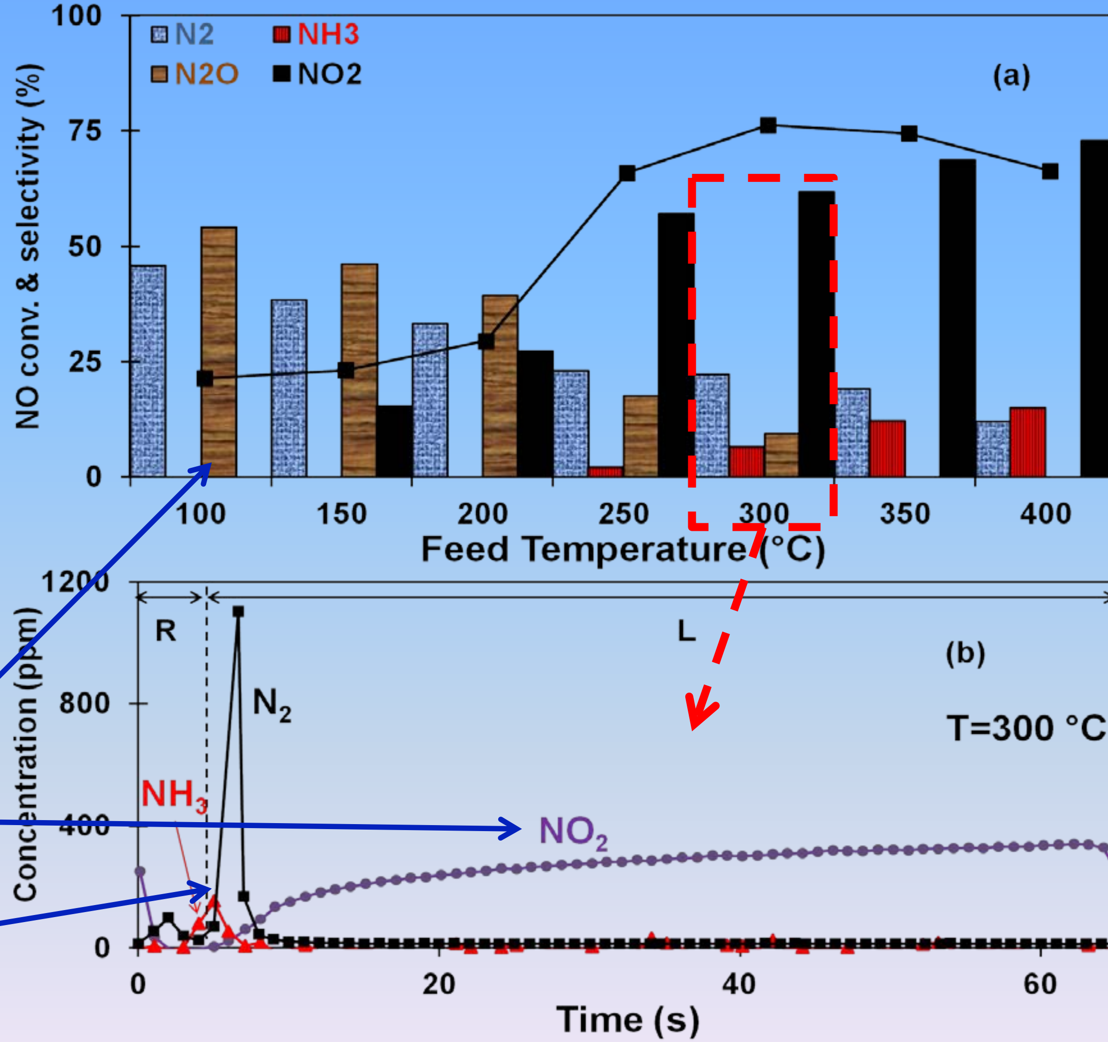


Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s
Temperature: 250°C

Washcoat:
Physical mixture of LNT1 & CuZ
2.1 g/in^3 LNT1, 0.9 g/in^3 CuZ

LNT & Cu/ZSM5 mixture:

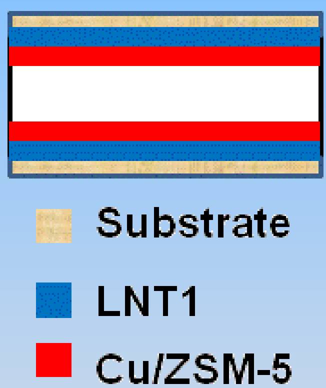
- *significant N_2O at low T*
- *significant NO_2 generation & breakthrough*
- *most N_2 made during lean*

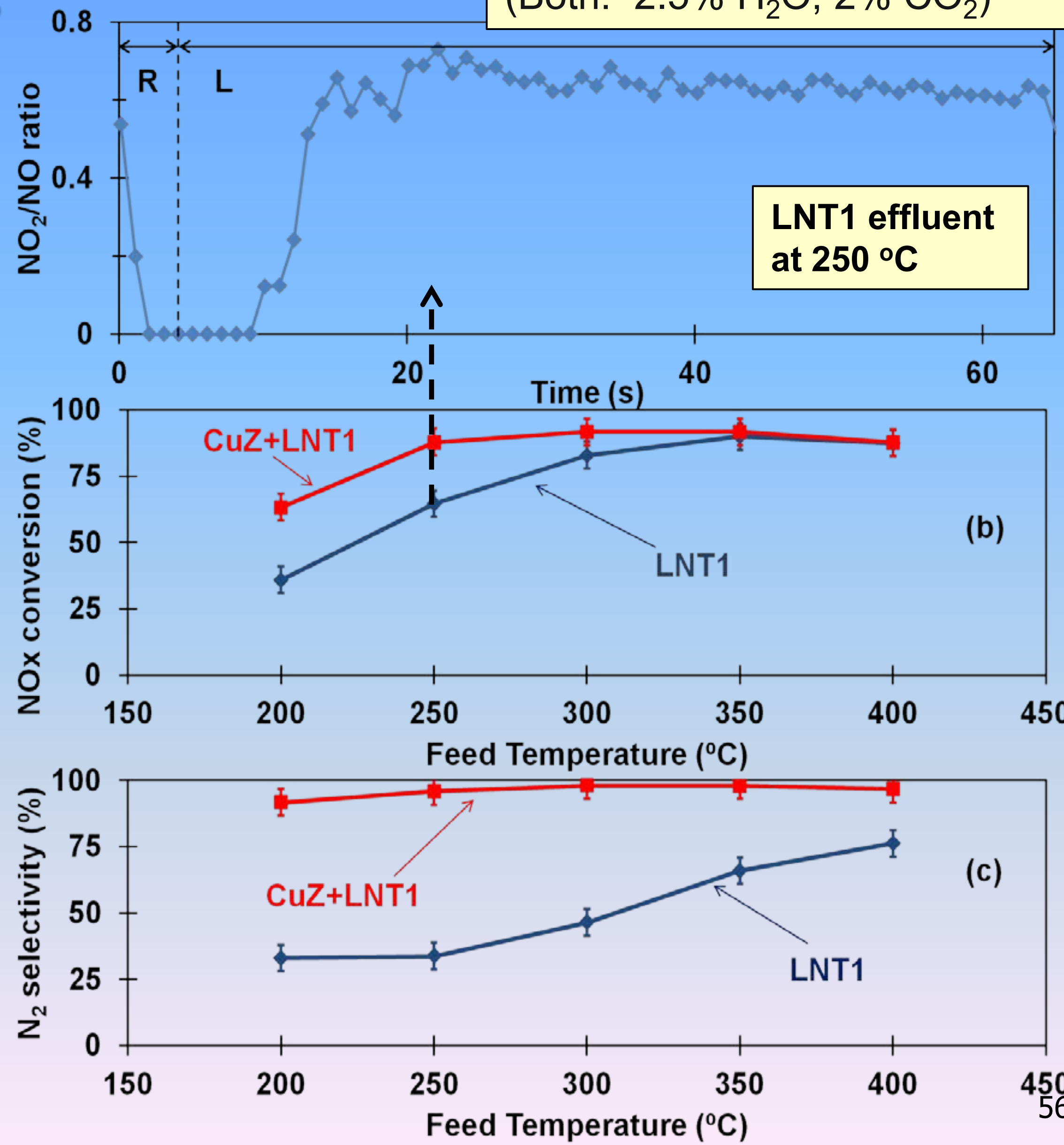


Liu, Y., M.P. Harold, and D. Luss, Appl. Catal. B. Environ. 121-122 (2012) 239-251

LNT/SCR: H_2 Reductant in Presence of CO_2 & H_2O

<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/SCR: Favorable NO_2/NOx ratio for SCR

$CO + H_2$ Results

Experiments

Reductant	CO_2 + H_2O?	Dual Layer Catalyst
H_2	No	LNT1/Cu-ZSM5, Fe-ZSM5
H_2	No	LNT1/Cu-ZSM5 (mixed layer)
H_2	Yes	LNT1/Cu-ZSM5
H_2 + CO	Yes	LNT1/Cu-ZSM5
H_2 + CO	Yes	LNT2/Cu-ZSM5
H_2 + CO	Yes	LNT3/Cu-ZSM5
H_2 + CO	Yes	LNT1+LNT3/Cu-ZSM5

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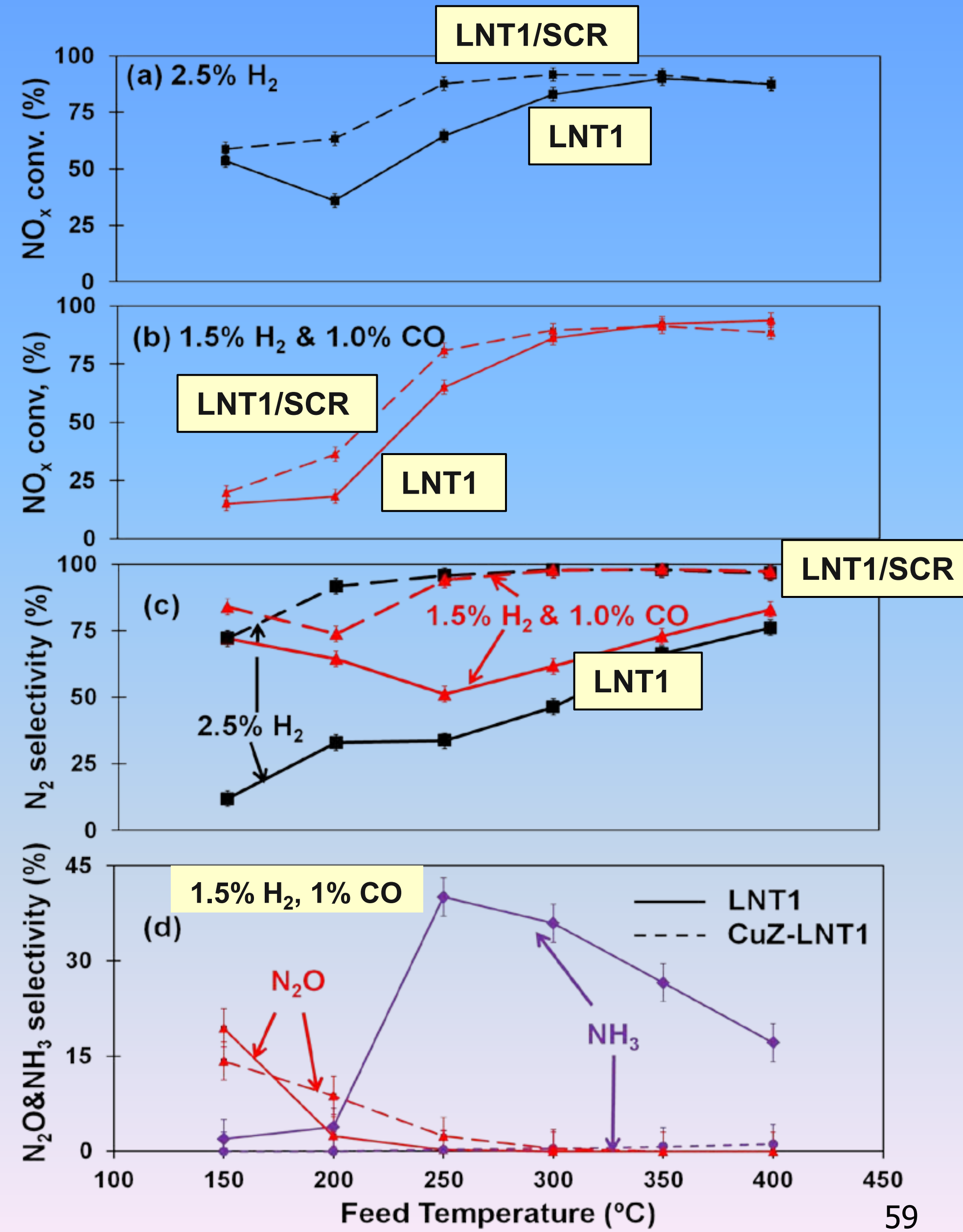
LNT/SCR with CO + H_2 Reductant

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)

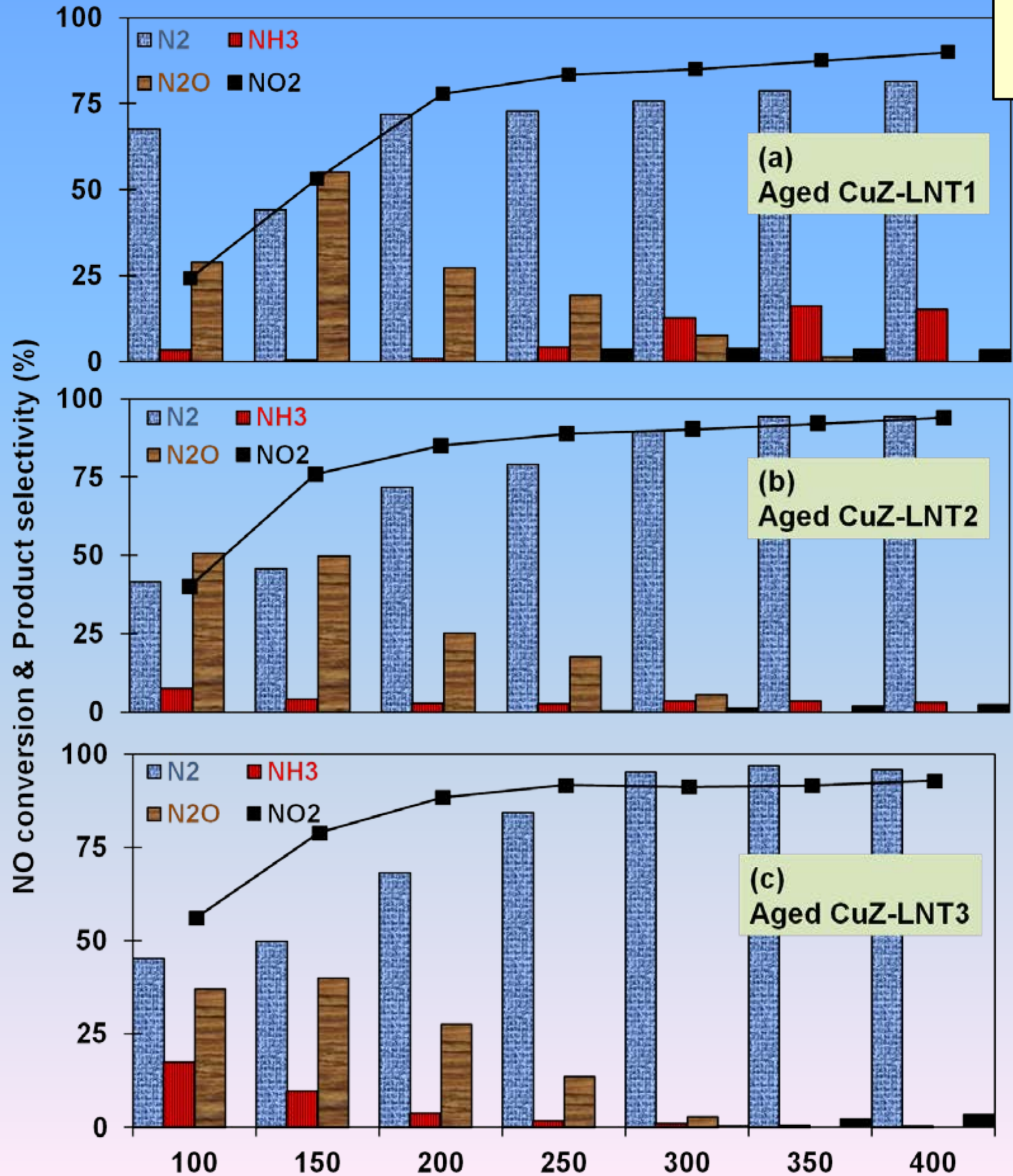


LNT: Overall lower NOx conversion with CO in feed

LNT/SCR: Increase in NOx conversion & N_2 selectivity

Ceria Loading Effect

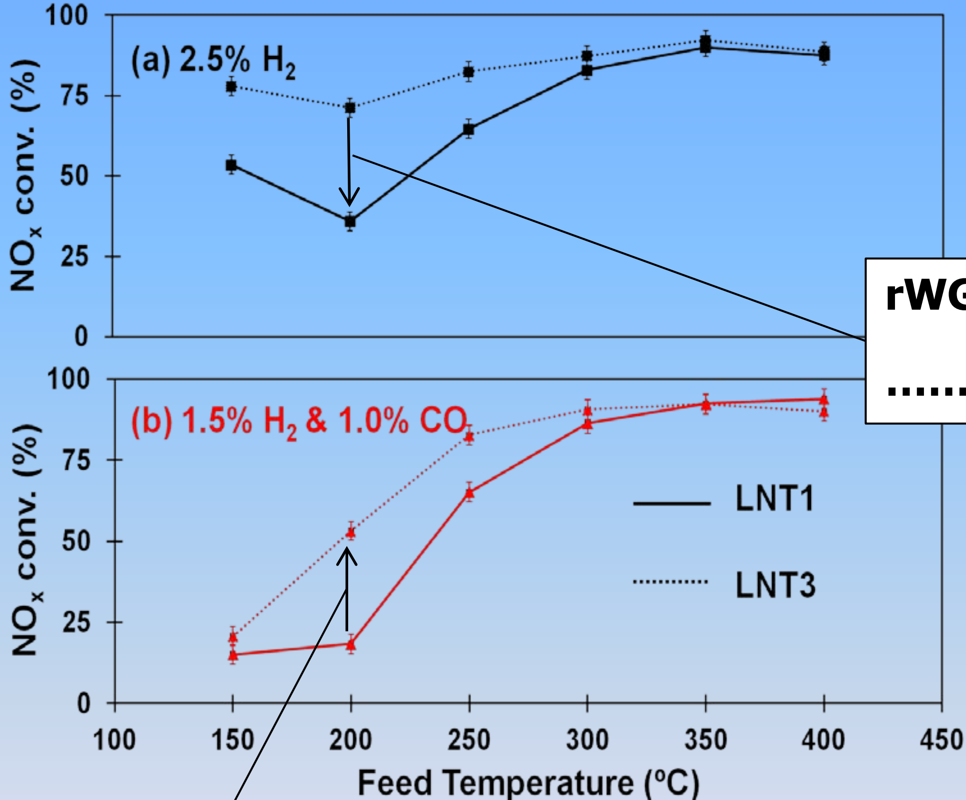
Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s



Ceria Additon

LNT: Impact of CeO_2 Addition

<u>Conditions:</u>
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)



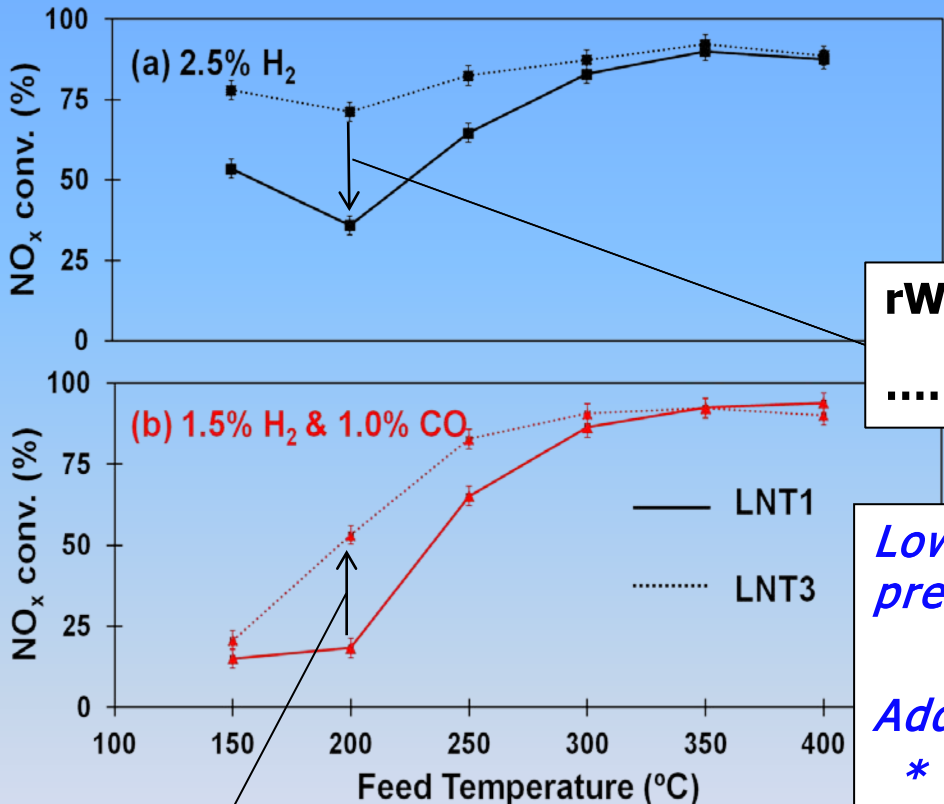
rWGS: $H_2 + CO_2 \leftrightarrow H_2O + CO$

……. CO adsorbs on Pt crystallites

WGS: $H_2O + CO \leftrightarrow H_2 + CO_2$

……. Cleans off Pt crystallites

LNT: Impact of CeO_2 Addition



<u>Conditions:</u>
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)

rWGS: H_2 + CO_2 ←→ H_2O + CO

……. CO adsorbs on Pt crystallites

Lower temperature performance not good in presence of CO – requires addl. measures

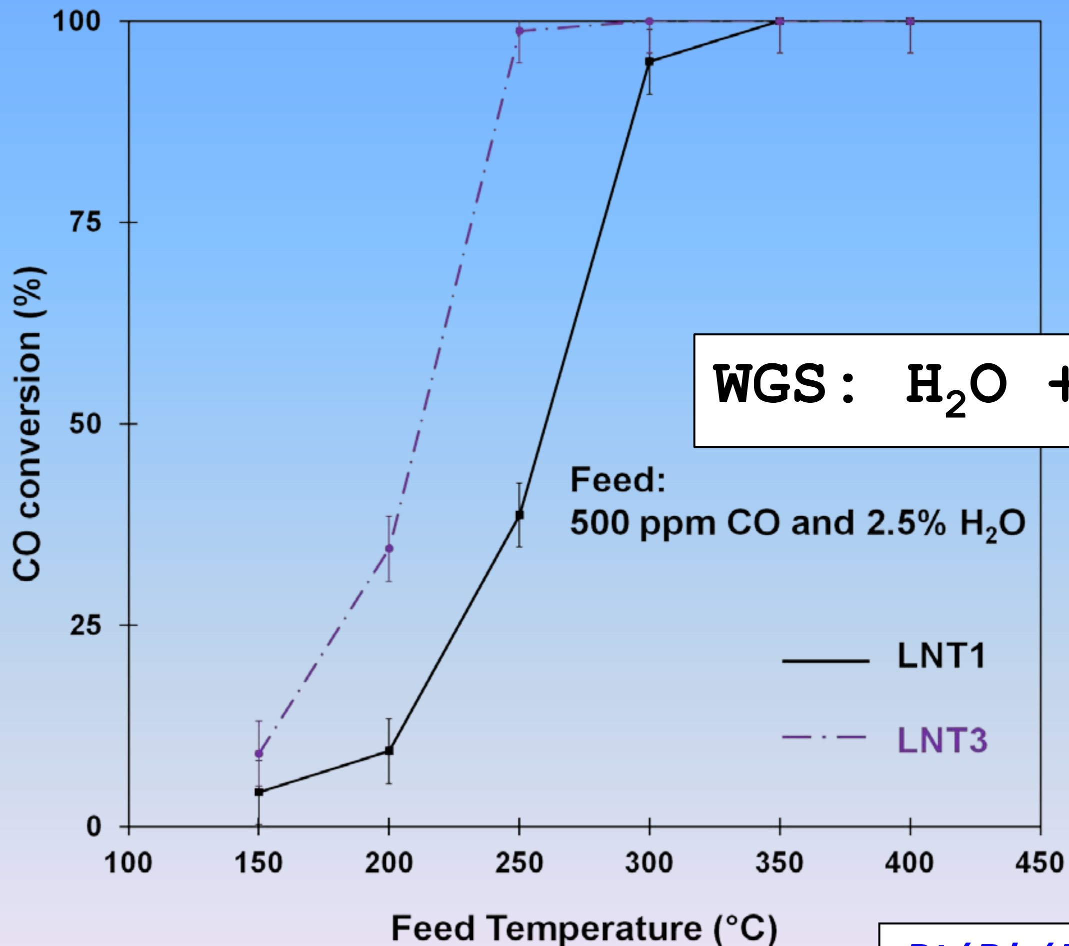
Addition of CeO_2 to LNT beneficial:

* *Provides additional NOx storage sites*
* *Mitigates CO inhibition*
* *Promotes WGS chemistry*

WGS: H_2O + CO ←→ H_2 + CO_2

……. Cleans off Pt crystallites

CeO_2 Promotion of WGS Reaction

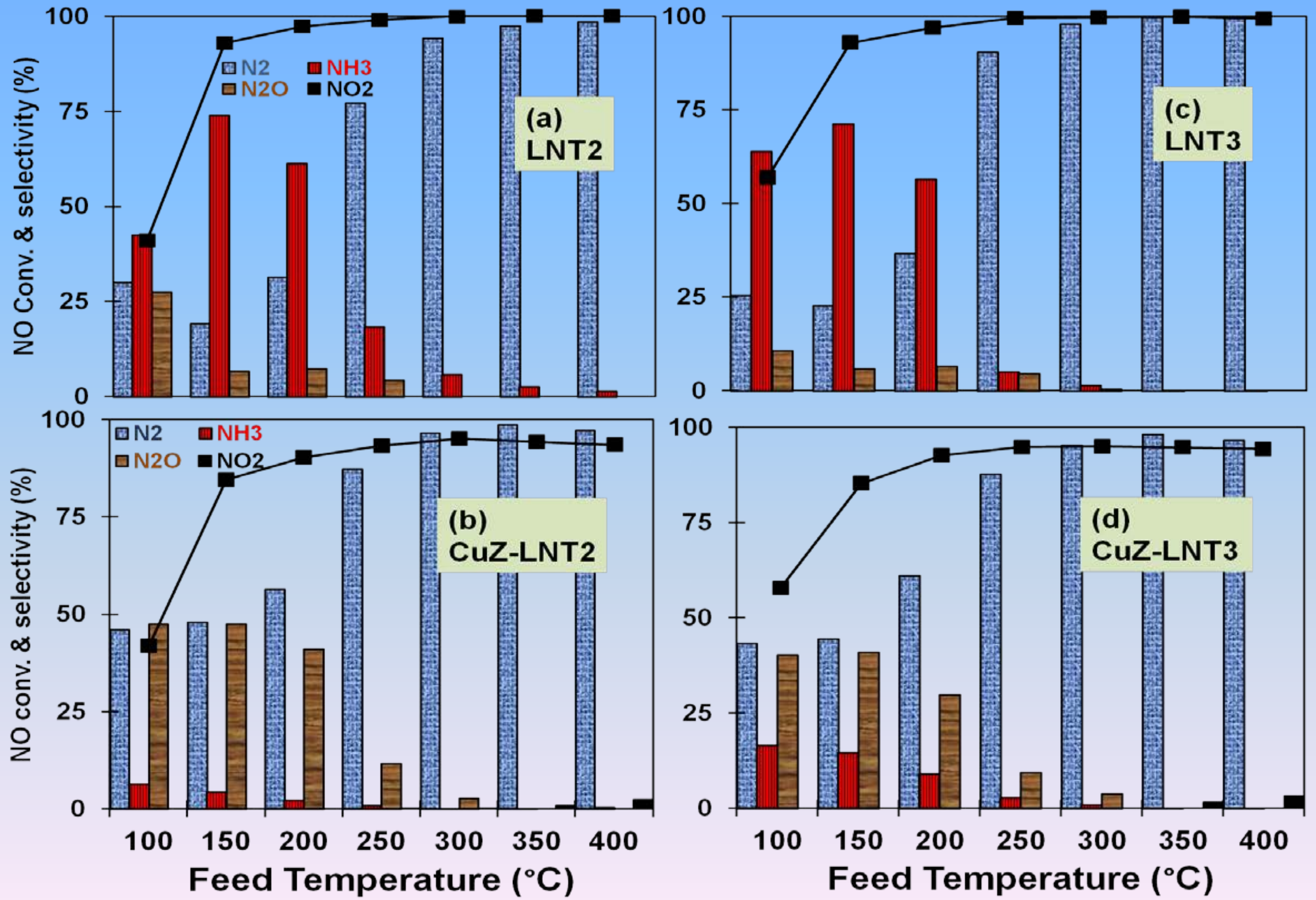


WGS: $H_2O + CO \leftrightarrow H_2 + CO_2$

Pt/Rh/BaO/CeO_2 catalyst exhibits enhanced water gas shift activity

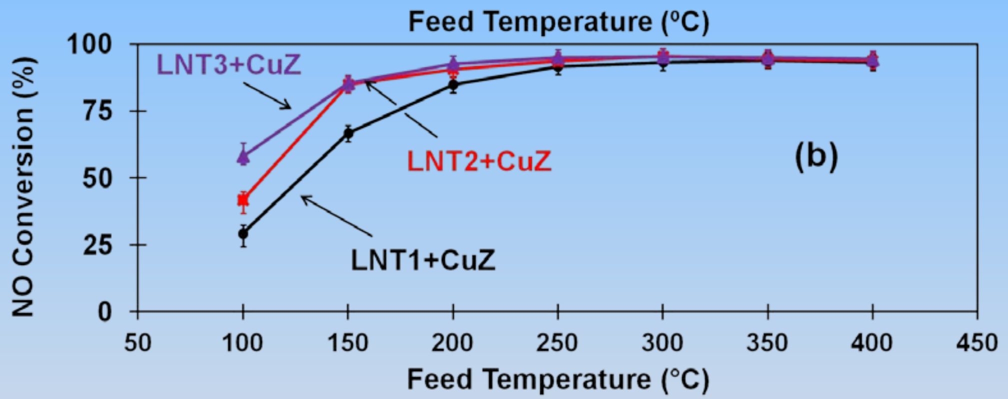
Comparison of LNT2 & LNT3: Ceria Loading Effect

Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s



Effect of Ceria on LNT/SCR

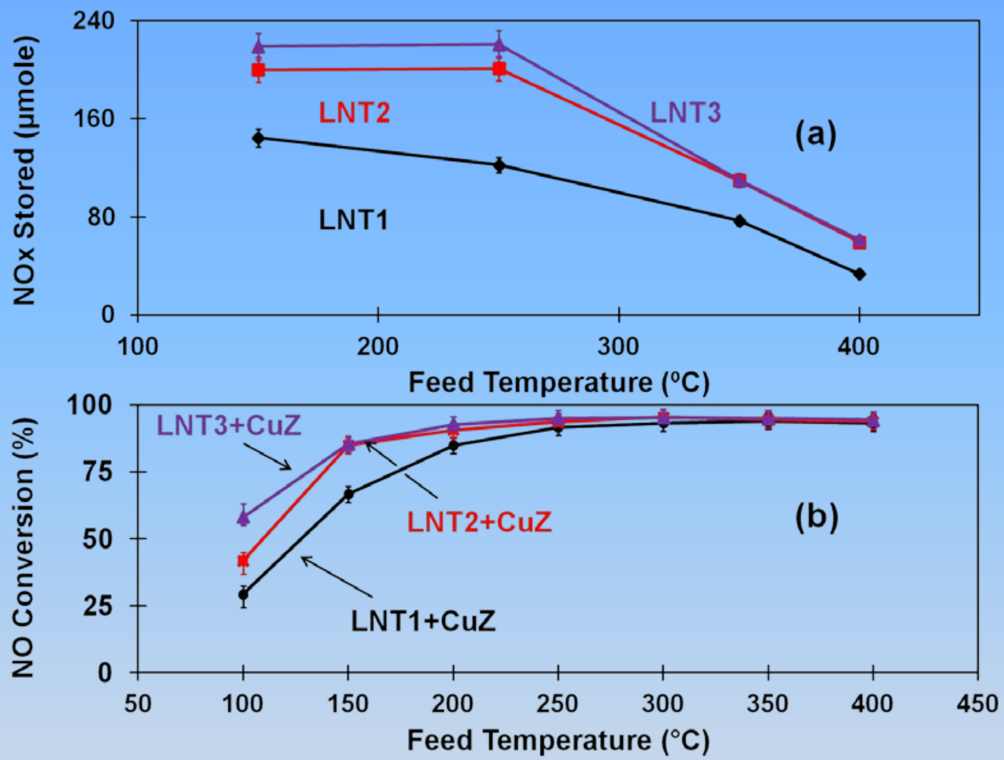
Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s



Ceria increases cycle-averaged NO conversion at low temperature

Effect of Ceria on LNT/SCR

<u>Conditions:</u>
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s

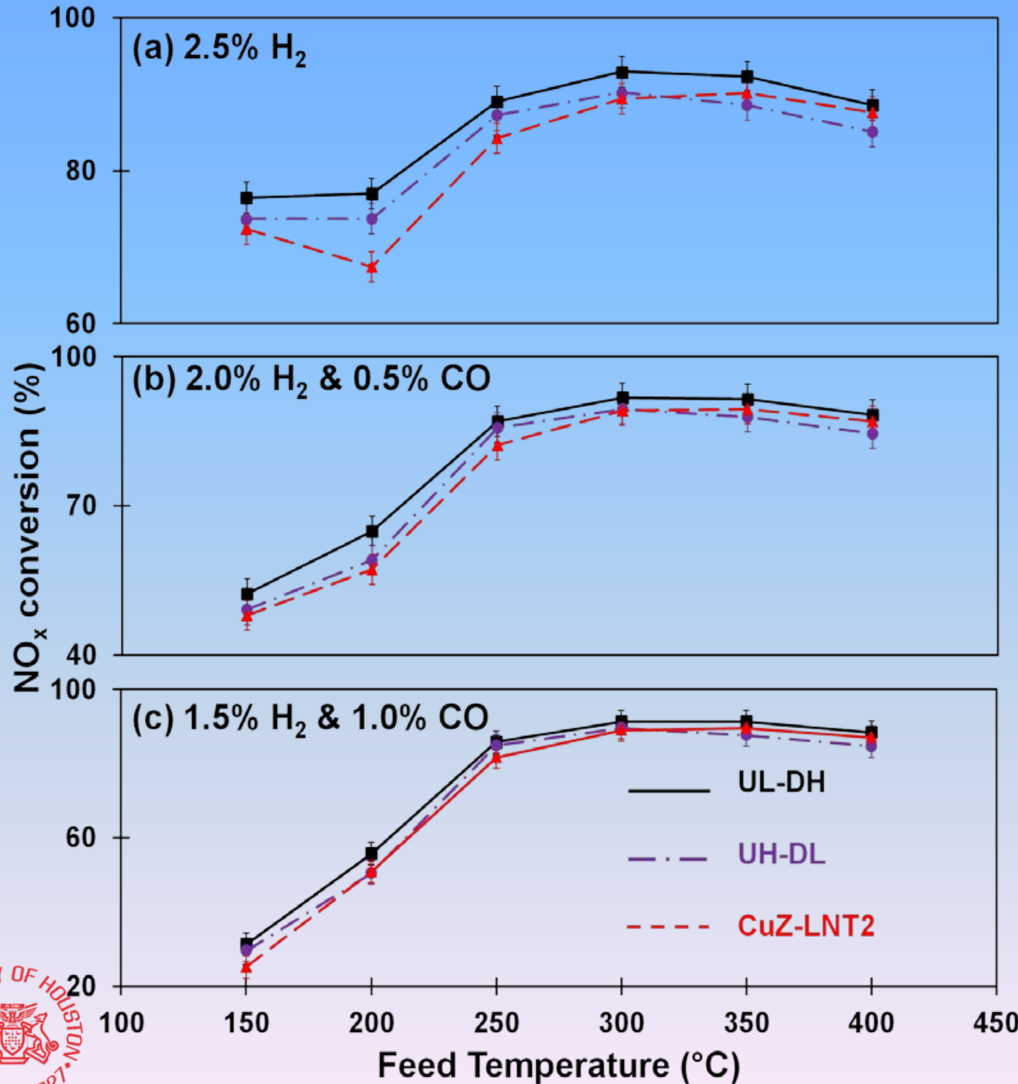


Roles of ceria in LNT/SCR:

Increases NOx storage & NO conversion at low temperature

Promotes WGS reaction

LNT/SCR: Ceria Zoning

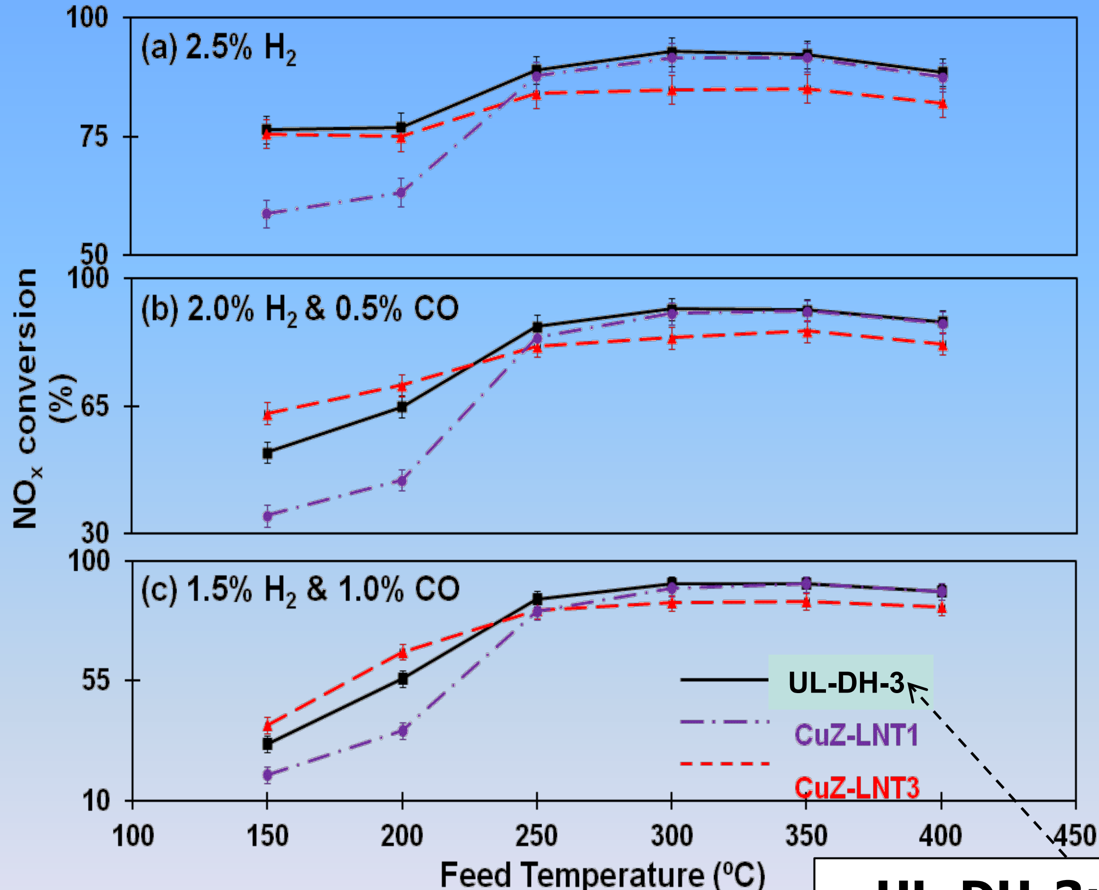


Sample	Upstream Ceria Level (wt.%)	Downstream Ceria Level (wt.%)
CuZ-LNT2	17	17
UL-DH	0	34
UH-DL	34	0

UL-DH > UH-DL > CuZ-LNT2

Nonuniform ceria works better

LNT/SCR Dual-Layer: CeO_2 Axial Zoning



Zoning of ceria:

Achieves beneficial trade-off

- *Approaches LNT3 performance at low temperature*
- *Approaches LNT1 performance at high temperature*

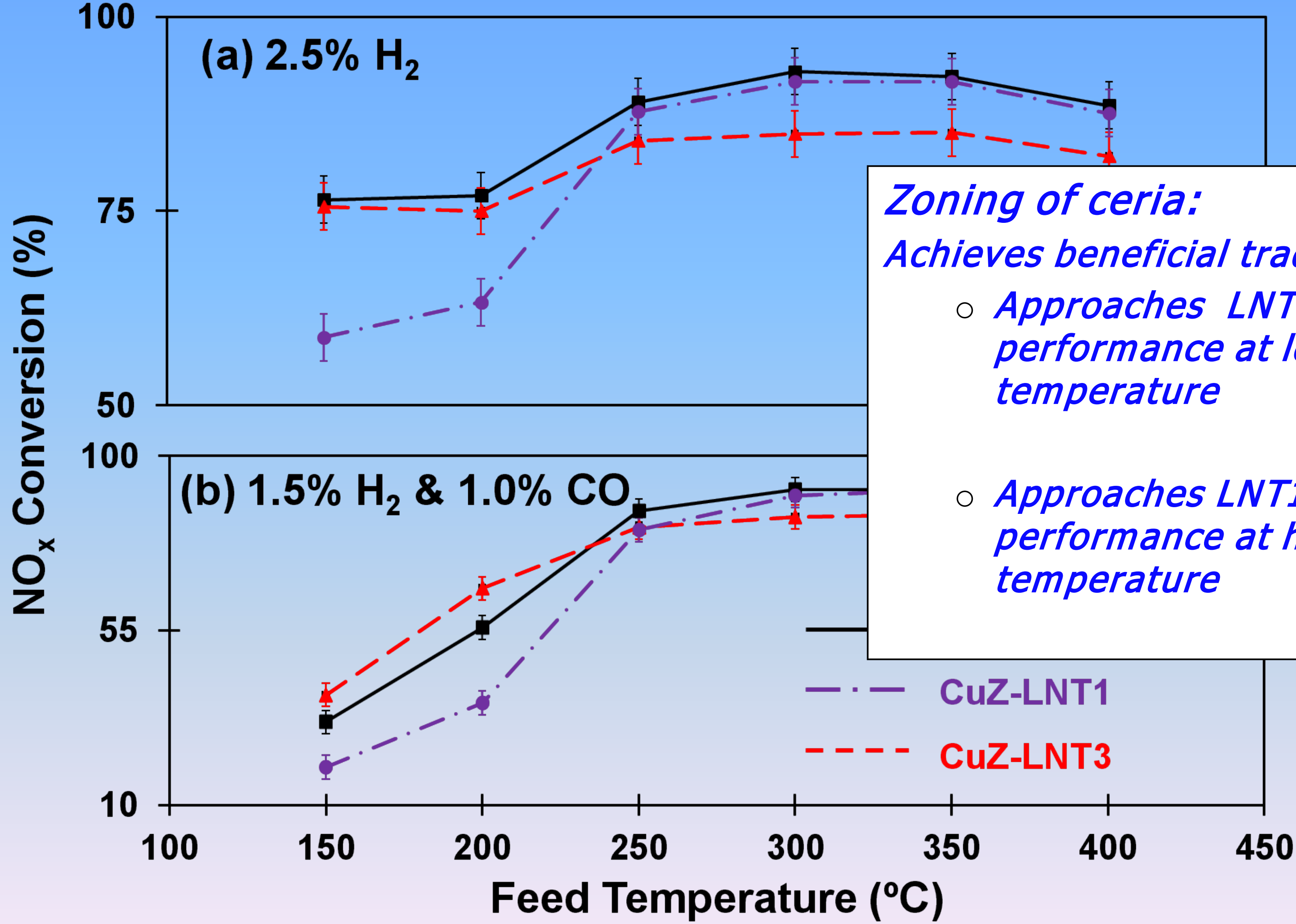
UL-DH-3:

- First half: CuZ-LNT1; aged
- Second half: CuZ-LNT3; 2.0 g/in^3

Liu, Y., Y. Zheng, M.P. Harold, and D. Luss, Appl. Catal. B. under review (2012).

Ceria Loading Effect

Conditions:
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s



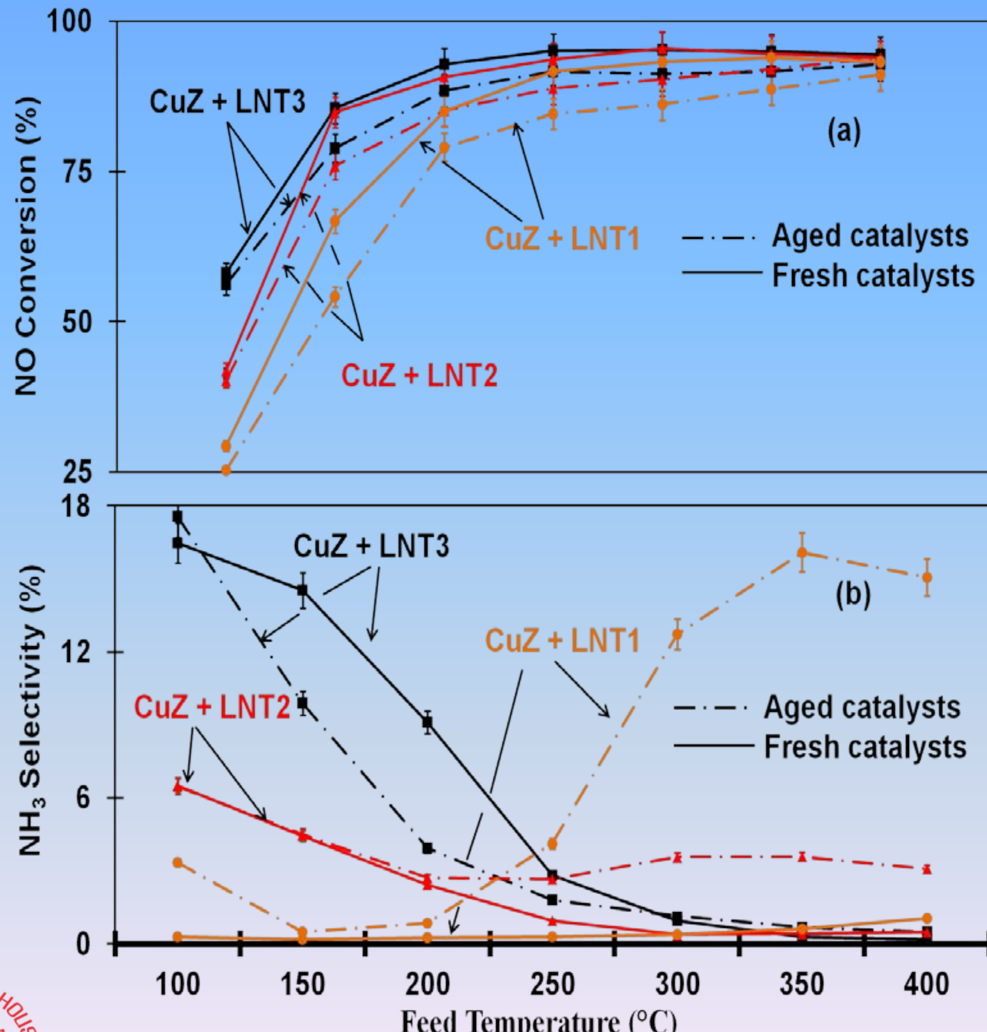
Zoning of ceria:

Achieves beneficial trade-off

- *Approaches LNT3 performance at low temperature*
- *Approaches LNT1 performance at high temperature*

Aging Effects

Aging Effects: Stabilization by Ceria



Aging: 600 °C for 100 hours in air

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

Aging reduces lowers NOx conversion for all temp.'s

Ceria-free LNT/SCR shows large NH_3 release

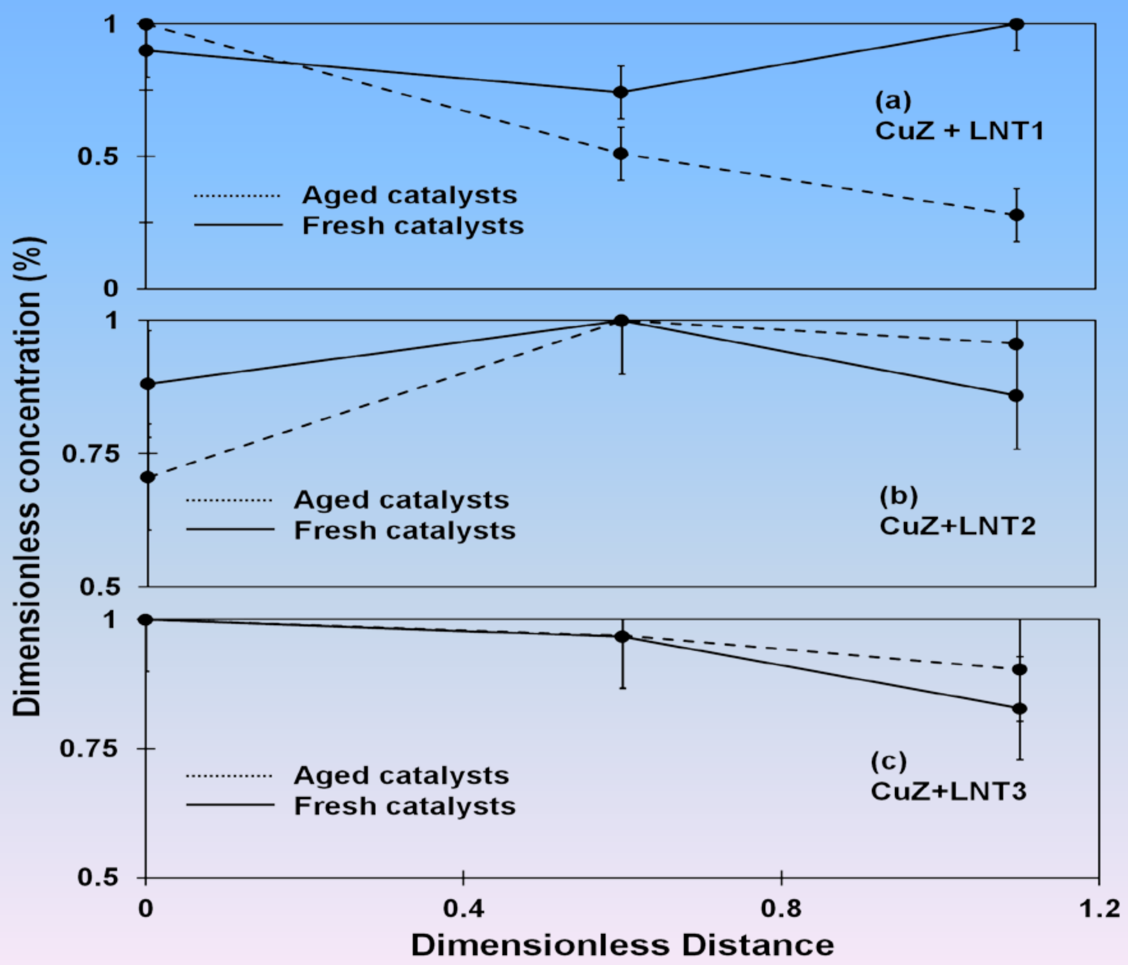
Ceria-based LNT/SCR shows less thermal degradation

SEM microprobe shows less Pt migration from LNT to SCR

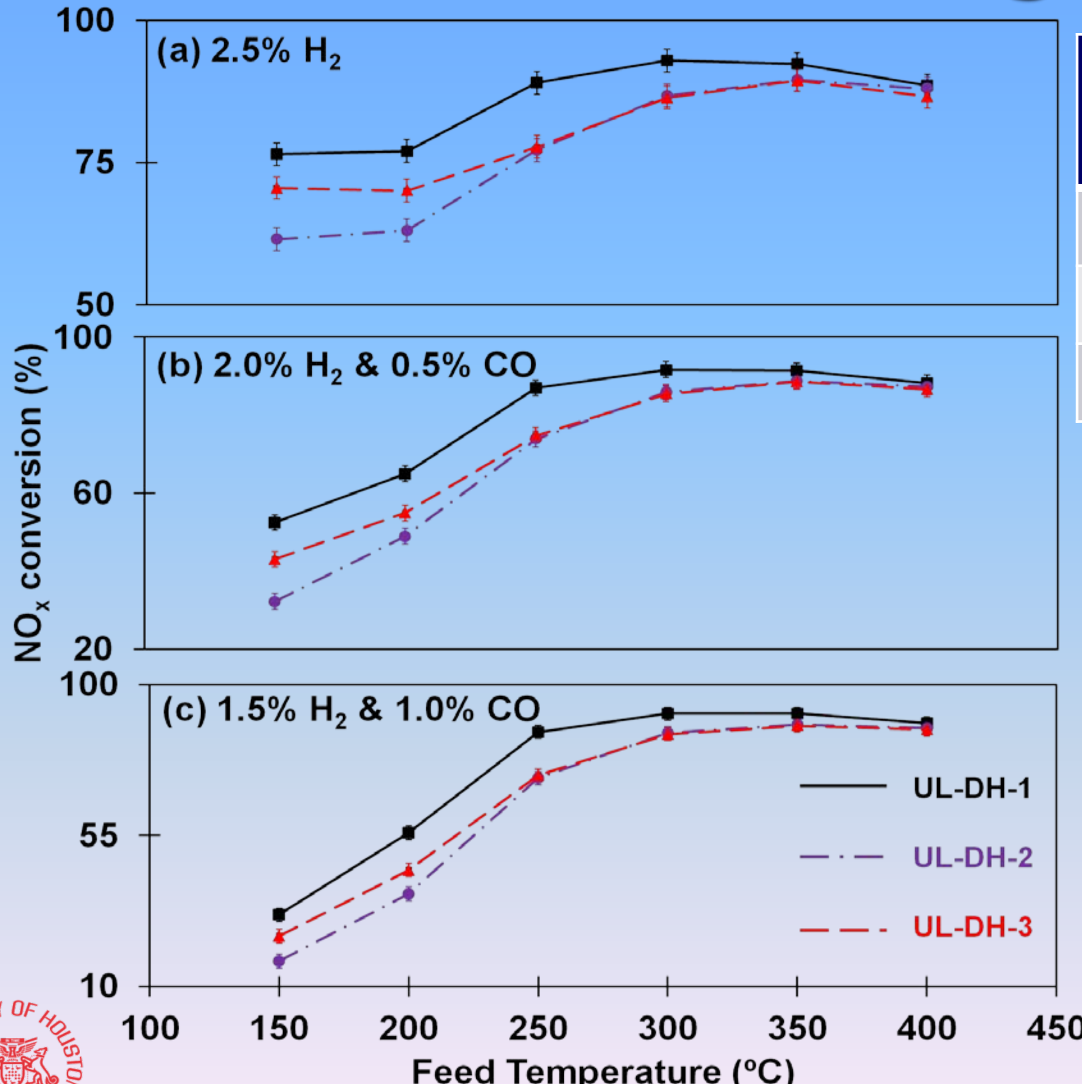
Ceria: Mitigation of Pt Migration

LNT/SCR interface

Pt/Pt_{max}



LNT/SCR: Effect of Aging & Loadinng

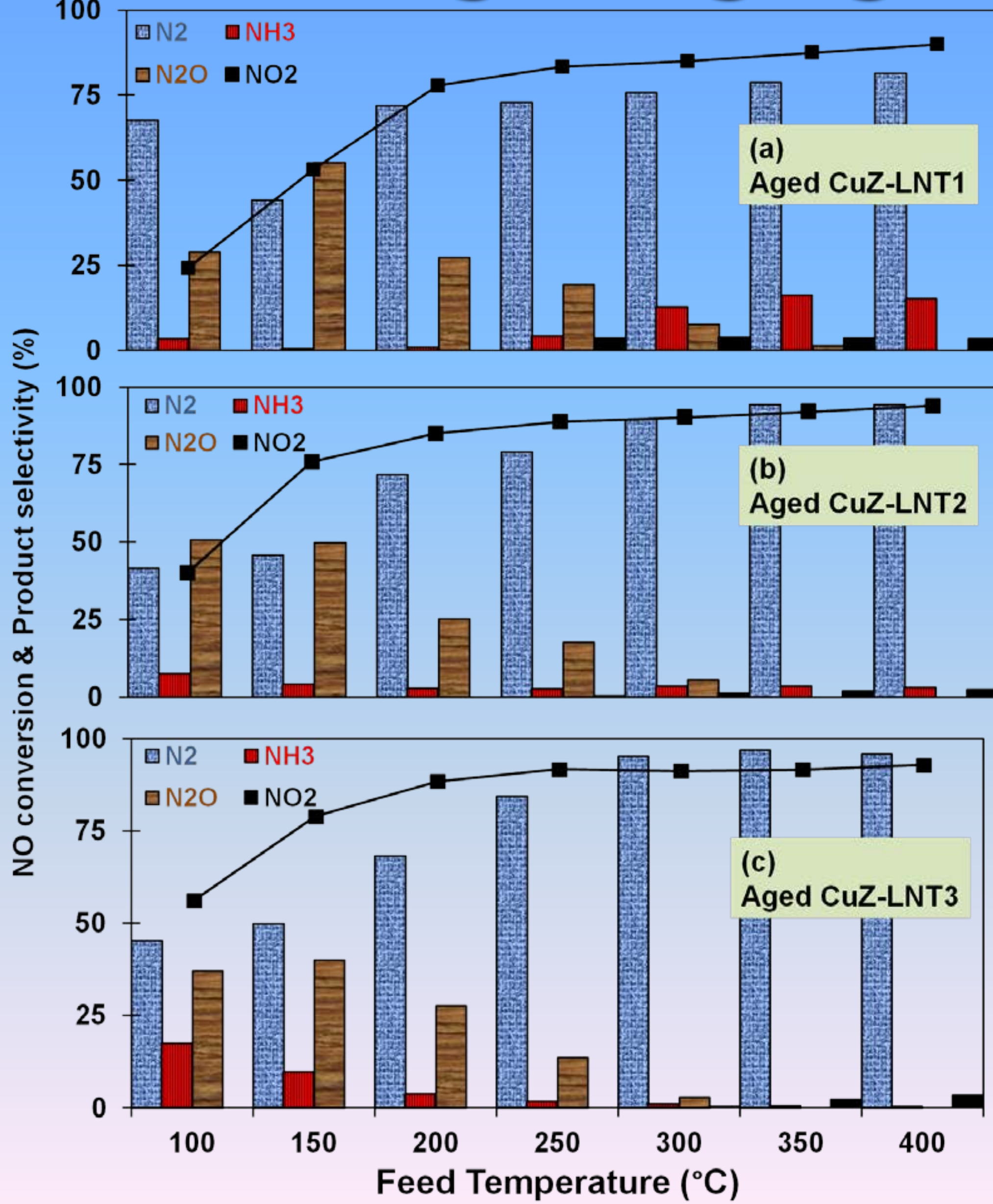


Sample	LNT1 Activity	LNT3 Activity	SCR Loading (g/in^3)
UL-DH-1	Fresh	Fresh	0.9
UL-DH-2	Aged	Fresh	0.9
UL-DH-3	Aged	Fresh	2.0

Improvement achieved with different reductant compositions

UL-DH-3 superior to UL-DH-2: Higher loading of CuZ layer

Ceria Loading & Aging Effects



<u>Conditions:</u>
Lean: 500 ppm NO, 5% O_2; 60s
Rich: 2.5% H_2; 5s

Aging: 600 ^{o}C for 100 hours

Increased ceria results in higher NO conversion and generally higher N_2 selectivity

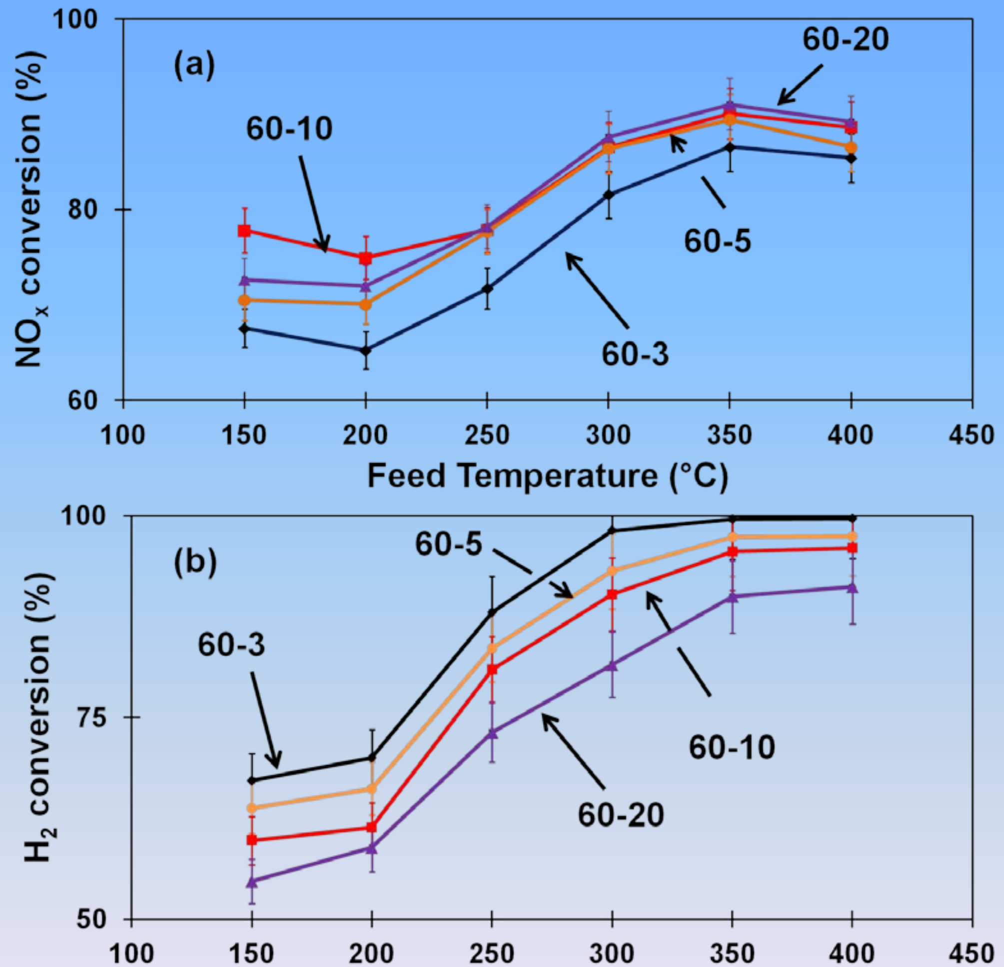
Ceria slows degradation by stabilizing Pt and Pt migration

Results Matrix

Reductant	CO_2 + H_2O?	Catalyst
H_2	Yes	LNT1/Cu-Z
H_2	No	LNT1/Cu-Z (mixed layer)
H_2 + CO	Yes	LNT1, LNT3
H_2 + CO	No	LNT1/Cu-Z → LNT3/Cu-Z
H_2 + CO	Yes	LNT1+LNT3/Cu-Z *zoned ceria*

Final step: optimize cycling parameters:
Total cycle time, reductant feed intensity

Optimization of Cycle Timing: Intensity of Reductant Pulse



Comparisons of (a) NO_x and (b) H_2 conversion under different lean-rich cycles using a 2.0 g/in^3 CuZ- Front Aged LNT1 back LNT3 dual-layer catalyst.

Catalyst: UL-DH-3
Lean: 500 ppm NO, 5% O_2,
(with 2.5% H_2O, 2% CO_2)

<u>Rich Feed:</u>

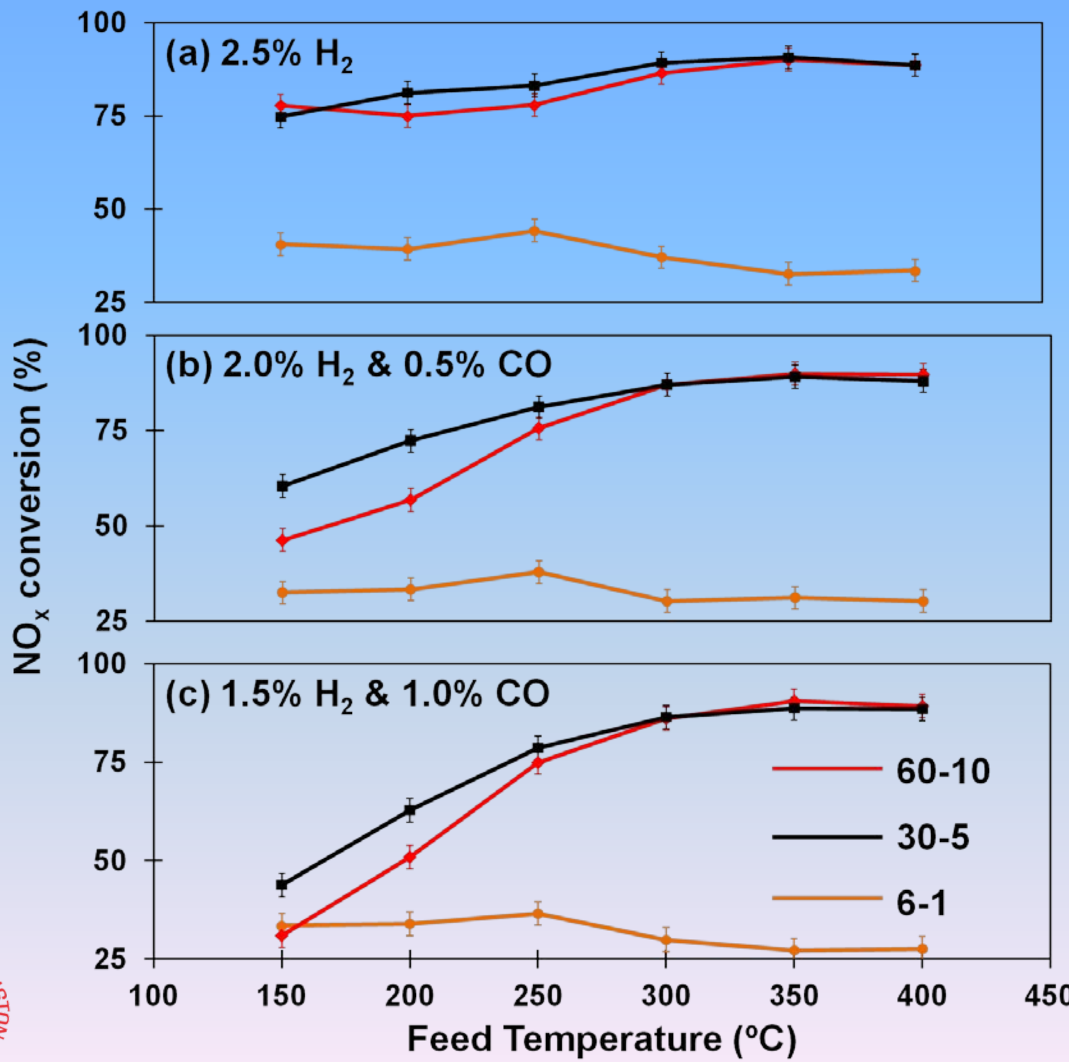
	C_{H2} (%)
60-20:	0.63
60-10:	1.25
60-5:	2.50
60-3:	4.17

2.5% H_2O, 2% CO_2

Optimal rich pulse time for fixed amt. reductant & storage time:
60 s lean, 10 s rich (1.25% H_2)

Liu, Y., M.P. Harold, and D. Luss, in preparation (2012).

Optimization of Cycle Timing: Total Cycle Time



Catalyst: UL-DH-3
Lean: 500 ppm NO, 5% O_2,
Rich: 2.5% H_2
(with 2.5% H_2O, 2% CO_2)

Varied lean/rich timing:

Lean	Rich
60 s	10 s
30 s	5 s
6 s	1 s

Optimal total cycle time with fixed reductant duty cycle:
30 s lean, 5 s rich