Modeling Studies of the Dual-Layer LNT/SCR Monolithic Catalyst

Mike Harold

Acknowledgements:

Bijesh Shakya, Yi Liu, Yang Zheng, Vemuri Balakotaiah, Dan Luss

Funding:

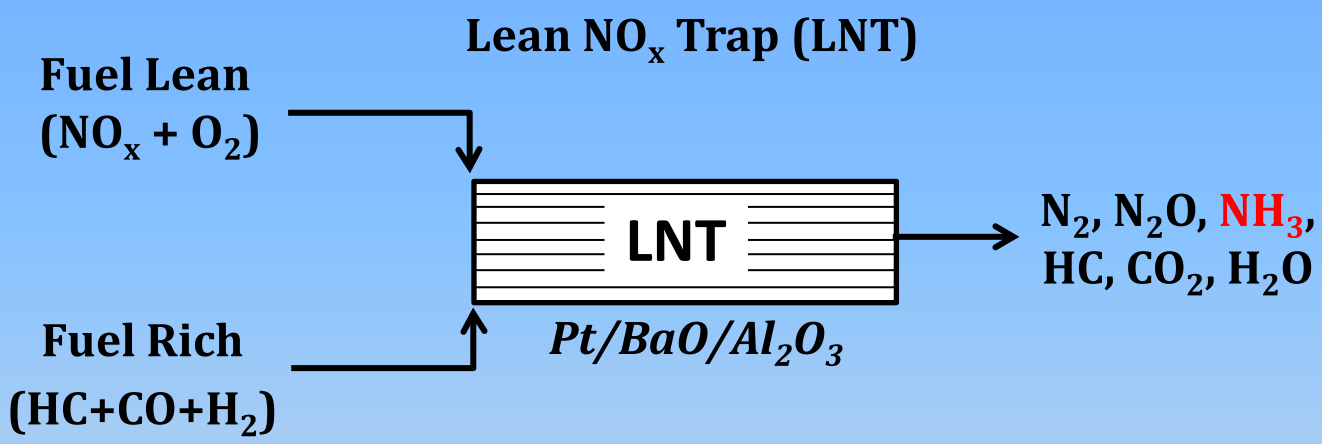
Motivation

http://solar.calfinder.com/blog/wp-content/uploads/2009/12/toxic-city-houston.jpg

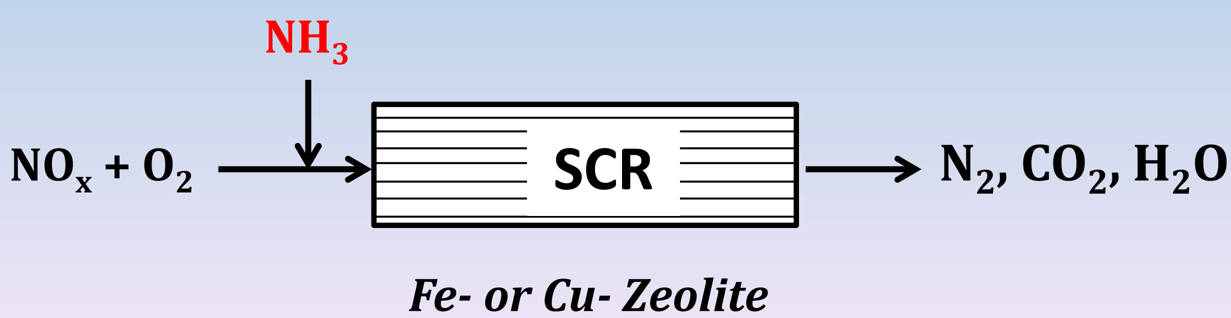
http://images.google.com/imgres?imgurl=http://www.utexas.edu/research/ceer/texaqs/images/downtown_view2

Technologies for Lean NO_x Reduction

NO_x Storage and Reduction (NSR)

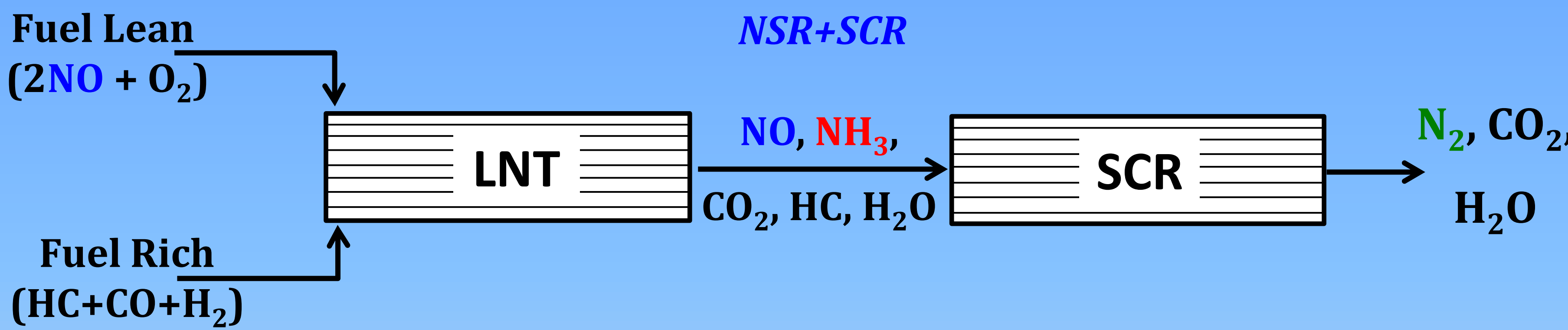


Selective Catalytic Reduction (SCR)



Background

Technologies for Lean NO_x Reduction



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

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

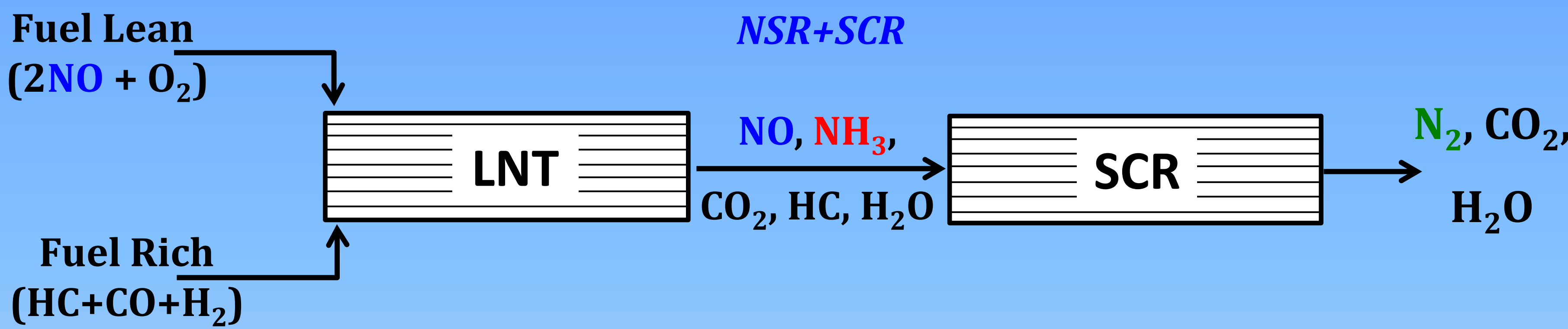
$$\text{OVERALL:} \quad 2NO + 4H_2 + O_2 \rightarrow N_2 + 4H_2O$$

$$X_{NOx}=0.5 \qquad S_{NH3}=1$$

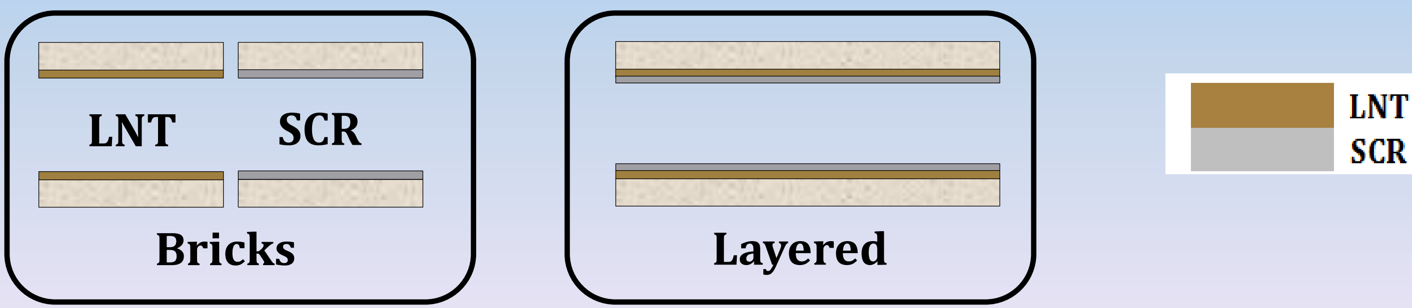
LNT does not need a highly effective NSR catalyst in the combined NSR/SCR application

Background

Technologies for Lean NO_x Reduction

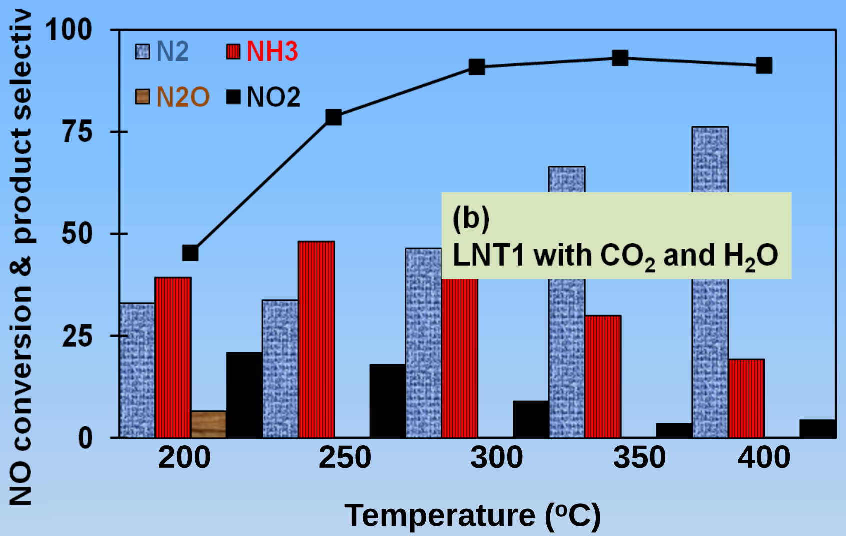


Compare:



LNT/SCR: H_2 Reductant With 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: H_2 Reductant With CO_2 & H_2O

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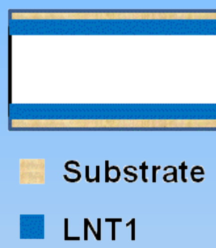
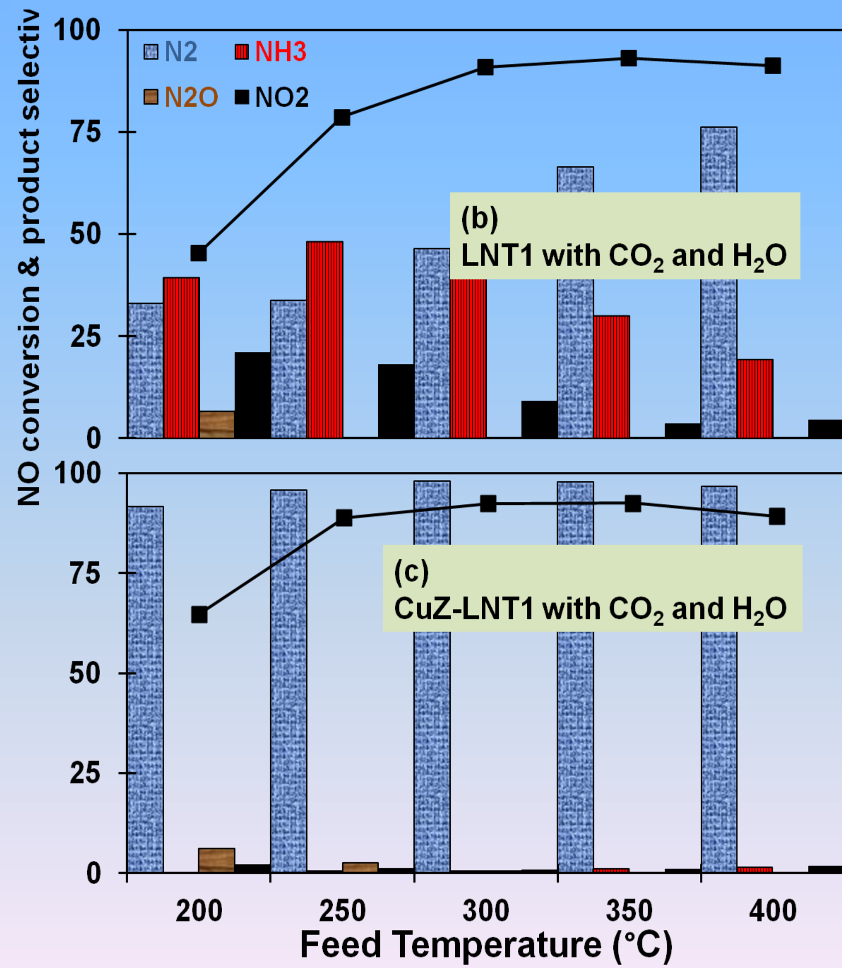
(Both: 2.5% H_2O, 2% CO_2)





Objective of Current Study

Conduct simulation studies of dual-layer LNT/SCR monolithic catalyst using global kinetics to

(i) elucidate the reactor behavior

(ii) identify optimal catalyst design & reactor operating strategies

Approach

- Develop & validate global kinetic model for low dispersion LNT catalysts
- Adopt kinetic model for SCR from the literature ‡
- Use LNT/SCR dual layer reactor model to study:
    - Effect of washcoat loading
    - Effect of temperature
    - Compare dual layer design to dual brick design

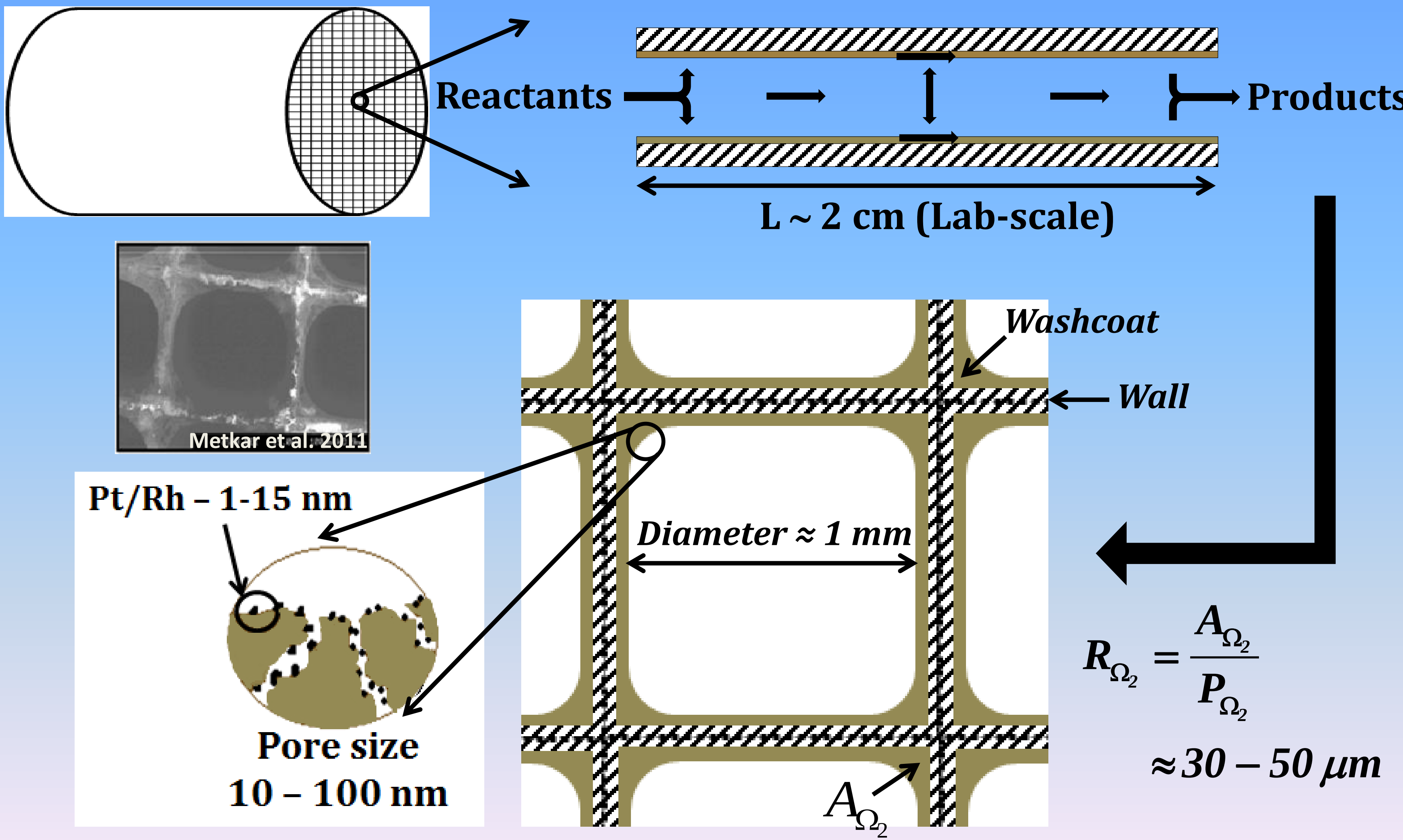
‡ Metkar et. al. 2012 / Chem. Eng. Sci. / doi: http://dx.doi.org/10.1016/j.ces.2012.09.008

Outline

- Model development (Multiple length-time scales, model equations)
- Model tuning and validation for LNT (LNT reactions, compare with experiments)
- Review SCR model‡ (SCR reactions, validations)
- Simulation results of dual layer LNT/SCR (concentration profiles, effect of washcoat/catalyst loading, effect of temperature, compare with brick config)
- Conclusions

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

Multiple Length/Time Scales



$$R_{\Omega_2} = \frac{A_{\Omega_2}}{P_{\Omega_2}}$$

$$\approx 30 - 50\ \mu m$$

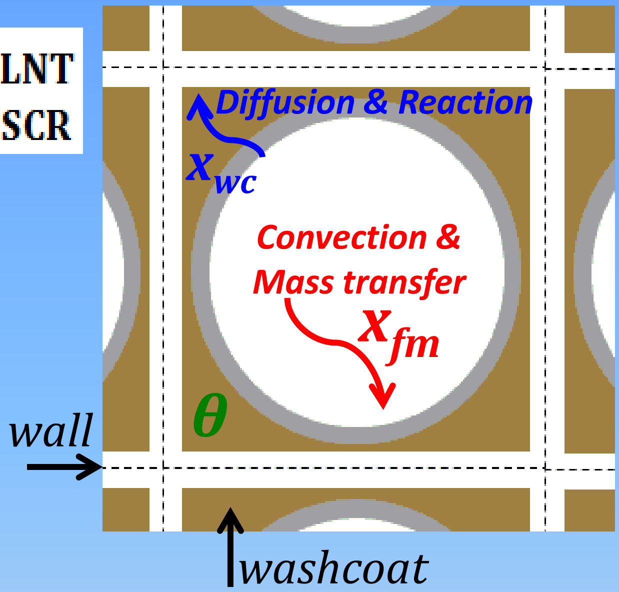
Model Development

Model equations

Fluid phase equation

$$\frac{\partial x_{fm,j}}{\partial t} = -\bar{u}\frac{\partial x_{fm,j}}{\partial z} - \frac{k_{me,j}(z)}{R_{\Omega_1}}(x_{fm,j} - x_{s,j})$$

$$(0 < z < L)$$



Washcoat equation

$$\varepsilon_{wc}\frac{\partial x_{wc,j}}{\partial t} = \frac{\partial}{\partial y}\left(D_{e,j}\frac{\partial x_{wc,j}}{\partial y}\right) + \frac{1}{C_{tm}}\sum_{r=1}^{rxn}\vartheta_{jr}R_r(\underline{x_{wc}},\underline{\theta},T)$$

Site balance

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{C^o}\sum_{r=1}^{rxn}\vartheta_{kr}R_r(\underline{x_{wc}},\underline{\theta},T)$$

Outline

- ❖ Model development (Multiple length-time scales, model equations) ✓
- ❖ Model tuning and validation for LNT
- ❖ Review SCR model[‡] (SCR reactions)
- ❖ Simulation results of dual layer LNT/SCR (concentration profiles, effect of washcoat/catalyst loading, effect of temperature)
- ❖ Summary and conclusions

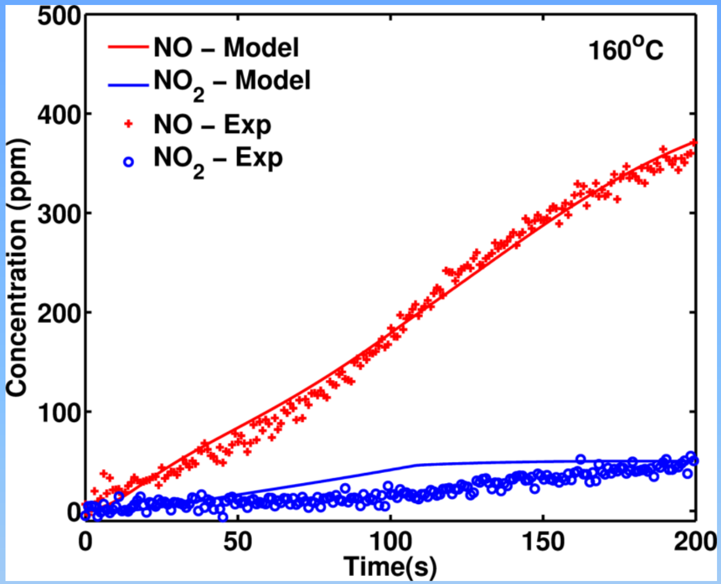
‡ Metkar et. al. 2012 / Chem. Eng. Sci. / doi: http://dx.doi.org/10.1016/j.ces.2012.09.008

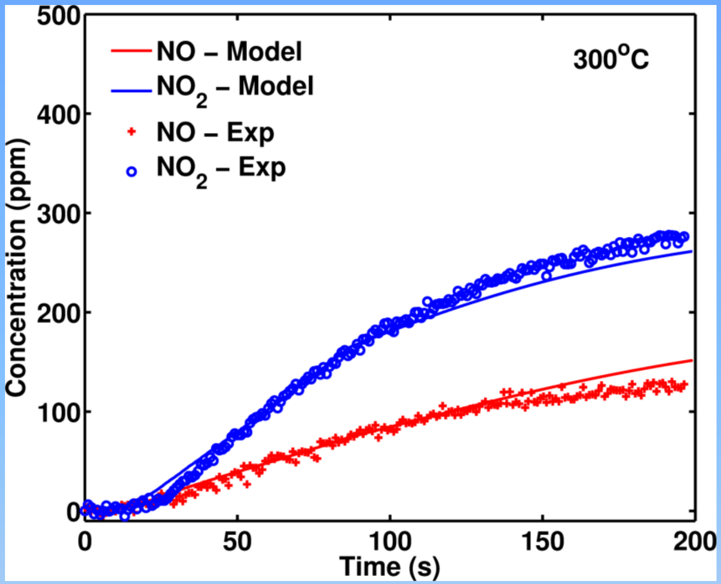
LNT – Reactions and Catalyst

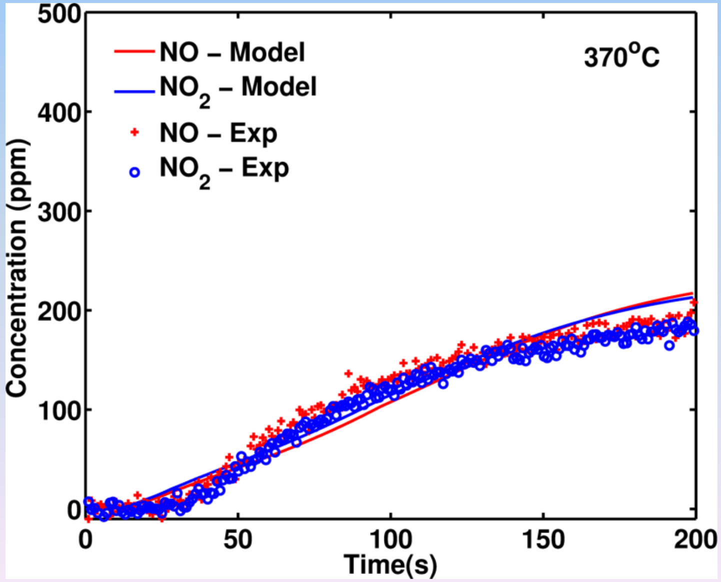
NO oxidation	1.	$NO + 0.5\ O_2 \rightarrow NO_2$
NO storage in the presence of O_2	2.	$2\ NO + 1.5\ O_2 + BaO_{(f)} \rightarrow Ba(NO_3)_{2\ (f)}$
	3.	$2\ NO + 1.5\ O_2 + BaO_{(S)} \rightarrow Ba(NO_3)_{2\ (S)}$
NO_2 Storage	4.	$2\ NO_2 + 0.5\ O_2 + BaO_{(f)} \rightarrow Ba(NO_3)_{2\ (f)}$
	5.	$3\ NO_2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

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

LNT – Model vs Exp ‡ - Storage







Conditions:

Lean inlet: 500 ppm NO + 5% O_2

GHSV: 60,000 hr^{-1} (based on monolith volume) (20 ms @ 300°C)

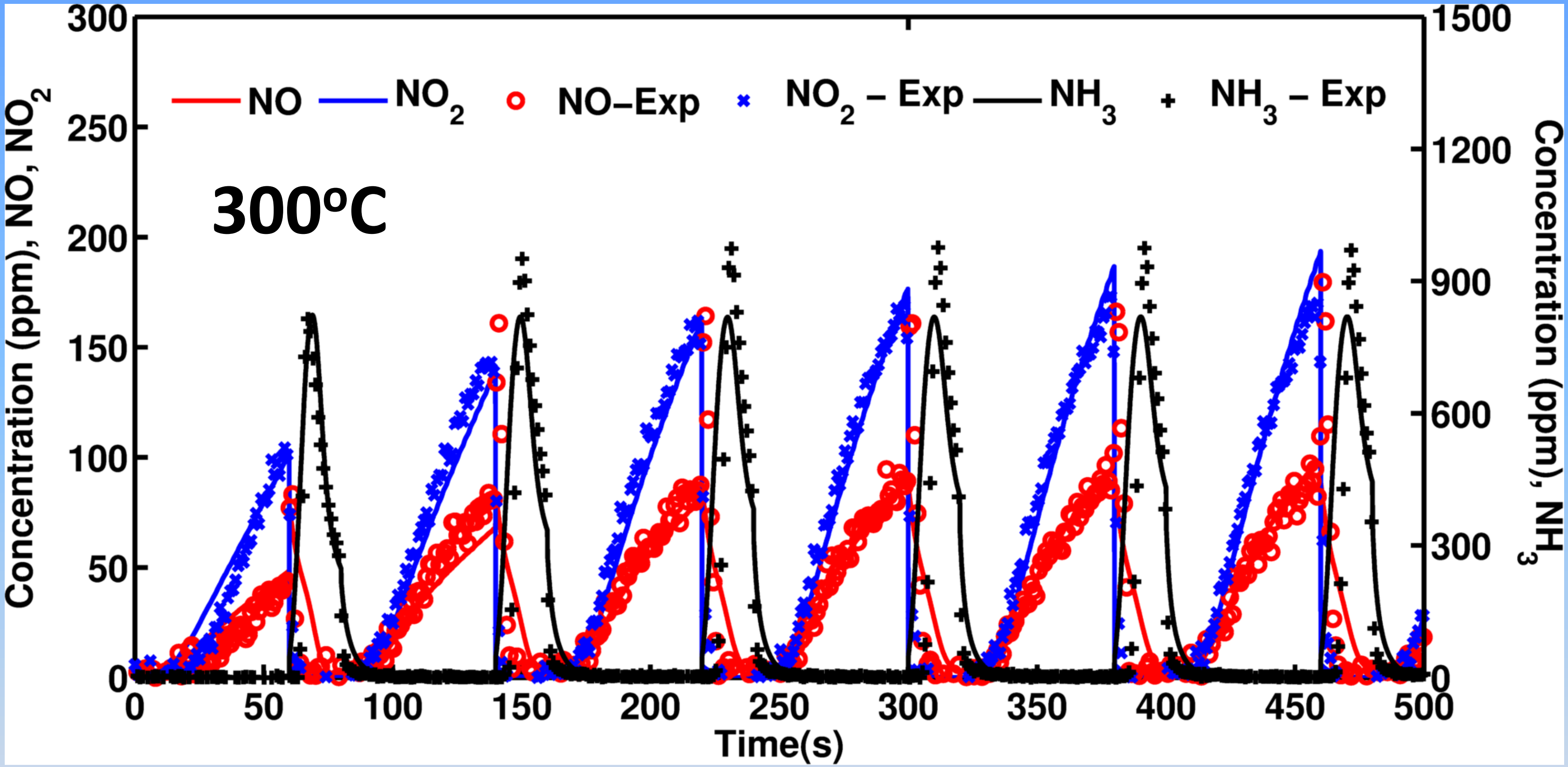
Catalyst:

2 cm long; 28 channels

400 cpsi; 30 μm washcoat

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

LNT – Model vs Exp ‡ – Cycling

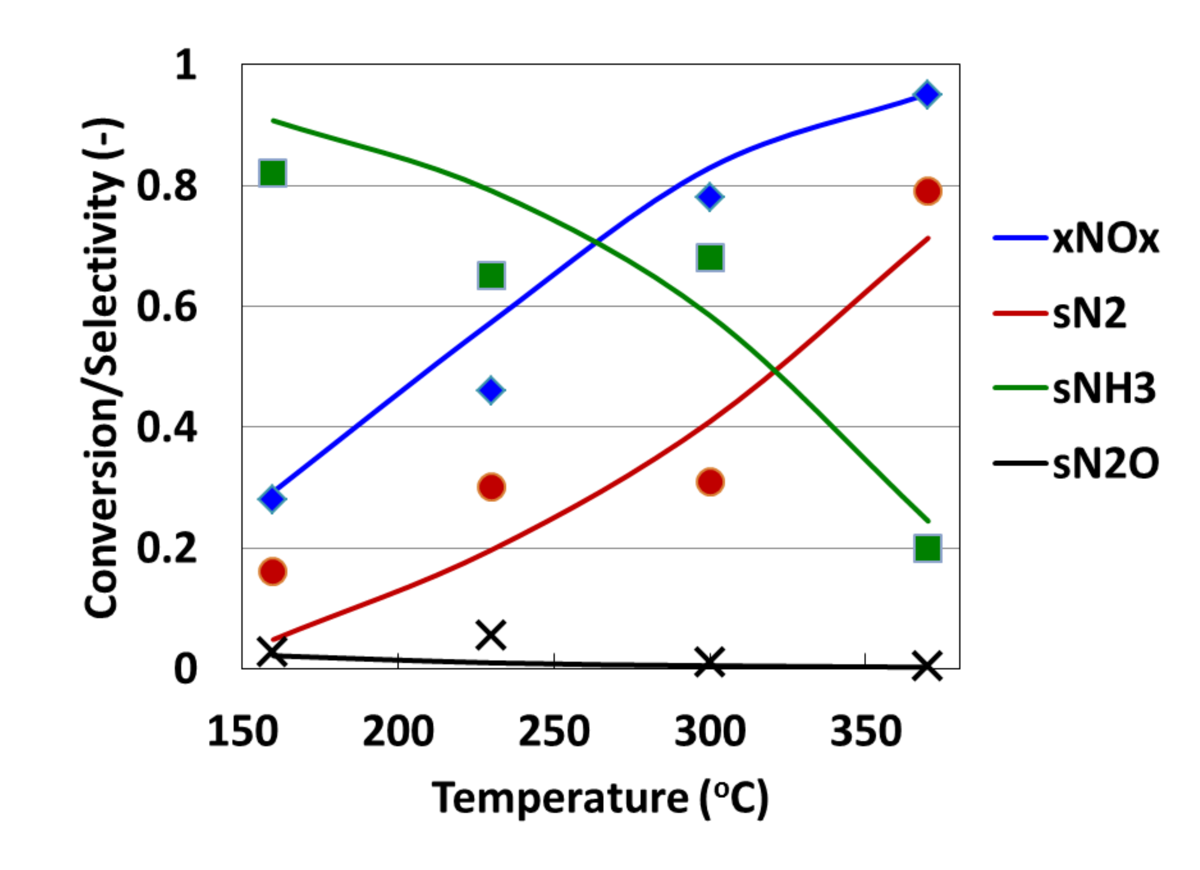


Conditions:
Lean inlet: 500 ppm NO + 5% O_2 in bal Ar / Duration: 60s
Rich inlet: 5000 ppm H_2 in bal Ar / Duration: 20s
Temperature: 300°C
GHSV: 60,000 hr^{-1} (based on monolith volume)

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

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

LNT – Model vs Exp ‡ - Regeneration



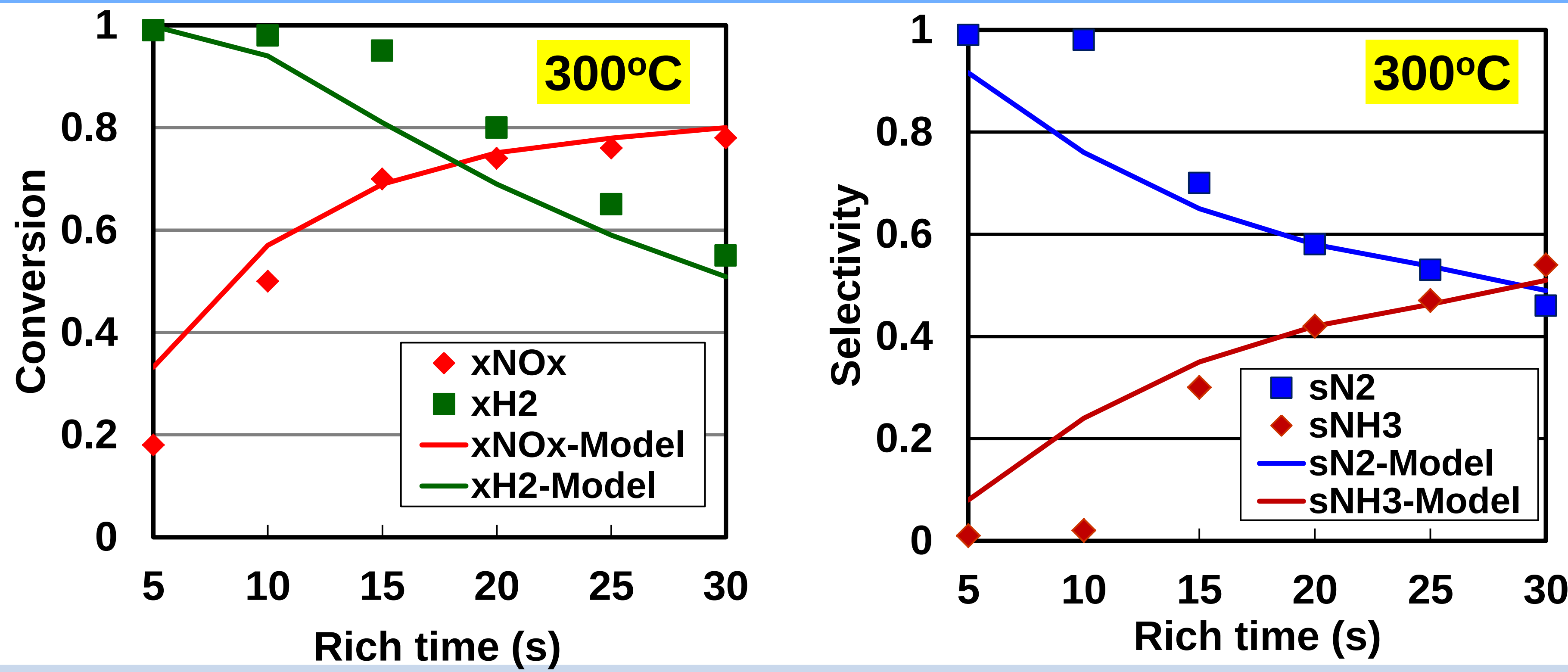
Conditions:
NOx stored: *1.5×10^{-5} moles*
Rich inlet: 1500 ppm H_2 – 200s
GHSV: 60,000 hr^{-1} (based on monolith volume)

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

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

LNT – Model vs Exp ‡

Effect of Rich phase duration



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

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

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

Outline

- Model development (Multiple length-time scales, model equations) ✓
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- Review SCR model‡ (SCR reactions)
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‡ Metkar et. al. 2012 / Chem. Eng. Sci. / doi: http://dx.doi.org/10.1016/j.ces.2012.09.008

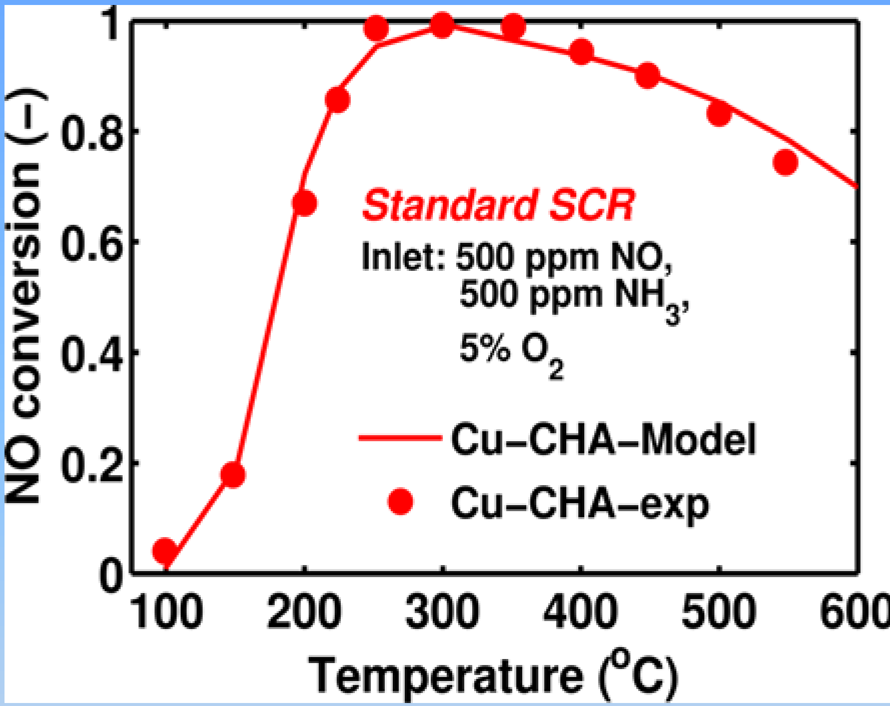
SCR‡ – Reactions and Catalyst

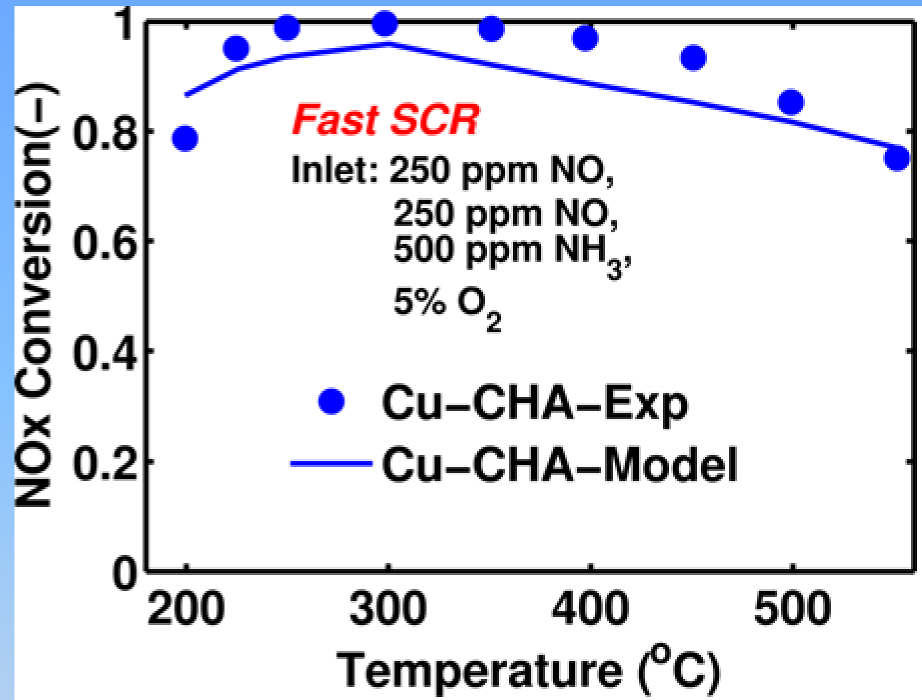
NH_3 adsorption / desorption	1.	$NH_3 + S$	→	$NH_3\text{-}S$
NH_3 oxidation	2.	$2NH_3\text{-}S + 1.5O_2$	→	$N_2 + 3H_2O + 2S$
NO oxidation	3.	$NO + ½\ O_2$	→	NO_2
Standard SCR	4.	$4NH_3\text{-}S + 4NO + O_2$	→	$4N_2 + 6H_2O + 4S$
Fast SCR	5.	$2NH_3\text{-}S + NO + NO_2$	→	$2N_2 + 3H_2O + 2S$
NO_2-SCR	6.	$4NH_3\text{-}S + 3NO_2$	→	$3.5N_2 + 6H_2O + 4S$
Ammonium nitrate formation	7.	$2NH_3\text{-}S + 2NO_2$	→	$N_2 + NH_4NO_3 + H_2O + 2S$
Ammonium nitrate decomposition	8.	NH_4NO_3	→	$N_2O + 2H_2O$

Sample	Cu (%)
Cu-Chabazite	2.48

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

SCR Results‡





"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*

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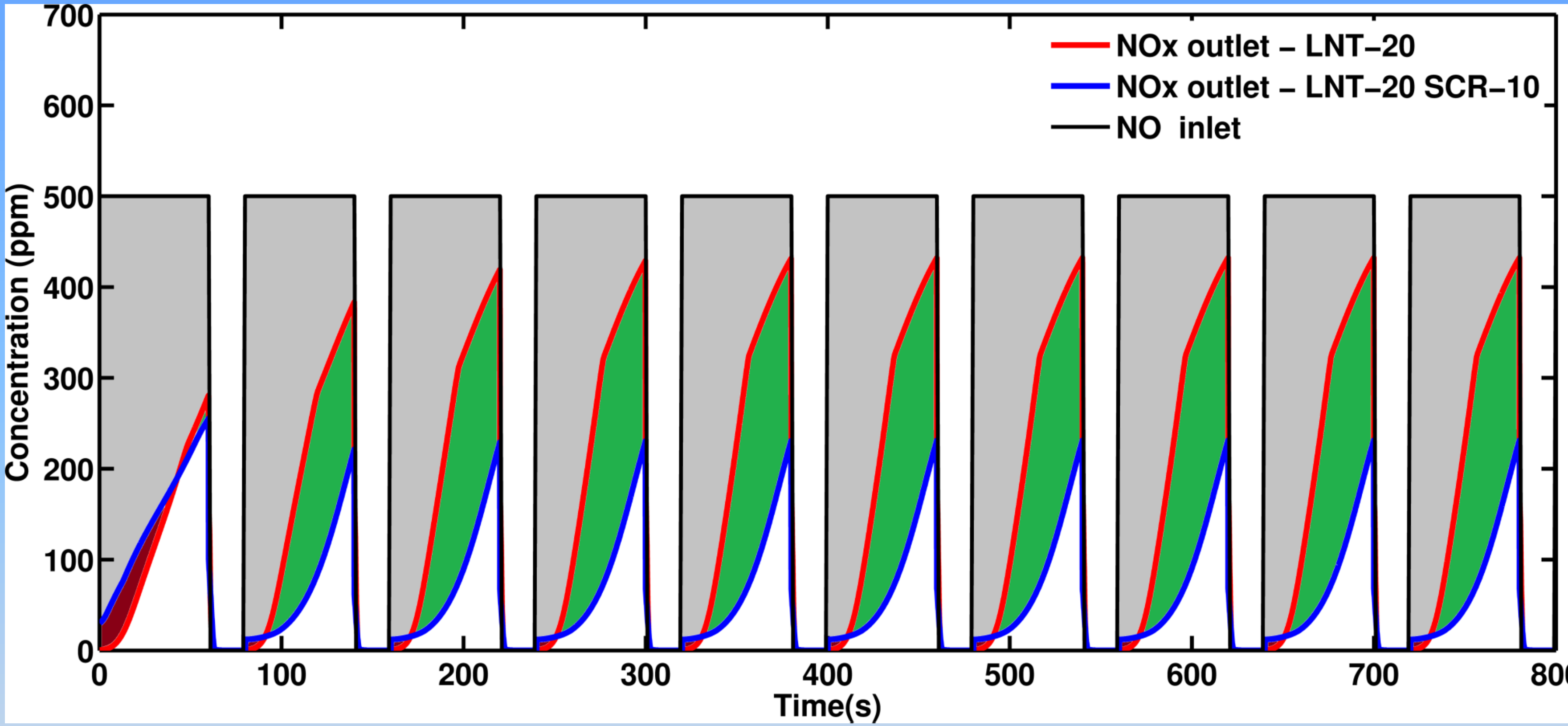
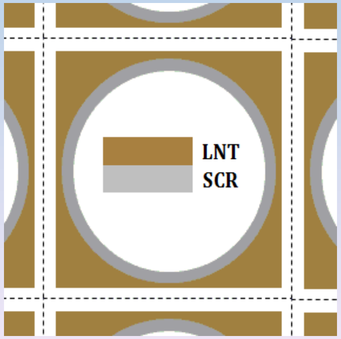
LNT/SCR – Effluent NO_x Profile



Washcoat thickness: LNT = 20 μm / SCR = 10 μm



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

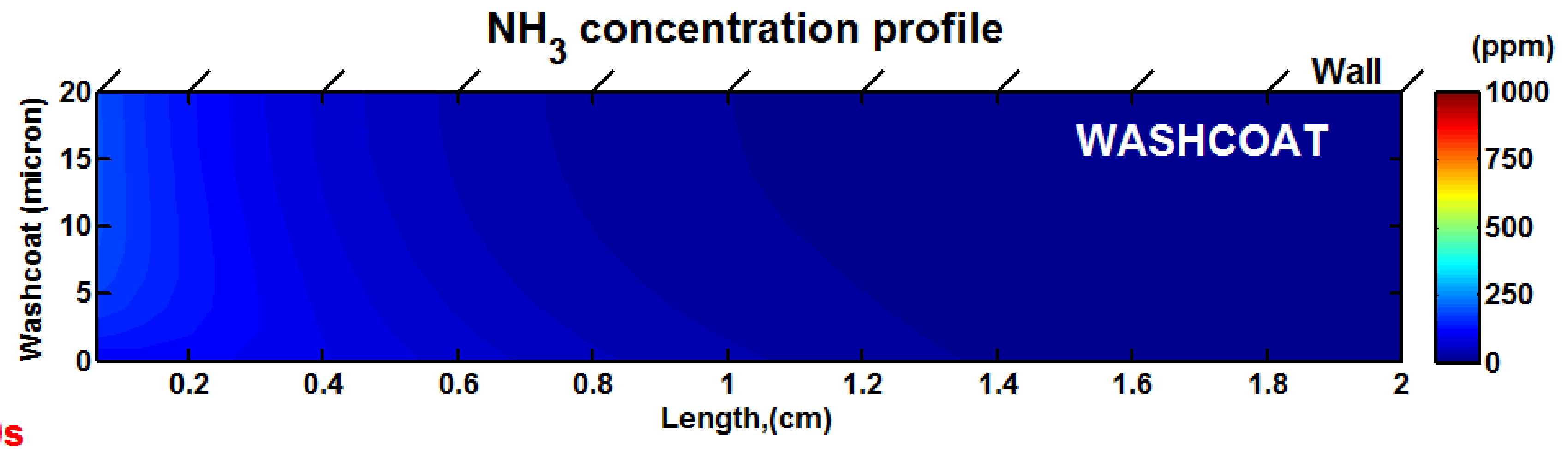
GHSV: 60,000 hr^{-1} (based on monolith volume); $\tau_c \approx$ 20ms

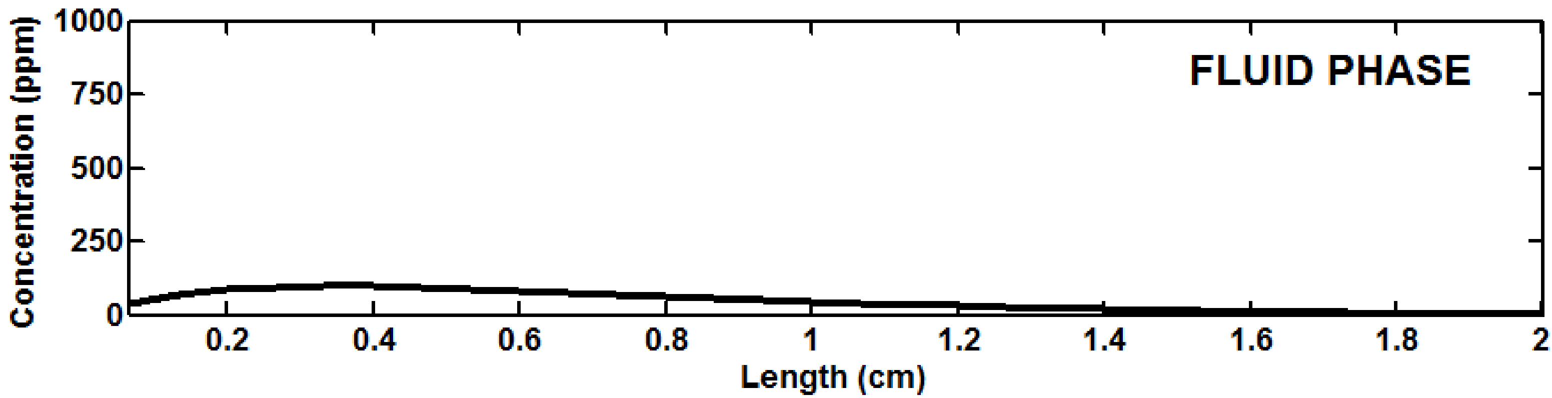
NH_3 Profile in LNT @ 300ºC

Cycle=1

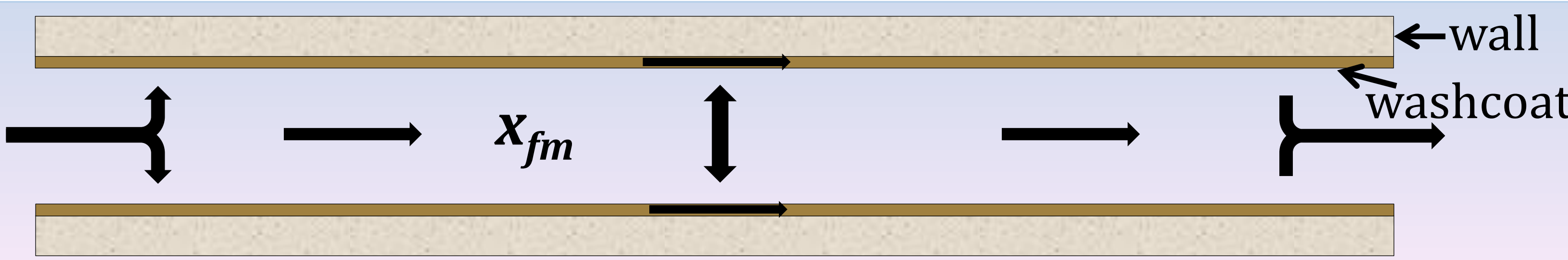
Time=60.0s

Lean

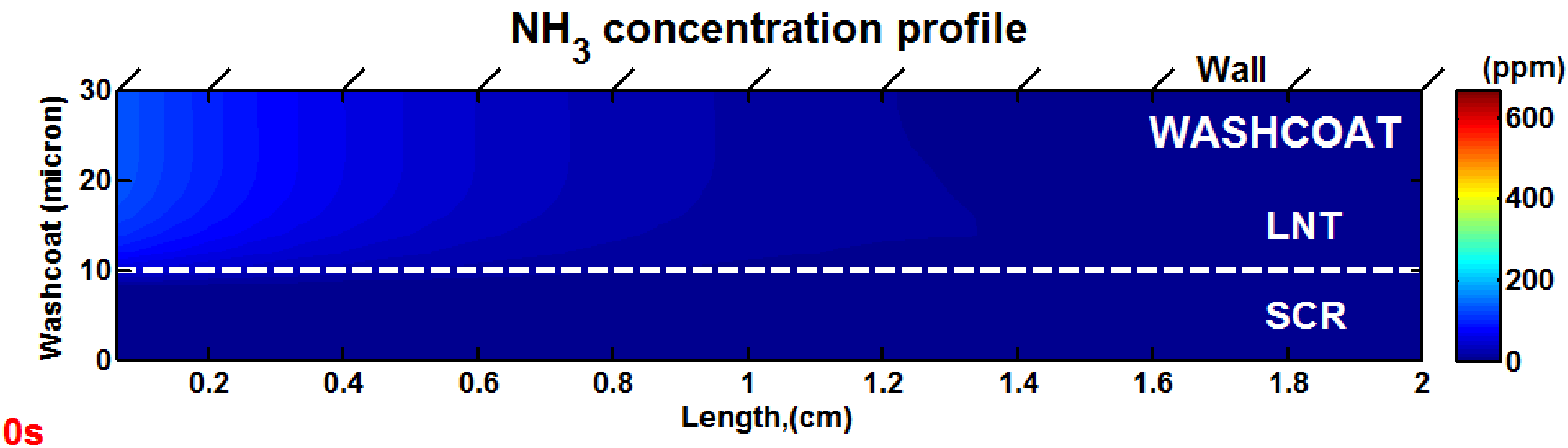




60s lean
20s rich



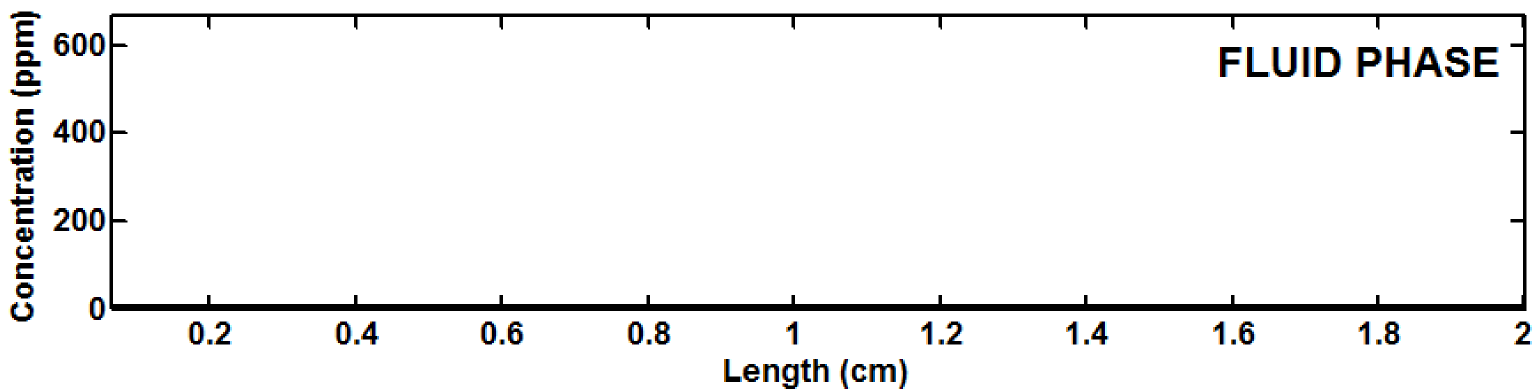
NH_3 Profile in LNT/SCR @ 300°C

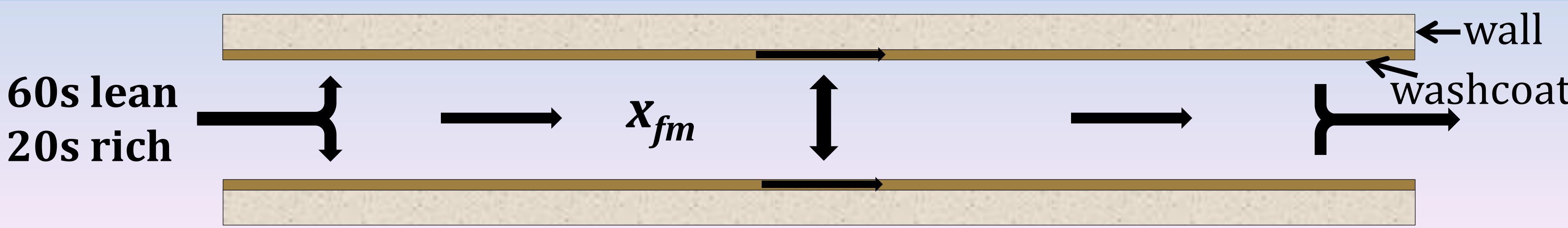


Cycle=1

Time=60.0s

Lean





Effect of SCR Washcoat Loading

Conditions:

Lean: 60s

500 ppm NO

5% O_2

Rich: 20s

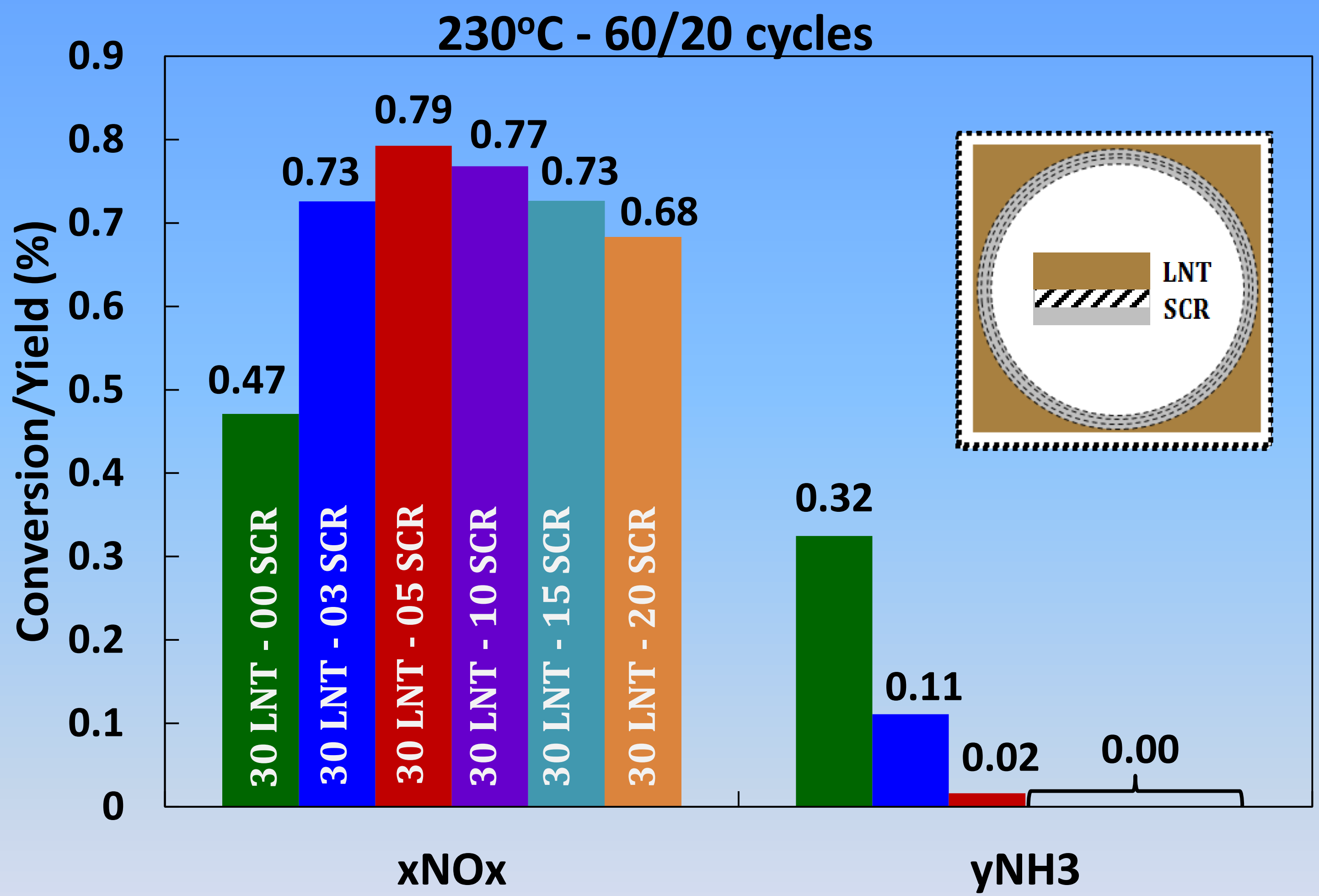
5000 ppm H_2

230°C

Washcoat Thickness:

LNT = 30 μm

SCR = 0-20μm

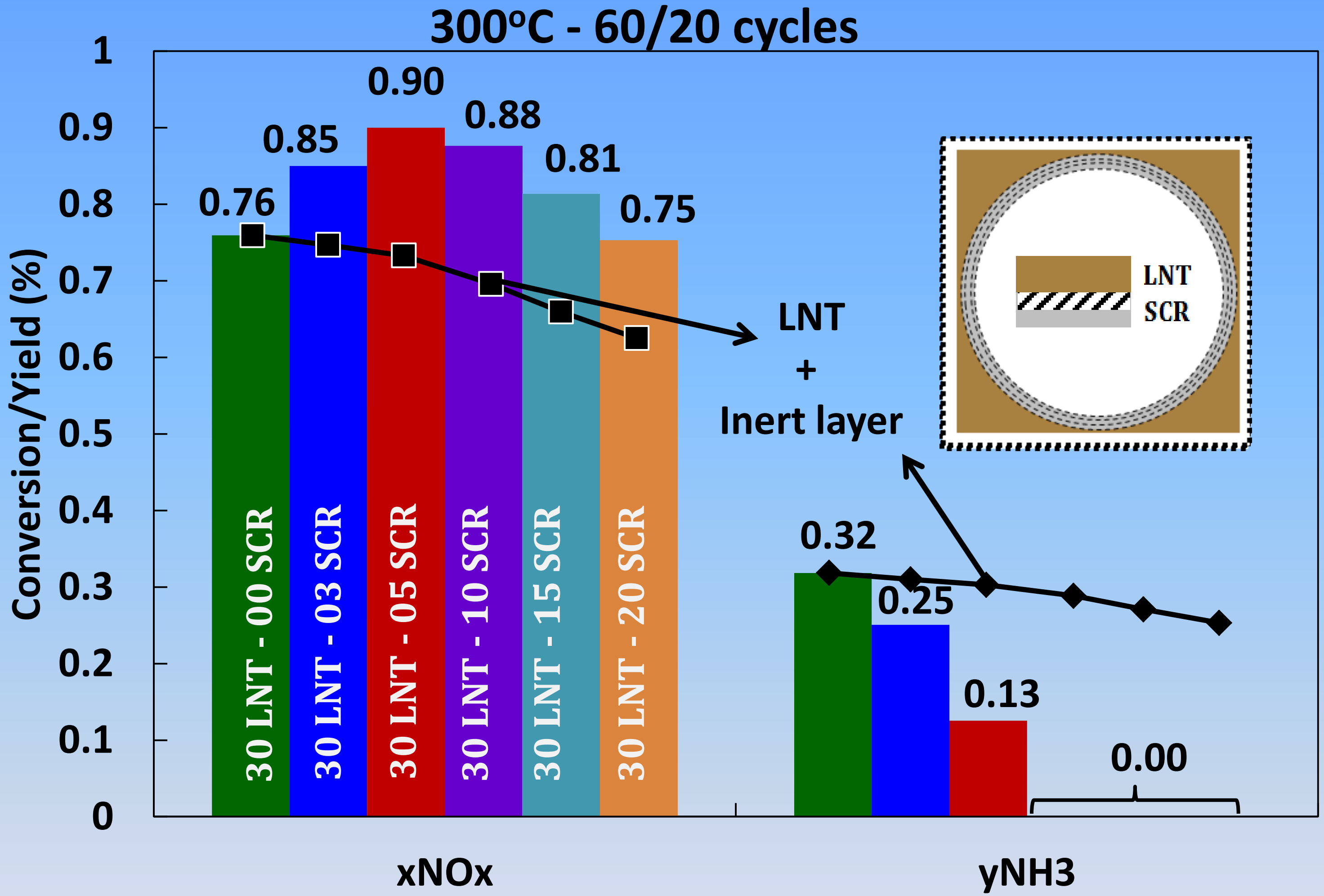


Excessive SCR loading leads to lower NOx conversion because of undesired diffusional limitation

Effect of SCR Washcoat Loading

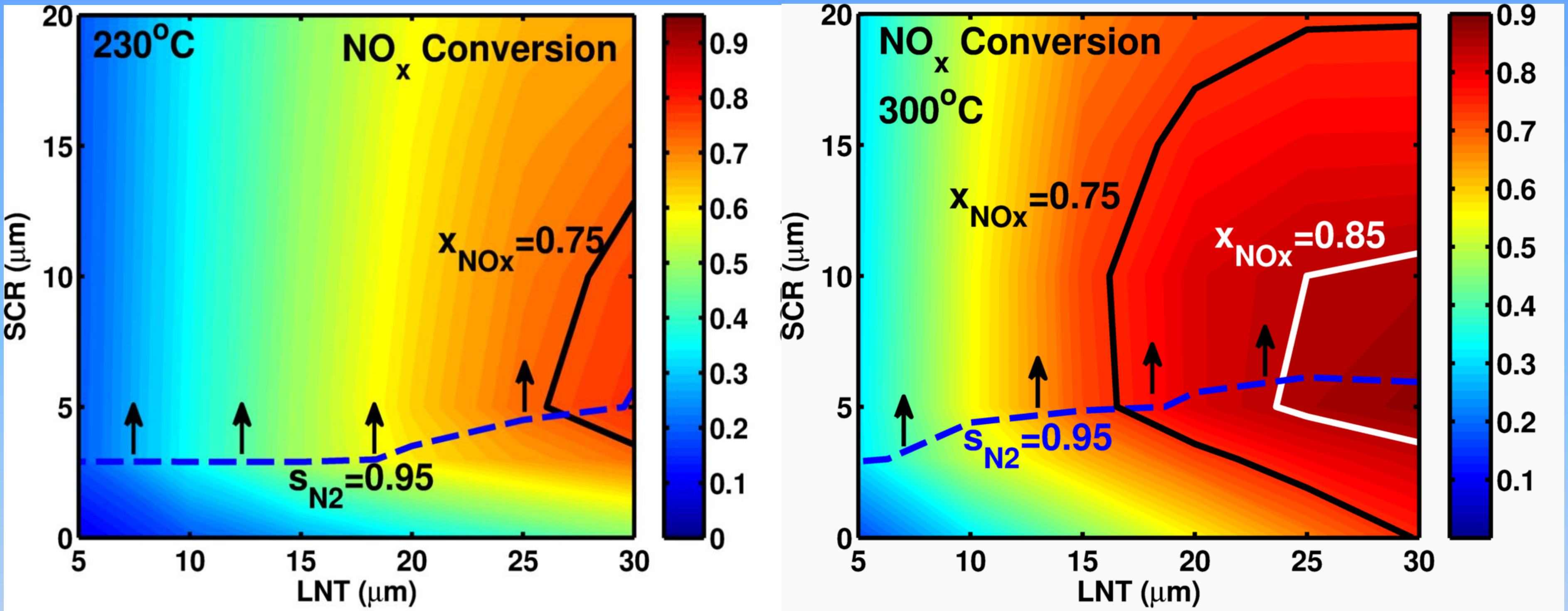
Conditions:
Lean: 60s
500 ppm NO
5% O_2
Rich: 20s
5000 ppm H_2
300°C

Washcoat Thickness:
LNT = 30 μm
SCR = 0-15 μm



Inert layer shows effect of diffusion w/o reaction

Effect of LNT/SCR Washcoat Loading



Conditions:

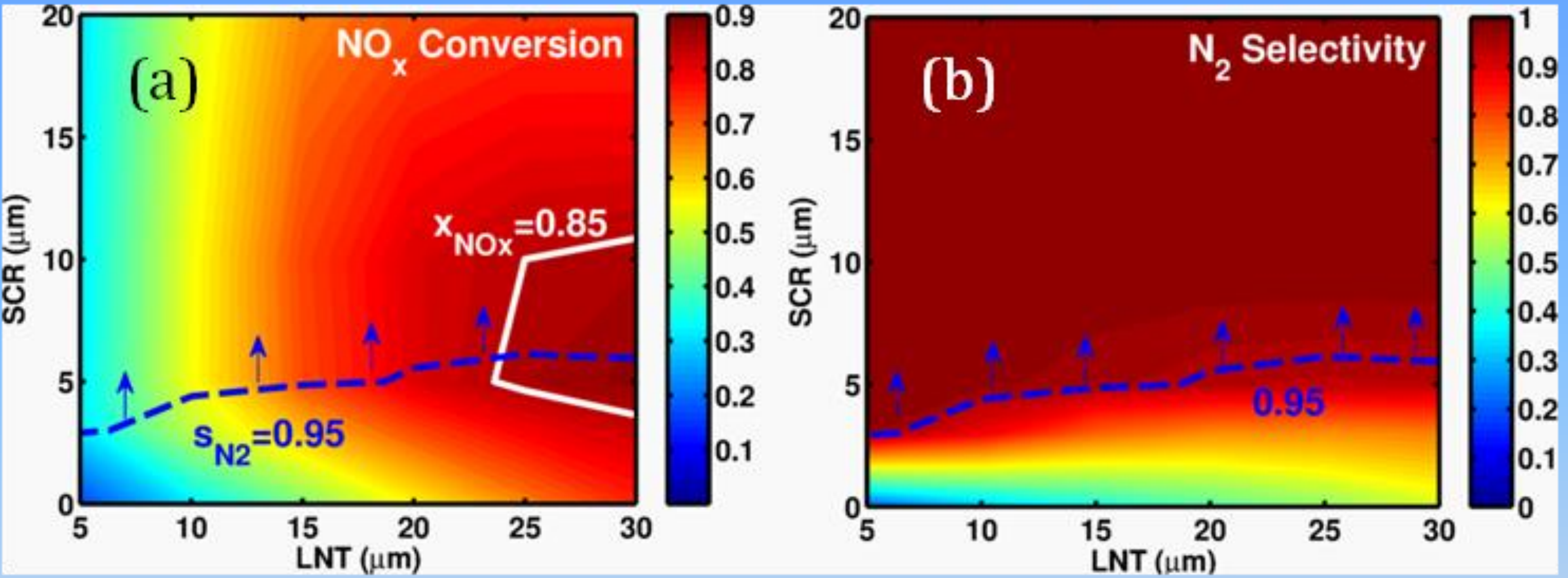
Lean inlet: 500 ppm NO + 5% O_2 in bal Ar / Duration: 60s

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

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

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

Effect of LNT/SCR Washcoat Loading



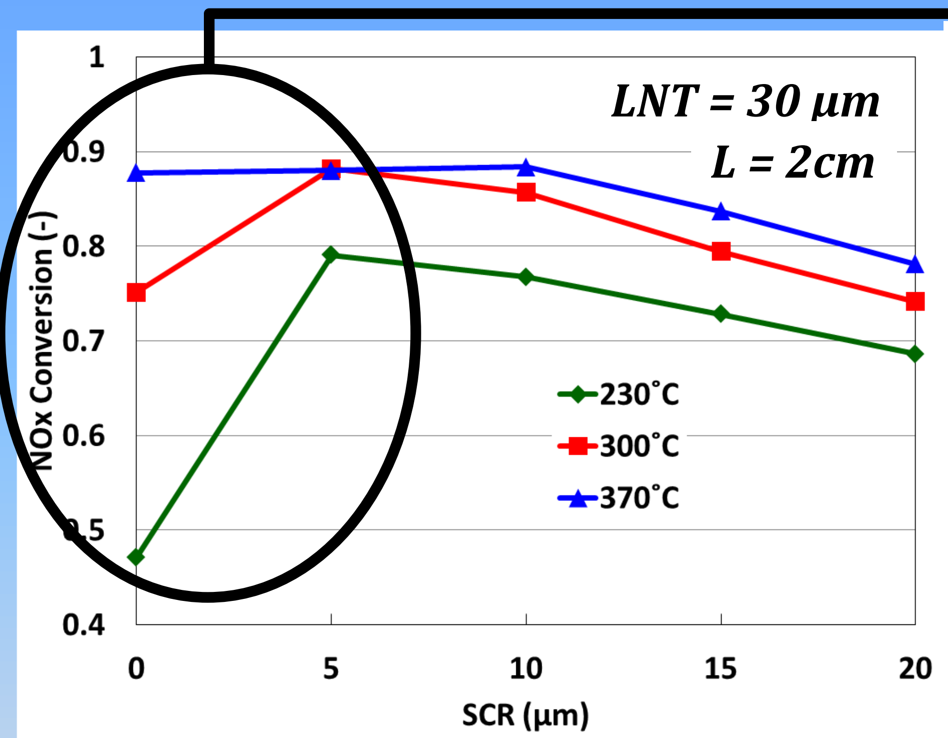
Conditions:

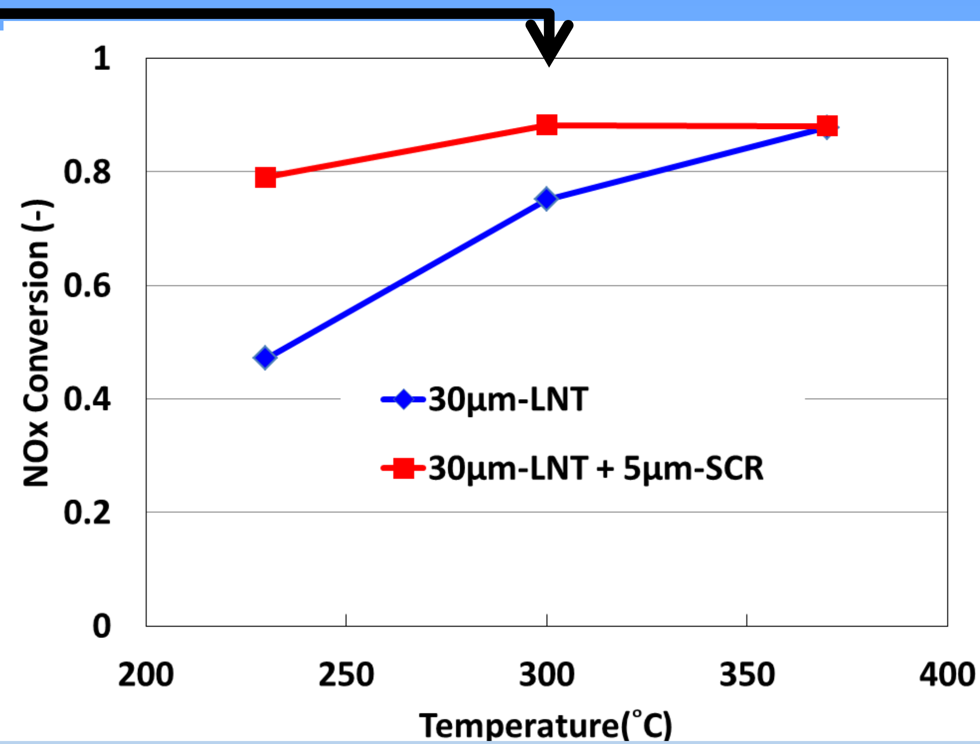
Lean inlet: 500 ppm NO + 5% O_2 in bal Ar / Duration: 60s

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

Temperature: 300°C ***GHSV:*** 60,000 hr^{-1} (based on monolith volume)

Effect of Temperature

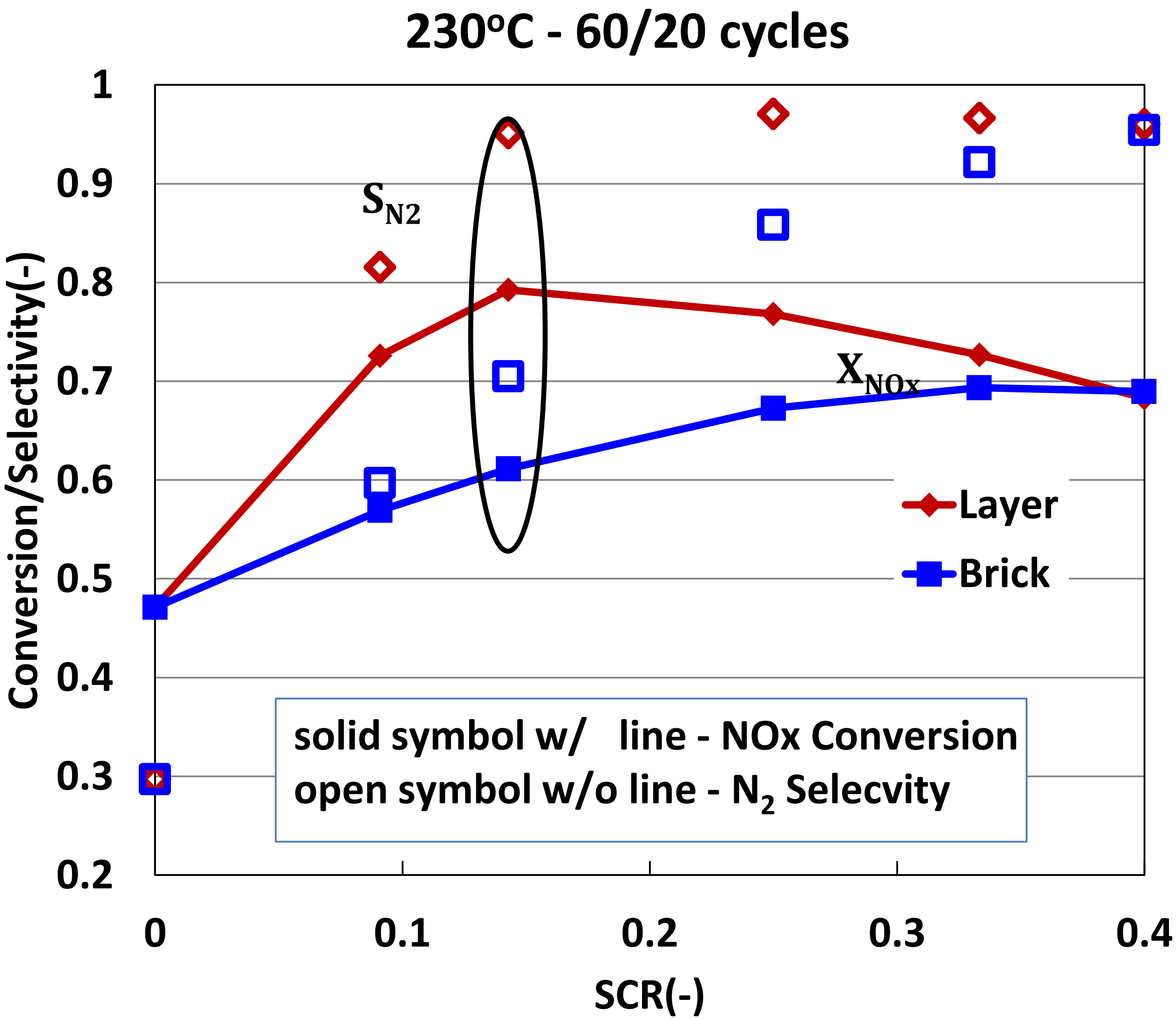




Conditions: Lean: 60s 500 ppm NO + 5% O_2
Rich: 20s 5000 ppm H_2

Impact of SCR becomes ***less significant*** *at* ***higher temperature*** ➔ *significant* ***NH_3 consumption*** *in* ***LNT***

Layered vs Brick



L = 2cm

LNT = 30 μm

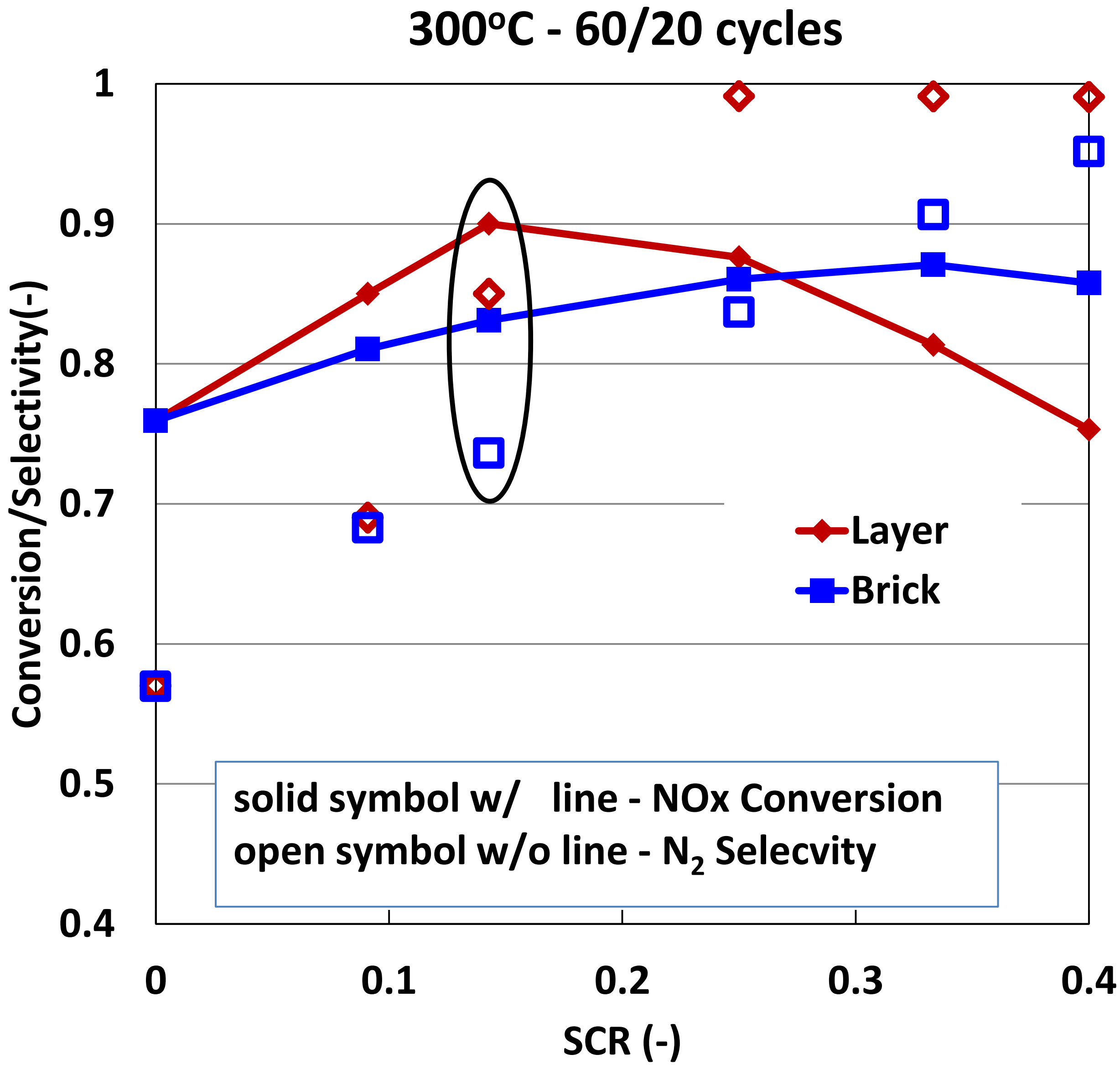
SCR	Layer (μm)	Brick (cm)	R_{Ω_2} (μm)
0.00	0	0.00	30
0.09	3	0.18	33
0.14	5	0.28	35
0.25	10	0.50	40
0.33	15	0.66	45
0.40	20	0.80	50

Conditions:

Lean: 60s 500 ppm NO + 5% O_2

Rich: 20s 5000 ppm H_2

Layered vs Brick



L = 2cm

LNT = 30 µm

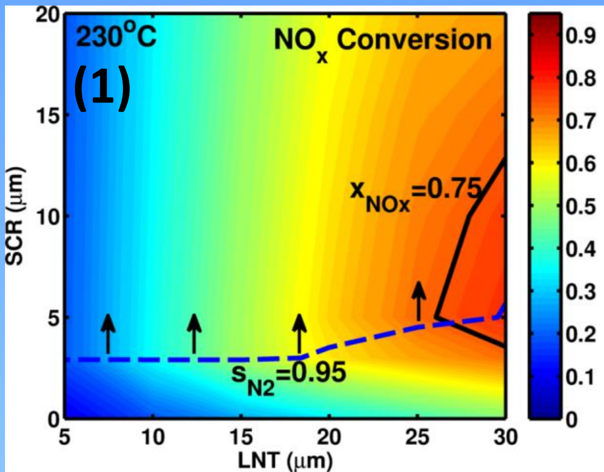
SCR	Layer (µm)	Brick (cm)	R_{Ω_2} (µm)
0.00	0	0.00	30
0.09	3	0.18	33
0.14	5	0.28	35
0.25	10	0.50	40
0.33	15	0.66	45
0.40	20	0.80	50

Conditions:

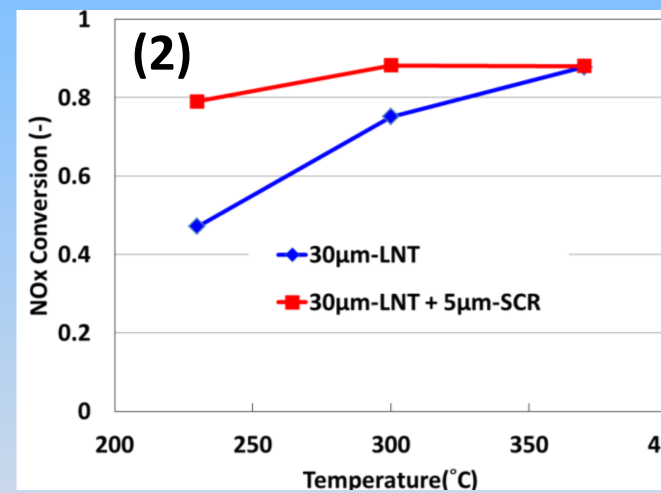
Lean: 60s 500 ppm NO + 5% O_2

Rich: 20s 5000 ppm H_2

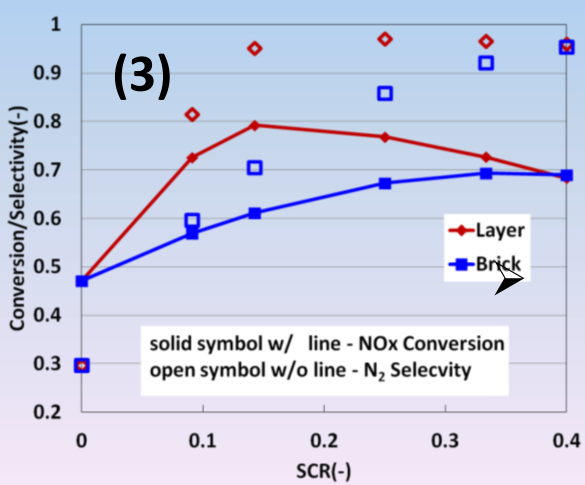
Summary and Conclusions



- Multiple combination of LNT and SCR can give same NOx conversion
- For a given LNT loading and temperature, there exists an SCR loading that gives max NOx conversion



- SCR function is diminished at higher temperature



- Better storage and utilization of generated NH_3 in dual layer configuration compared to brick

THANK YOU FOR YOUR ATTENTION!

Acknowledgements: