Cullen College of Engineering
Department of Chemical and Biomolecular Engineering

TEXAS CENTER FOR CLEAN
ENGINES, EMISSIONS & FUELS
University of Houston

Fast Cycling NSR + SCR Over Dual-Layer Catalysts

Yang Zheng, Mengmeng Li, Dan Luss, and Mike Harold

Department of Chemical and Biomolecular Engineering

Texas Center for Clean Engines, Emissions & Fuels

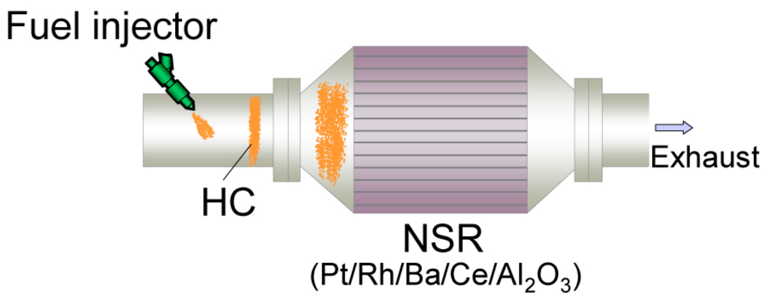
University of Houston, Houston TX

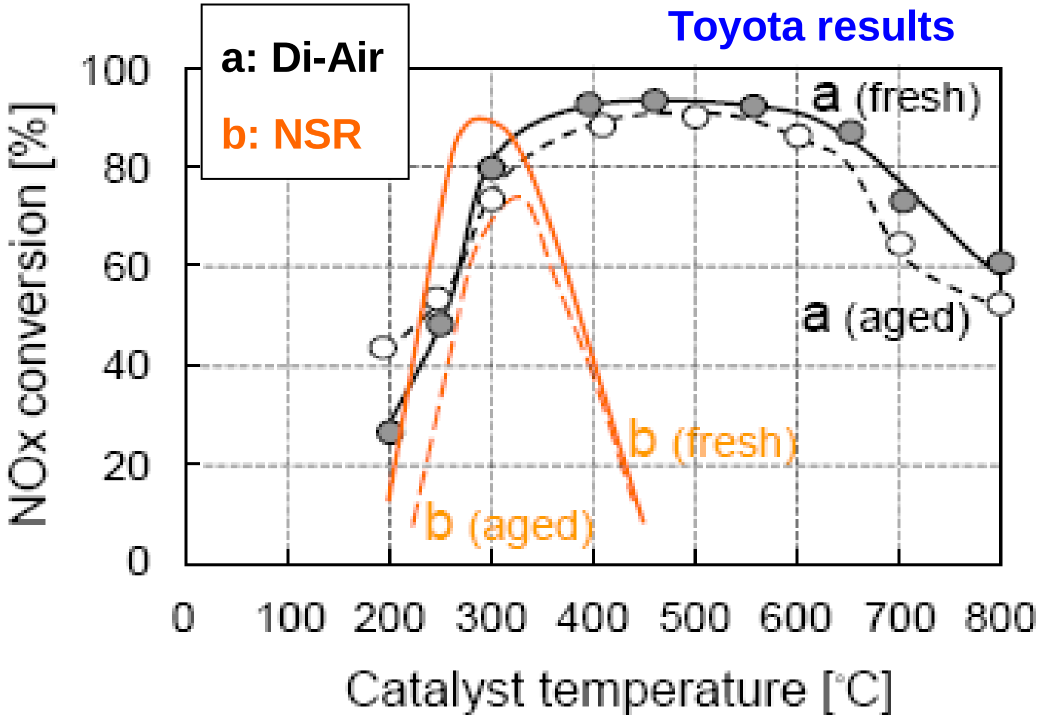
2015 CLEERS Meeting

Acknowledgements: *NSF + DOE, BASF, UH-TXCEF*

Rapid HC Pulsing on NOx Storage & Reduction Catalyst

Lean-burn emission control:
an enabler of clean and fuel-efficient light-duty vehicles





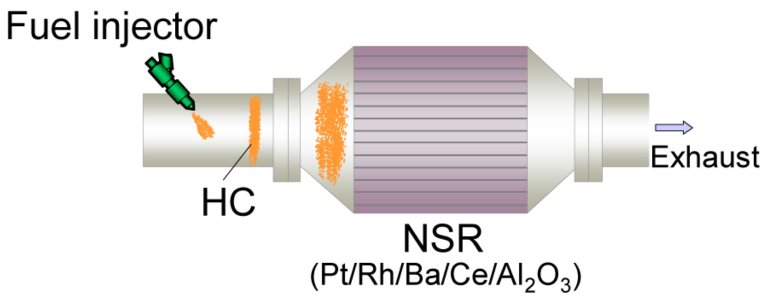
Toyota's Di-Air:

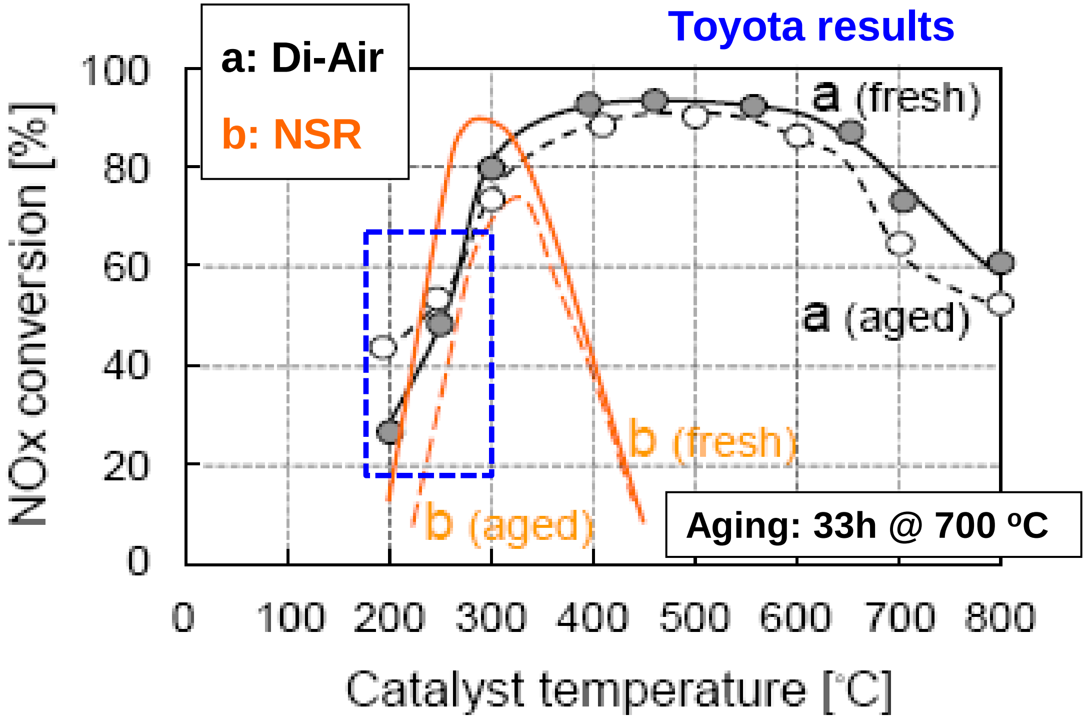
Diesel NOx aftertreatment by Adsorbed intermediate reductants (0.3~2.5 Hz)

[1] Bisaiji, Y., Yoshida, K., Inoue , M., Takagi, N. et al.SAE Int. J. Fuels Lubr. 5(3):2012
[2] Perng, C.C.Y., Easterling, V.G., Harold, M.P., Catalysis Today 231:125-134, 2014,

Evidence for Low Temperature Enhancement?

Lean-burn emission control:
an enabler of clean and fuel-efficient light-duty vehicles



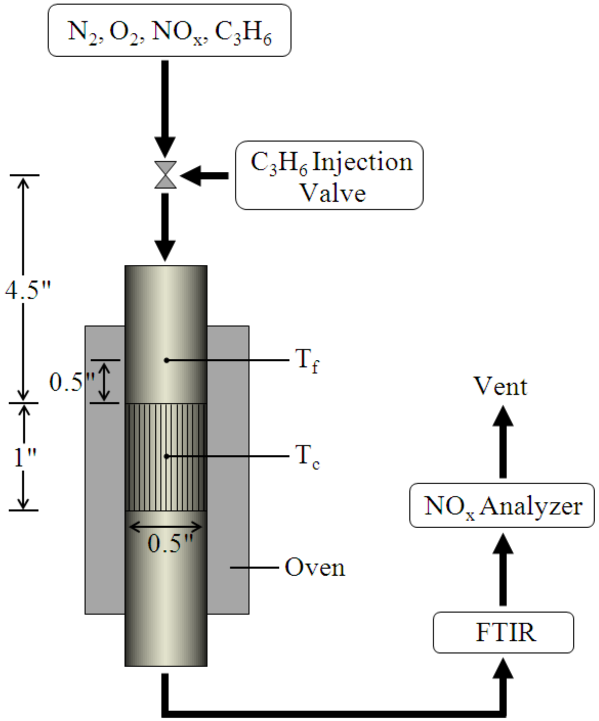


Toyota's Di-Air:

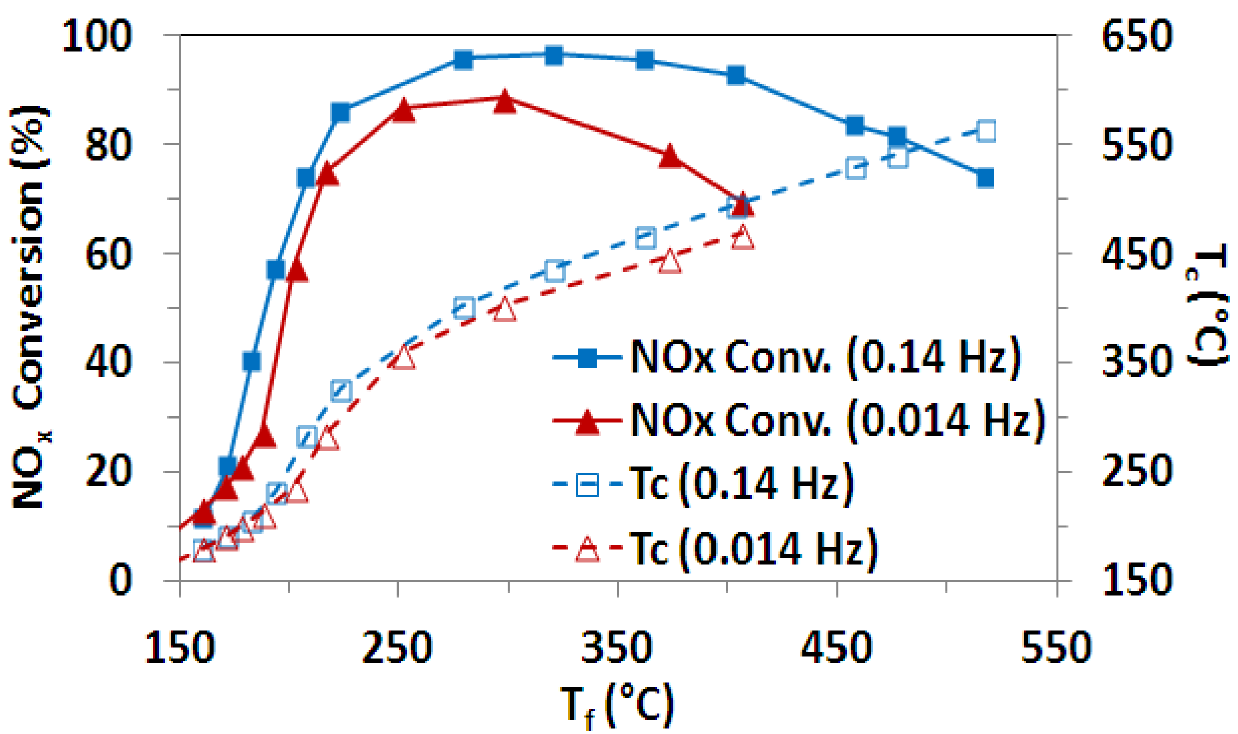
Diesel NOx aftertreatment by Adsorbed intermediate reductants (0.3~2.5 Hz)

[1] Bisaiji, Y., Yoshida, K., Inoue , M., Takagi, N. et al.SAE Int. J. Fuels Lubr. 5(3):2012
[2] Perng, C.C.Y., Easterling, V.G., Harold, M.P., Catalysis Today 231:125-134, 2014,

Confirmation Study of Rapid Cycling



UH results



Feed: 5% O_2 & 700 ppm NO

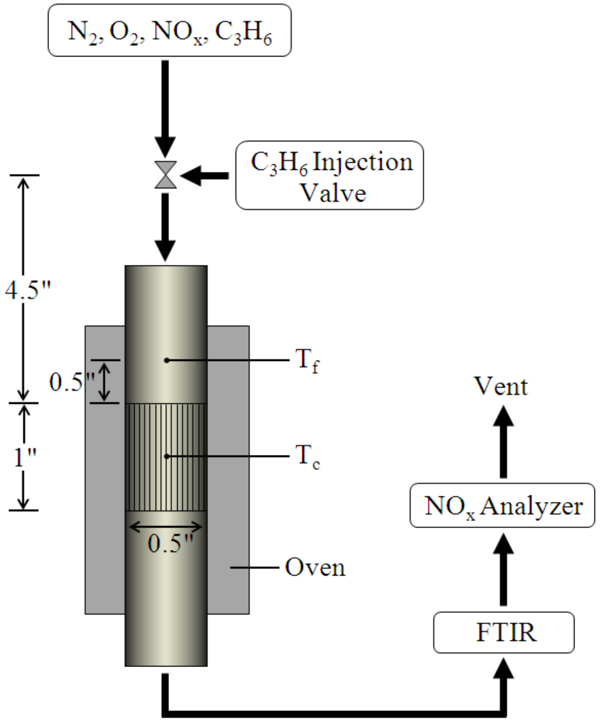
Rich Phase C_3H_6 = 1.75%

Rich duty cycle = 14.3%

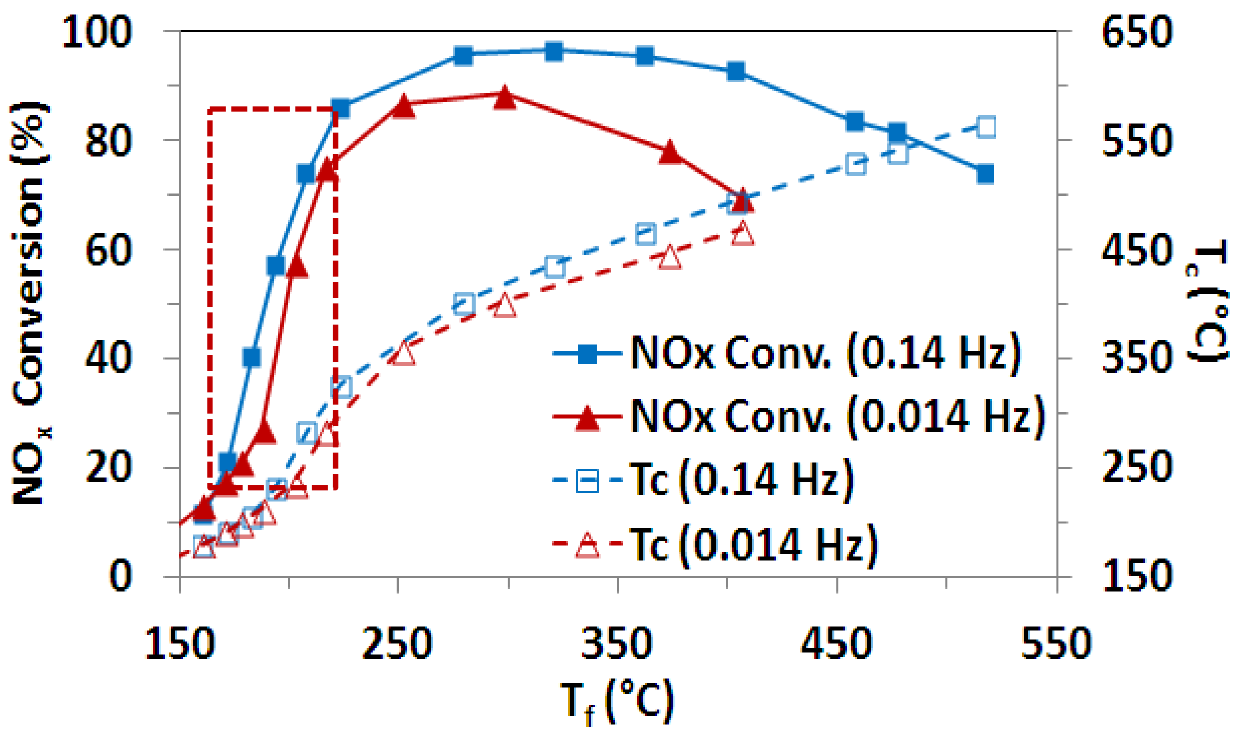
[1] Bisaiji, Y., Yoshida, K., Inoue , M., Takagi, N. et al.SAE Int. J. Fuels Lubr. 5(3):2012

[2] Perng, C.C.Y., Easterling, V.G., Harold, M.P., Catalysis Today 231:125-134, 2014,

Further Evidence for Low Temperature Enhancement



UH results



Feed: 5% O_2 & 700 ppm NO

Rich Phase C_3H_6 = 1.75%

Rich duty cycle = 14.3%

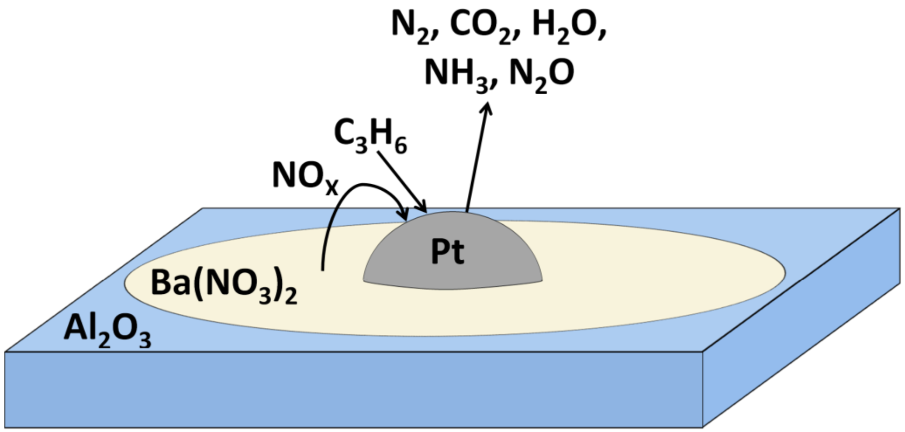
[1] Bisaiji, Y., Yoshida, K., Inoue , M., Takagi, N. et al.SAE Int. J. Fuels Lubr. 5(3):2012

[2] Perng, C.C.Y., Easterling, V.G., Harold, M.P., Catalysis Today 231:125-134, 2014,

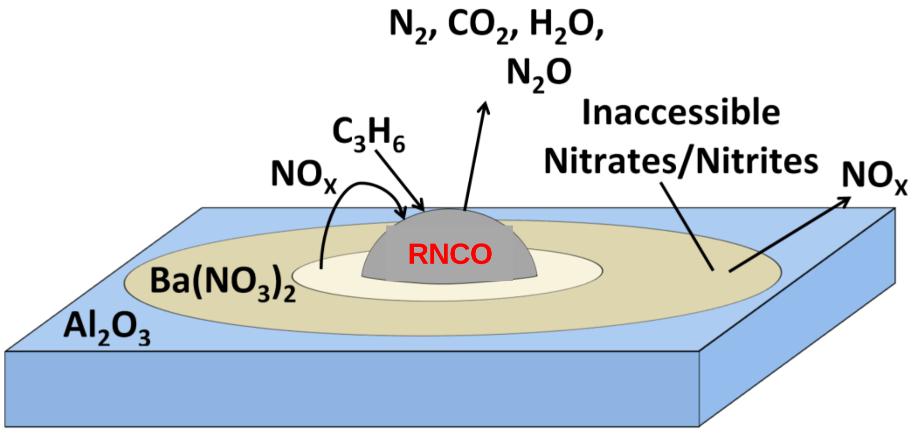
Rapid Injection Mechanism

- Only NOx stored in close proximity to Pt is utilized
- Generation of "RNCO" species on Pt and proximal storage sites leads to highly selective conversion to N_2
- Key: Intermediate species survives higher temperatures
- Need time for intermediate to accumulate on catalyst

Low Injection Frequency



High Injection Frequency



Questions

- Is there low temperature enhancement of NOx conversion during rapid cycling?
- Does the choice of hydrocarbon matter?
- How important are nonisothermal effects?
- Could addition of SCR function help?
- What is the optimal catalyst composition & architecture and operating strategy?
- Can this process be modeled?

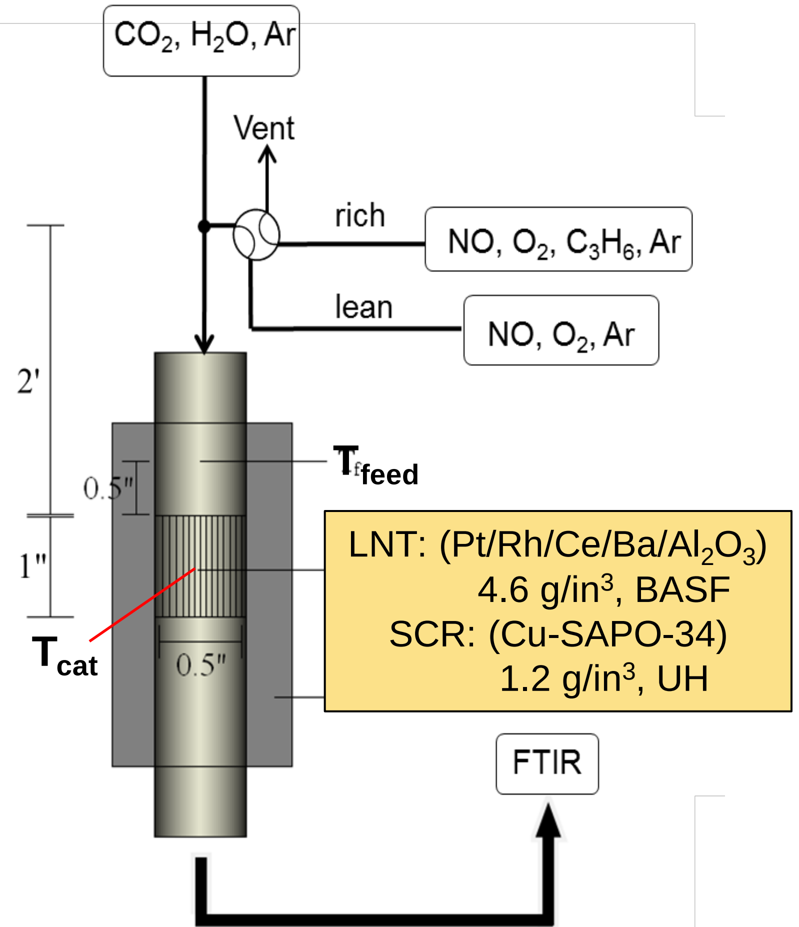
Objectives of Current Study

- Conduct systematic study on effect rapid hydrocarbon injection using various reductants during fast cycling NSR
- Investigate behavior over wide temperature range
- Evaluate impact of adding SCR function
- Provide further insight into fast cycling effects & mechanism

Feed Conditions

Cycling test (GHSV=80,000h^{-1})

Gas	Lean	Rich
NO	300 ppm	300 ppm
C_3H_6	—	1.8%
O_2	10%	5%
CO_2	5%	5%
H_2O	3.5%	3.5%
$\lambda = \frac{AFR}{AFR_{stoich}}$	$\lambda_{avg.}$=1.81	$\lambda_{rich.}$=0.89



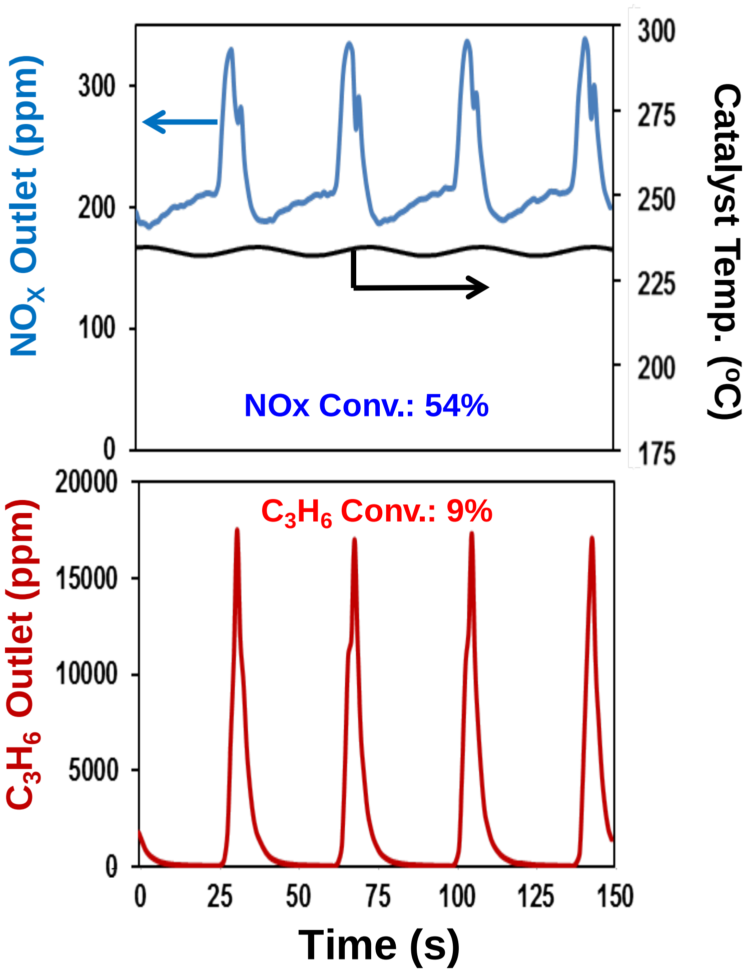
Rich cycle duty (rich period/cycle time) is fixed at **14.3%**, 60/10s, 30/5s, 6/1s
(0.014Hz) (0.028Hz) (0.14Hz)

All Catalysts were aged at **700 °C for 33h in air**

Impact of Cycling Frequency on Transient Behavior

225 °C feed temperature

a) LNT 30/5s

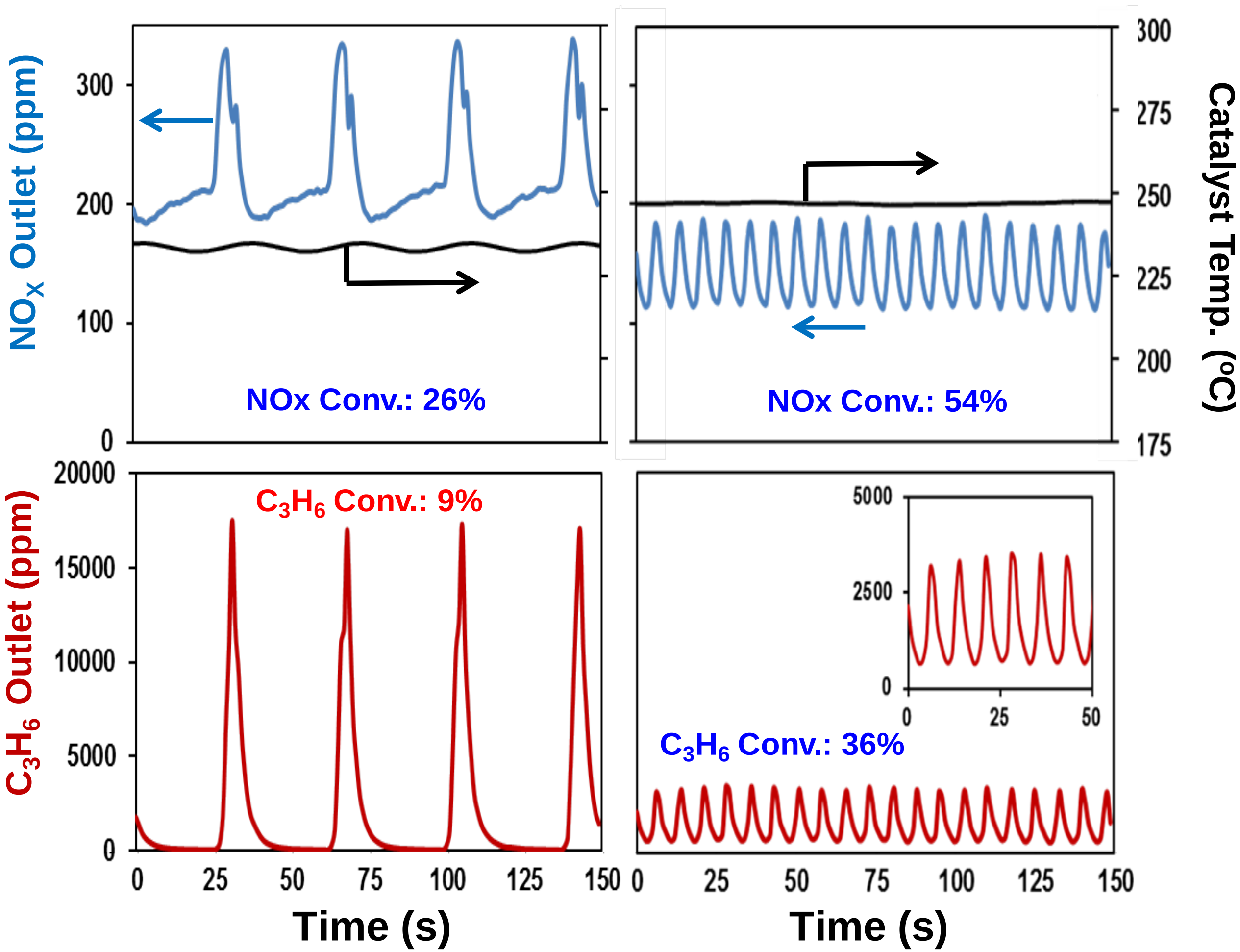


C_3H_6 feed 1.8%

Impact of Cycling Frequency on Transient Behavior

225 ^oC feed temperature

a) LNT 30/5s → b) LNT 6/1s

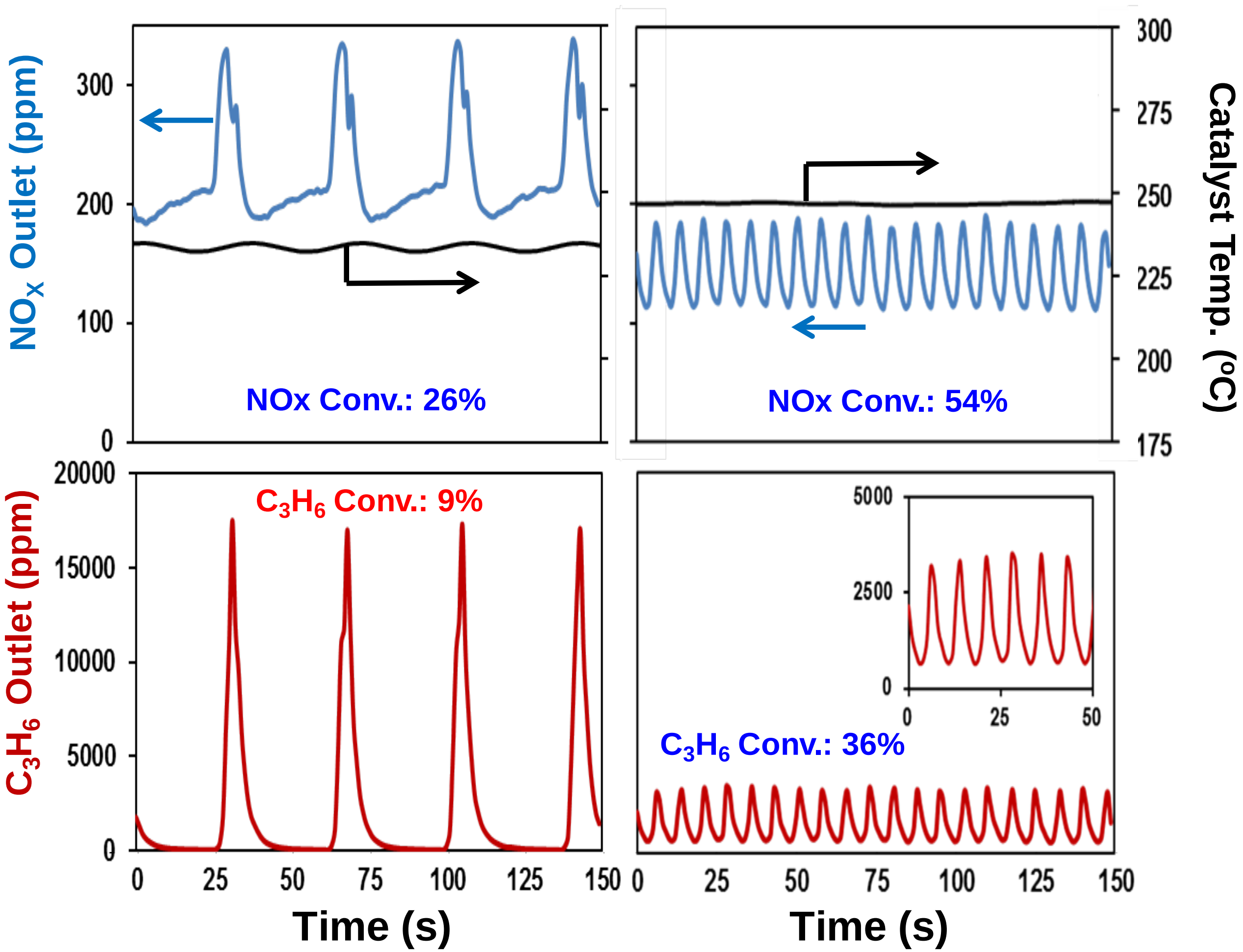


C_3H_6 feed 1.8%

Impact of Cycling Frequency on Transient Behavior

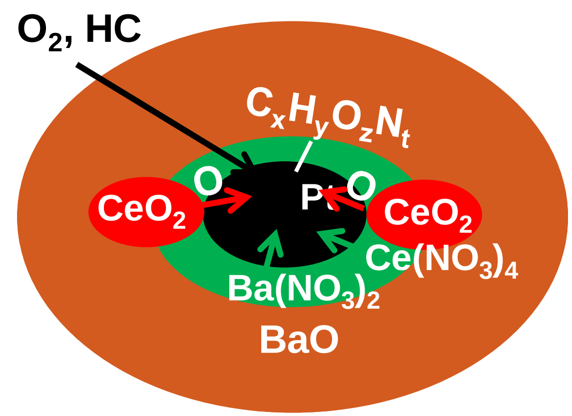
225 ^oC feed temperature

a) LNT 30/5s → b) LNT 6/1s



C_3H_6 feed 1.8%

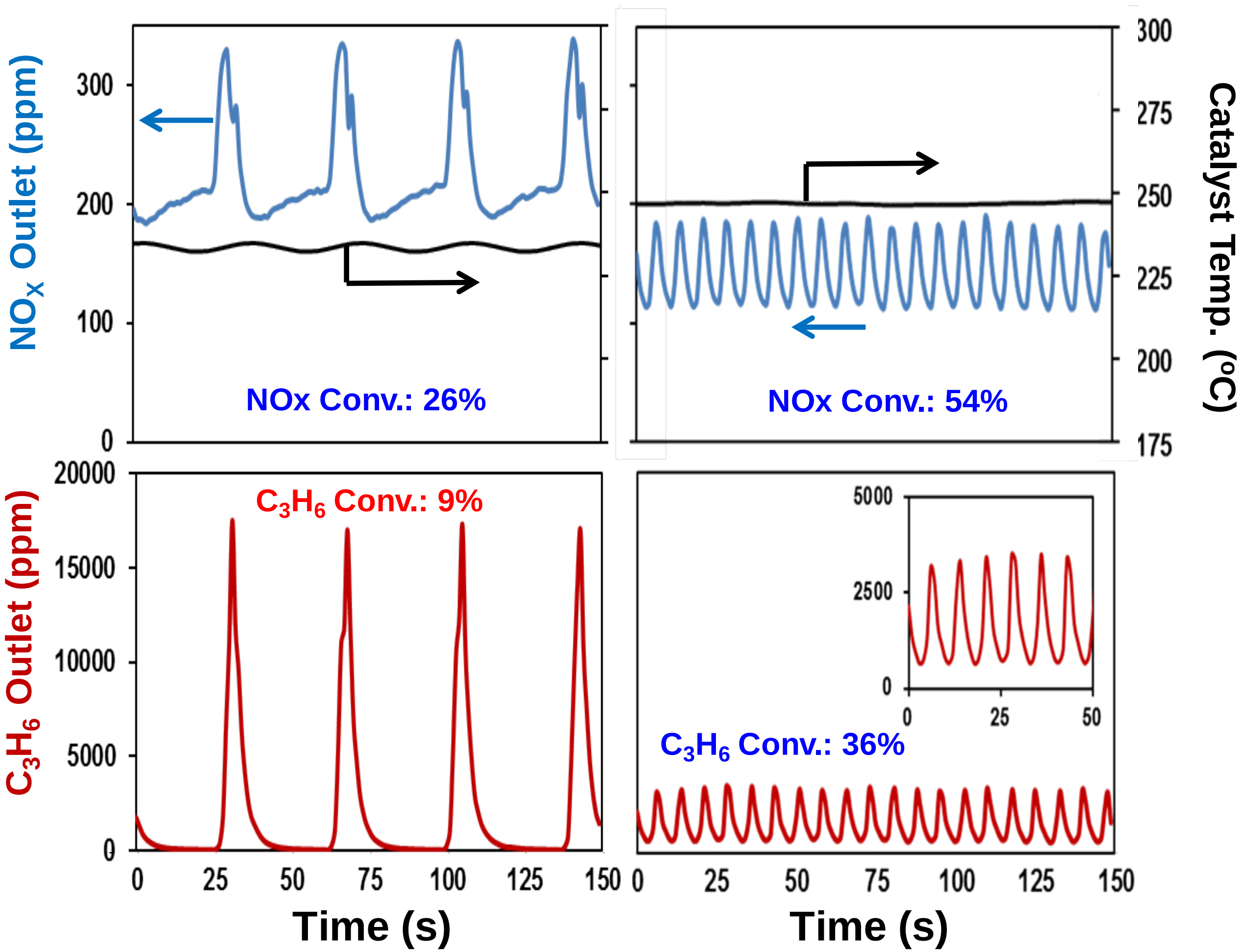
Reduction



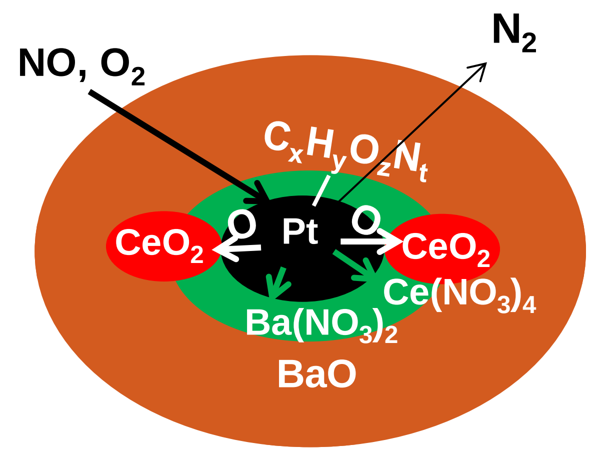
Impact of Cycling Frequency on Transient Behavior

225 °C feed temperature

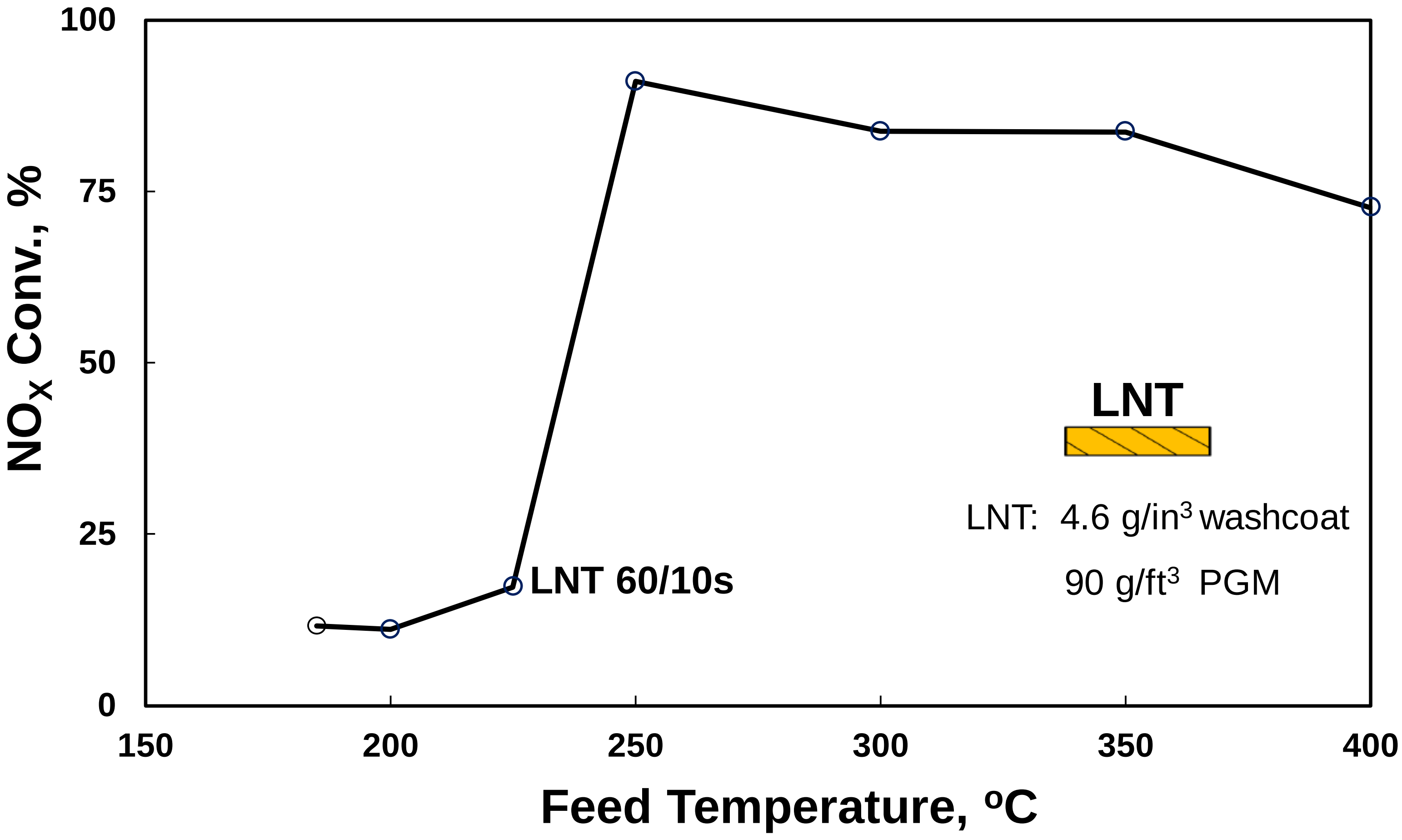
a) LNT 30/5s → b) LNT 6/1s



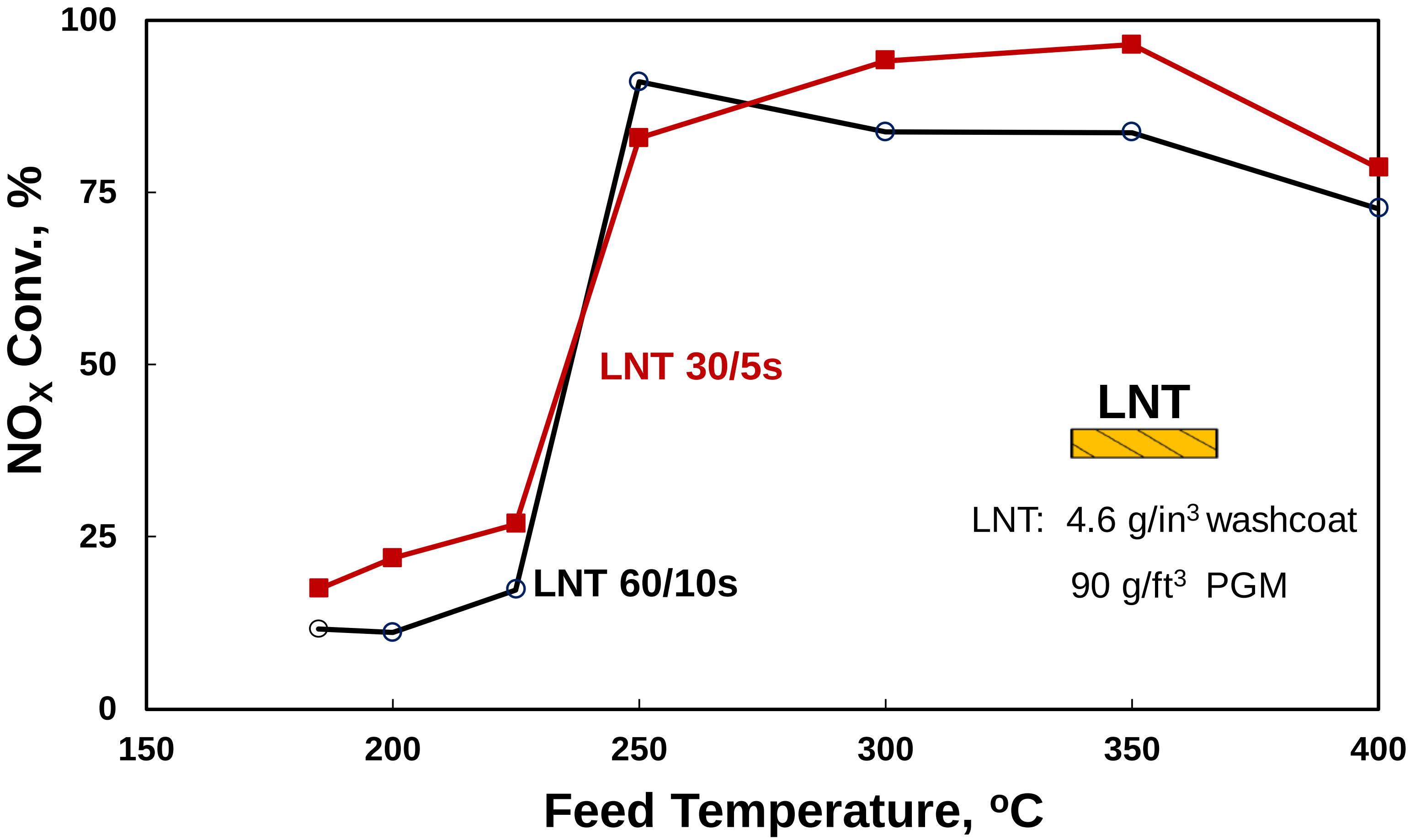
C_3H_6 feed 1.8%



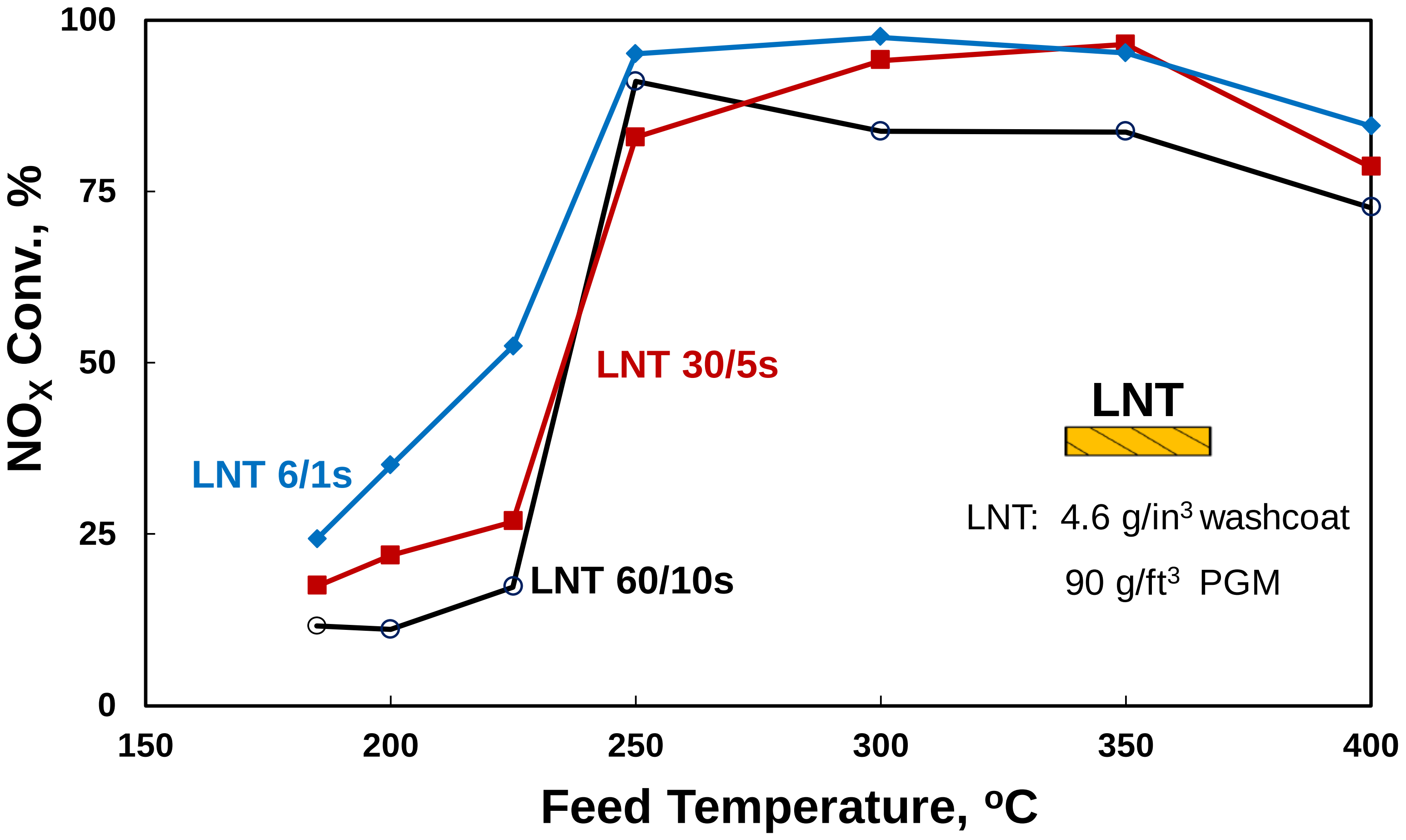
Impact of Cycling Frequency



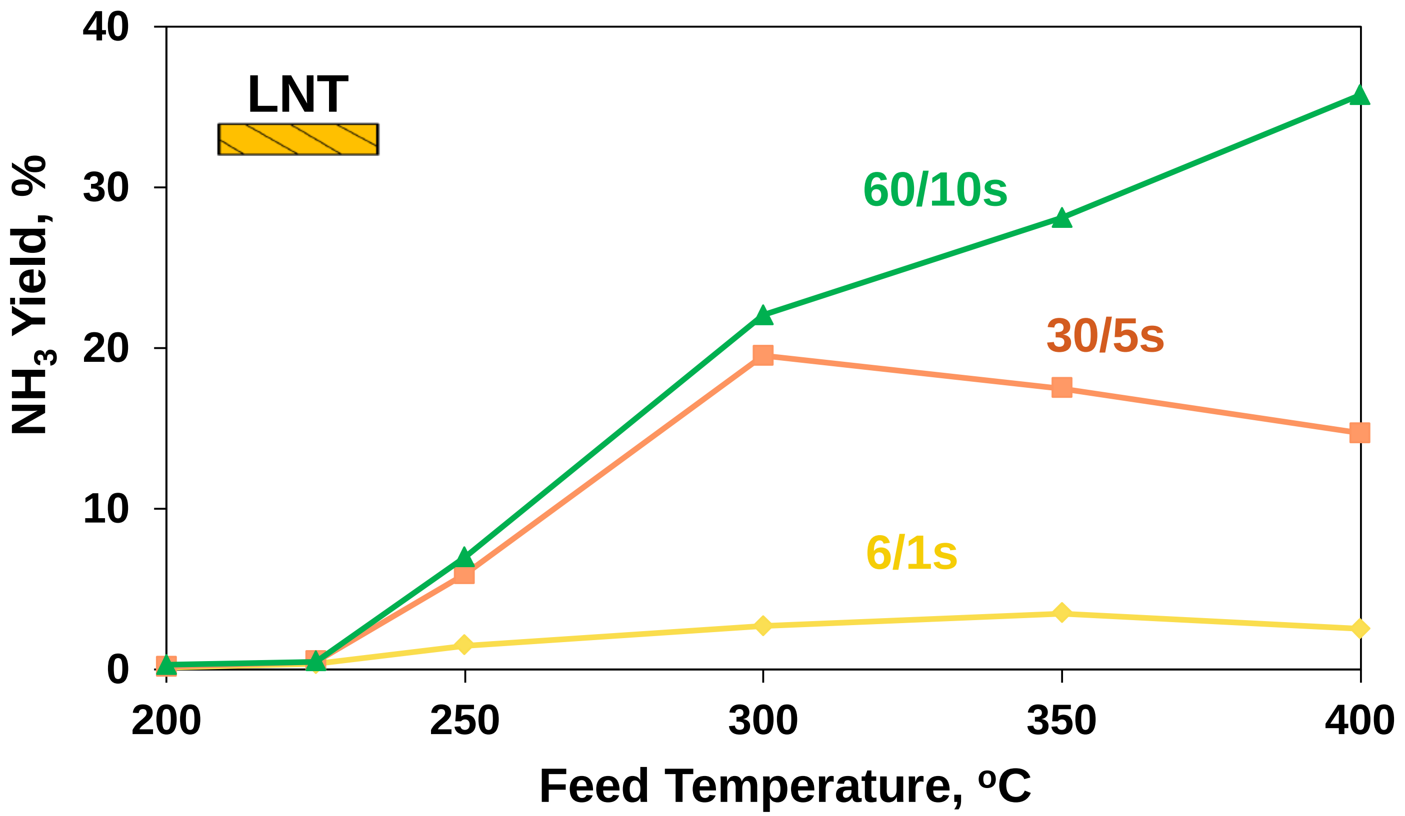
Impact of Cycling Frequency



Impact of Cycling Frequency



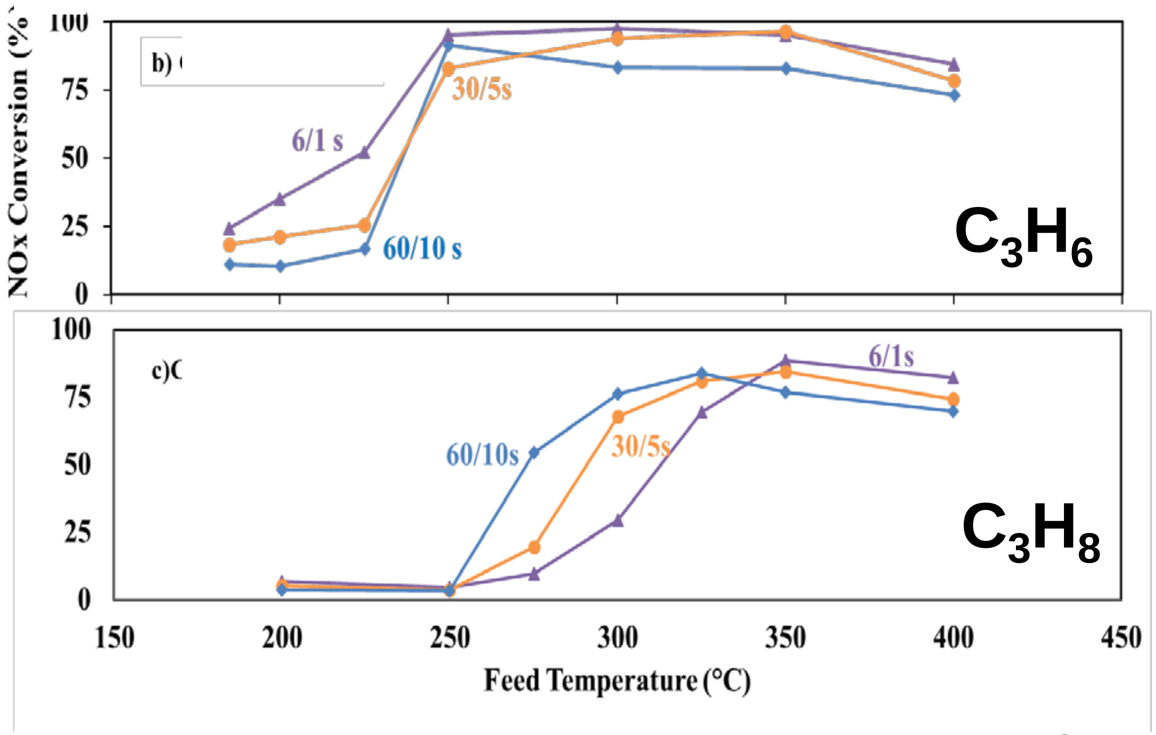
Evidence for a Non-NH_3 Mechanism



Suggests non-NH_3 mechanism for NOx reduction

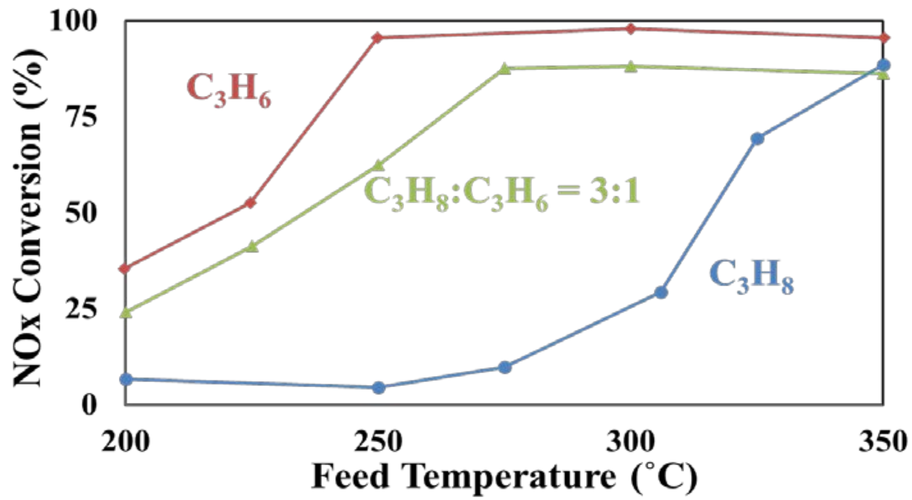
Reductant Comparison: Propene vs. Propane

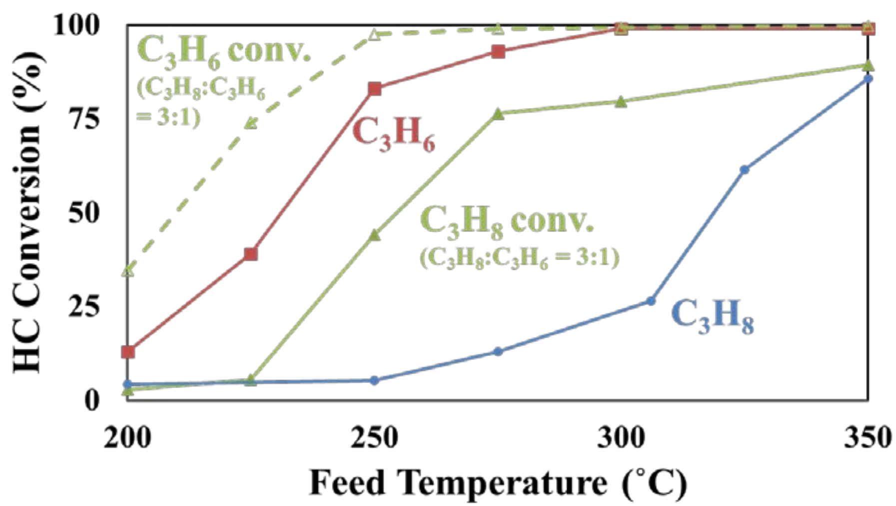
	Rich	
	C_3H_6	C_3H_8
NO (ppm)	300	300
O_2 (%)*	5	5
H_2 (%)	-	-
C_3H_6 (%)	1.8	-
C_3H_8 (%)	-	1.62



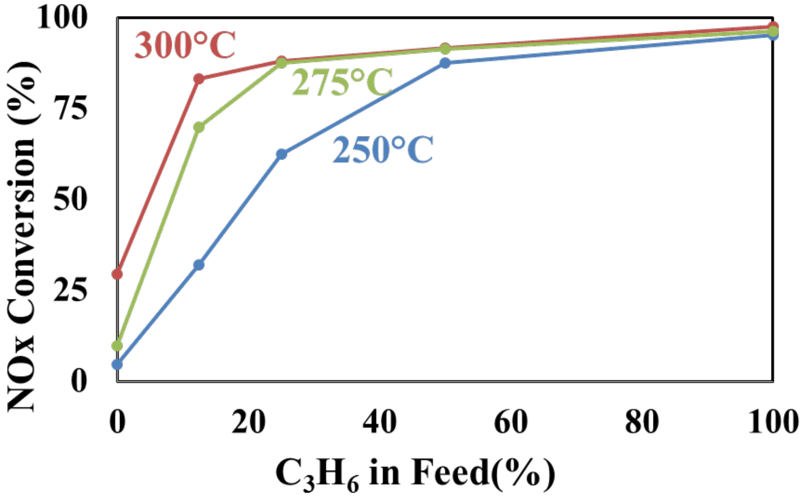
Fast Cycling with Propene + Propane Mixture

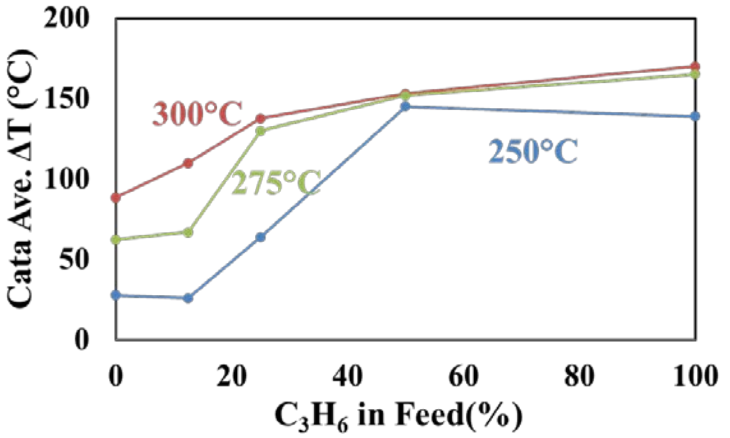
- Replacement of fraction of C_3H_8 with C_3H_6 leads to significant enhancement in NOx conversion

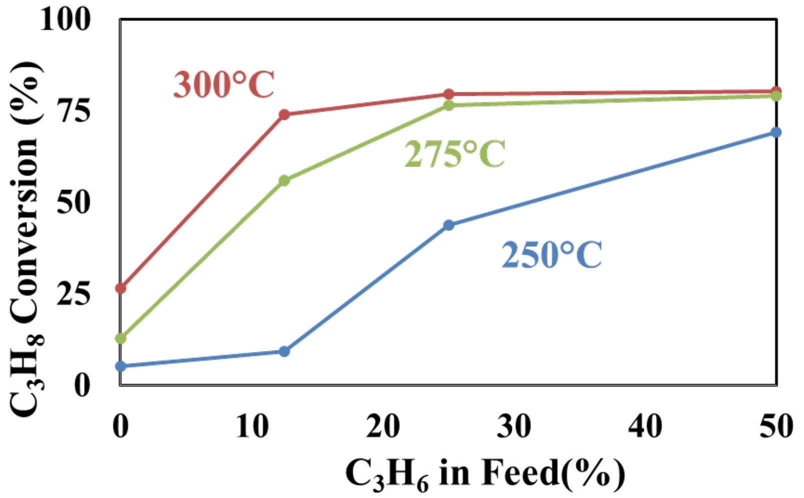




Fast Cycling with Propene + Propane Mixture



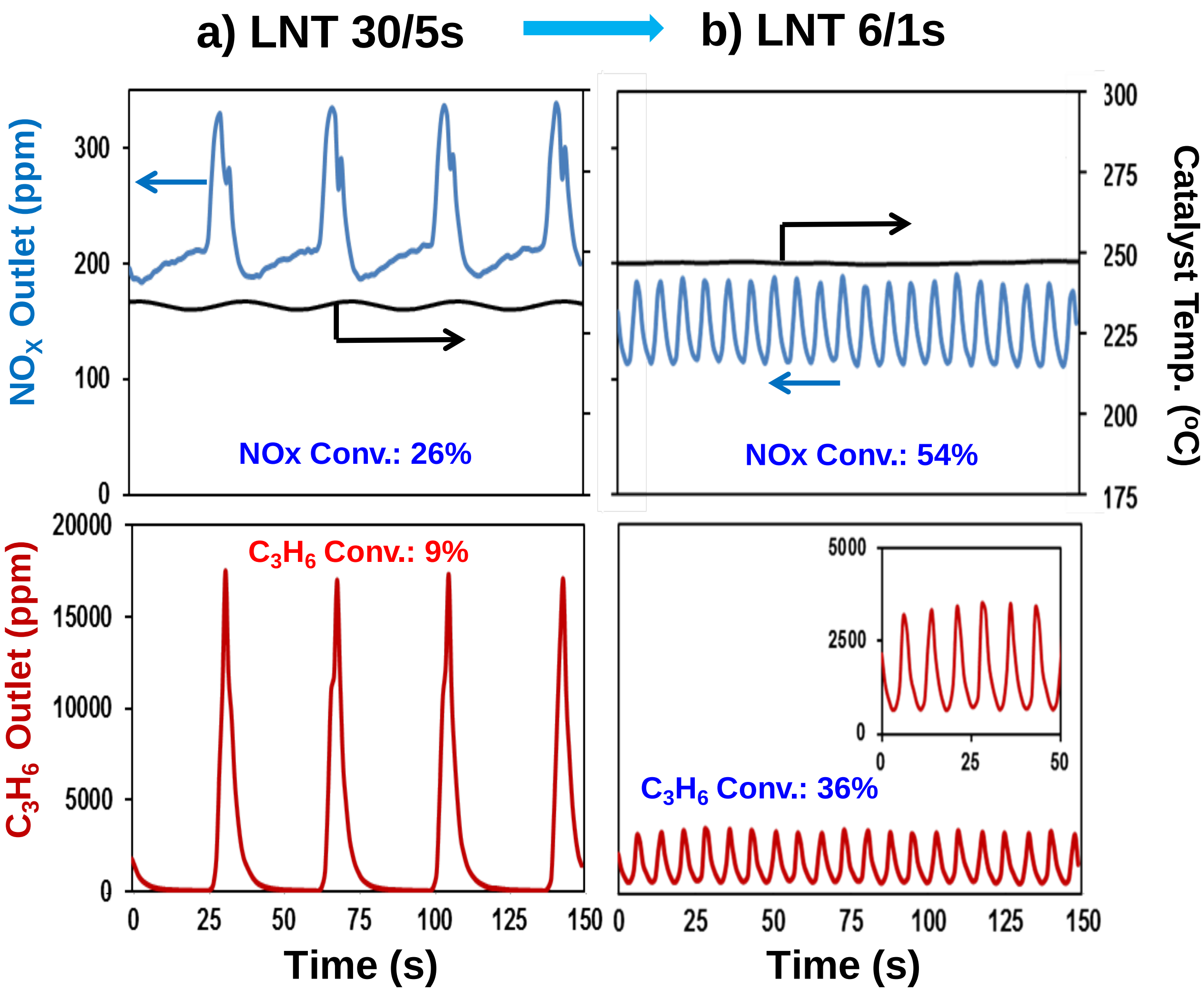




- Effect of C_3H_6 addition is nonlinear

Impact of Cycling Frequency on Transient Behavior

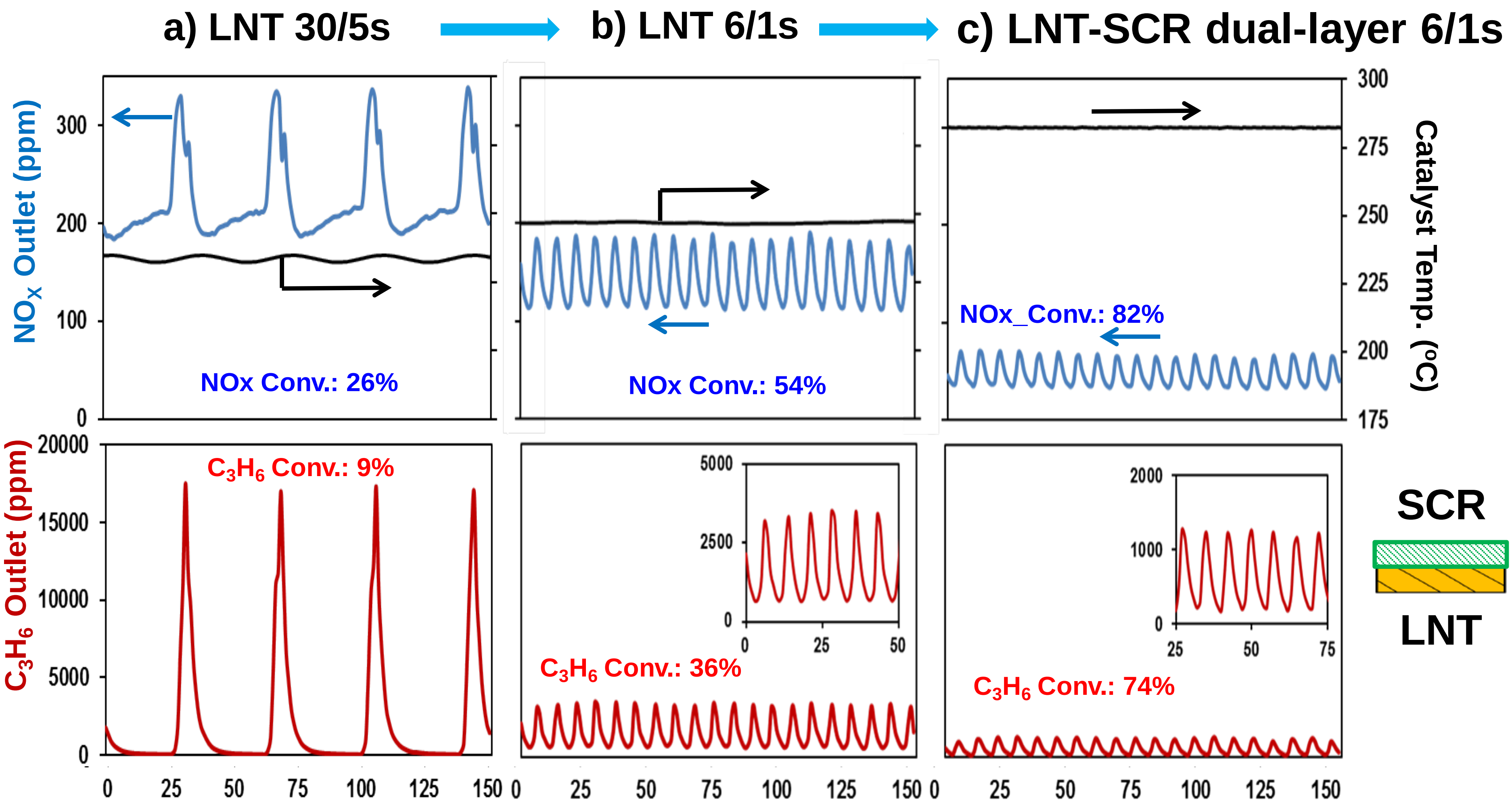
225 ^oC feed temperature



C_3H_6 feed 1.8%

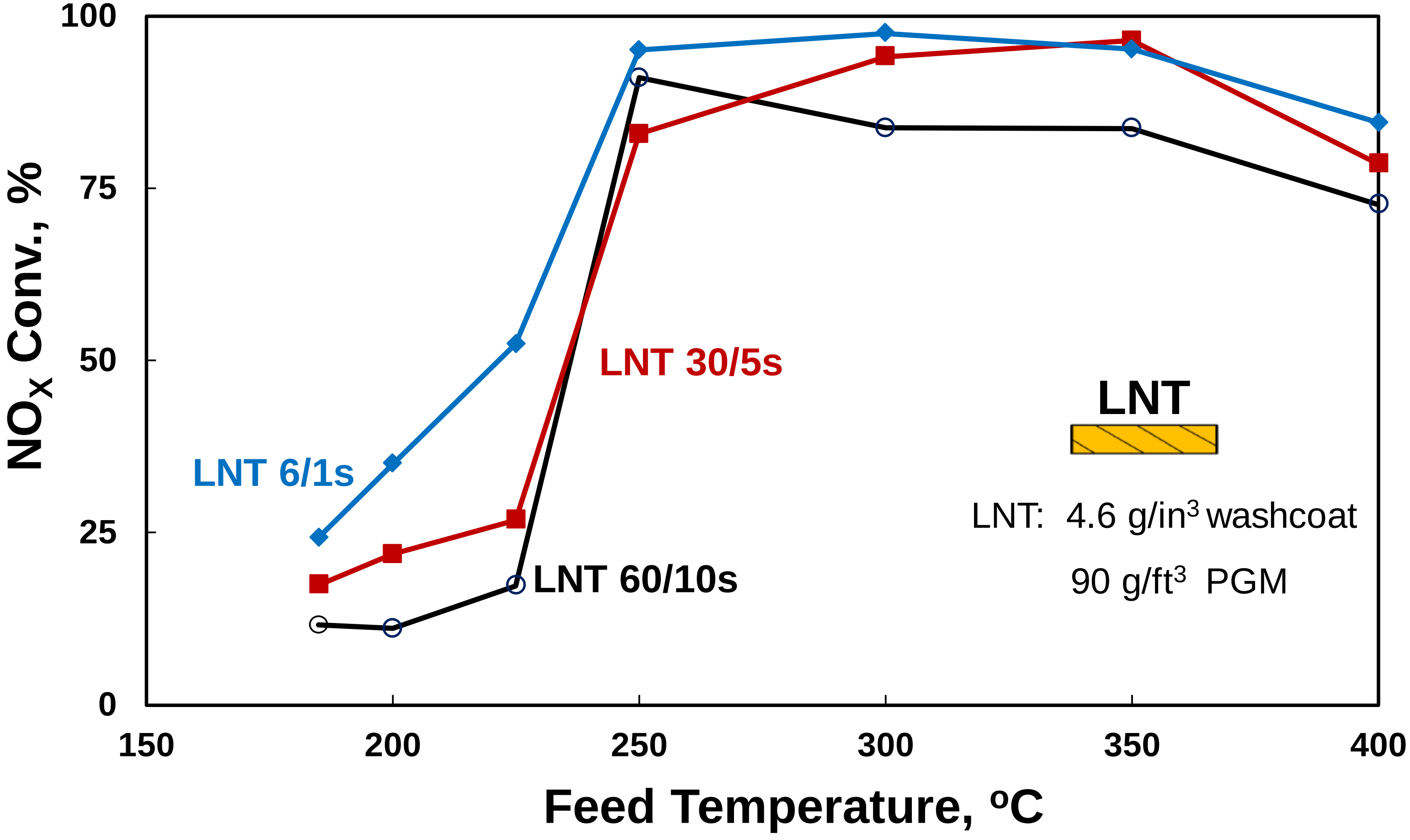
Impact of SCR Top Layer

225 ^oC feed temperature

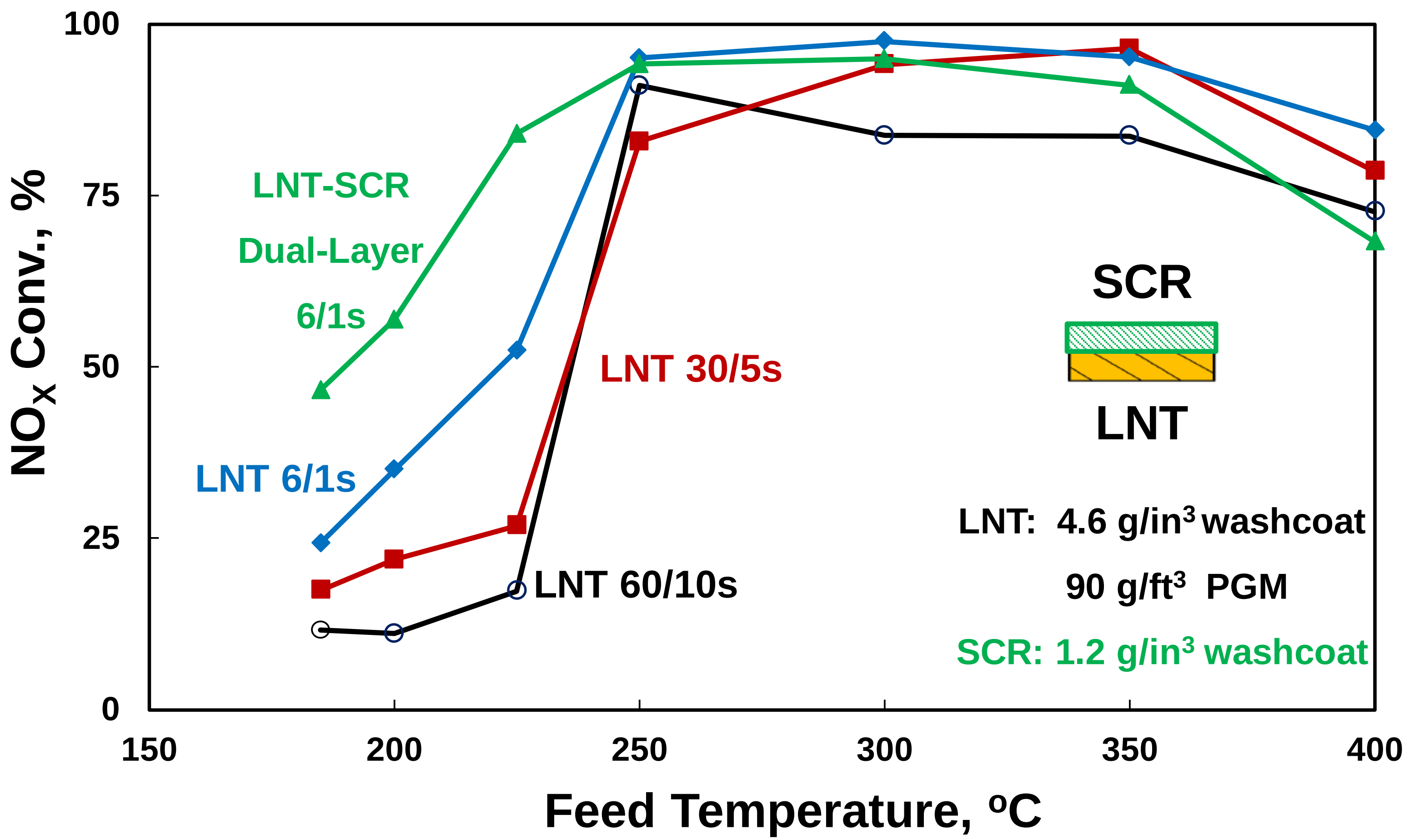


C_3H_6 feed 1.8%

Impact of Cycling Frequency



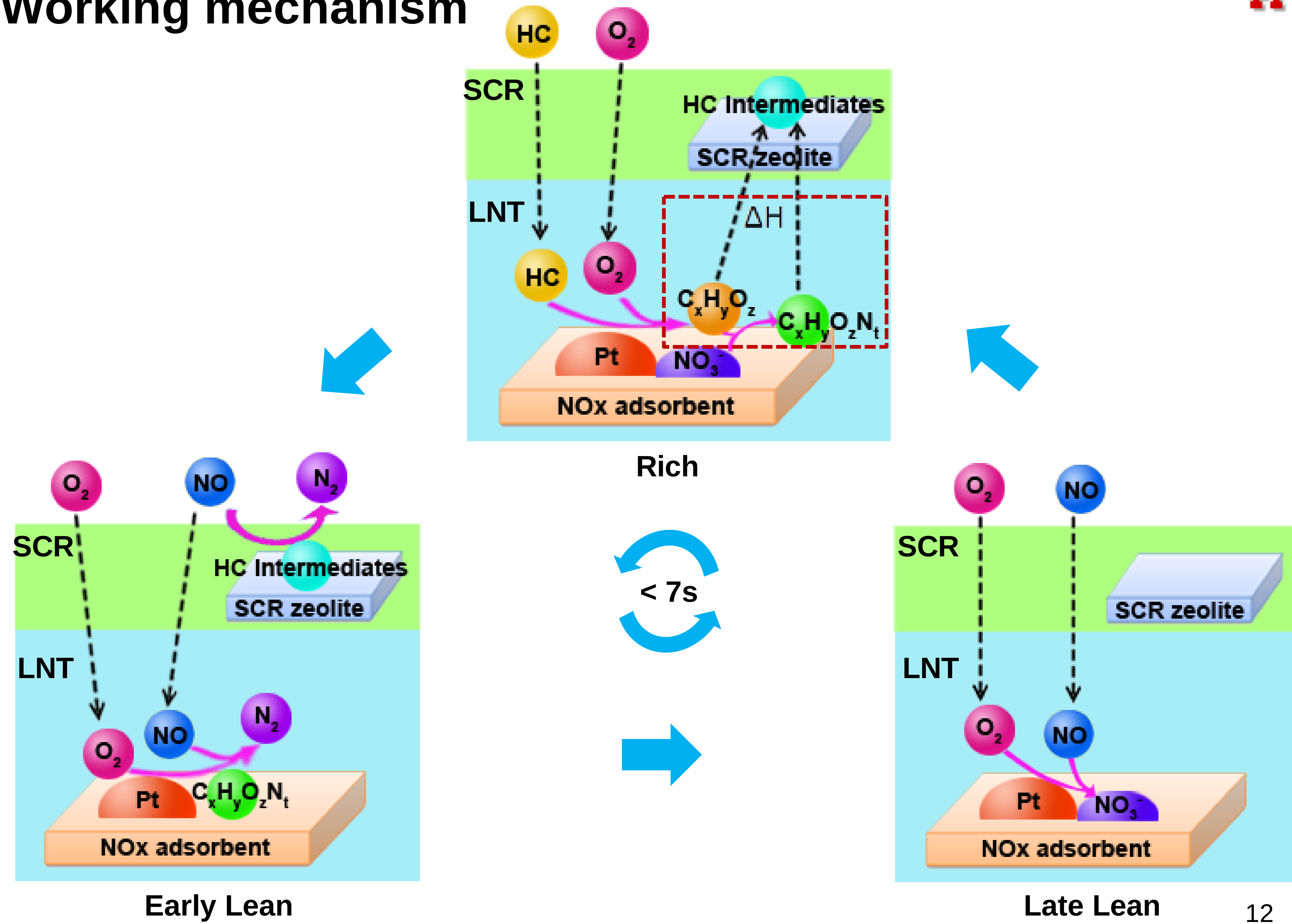
Impact of SCR Top Layer



Non NH_3 pathway: LNT-assisted HC-SCR by Ford

[1] Xu, L., McCabe, R., Dearth, M., and Ruona, W., SAE Int. J. Fuels Lubr. 3(1): 37-49, 2010

Working mechanism



Modeling Challenge

- Sensitive dependence on pulse shape & frequency
- Highly nonisothermal
- Rapid transients may preclude classical approach of mass & heat transfer coefficients
- May require full-blown simulation of 3-D mass, heat & momentum balances with detailed chemistry
- Fast cycling involves complex storage & reaction chemistry
- etc.

Conclusions

- Higher NO_x conversion at increased injections frequency using propylene
- High frequency injection gives elevated buy nearly time-invariant catalyst temperature
- Enhancement appears to span wider temperature window than first communicated
- Reductant type important: Enhancement not observed using C_3H_8 but is observed using C_3H_6
- Mechanism for N_2 formation different than conventional NSR; e.g. RNCO + NOx $\rightarrow$ N_2
- Addition of SCR top layer beneficial to conversion
- Opens the door for development of tailored multi-functional catalysts
- Slip of hydrocarbon may require downstream elimination measures

Acknowledgements

TEXAS CENTER FOR CLEAN
ENGINES, EMISSIONS & FUELS
University of Houston

BASF
The Chemical Company

Thank you!

Questions ?

Top-layer impact