



# Synergy of LNT and SCR Catalysts in Coupled LNT-SCR Systems

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# Synergy of LNT and SCR Catalysts in Coupled LNT-SCR Systems

## Overview:

- Coupled LNT-SCR systems: concept and development
- Role of HC<sub>s</sub> in NO<sub>x</sub> reduction over coupled LNT-SCR (Cu-CHA) system
- NO<sub>x</sub> reduction using HC<sub>s</sub> and NH<sub>3</sub> over Cu-CHA
- Mitigation of N<sub>2</sub>O and H<sub>2</sub>S emissions over Cu-CHA in LNT-SCR configuration
- Plasma-assisted LNT catalyst regeneration
- Summary

# LNT-SCR Concept: Utilization of *In Situ* NH<sub>3</sub>

- “Classical” explanation:
  - LNT produces NH<sub>3</sub> during rich purges (similar to TWC under rich engine conditions)
  - NH<sub>3</sub> stores on downstream SCR catalyst
  - Stored NH<sub>3</sub> reacts with “breakthrough” NOx during lean operation
  - Similar to urea-SCR except that NH<sub>3</sub> is generated “in-situ” or “passively” by the LNT

D. Chatterjee, P. Kočí, V. Schmeisser, M. Marek, M. Weibel, B. Krutzsch, Catal. Today 151 (2010) 395.

P. Forzatti, L. Lietti, Catal. Today 155 (2010) 131.

A. Lindholm, H. Sjövall, L. Olsson, Appl. Catal. B 98 (2010) 112.

L. Xu, R. McCabe, M. Dearth, W. Ruona, SAE Technical Paper 2010-01-0305 (2010).

E.C. Corbos, M. Haneda, X. Cortois, P. Marecot, D. Duprez, H. Hamada, Appl. Catal. A 365 (2009) 187-193.

F. Plát, S. Bártová, J. Štěpánek, P. Kočí, M. Marek, Ind. Eng. Chem. Res. 49 (2010) 10348.

## LNT-SCR Concept: History

- First U.S. patent to DaimlerChrysler in 2001 (US 6,176,079)
- Other U.S. patents to SwRI, Ford, Eaton, DaimlerChrysler, GM, BASF, Umicore, Johnson-Matthey
- First open literature publications:  
2006, Eaton Corp. , use of LNT-SCR system for HDD applications  
2006-2007, Ford, use of LNT-SCR for LDD applications
- First application: Daimler, BlueTEC Mercedes E320 (introduced in October 2006 in U.S.)
- 2<sup>nd</sup> generation LNT-SCR system reported by Ford in 2009  
(Fe-zeolite SCR catalyst replaced by Cu-CHA)
- LNT-SCR system models published:  
2009-2010: Daimler group  
2010: Kočí et al.  
2012: Balakotaiah et al.

# LNT-SCR Concept: Applications



BlueTEC Mercedes E320 (MY 2007 in U.S.)  
and E300 (MY2008 in Europe)

V6 CDI engine

- Aimed at Tier II Bin 8, corresponding to ca. 50% NOx conversion requirement
- DOC-LNT-CDPF-SCR exhaust catalyst configuration
- Function of SCR catalyst appears to have been mainly for avoidance of NH<sub>3</sub> slip
- Used in MY2007-2009
- Superceded by BlueTEC II urea-SCR system (Tier II, Bin 5)

M. Weibel, N. Waldbüßer, R. Wunsch, D. Chatterjee, B. Bandl-Konrad, B. Krutzsch, Top. Catal. 52 (2009) 1702.  
J. Schommers, H. Breitbach, AutoTechnology, 7(3) (2007) 48.

## 2<sup>nd</sup> Generation LNT + SCR

- Key points:
  - enabled by advances to both LNT catalyst technology and SCR catalyst technology
  - NH<sub>3</sub> *in situ* mechanism does not fully explain LNT+SCR vehicle data: HC-SCR in Cu-CHA catalyst also contributes to NOx reduction
  - Cu-CHA also plays active role in mitigation of N<sub>2</sub>O and H<sub>2</sub>S emissions
  - excellent NOx reduction activity of Cu-CHA catalyst (and stability w.r.t. aging) enables decrease in LNT PGM loadings

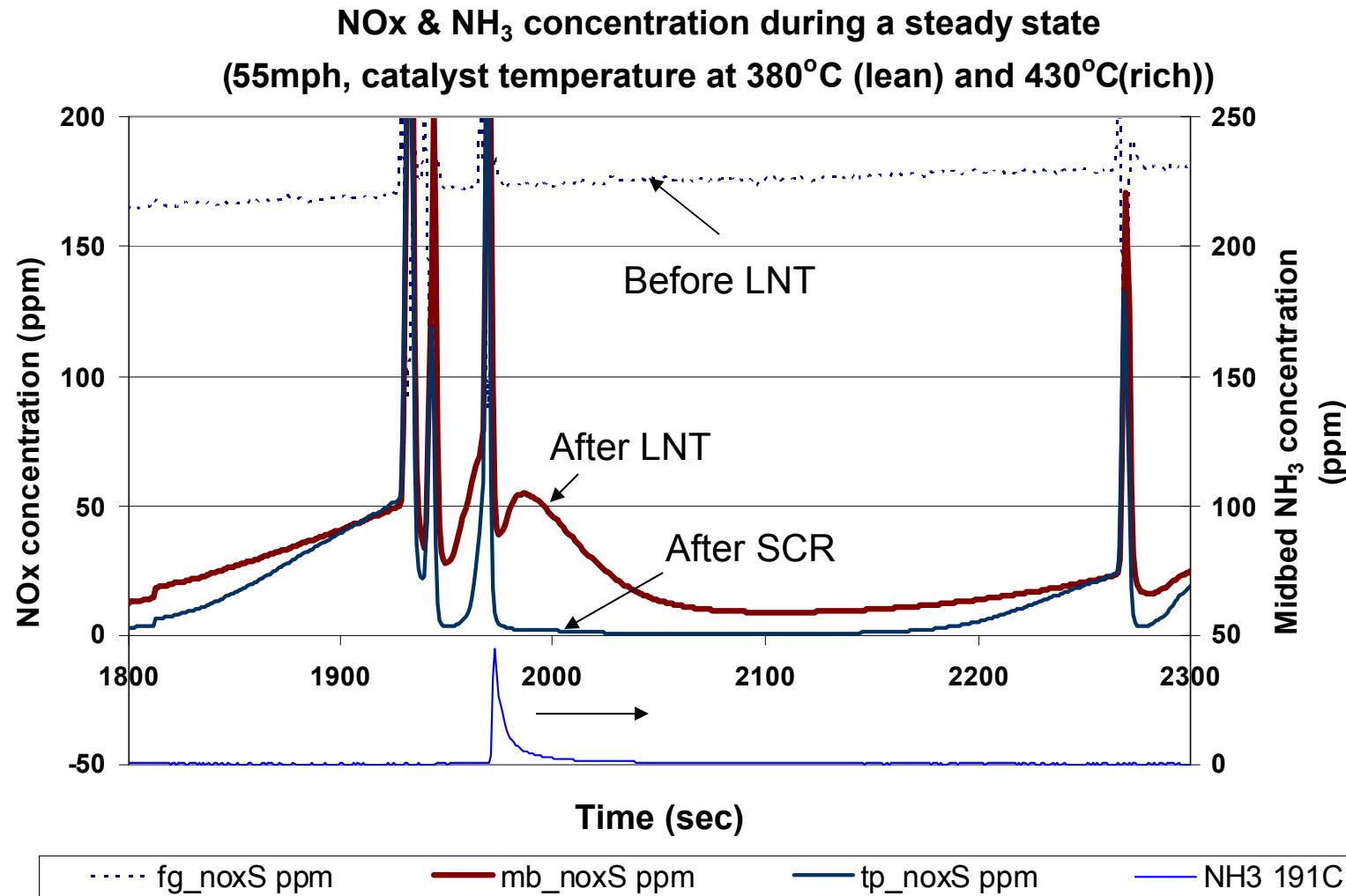
L. Xu, R. McCabe, M. Dearth, W. Ruona, SAE Technical Paper, 2010-01-0305.

L. Xu, R. McCabe, P. Tennison, H.-W. Jen, SAE Technical Paper, 2011-01-0308.

J. Wang, Y. Ji, Z. He, M. Crocker, M. Dearth, R.W. McCabe, Appl. Catal. B 111-112 (2012) 562.

# Vehicle Testing: Steady-Speed

## (Ford data: R. McCabe and M. Dearth)

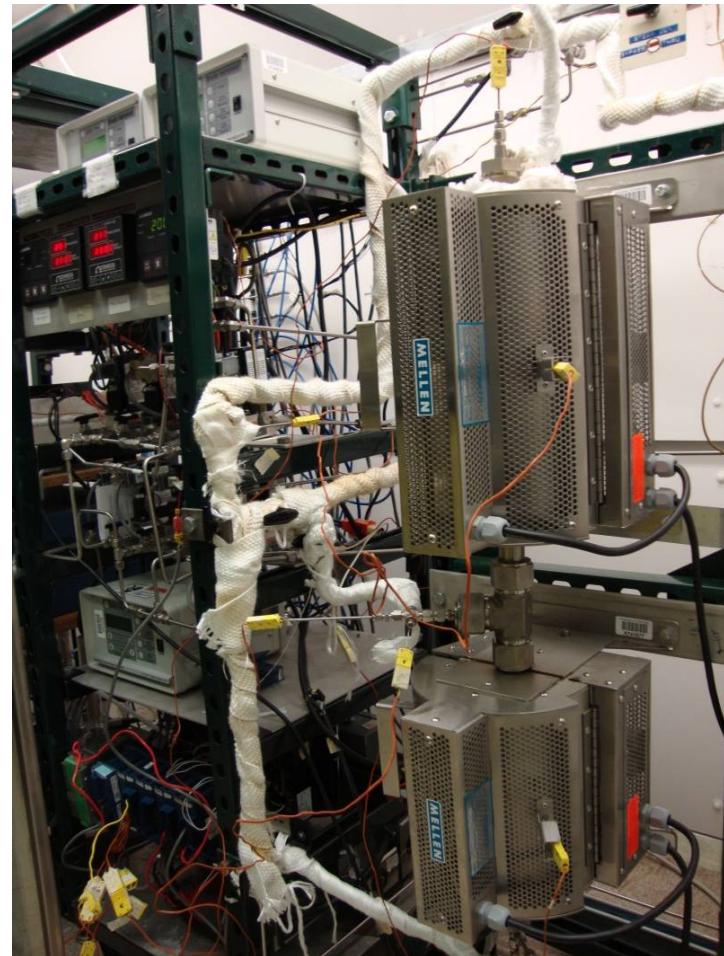


NH<sub>3</sub> produced cannot explain extra NOx conversion by SCR catalyst

# Reactor Studies

## LNT-SCR studies:

- BASF catalysts:  
Low PGM-loaded LNT +  
Cu-chabazite SCR catalyst
- 3" x 0.9" cores, de-greened at 500 °C  
for 5 h under L/R cycling
- Separate catalysts/reactors with gas  
sampling at three positions
- 60 s lean/5 s rich cycles
- Gas analysis using FTIR gas analyzer

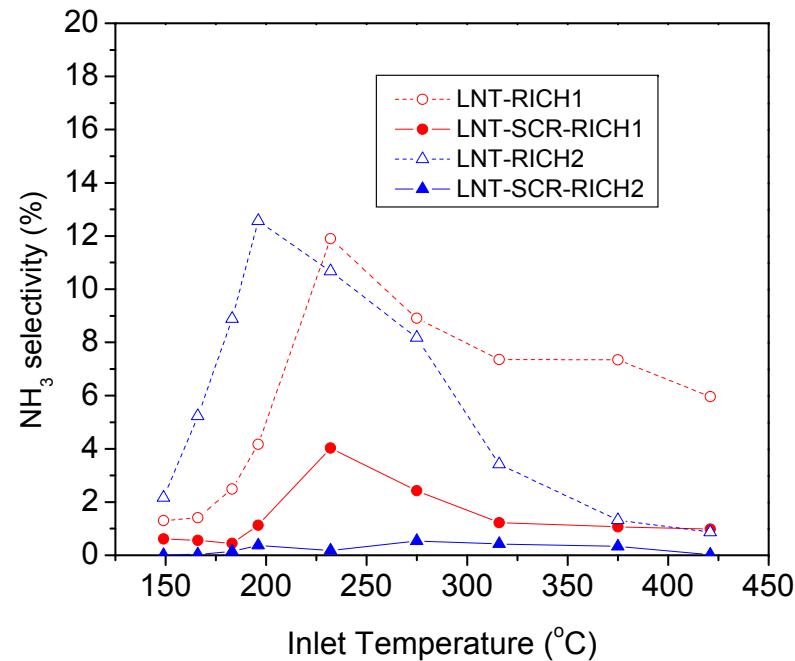
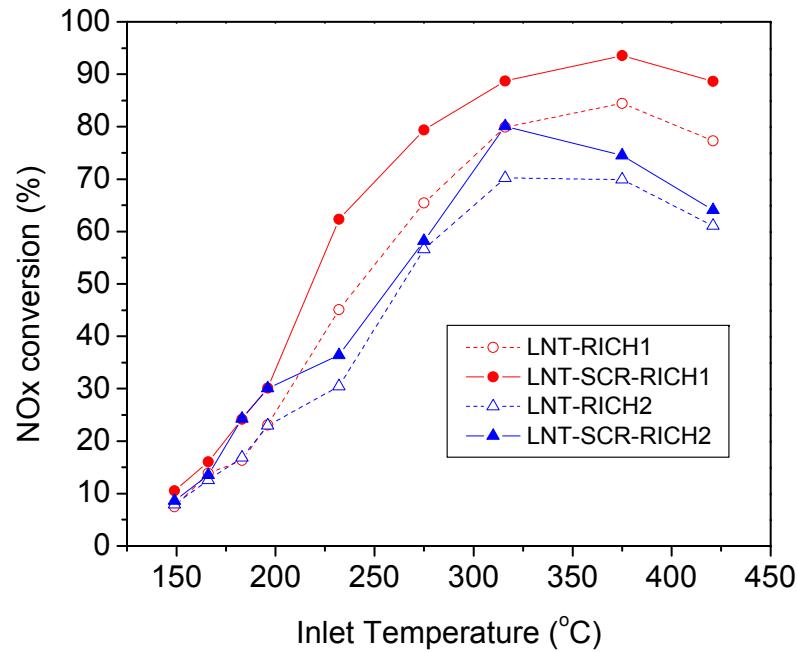


# NO<sub>x</sub> and NH<sub>3</sub> Conversion in LNT-SCR System: Effect of Added Propene (Rich Phase)

60 s lean – 5 s rich cycles:

Rich condition #1: 1% CO, 0.3% H<sub>2</sub>, 3333 ppm C<sub>3</sub>H<sub>6</sub>

Rich condition #2: 1% CO, 0.3% H<sub>2</sub>



Benefit of SCR catalyst most apparent when hydrocarbon (propene) is present  
→ SCR catalyst is able to utilize propene - or a derivative thereof - as a reductant

# Nitrogen Balance Across SCR Catalyst

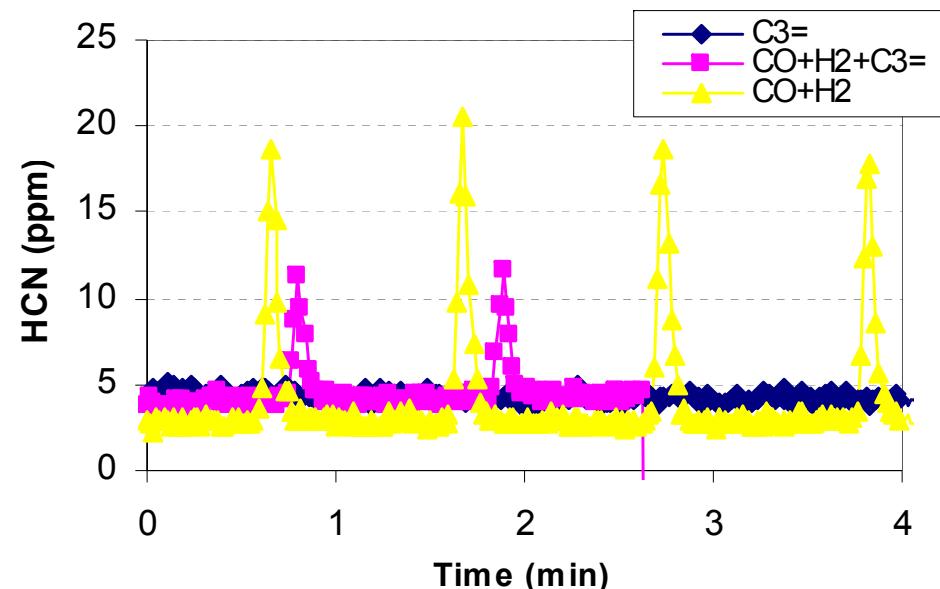
**Reductant = 1% CO + 0.3% H<sub>2</sub> + 3333 ppm C<sub>3</sub>H<sub>6</sub>**

LNT Inlet Temperature (°C)	NH <sub>3</sub> converted over SCR catalyst (ppm)	NOx converted over SCR catalyst (ppm)	NH <sub>3</sub> converted – NOx converted (ppm)
149	0.1	9.3	-9.1
166	0.3	6.7	-6.3
183	0.9	23.9	-23.0
196	1.9	21.5	-19.6
232	8.7	52.6	-43.9
275	11.9	42.4	-30.5
316	14.6	26.8	-12.2
375	15.9	27.7	-11.8
421	11.4	34.7	-23.3

# Speciation Study of LNT Exhaust Gas

- FT-IR applied to study formation of potential NOx reductants over LNT (other than NH<sub>3</sub>); only HCN is consistently observed in gas phase, but in low concentrations
- GC-MS also failed to detect significant gas phase organo-N species
- Hence, formation of organo-nitrogen species over LNT does not appear to be important for SCR

➤ Slipped hydrocarbon is responsible for NOx reduction in SCR catalyst

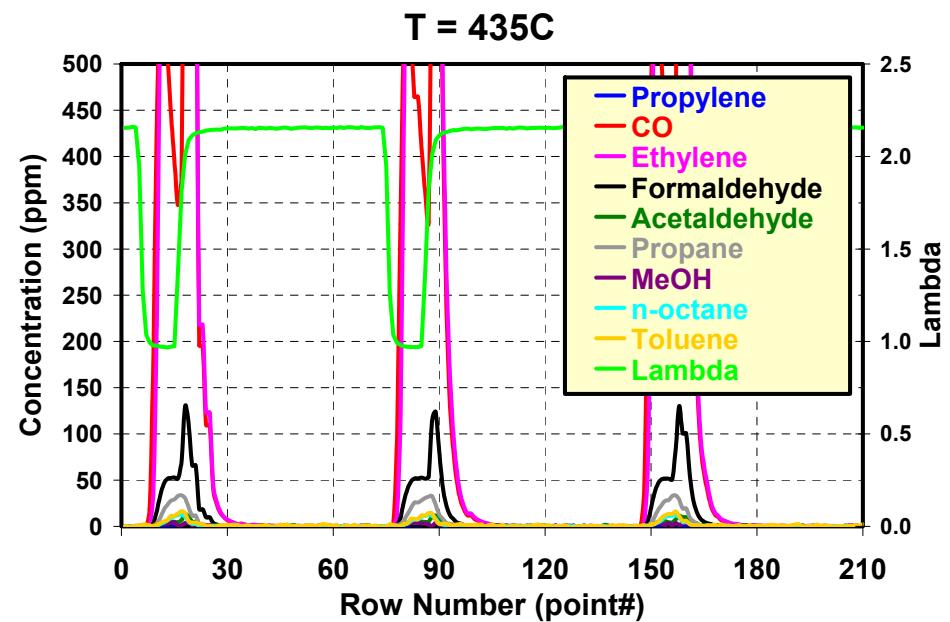
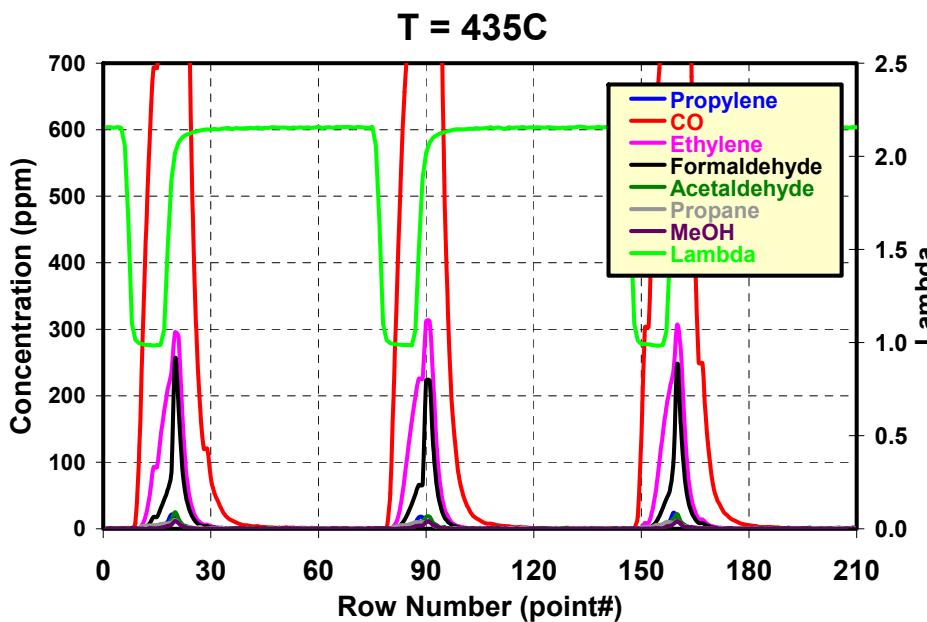
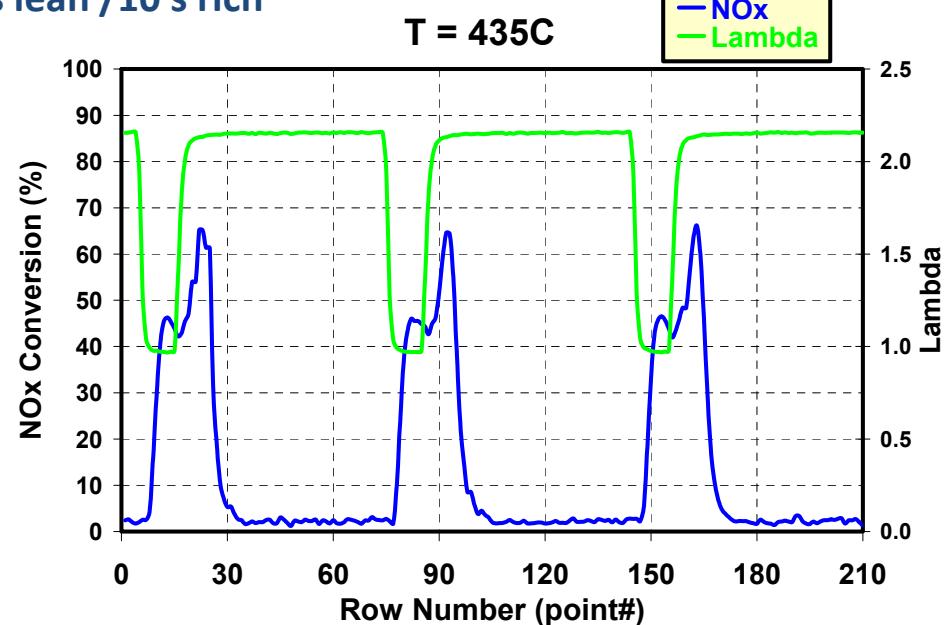
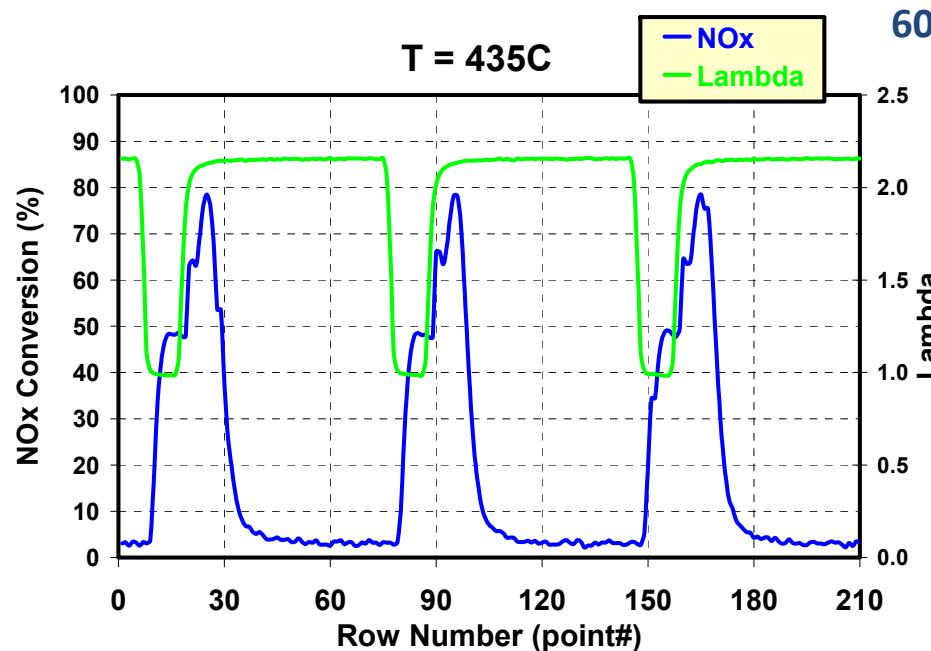


Measured HCN downstream of LNT during lean/rich cycling (for 3 different reductant mixtures)

Propylene

## Lean/Rich Cycling over SCR Catalyst

Ethylene

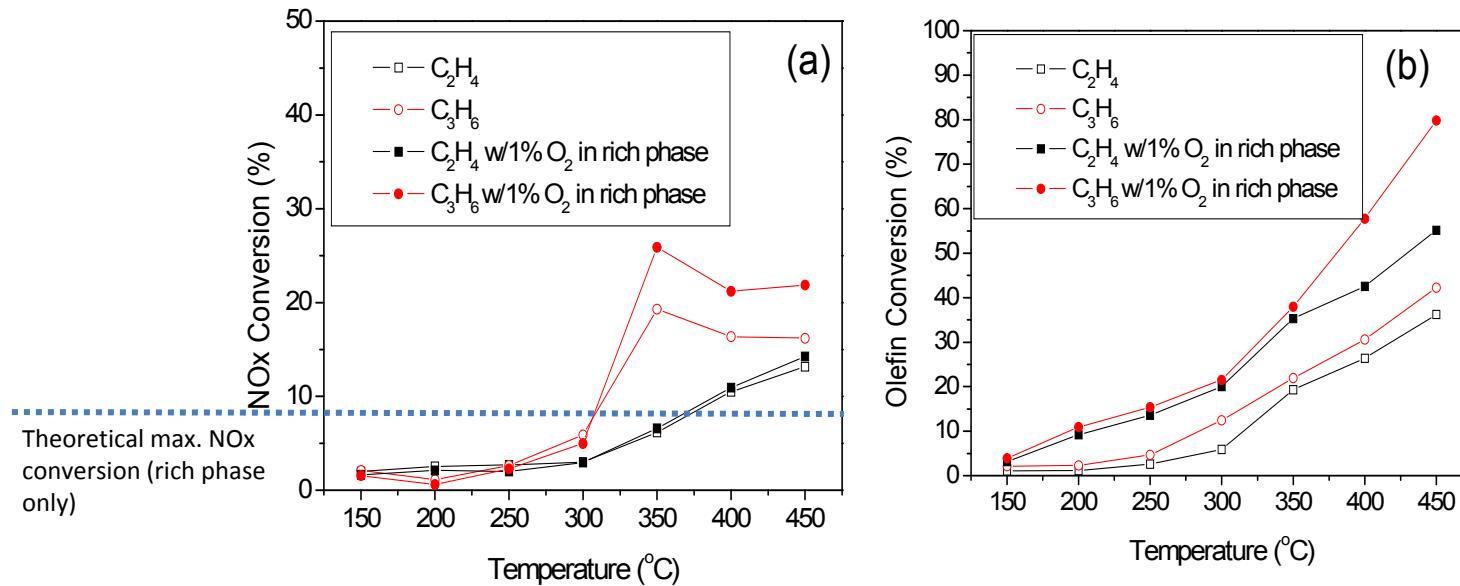


# NOx Conversion over Cu-zeolite SCR Catalyst During Lean-rich Cycling: C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> as Rich Phase Reductants

## SCR catalyst only:

Lean (60 s): 300 ppm NO, 8% O<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, N<sub>2</sub> as balance;

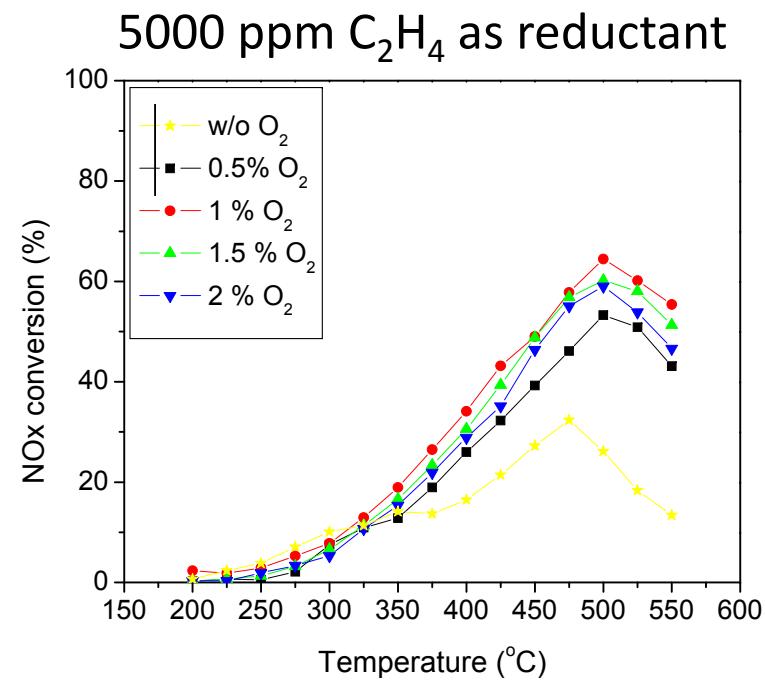
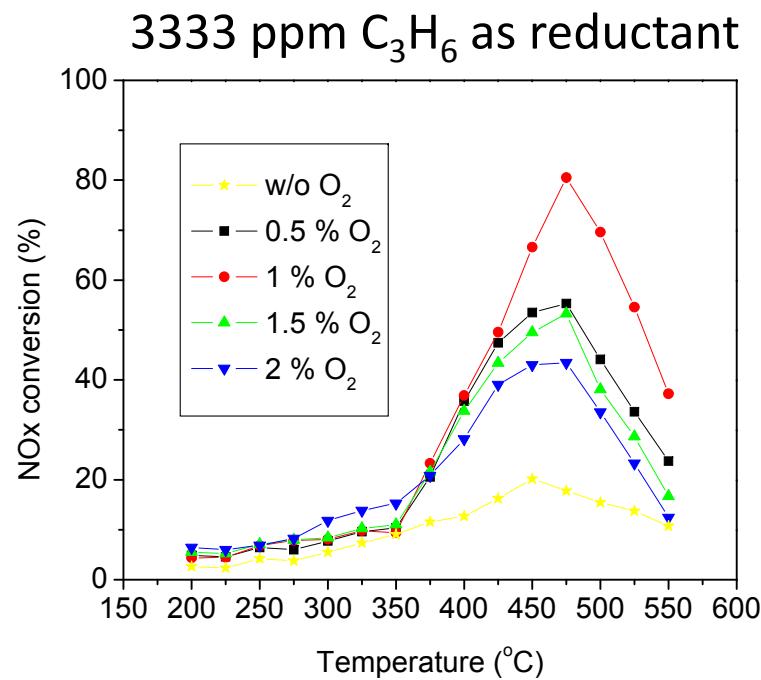
Rich (5 s): 300 ppm NO, 3333 ppm C<sub>3</sub>H<sub>6</sub> or 5000 ppm C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub> as indicated, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, N<sub>2</sub> as balance



- Cycle-averaged NOx conversion is higher than theoretical value if NOx is only reduced during rich phase => hydrocarbon storage + lean phase NOx reduction
- NOx conversion is sensitive to O<sub>2</sub> content of feed

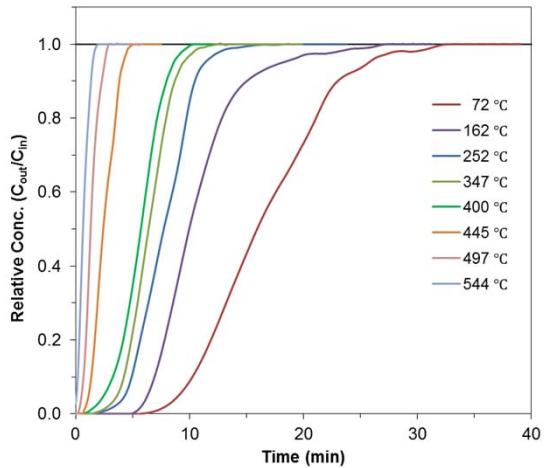
# Steady State NOx Conversion over Cu-zeolite SCR Catalyst

Conditions: 300 ppm NO, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, N<sub>2</sub> balance, GHSV = 30,000 h<sup>-1</sup>

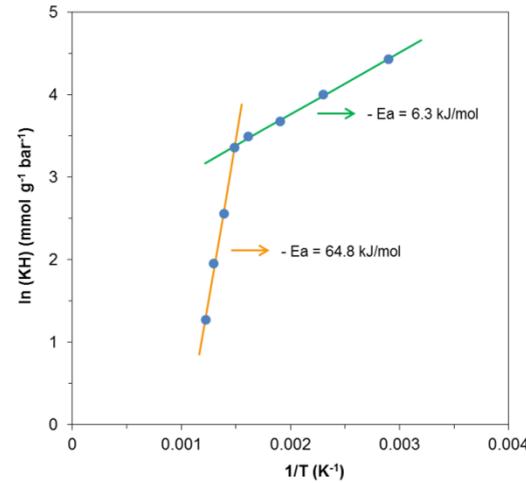


- Propylene and ethylene show moderate activity for NOx reduction over SCR catalyst under steady-state and cycling conditions
- NOx conversion is sensitive to O<sub>2</sub> content of feed

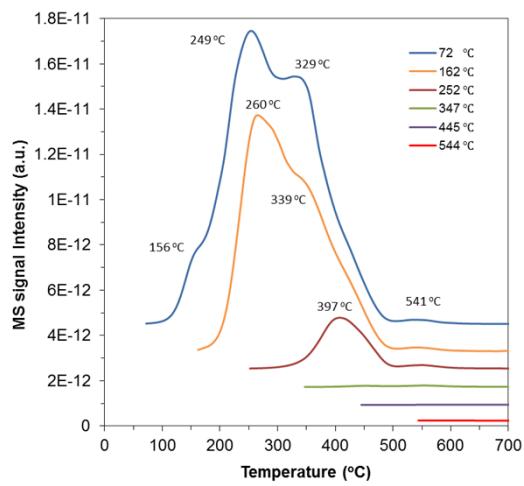
# Adsorption of C<sub>3</sub>H<sub>6</sub> on Cu-chabazite SCR Catalyst



Breakthrough curves for C<sub>3</sub>H<sub>6</sub> adsorption on Cu-CHA



Arrhenius plot of Henry's constant values obtained from Langmuir isotherm model



C<sub>3</sub>H<sub>6</sub>-TPD profiles obtained after evacuation of the C<sub>3</sub>H<sub>6</sub> saturated Cu-CHA samples

- Maximum C<sub>3</sub>H<sub>6</sub> loading (72 °C) = 3.6 wt%
- Magnitude of heats of adsorption consistent with chemi- and physisorption; chemisorption is indicated to be strong
- TPD experiments (Cu-CHA and Cu-leached samples): desorption peak at 250 °C due to propene adsorbed on Cu<sup>2+</sup>; desorption peaks at 150 °C and 330 °C due to propene adsorbed on (non-Cu) acidic sites in zeolite
- In addition to propene, many other desorbed species are observed: C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, etc.

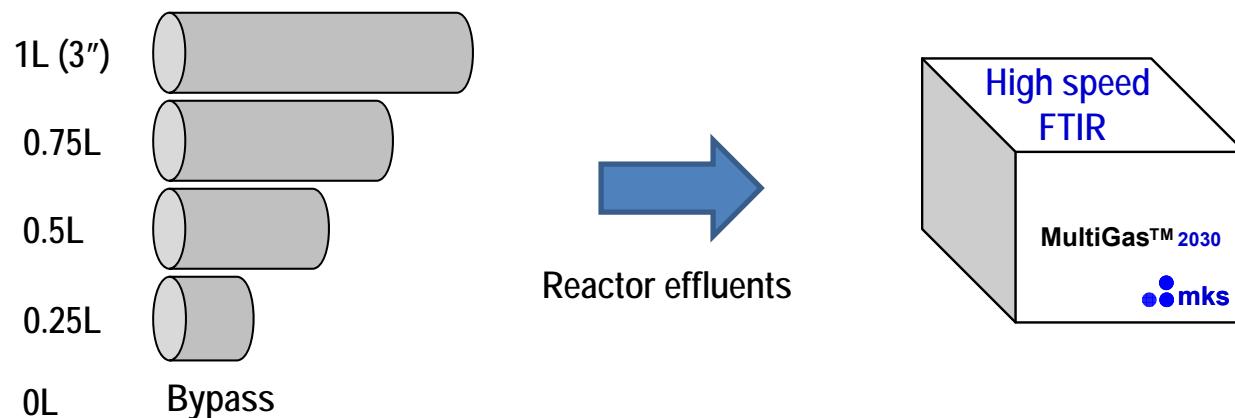
# Spatiotemporal Analysis of NOx Reduction by NH<sub>3</sub> & C<sub>3</sub>H<sub>6</sub> over Cu-chabazite During Lean/Rich Cycling

- Bench-reactor experimental conditions

	NH <sub>3</sub>		C <sub>3</sub> H <sub>6</sub>		NH <sub>3</sub> + C <sub>3</sub> H <sub>6</sub>	
	Lean (60 s)	Rich (5 s)	Lean (60 s)	Rich (5 s)	Lean (60 s)	Rich (5 s)
NO (ppm)	300	300	300	300	300	300
O <sub>2</sub> (%)	8	1	8	1	8	1
C <sub>3</sub> H <sub>6</sub> (ppm)	0	0	0	3333	0	3333
NH <sub>3</sub> (ppm)	0	300	0	0	0	300
CO <sub>2</sub> (%)	5	5	5	5	5	5
H <sub>2</sub> O (%)	5	5	5	5	5	5
N <sub>2</sub> (%)	Balance	Balance	Balance	Balance	Balance	Balance

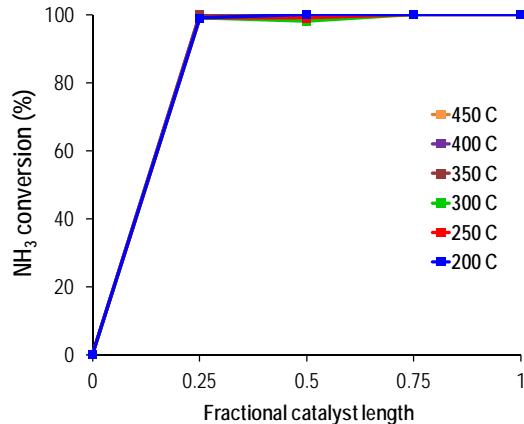
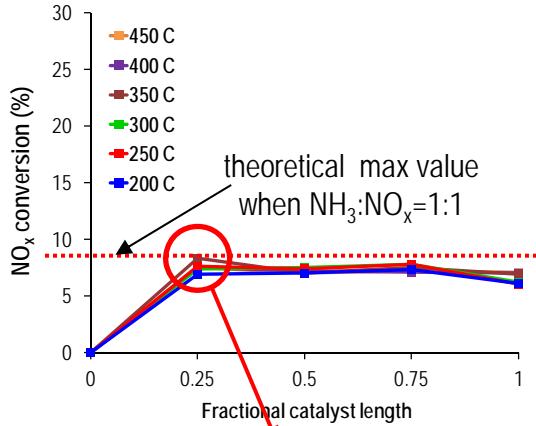
- Total flow: 13.7 L/min (equivalent to 30K SV for 3-in core: 1L)
- Temperature: 200, 250, 300, 350, 400, 450 °C

- Spatiotemporal resolution of reactions

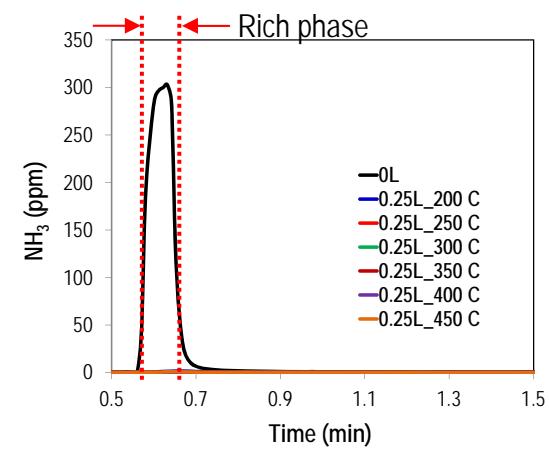
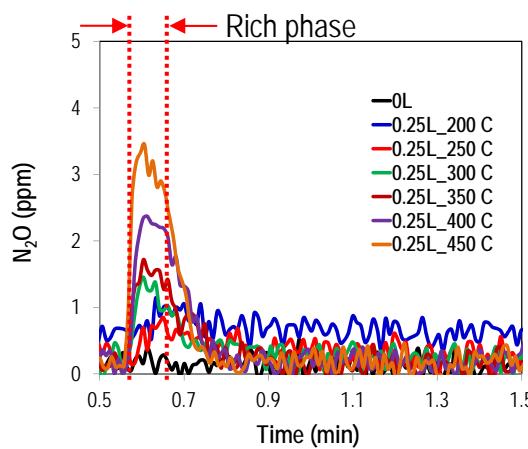
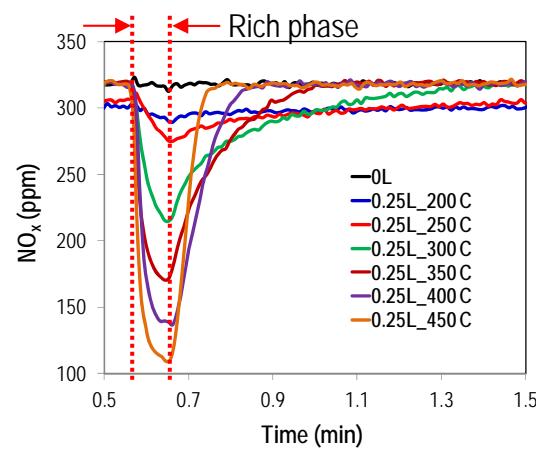


# NO<sub>x</sub> Reduction by NH<sub>3</sub>

**Reductant: 300 ppm NH<sub>3</sub>**



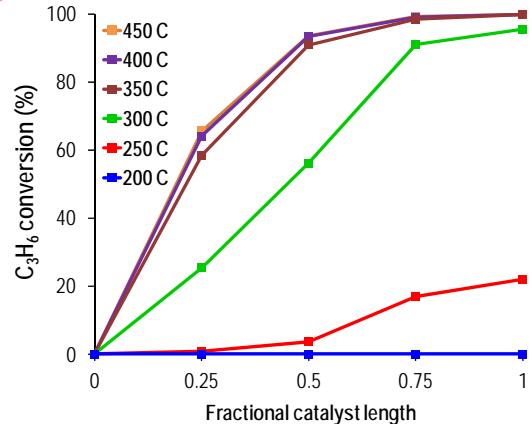
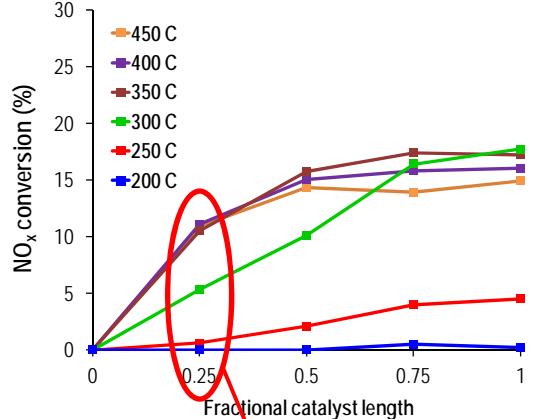
- Total consumption of NH<sub>3</sub> with near stoichiometric NO<sub>x</sub> reduction within 1<sup>st</sup> ¼ catalyst at all temps.



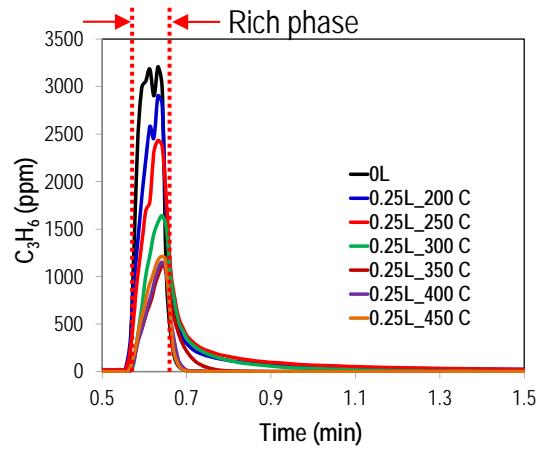
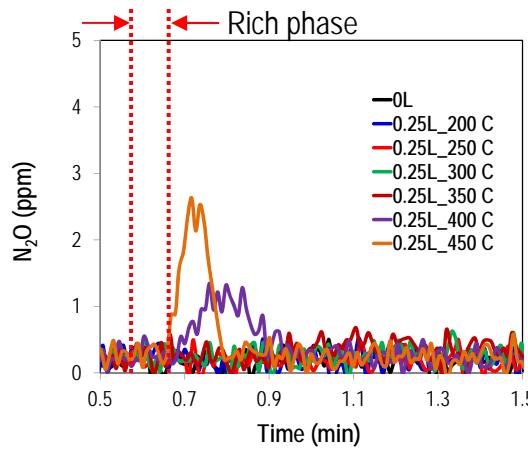
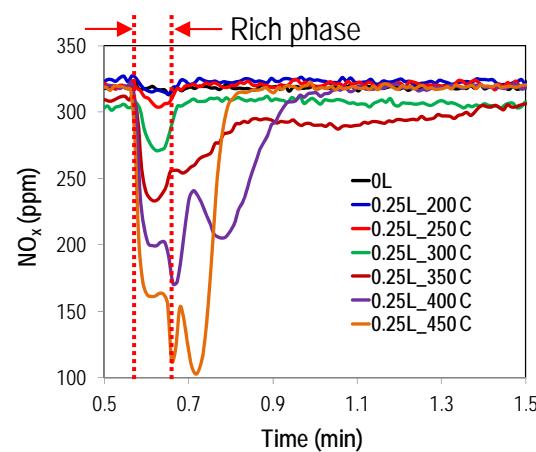
- NO<sub>x</sub> reduction occurs both in rich & lean phases
- Greater portion of NO<sub>x</sub> reduction in lean phase at lower temperatures
  - Due to lower reduction rate & higher NH<sub>3</sub> storage

# Significant NOx Reduction by C<sub>3</sub>H<sub>6</sub> Above 250 °C

**Reductant: 3333 ppm C<sub>3</sub>H<sub>6</sub>**



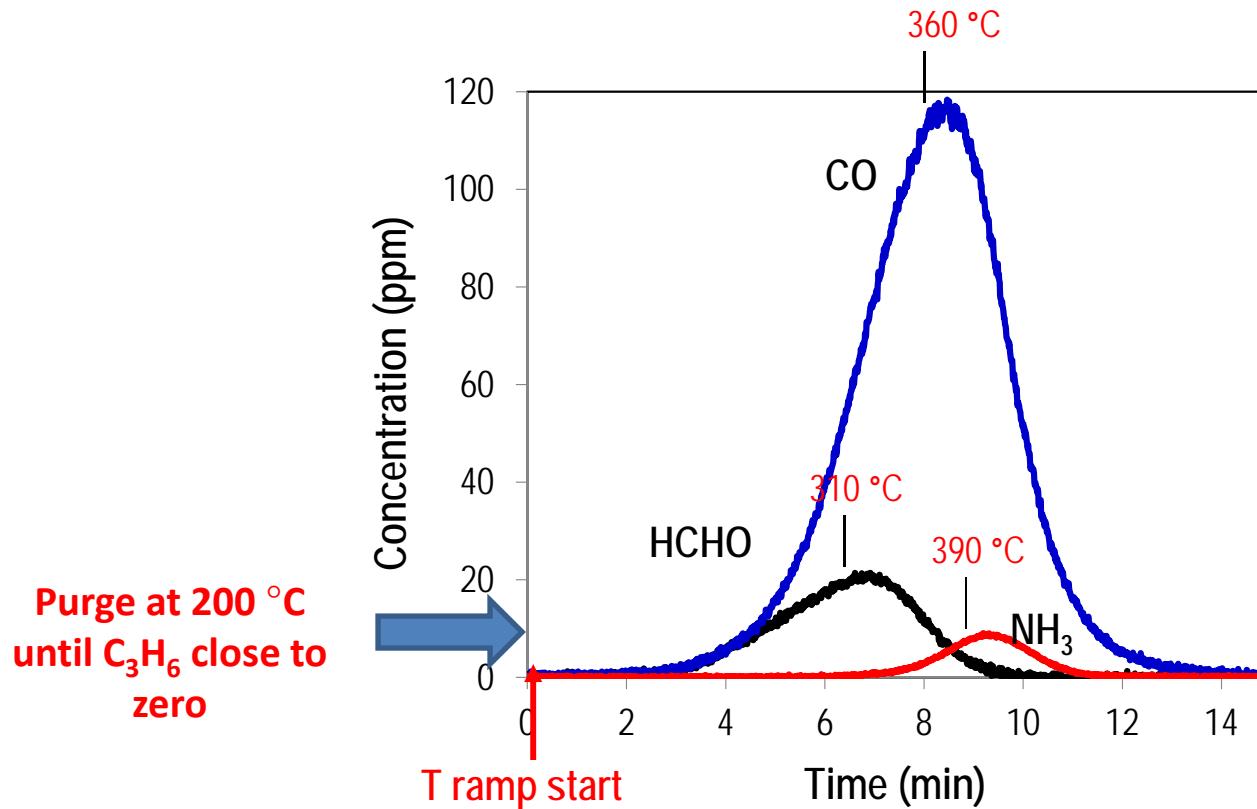
- Up to ~20% NOx conversion
- Best performance at 350 °C
- Entire length used except at 400-450 °C



- NOx reduction occurs both in rich & lean phases (3 “regimes” at 350, 400, 450 °C)
- Greater portion of NOx reduction in lean phase at 300 °C than at 450 °C
  - Due to lower reduction rate & higher C<sub>3</sub>H<sub>6</sub> storage (see peak tails)

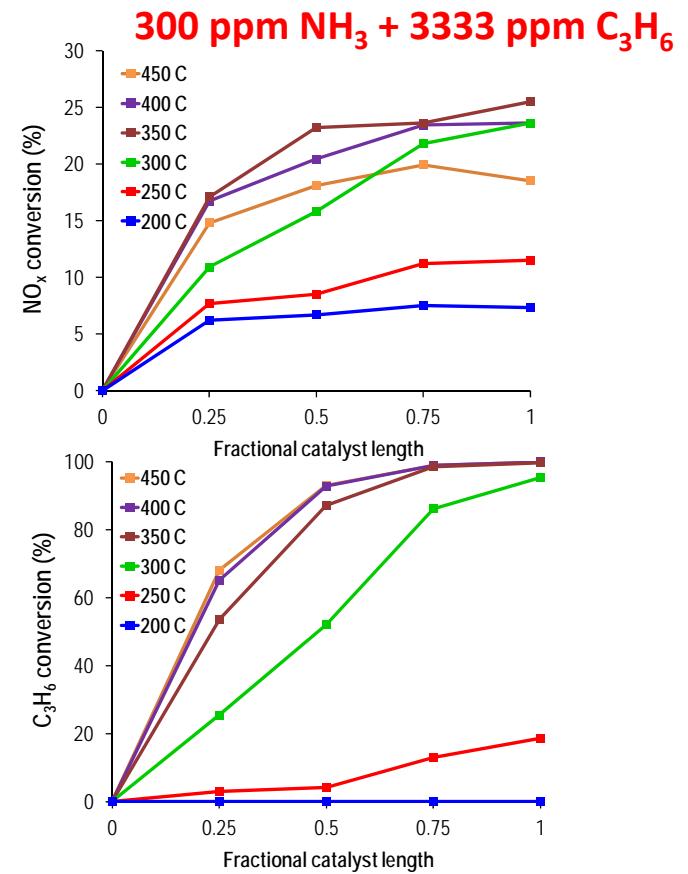
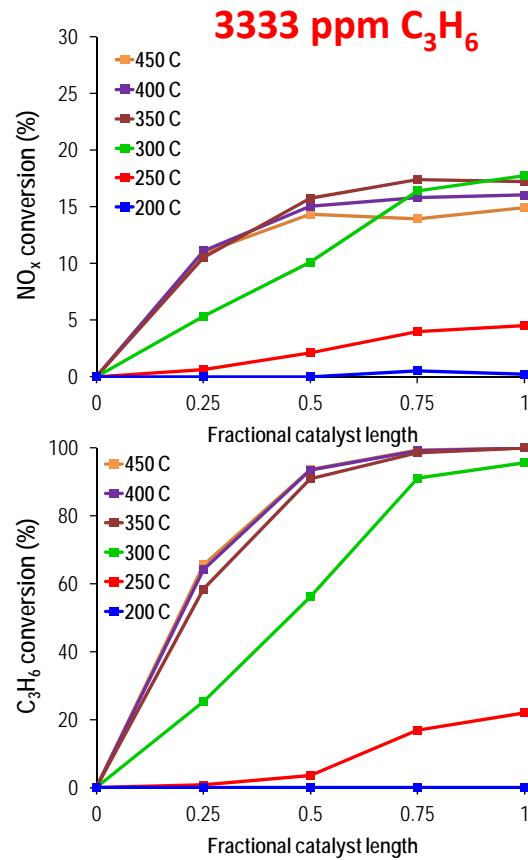
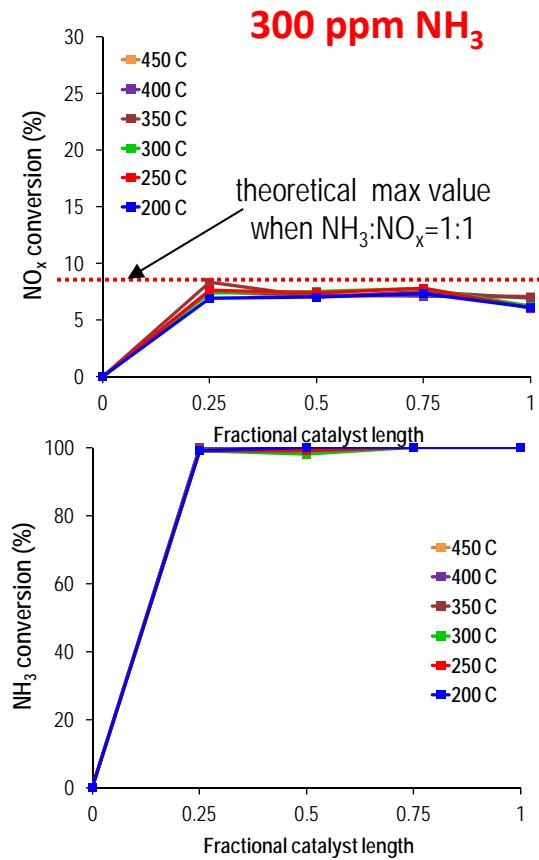
# NH<sub>3</sub> Could be Surface Intermediate

Temperature ramp (200 → 500 °C) after C<sub>3</sub>H<sub>6</sub> cycling at 450 °C → 200 °C;  
catalyst was purged with O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> at 200 °C before the TPD

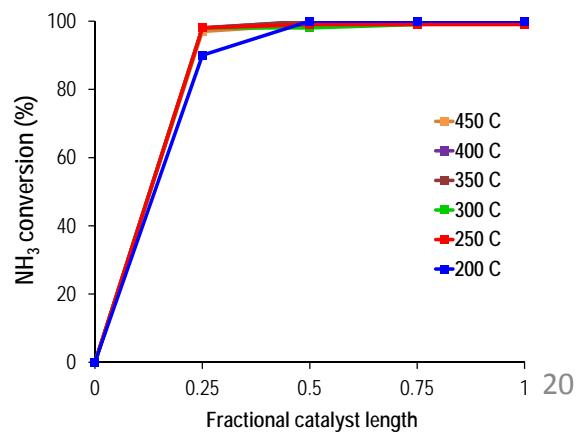


- High-T release of NH<sub>3</sub> suggests its formation, storage & usage on surface only
  - Could explain “3<sup>rd</sup>” NOx reduction regime (peak in lean phase) observed during C<sub>3</sub>H<sub>6</sub> cycling at 350, 400, 450 °C

# Effects of $\text{NH}_3$ & $\text{C}_3\text{H}_6$ on NOx Reduction are Additive



- Spatial profiles of  $\text{NH}_3$  &  $\text{C}_3\text{H}_6$  utilization virtually unaffected by co-feeding



# $^{15}\text{N}^{18}\text{O}$ Experiments Performed to Probe the Chemistry of $\text{NH}_3$ Intermediate

- Bench-reactor experimental conditions

	$\text{NH}_3$		$\text{C}_3\text{H}_6$		$\text{NH}_3 + \text{C}_3\text{H}_6$	
	Lean (60 s)	Rich (5 s)	Lean (60 s)	Rich (5 s)	Lean (60 s)	Rich (5 s)
$^{15}\text{N}^{18}\text{O}$ (ppm)	600	600	600	600	600	600
$\text{O}_2$ (%)	8	1	8	1	8	1
$\text{C}_3\text{H}_6$ (ppm)	0	0	0	3333	0	3333
$\text{NH}_3$ (ppm)	0	600	0	0	0	600
$\text{CO}_2$ (%)	5	5	5	5	5	5
$\text{H}_2\text{O}$ (%)	5	5	5	5	5	5
Ar (%)	Balance	Balance	Balance	Balance	Balance	Balance

- Total flow: 6.9 L/min
- Catalyst length: 0.75 in
- Temperature: 350 °C

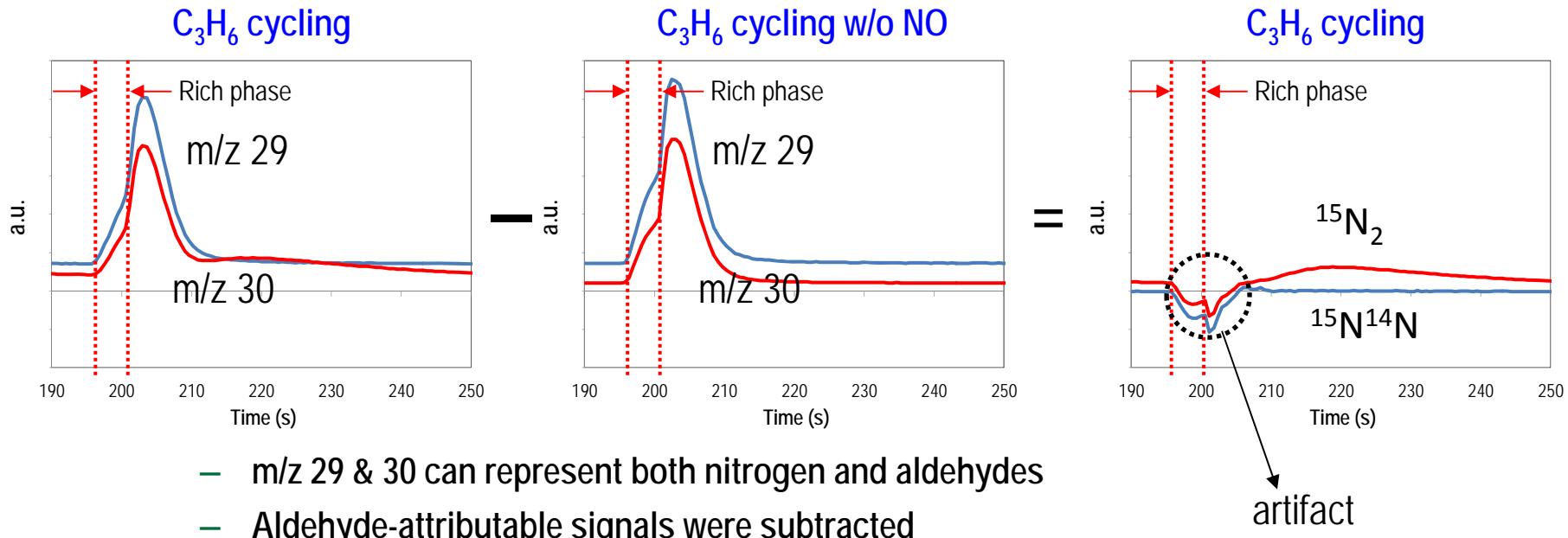
*Note: higher NO,  $\text{NH}_3$  concentrations & lower flow rate used to facilitate MS analysis*

## $^{15}\text{N}^{18}\text{O}$ Experiments Performed to Probe the Chemistry of $\text{NH}_3$ Intermediate (cont.)

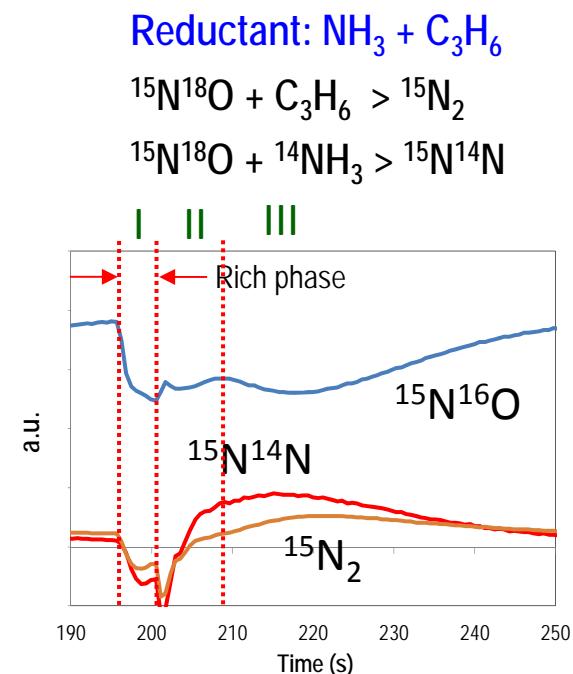
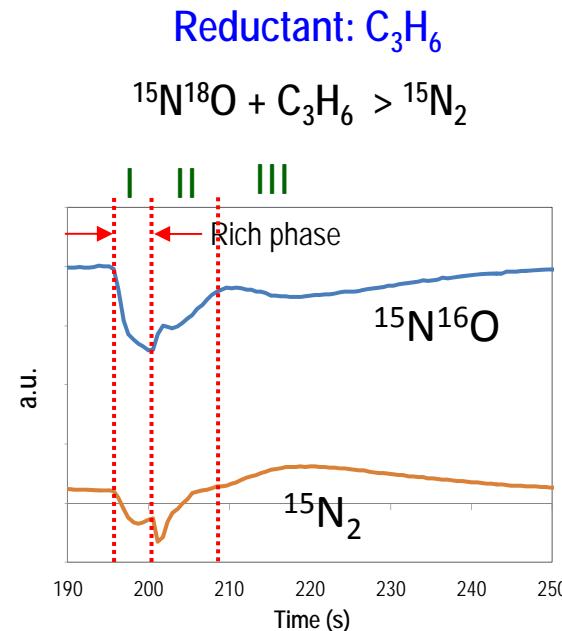
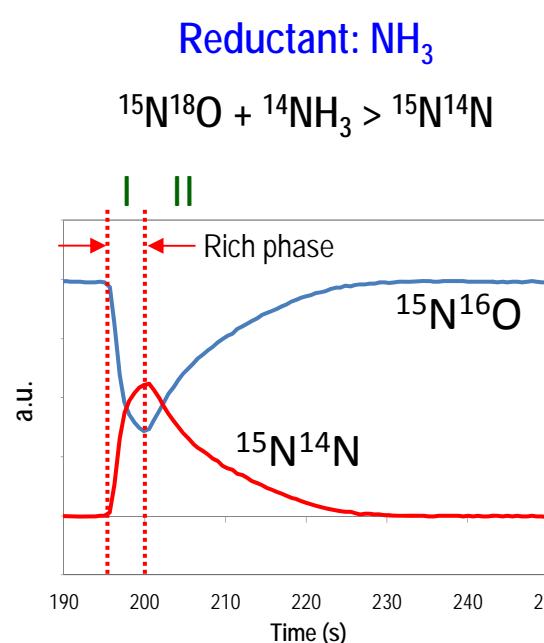
- Gas effluent analysis

- Mass spectrometer (EI, quadrupole)
- Monitored mass-to-charge ratios ( $m/z$ ):
  - Reductants: 24 ( $\text{C}_2\text{H}_4$ ), 28 ( $\text{CO}, \text{C}_2\text{H}_4$ ), 29 & 30 (aldehydes), 41 ( $\text{C}_3\text{H}_6$ )
  - $\text{O}_2$ : 34 ( $^{18}\text{O}^{16}\text{O}$ )
  - NO: 31 ( $^{15}\text{N}^{16}\text{O}$  major component at outlet)
  - $\text{N}_2$ : 29 ( $^{15}\text{N}^{14}\text{N}$ ), 30 ( $^{15}\text{N}_2$ )

- Cross-sensitivity issues have been considered



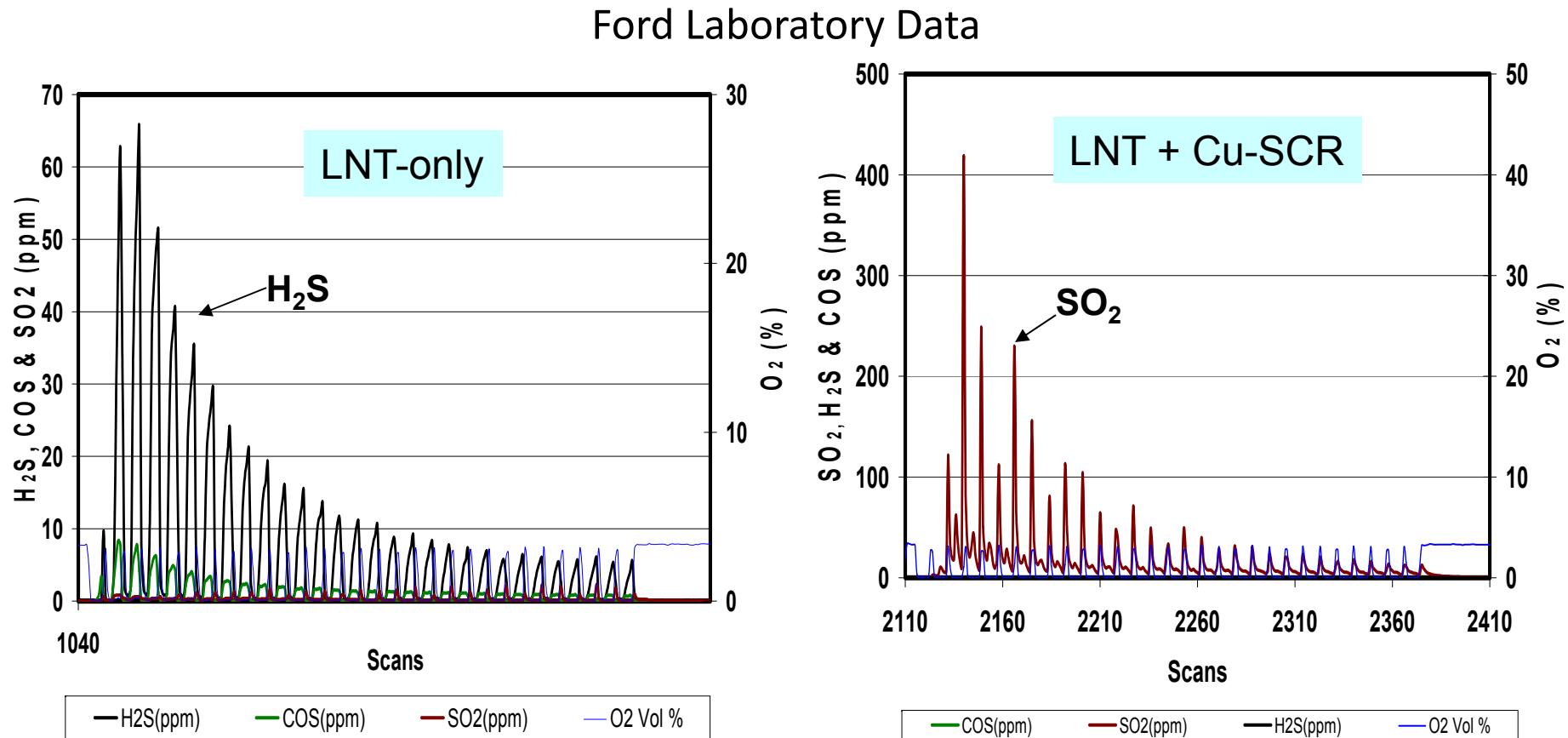
# $\text{C}_3\text{H}_6$ Contributes to $\text{NH}_3$ Formation but Inhibits $\text{NH}_3\text{-NO}$ Reaction



- 2 regimes of  $^{15}\text{NO}$  reduction during  $\text{NH}_3$  cycling
  - Rich phase (I); early lean phase (II)
- 3 regimes of  $^{15}\text{NO}$  reduction during  $\text{C}_3\text{H}_6$  cycling
  - Rich phase (I); early lean phase (II); mid lean phase (III; starts when HC's are depleted)
- Regimes I & II of  $^{15}\text{NO}$  reduction during  $\text{C}_3\text{H}_6$  cycling lead exclusively to  $^{15}\text{NH}_3$ 
  - Third regime (III) utilizes stored  $^{15}\text{NH}_3$  producing  $^{15}\text{N}_2$
- Adsorbed hydrocarbons slow kinetics of  $\text{NH}_3$  utilization (i.e.,  $^{15}\text{N}^{14}\text{N}$  formation)
  - cf. unaffected  $\text{NH}_3$  storage capacity & additive effect on cycle-averaged NO conversion

# Mitigation of H<sub>2</sub>S Emissions by Cu-CHA SCR Catalyst

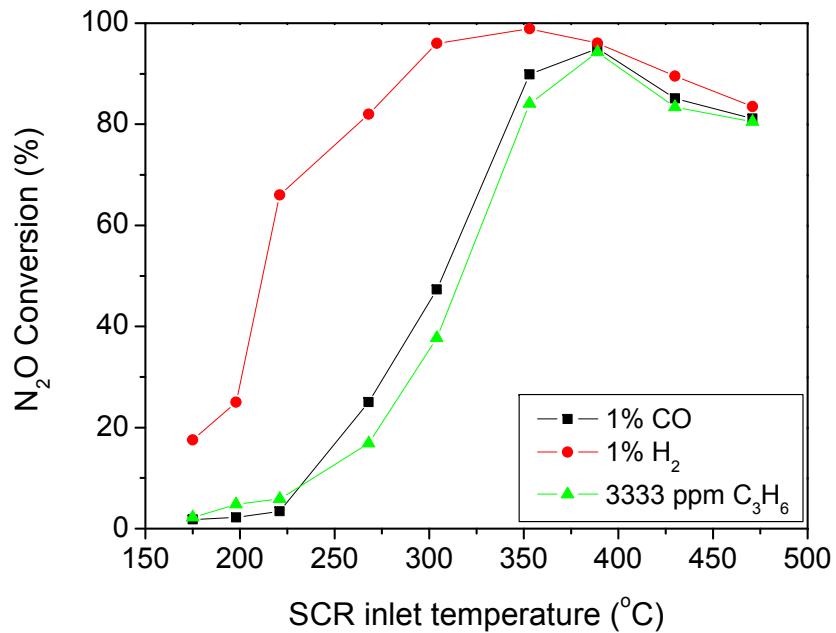
## Desulfation Comparison: LNT-only vs. LNT-SCR



Cu-CHA SCR catalyst virtually eliminates H<sub>2</sub>S emissions produced by LNT during rich high-temperature desulfation (H<sub>2</sub>S from LNT converted to SO<sub>2</sub>) – more detail in SAE 2009-01-0285 (L. Xu et al.)

# $\text{N}_2\text{O}$ Reduction Over Cu-CHA SCR Catalyst

Cycle-averaged  $\text{N}_2\text{O}$  conversion over SCR catalyst during  
60 s lean/5 s rich cycling :

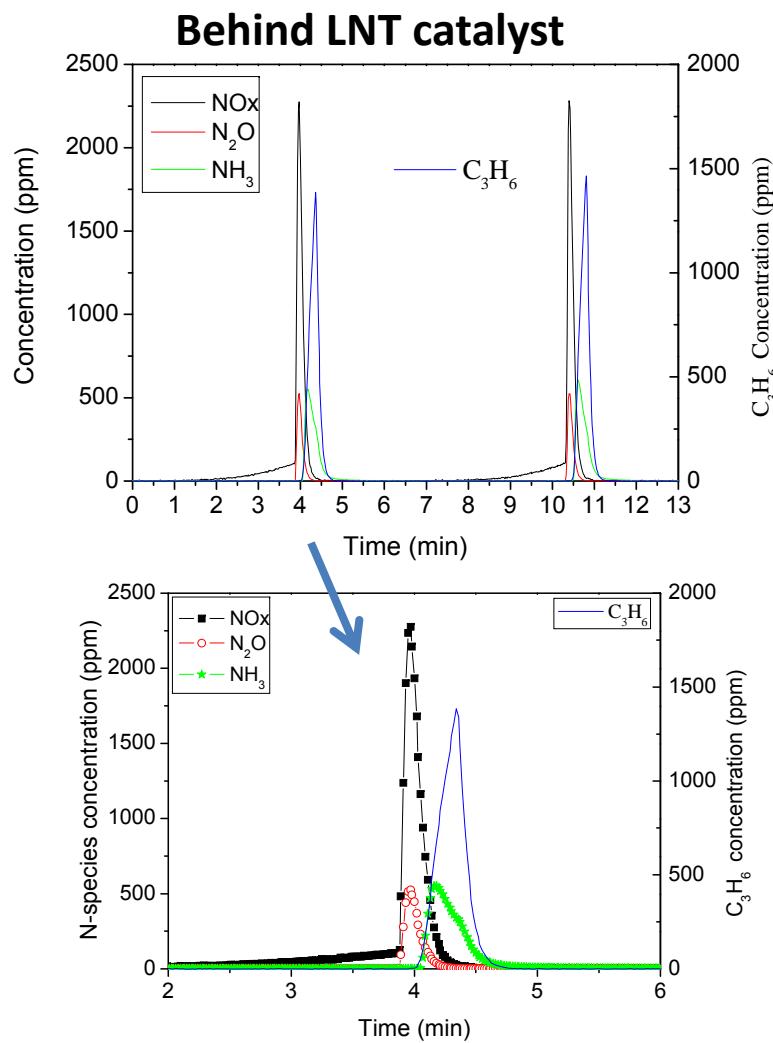


Lean: 300 ppm NO, 8% O<sub>2</sub>, 5% CO<sub>2</sub>,  
5% H<sub>2</sub>O, N<sub>2</sub> as balance;  
Rich: 300 ppm NO, 1% H<sub>2</sub> or 1% CO  
or 3333 ppm C<sub>3</sub>H<sub>6</sub> as reductant,  
5% CO<sub>2</sub>, 5% H<sub>2</sub>O, N<sub>2</sub> as balance;  
GHSV = 30,000 h<sup>-1</sup>

- H<sub>2</sub> best reductant for N<sub>2</sub>O
- No reductant breakthrough from LNT observed at ≥400 °C, hence N<sub>2</sub>O conversion tails off (implies that N<sub>2</sub>O decomposition must be occurring)

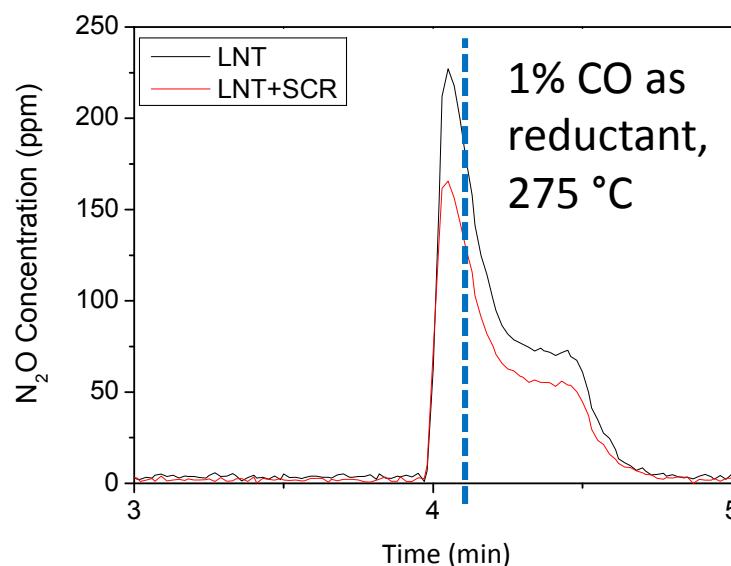
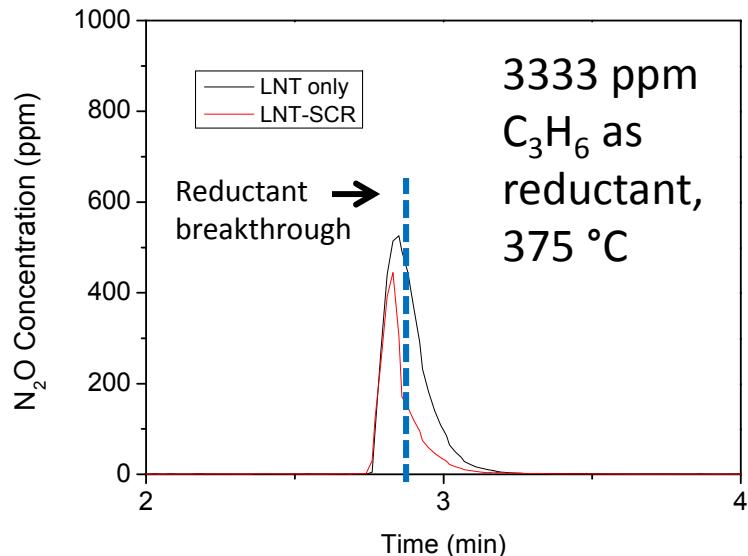
# $\text{N}_2\text{O}$ Reduction Over Cu-CHA SCR Catalyst

Comparison of gas composition behind LNT and SCR catalysts during lean-rich cycling  
(1%  $\text{C}_3\text{H}_6$  as reductant, 360 s lean, 30 s rich; 375 °C)



- As expected NOx and  $\text{N}_2\text{O}$  breakthrough LNT catalyst before  $\text{NH}_3$  and  $\text{C}_3\text{H}_6$
- Significant conversion of NOx,  $\text{NH}_3$ ,  $\text{C}_3\text{H}_6$  and  $\text{N}_2\text{O}$  over SCR catalyst

# $\text{N}_2\text{O}$ Reduction Over Cu-CHA SCR Catalyst



Comparison of  $\text{N}_2\text{O}$  concentrations behind LNT & SCR catalysts (360 s lean, 30 s rich):

- Increased  $\text{N}_2\text{O}$  formation over LNT when using CO as reductant, compared to  $\text{H}_2$  (consistent with Abdulhamid *et al.* and LePhuc *et al.*)
- For CO,  $\text{N}_2\text{O}$  formation observed at L-R and R-L transition (consistent with Elizundia *et al.*)
- Some  $\text{N}_2\text{O}$  conversion occurs before reductant has broken through, implying  $\text{N}_2\text{O}$  decomposition

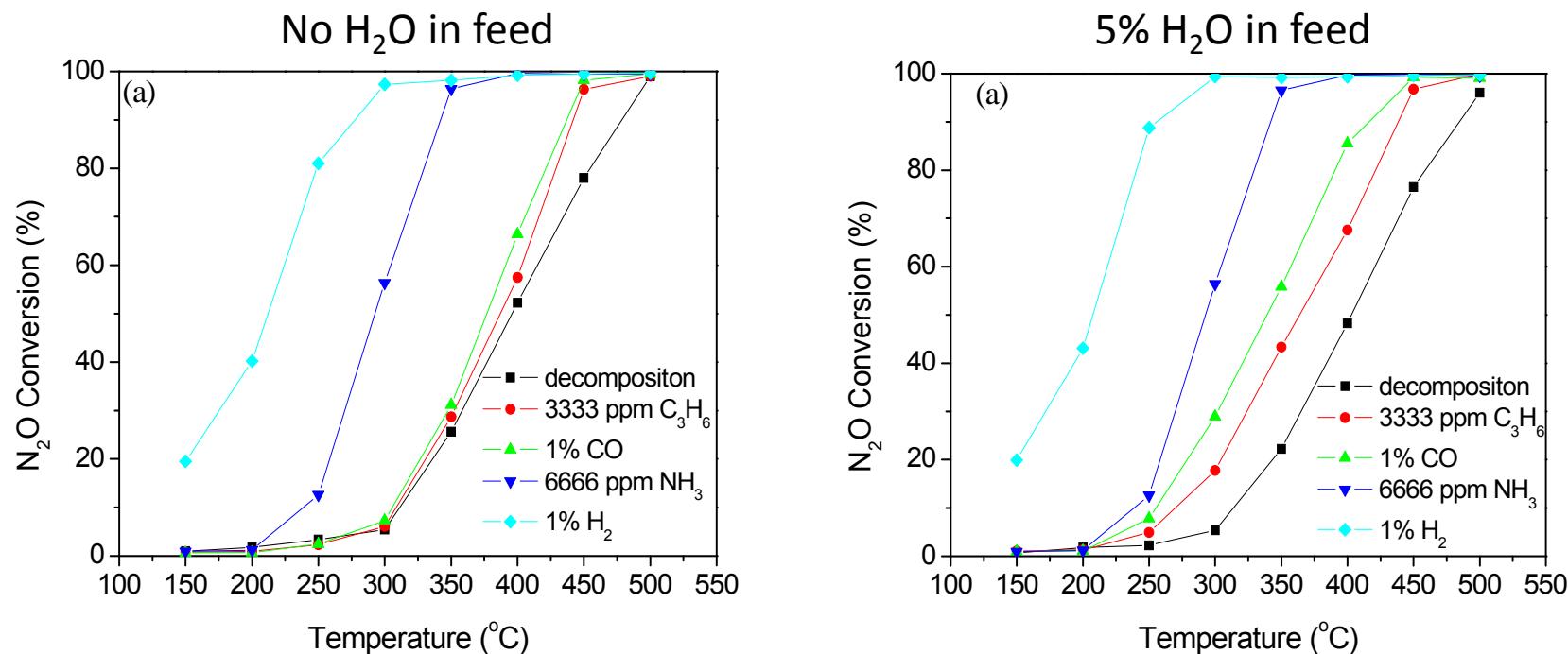
H. Abdulhamid, E. Fridell, M. Skoglundh, Top. Catal. 30/31 (2004) 161.

N. Le Phuc, X. Cortois, F. Can, S. Berland, S. Royer, P. Marecot, D. Duprez, Catal. Today 176 (2011) 424.

U. Elizundia, D. Duraiswami, B. Pereda-Ayo, R. Lopez-Fonscea, J.R. Gonzalez-Velasco, Catal. Today, 176 (2011) 324.

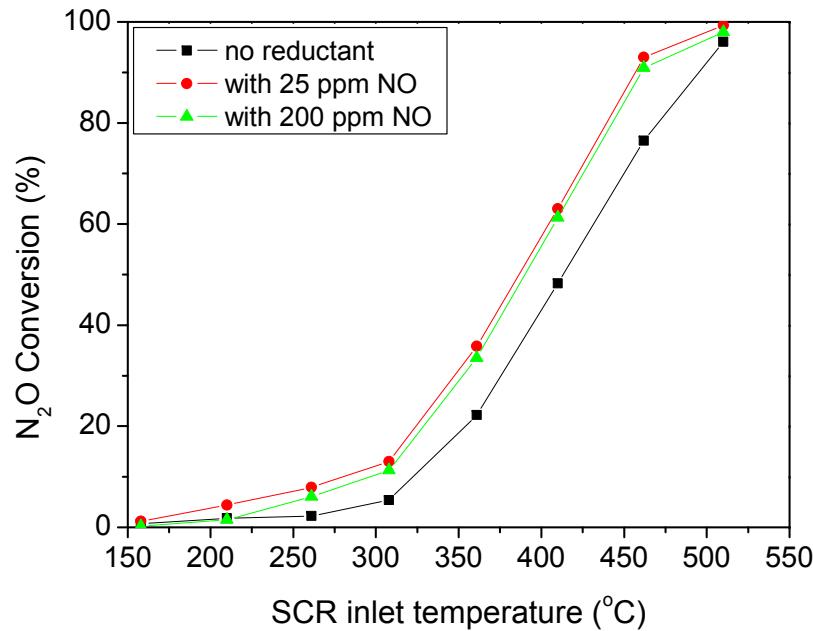
# $\text{N}_2\text{O}$ Reduction Over Cu-CHA SCR Catalyst: Steady-state Continuous Flow (1)

Feed: 100 ppm  $\text{N}_2\text{O}$ , 5%  $\text{CO}_2$ , reductant as shown, bal.  $\text{N}_2$ ; GHSV = 30,000  $\text{h}^{-1}$



- $\text{H}_2$  best reductant, followed by  $\text{NH}_3$
- $\text{N}_2\text{O}$  reduction not inhibited by water; v. slight inhibition of decomposition reaction
- Slight promoting effect with water for reduction using CO or  $\text{C}_3\text{H}_6$ : implies *in situ* formation of  $\text{H}_2$  via WGS or steam reforming

# $\text{N}_2\text{O}$ Reduction Over Cu-CHA SCR Catalyst: Steady-state Continuous Flow (2)



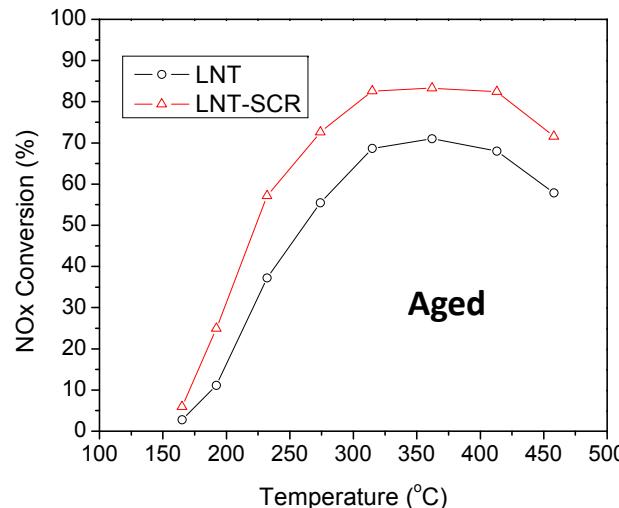
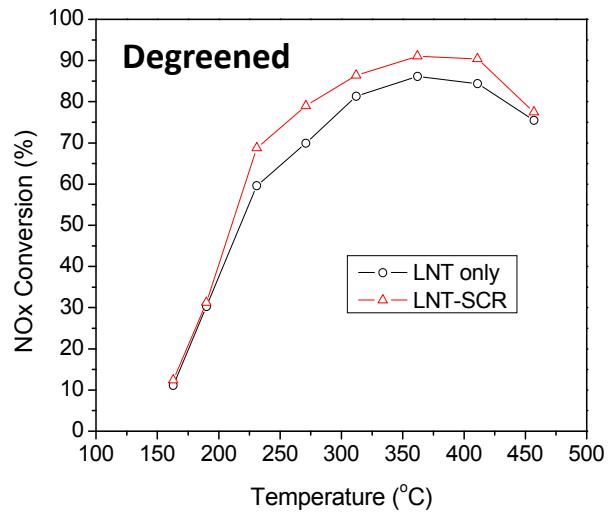
Feed: 100 ppm  $\text{N}_2\text{O}$ , 5%  $\text{CO}_2$ , NO as shown, bal.  $\text{N}_2$ ; GHSV = 30,000  $\text{h}^{-1}$

- $\text{N}_2\text{O}$  decomposition is weakly promoted by NO, e.g.:  $\text{N}_2\text{O} + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2$
- Effect appears to be catalytic, rather than stoichiometric (e.g., may facilitate migration of adsorbed O through  $\text{NO}_2$  intermediates, enhancing the recombination of O atoms)\*

\* Pérez-Ramírez J, Kapteijn F, Mul G, Moulijn JA (2002) J Catal 208: 211.

Kaucký D, Sobalík Z, Schwarze M, Vondrová A, Wichterlová B (2006) J Catal 238:293.

# LNT-SCR System Aging



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<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>; rich (5 s): 2.5% CO, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>. GHSV = 60,000 h<sup>-1</sup>.

- 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<sub>3</sub> and increased NOx slip available for reaction
- Hence, SCR catalyst helps to compensate for deterioration in LNT NOx conversion

# The 150 °C Challenge: Non-thermal Plasma-Assisted NO<sub>x</sub> Storage-Reduction on Perovskite LNT Catalysts

- Limiting factors for LNT operation at low temperatures are ability to:
  - (i) store NO<sub>x</sub>
  - (ii) regenerate storage sites
  - (iii) reduce released NO<sub>x</sub>
- Concept:
  - apply perovskites for (i)
  - apply non-thermal plasma for (ii) and (iii)\*

Catalyst	NO <sub>x</sub> storage capacity ( $\mu\text{mol/g}$ )				
	30 °C	100 °C	200 °C	300 °C	400 °C
Pt/30BaO/Al <sub>2</sub> O <sub>3</sub>	86.9	152.1	219.6	398.9	508.1
LaMn <sub>0.9</sub> Fe <sub>0.1</sub> O <sub>3</sub>	380.5	371.6	385.4	392.3	306.3

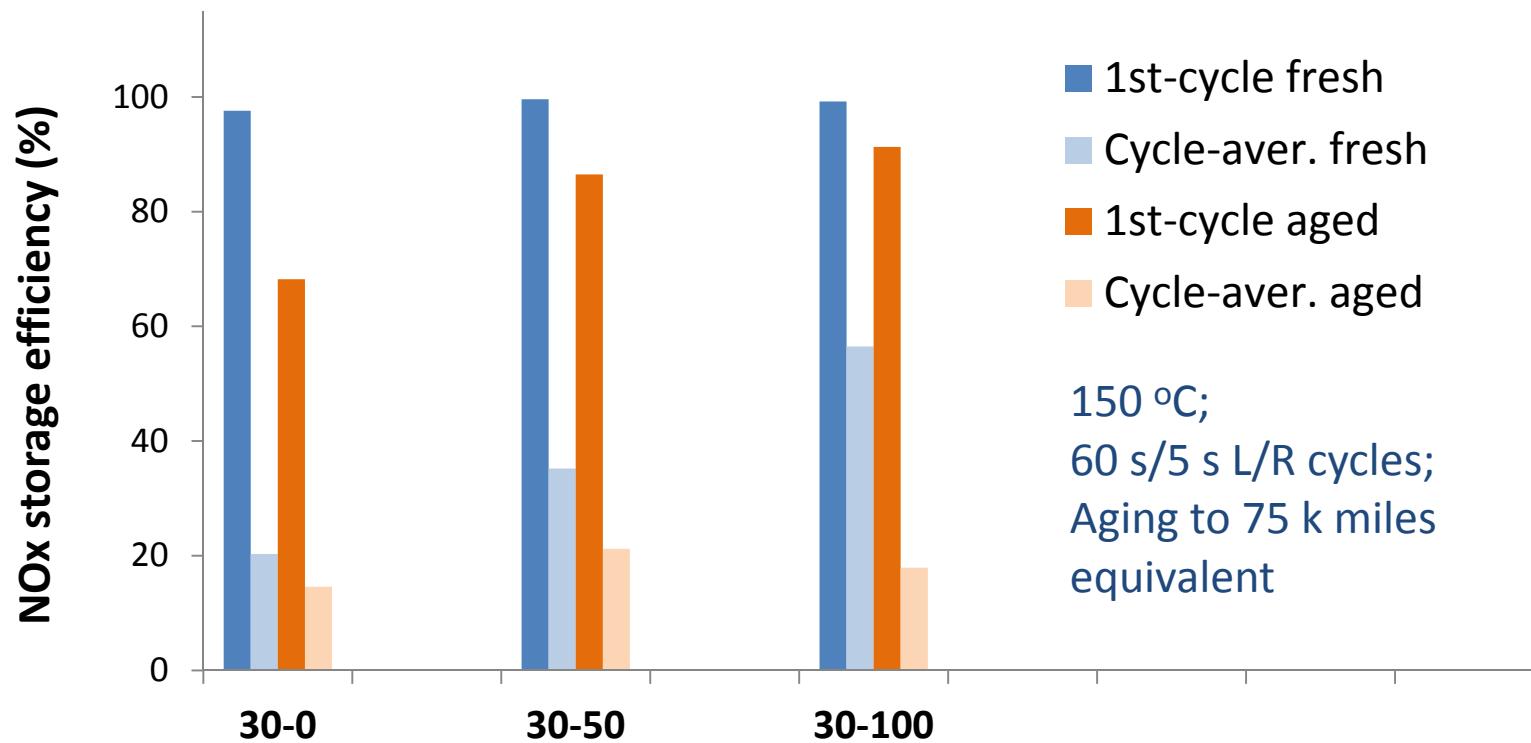
500 ppm NO, 8% O<sub>2</sub>, N<sub>2</sub> bal., 50 min, GHSV = 30,000 h<sup>-1</sup>

\* Production of H<sub>2</sub>-rich gas for LNT regeneration using plasmatron fuel reformer:

L. Bromberg, D.R. Cohen, A. Rabinovich, J. Heywood, Int. J. Hydrogen Energy, 26 (2001) 1115.

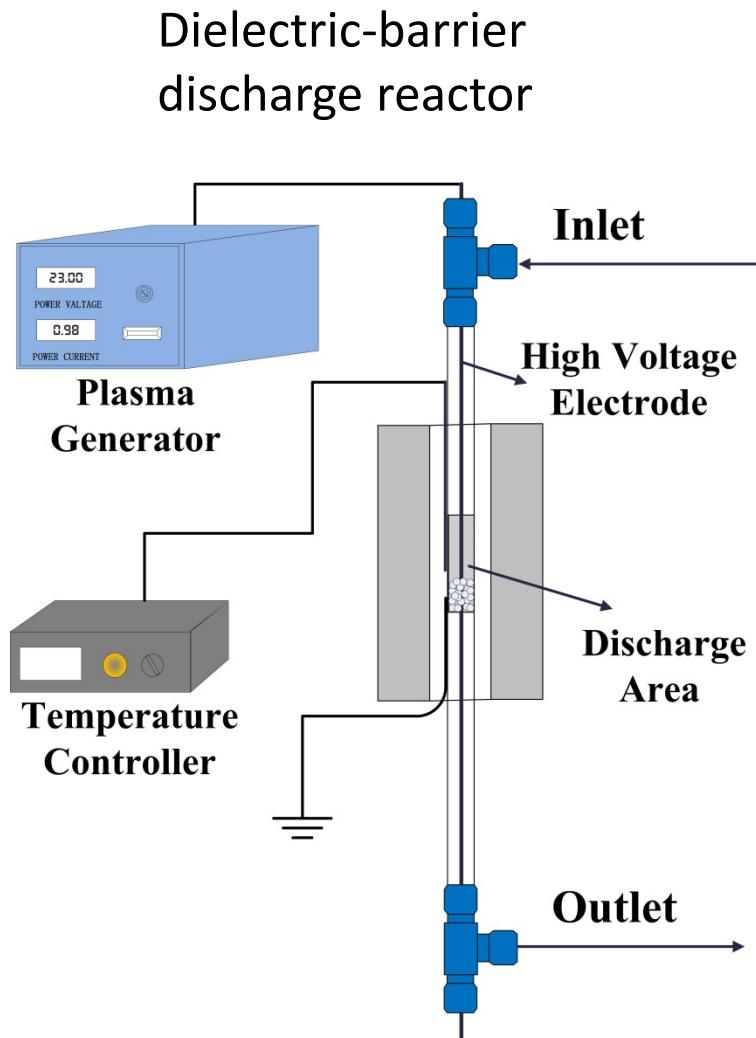
R. Mital, B.J. Stroia, R.C. Yu, U.S. patent 7,377,101 (2008).

# Comparison of First Cycle and Cycle-averaged NOx Storage Capacities for Fully Formulated LNT Catalysts



- LNT performance severely limited at 150 °C by ability to regenerate NOx storage sites

# Non-thermal Plasma-Assisted NO<sub>x</sub> Storage-Reduction: Experimental Details



H<sub>2</sub> or Ar non-thermal plasma applied in rich phase

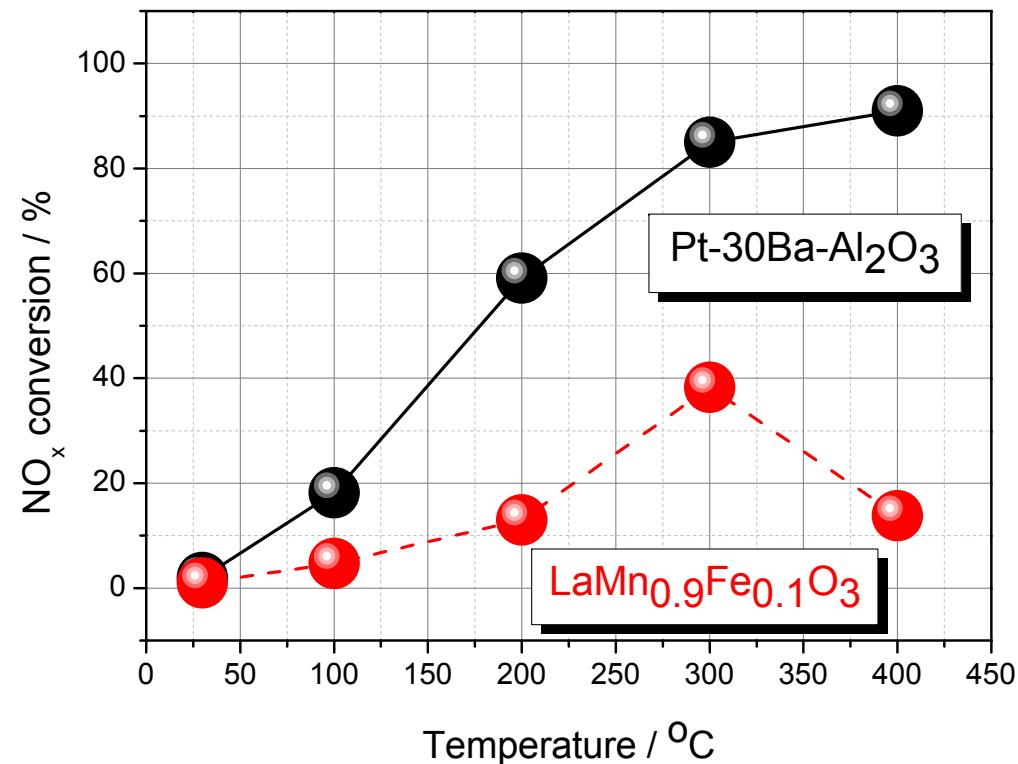
Discharge power = 20 w

Effluent gases analyzed using MS

A.J. Zhang, A.M. Zhu, J. Guo, Y. Xu, C. Shi,  
*Chem. Eng. J.*, 156 (2010) 601.

# NO<sub>x</sub> Conversion Under Lean-Rich Cycling

## w/o NTP: LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub>



Lean (10 min): 500 ppm NO,  
8% O<sub>2</sub>, bal. Ar

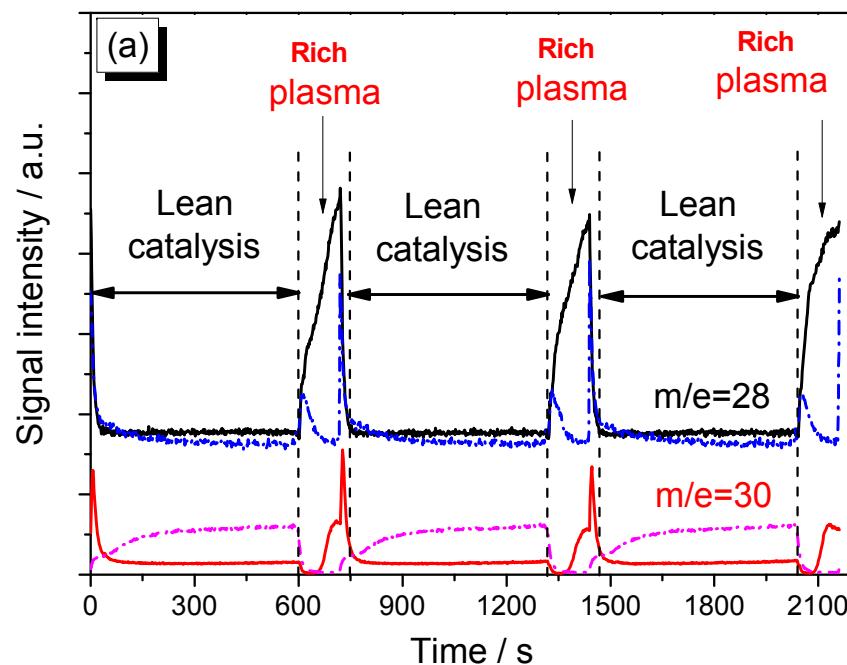
Rich (2 min): 1% H<sub>2</sub>, bal. Ar;  
GHSV = 10,000 h<sup>-1</sup>

Catalyst pre-treatment in 1%  
H<sub>2</sub> at 500 °C for 1 h

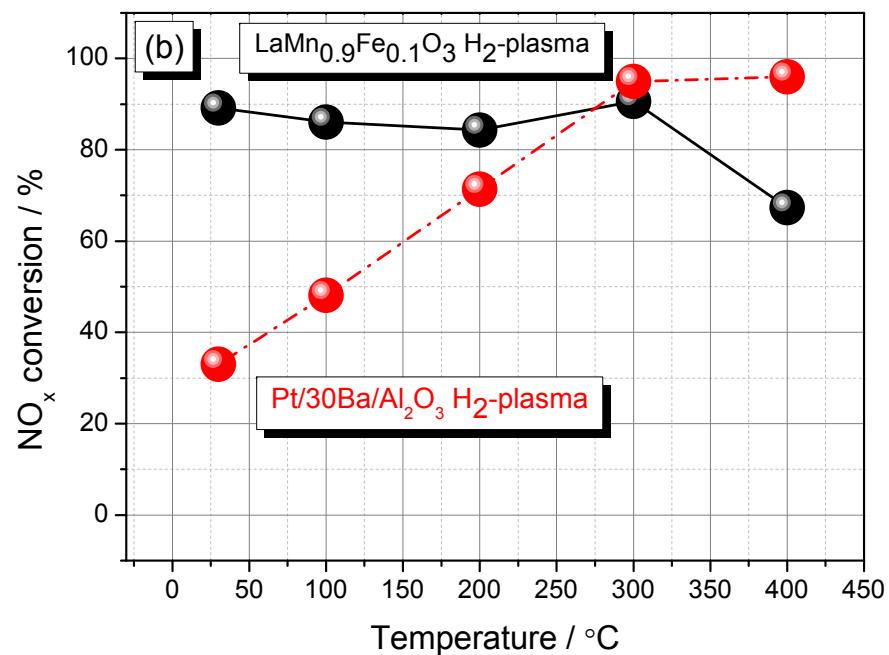
- Low rich phase NO<sub>x</sub> reduction activity of LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> responsible for poor NO<sub>x</sub> conversion under lean-rich cycling

# NO<sub>x</sub> Conversion Under Lean-Rich Cycling with NTP: LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub>

N<sub>2</sub> and NO<sub>x</sub> profiles (T = 30 °C)  
Solid line: H<sub>2</sub> plasma; dotted: Ar plasma



Cycle –averaged NO<sub>x</sub> conversion



- 90% NO<sub>x</sub> conversion obtained at 30 °C for LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> under these conditions

C. Shi, Z. Zhang, M. Crocker, L. Xu, C. Wang, C. Au, A. Zhu, *Catalysis Today* (2013),  
<http://dx.doi.org/10.1016/j.cattod.2013.03.008>

## Summary (1)

- Reactor studies have shown that a hydrocarbon-based NOx reduction pathway (ethylene and propylene studied) can operate on a Cu-chabazite SCR catalyst in parallel with the NH<sub>3</sub>-SCR pathway
- The contribution of hydrocarbons to NOx reduction is most evident under conditions of low NH<sub>3</sub> availability
- NH<sub>3</sub> is formed as an intermediate in NOx reduction by propene on the SCR catalyst
- The presence of propene slows the kinetics of (co-fed) NH<sub>3</sub> utilization by NOx on the SCR catalyst, but doesn't affect cycle-averaged NH<sub>3</sub> utilization (60 s lean/5 s rich cycles) except at *very* high concentrations
- Propene adsorbs strongly in the Cu-chabazite catalyst; at high temperatures, propene is converted to a variety of products (via oligomerization, cracking, oxidation, etc.)

## Summary (2)

- The synergy of coupled LNT-SCR systems results in significant operational benefits:
  - higher system NOx conversion due to ability of SCR catalyst to utilize NH<sub>3</sub> and HCs for NOx reduction
  - lower NH<sub>3</sub> and HC emissions
  - lower H<sub>2</sub>S and N<sub>2</sub>O emissions
  - ability to compensate for decreased LNT activity after aging (NOx reduction increasingly shifted towards SCR catalyst)
- The use of NTP, combined with perovskites possessing high NOx storage capacity, represents a promising approach for low temperature NOx storage-reduction

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