Laboratory Product Speciation Studies of the LNT + *in situ* SCR NOx Emission Control Concept

M. Crocker, V. Easterling, J. Wang

University of Kentucky Center for Applied Energy Research

M. Dearth, R.W. McCabe, J. Theis

Ford Motor Co.

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Project Overview

- Project team:

  University of Houston, University of Kentucky, Ford, ORNL, BASF

- Project goal:

  Identify the NOx reduction mechanisms operative in LNT and *in situ* catalysts, and to use this knowledge to design optimized LNT-SCR systems in terms of catalyst architecture and operating strategies

- Approach:

  U. Kentucky and Ford focusing on mechanistic and performance data to support modeling efforts at U. Houston:

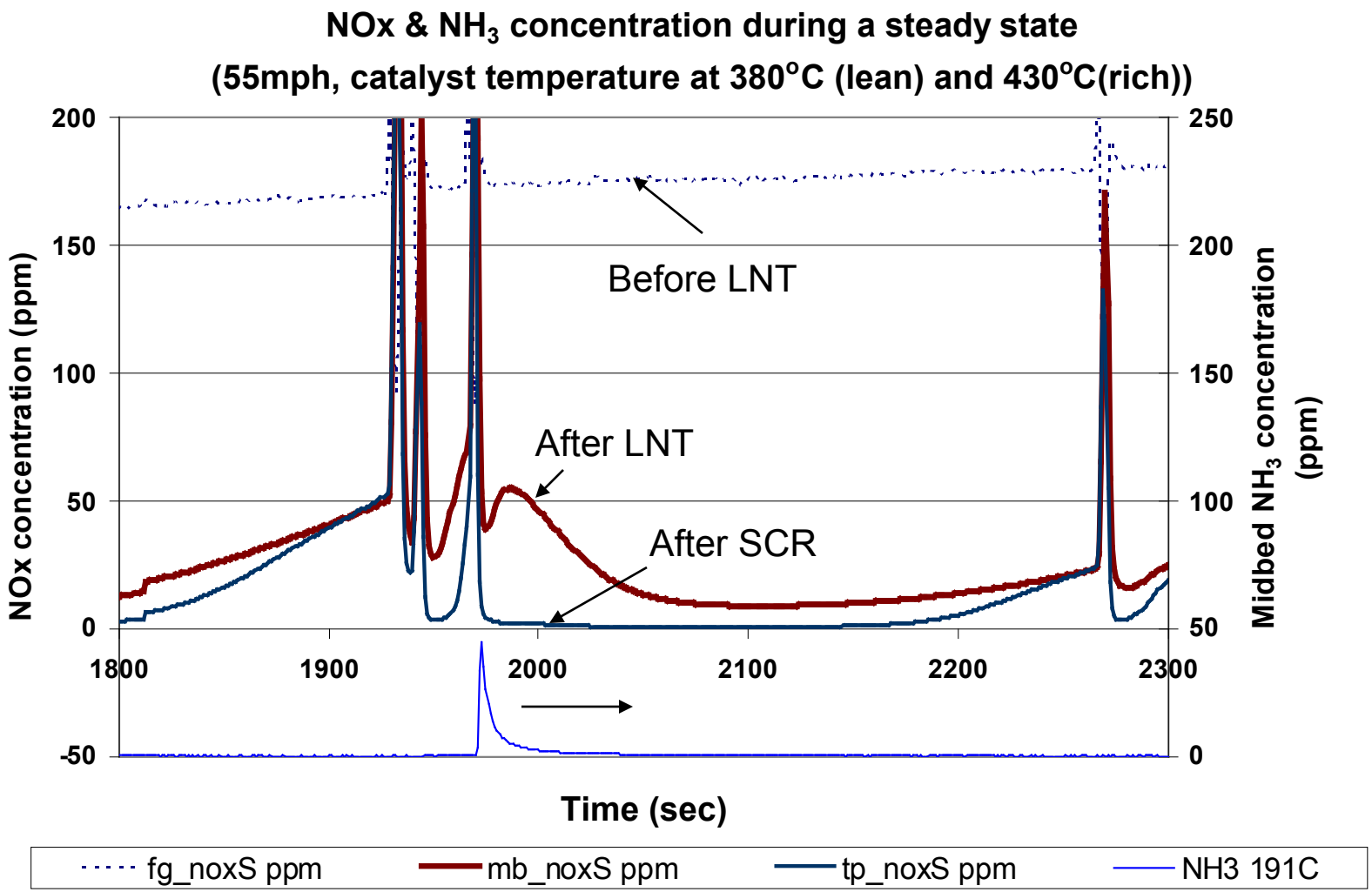
  - reactor studies and catalyst characterization
  - spaciMS studies
  - in situ DRIFTS studies
  - vehicle studies

Background: *In Situ* NH_3 Mechanism

- "Classical" explanation:
  - LNT produces NH_3 during rich purges (similar to TWC under rich engine conditions)
  - NH_3 stores on downstream SCR catalyst
  - Stored NH_3 reacts with "breakthrough" NOx during lean operation
  - Similar to urea-SCR except that NH_3 is generated "in-situ" or "passively" by the LNT

- NH_3 *in situ* mechanism does not appear to fully explain LNT+SCR data

Vehicle Testing: Steady-Speed

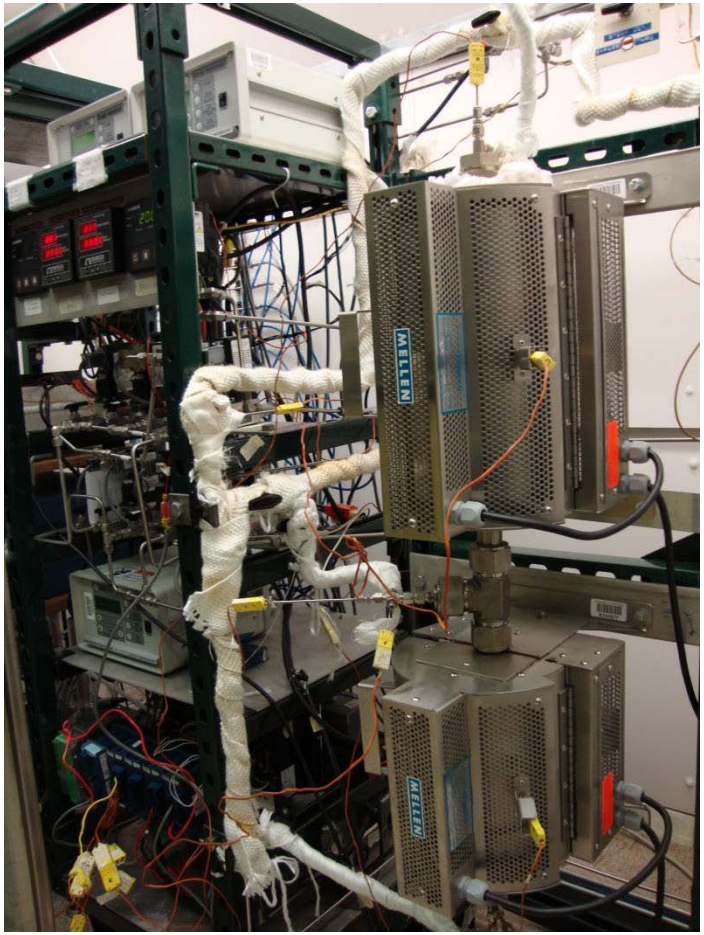


NH_3 produced cannot explain extra NOx conversion by SCR catalyst

Reactor Studies

LNT-SCR studies:

- Low PGM-loaded LNT used, with Cu-zeolite SCR catalyst
- 3” x 0.9” cores, de-greened at 500 ºC for 5 h under L/R cycling
- Two reactor configurations examined:
  (i) separate catalysts/reactors with gas sampling at three positions;
  (ii) close-coupled catalysts (one reactor) with gas sampling at reactor inlet and outlet
- 60 s lean/5 s rich cycles
- Gas analysis using FTIR gas analyzer

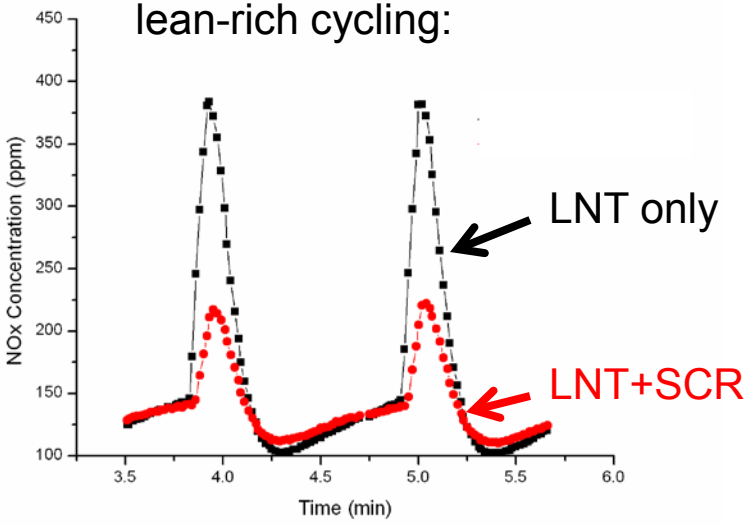


NOx Conversion in the LNT-SCR System: Results for Different Reductants (233 °C)

Reductant [a]	Total NOx conversion over SCR catalyst (%)	NOx conversion over SCR catalyst during lean phase (%)	NOx conversion over SCR catalyst during rich phase (%)
$CO + H_2 + C_3H_6$	15.3	5.9	9.6
$CO + H_2$	3.6	3.45	0.15
C_3H_6	8.0	0.8	7.2

[a] CO = 1%; H_2 = 0.3%; C_3H_6 = 3333 ppm; 0.5% O_2 also present in rich phase

$CO+H_2+C_3H_6$ as reductant, lean-rich cycling:



When propene is added as rich phase reductant, NOx conversion over SCR catalyst mainly occurs in rich phase (as opposed to lean phase for conventional NH_3 route)

Nitrogen Balance Across SCR Catalyst

Close-coupled Configuration; Reductant = 1% CO + 0.3% H_2 + 3333 ppm C_3H_6

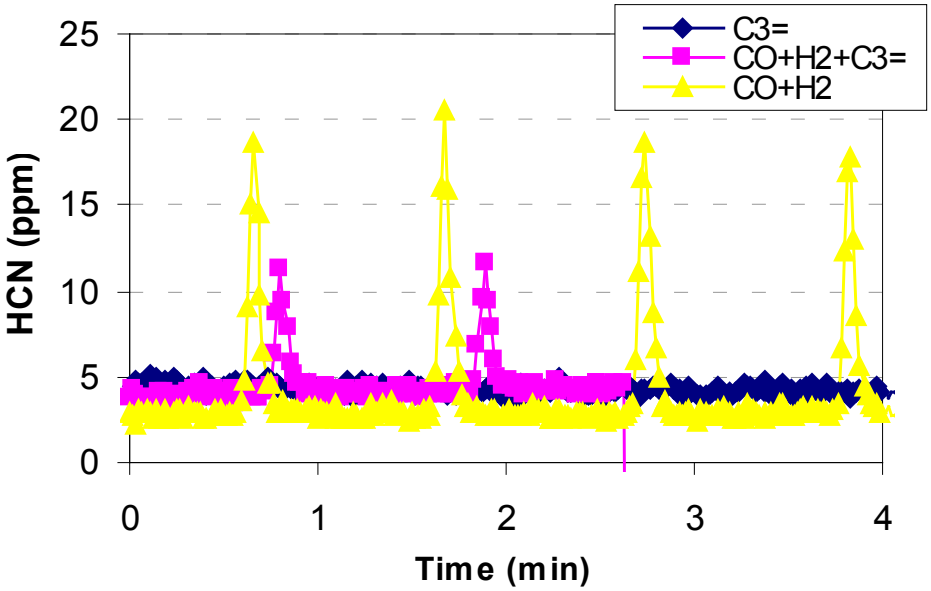
LNT Inlet Temperature (°C)	NH_3 converted over SCR catalyst (ppm)	NOx converted over SCR catalyst (ppm)	NH_3 converted – NOx converted (ppm)
149	0.1	9.3	-9.1
166	0.3	6.7	-6.3
183	0.9	23.9	-23.0
196	1.9	21.5	-19.6
232	8.7	52.6	-43.9
275	11.9	42.4	-30.5
316	14.6	26.8	-12.2
375	15.9	27.7	-11.8
421	11.4	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_3); only HCN is consistently observed, but in low concentrations

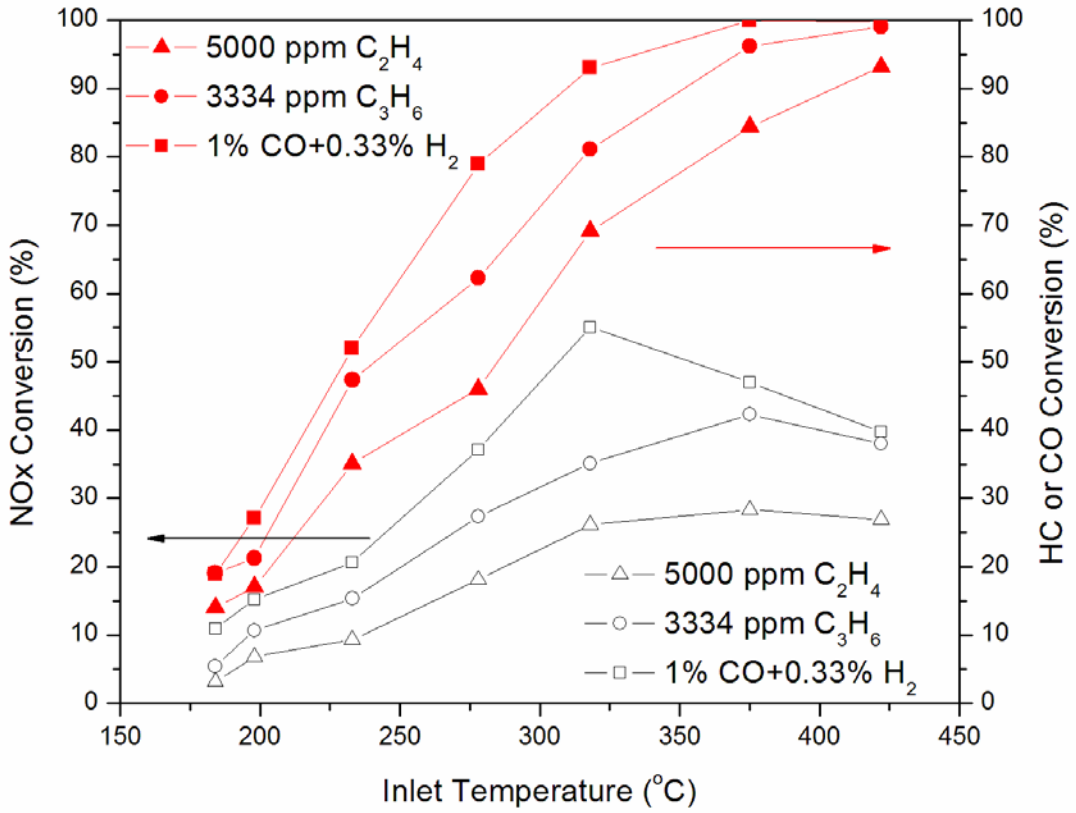
Hence, formation of organo-nitrogen species over LNT does not appear to be important

➢ Slipped hydrocarbon is responsible for NOx reduction in SCR catalyst



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

Steady State Reaction over SCR Catalyst



Feed gas:
300 ppm NO, 5% CO_2,
5% H_2O, N_2 balance,
GHSV = 30,000 h^{-1},
reductant as shown

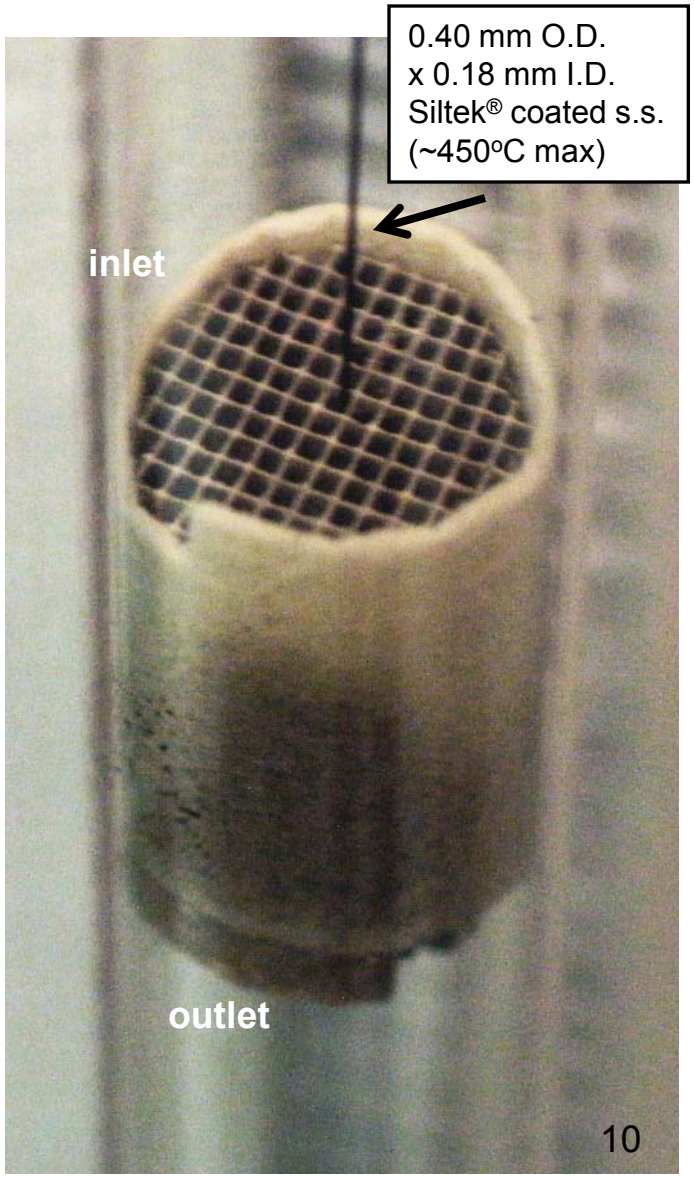
- SCR catalyst is active for NOx reduction using ethylene, propylene and CO/H_2 as reductants
- Can be significant for NOx conversion under conditions when there is little formation of NH_3

Spatiotemporal Study of LNT NH_3 Selectivity

SpaciMS - Spatially resolved capillary inlet MS

- Sampling probe can be positioned at multiple axial and/or radial positions to build up detailed spatio-temporal picture of reactions and breakthrough fronts
- Ford set-up makes use of V&F AirSense 2000 ™ CI-MS (improved sensitivity for NH_3); data typically taken at 12 points along length of catalyst

- Metal capillary heated using low voltage AC current.
- Diameter of catalyst channel (400/ 6) is ~1 mm and flow is ~30 mL/min @ 30,000 $h^{-1}$and 20 ^oC
- 14 mL/min (ambient) volume extracted from channel.
- Residence time (t_R) of gas in channel ~60 msec.
- MS measurement cycle ~10 msec.



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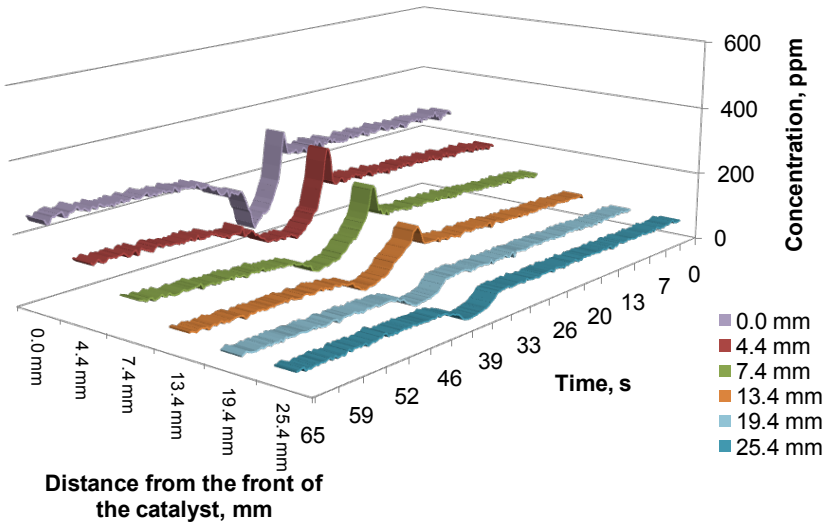
J.-S. Choi, W.P. Partridge, C.S. Daw, Appl. Catal. A: Gen. 293 (2005) 24.

SpaciMS Study of NH_3 Evolution in LNT Catalysts (1):
Degreened catalyst, low OSC, 250 ºC, H_2 as reductant

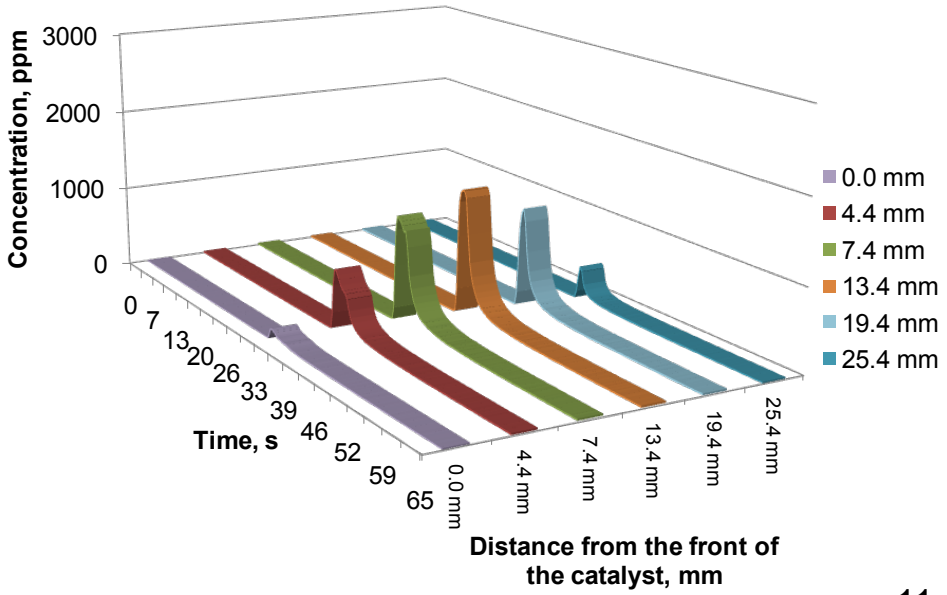
NO evolution



NO evolution:

NO concentration peaks near front of catalyst:
- NOx storage mainly in front portion
- NOx released to gas phase subsequently undergoes consumption downstream

NH_3 evolution

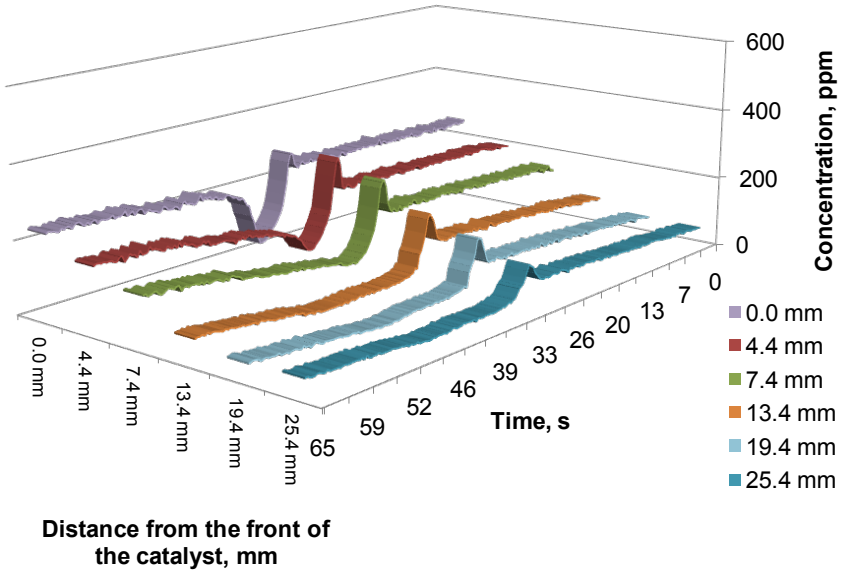


NH_3 evolution:

NH_3 concentration peaks near middle of catalyst:
- possible correlation with H_2 (from prior v
- NH_3 released to gas phase subsequentl undergoes consumption downstream

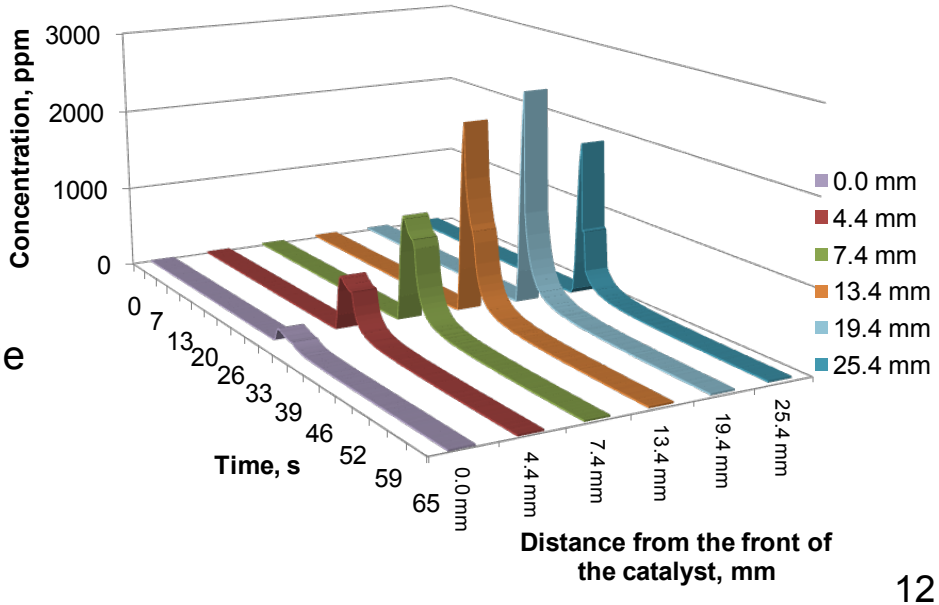
SpaciMS Study of NH_3 Evolution in LNT Catalysts (2):
Aged catalyst (24 h, 800 ºC, lean), low OSC, 250 ºC, H_2 as reductant

NO evolution



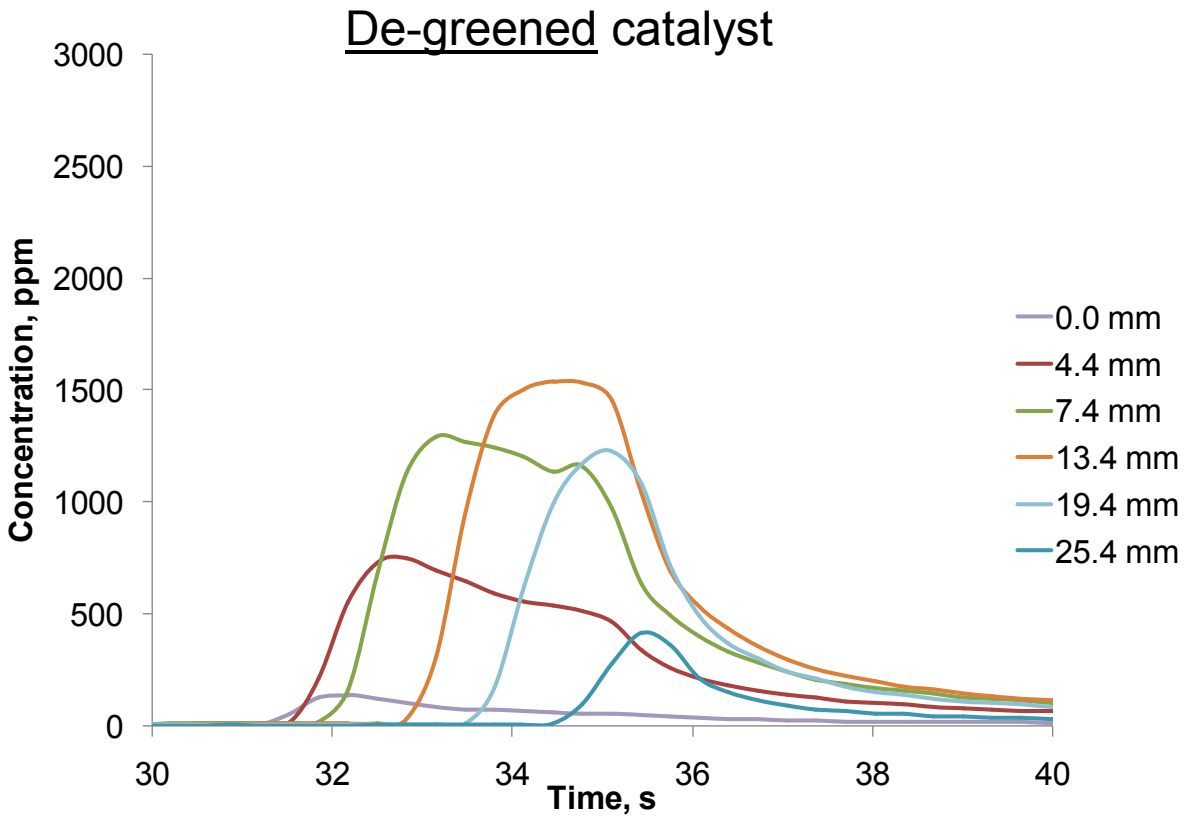
NO evolution:
NO concentration peaks near middle of catalyst:
- NOx storage & reduction zone "stretched" after catalyst aging due to loss of NOx storage capacity

NH_3 evolution



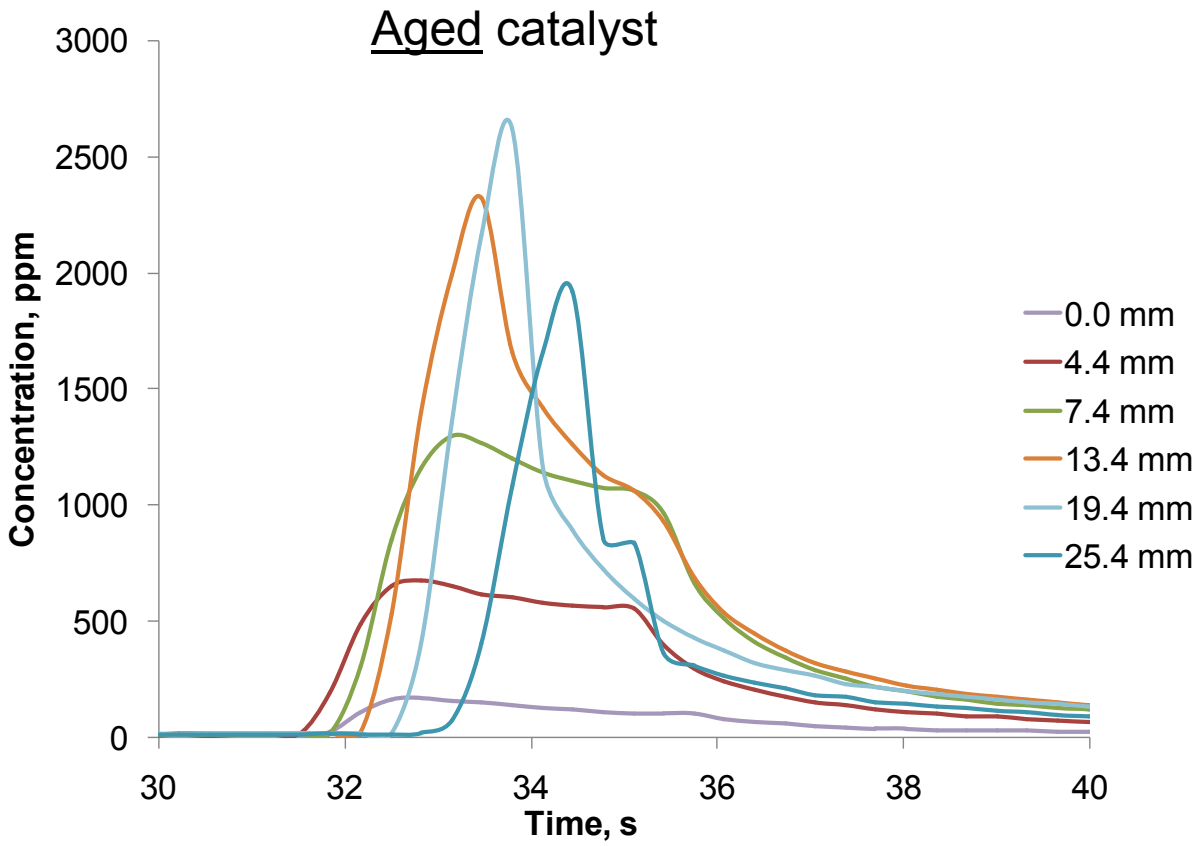
NH_3 evolution:
NH_3 concentration peaks near rear of catalyst:
- consistent with "stretching" of NOx storage & reduction zone
- formed NH_3 has less opportunity to be consumed via reaction with NOx or O_2, hence NH_3 emissions increase

2D Representation of NH_3 Concentration Profiles



- Time lag in NH_3 release indicates that boundary between lean and rich conditions moves relatively slowly through catalyst, due to high concentration of stored NOx (and O_2) in front region of catalyst)

2D Representation of NH_3 Concentration Profiles

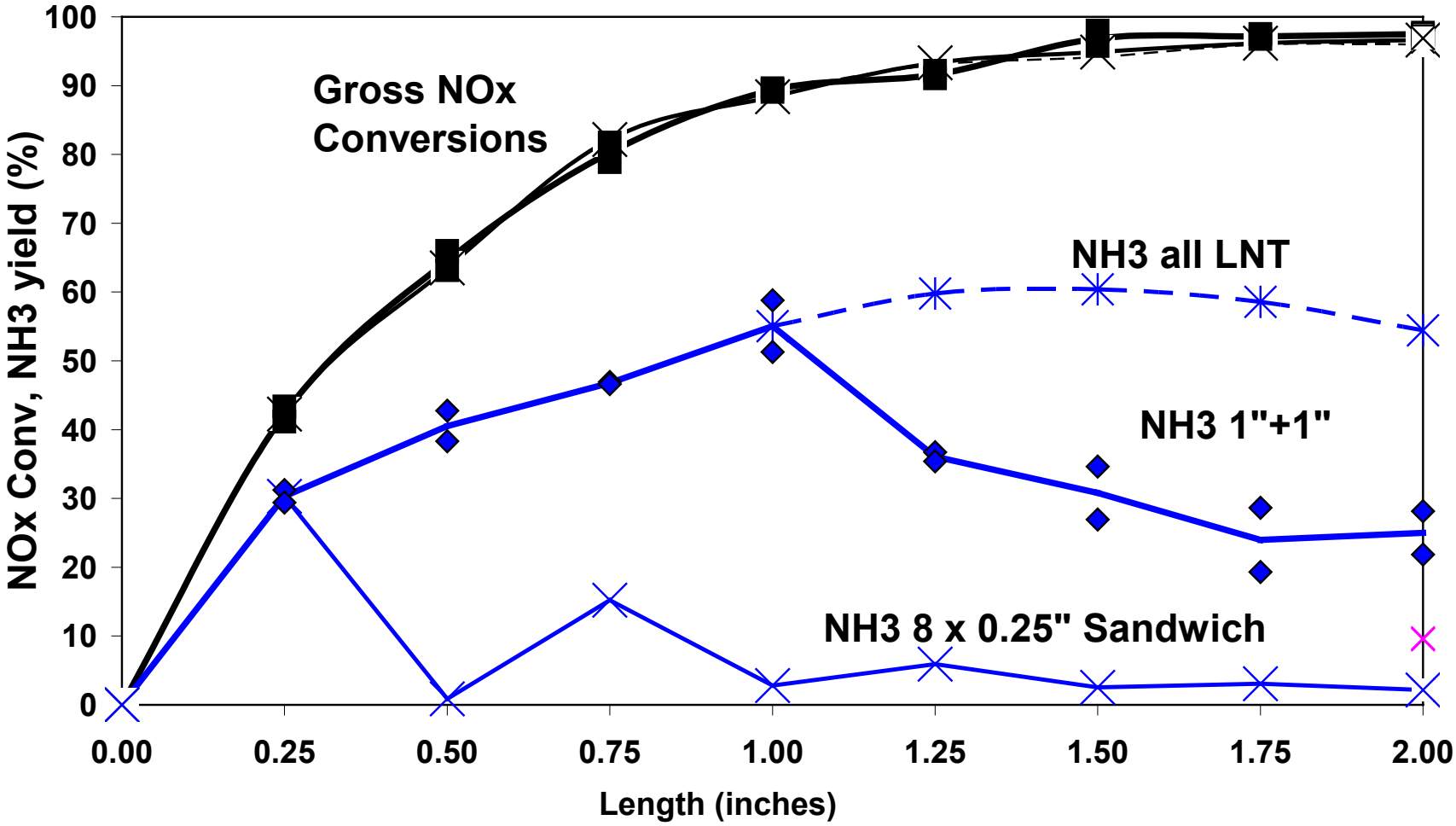


- Little time lag in NH_3 release: boundary between lean and rich conditions moves rapidly through catalyst, due to low concentration of stored NOx and O_2 in front region of catalyst
  => can be expected to result in high H_2/NOx ratios at Pt

Spatial Study of NH_3 Evolution - Effect of Catalyst Configuration: 2" LNT vs. 1"+1" LNT-SCR, vs. 8 x 0.25" LNT-SCR sandwich

Catalysts aged 20 h at 800 ºC; catalysts evaluated at 275 ºC on 60/5 s cycle

4% CO + 1.3% H_2 + 2500 ppm C_2H_4 + 1% O_2 during rich purges, λ = 0.86



Conclusions

- Reactor studies have shown that a hydrocarbon-based NOx reduction mechanism can operate in the SCR catalyst in parallel with the NH_3-SCR mechanism
- The hydrocarbon pathway is characterized by NOx conversion proceeding in both the lean and rich phases, unlike the NH_3 pathway which operates mainly in the lean phase
- SpaciMS indicates significant changes w.r.t. NH_3 release upon LNT aging:
  - for aged catalysts, NOx storage zone is stretched along entire length of catalyst
  - consequently, NH_3 evolution increases along length of catalyst (less opportunity for NH_3 to be consumed in rear of catalyst by O_2)
  - reductant front travels faster through aged catalyst
- NH_3 emissions are heavily influenced by LNT-SCR system architecture

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  C.Z. Wan (BASF)