Assessing Monolith Length Effect on LNT Performance

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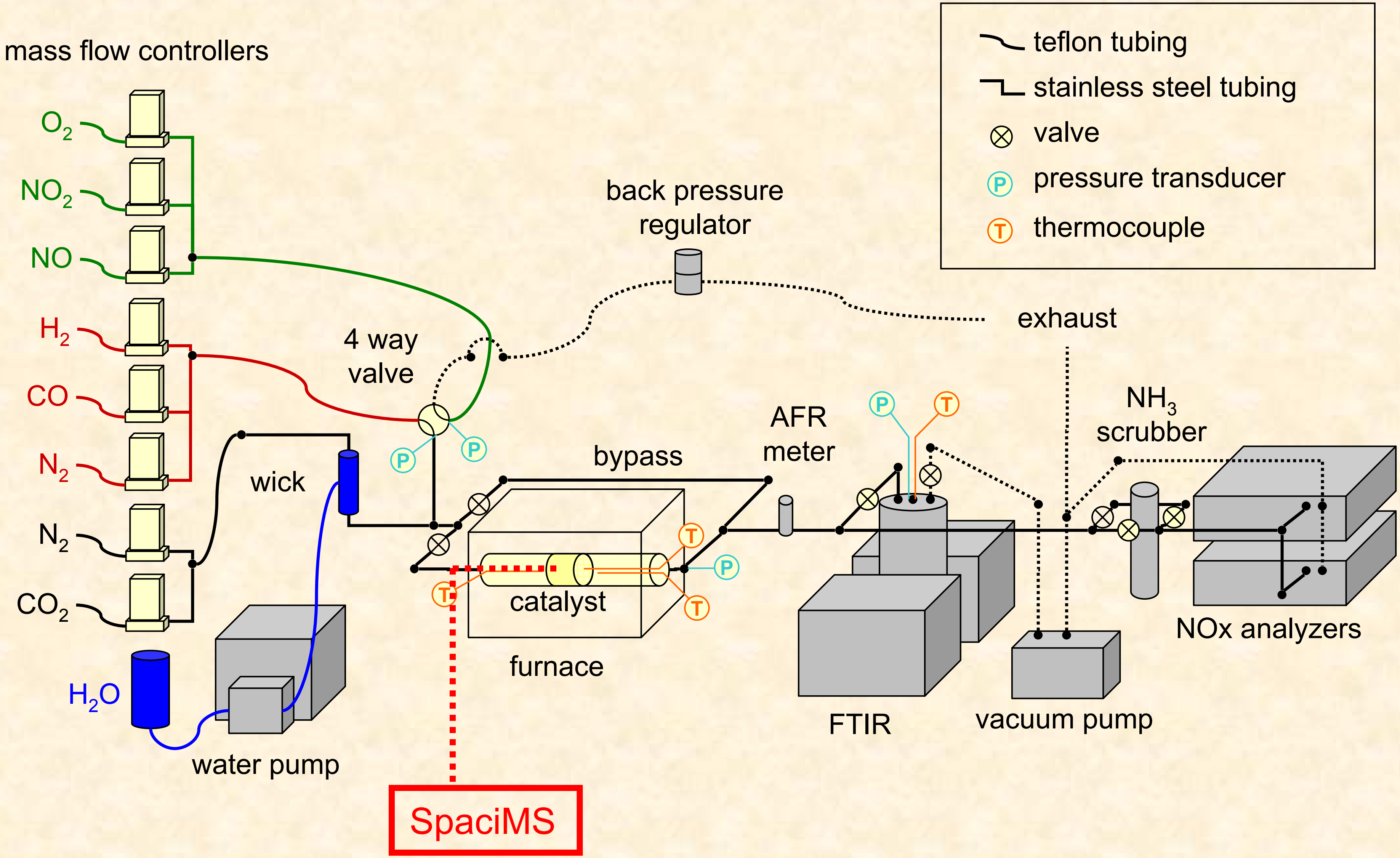
9th CLEERS Workshop, University of Michigan, Dearborn

May 4, 2006

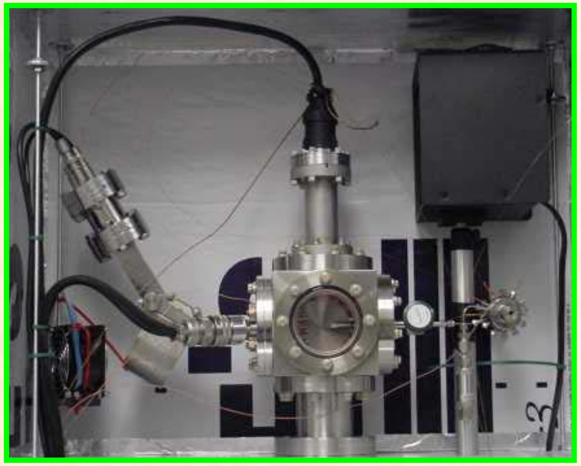
This work is designed to determine if/how monolith length affects LNT performance

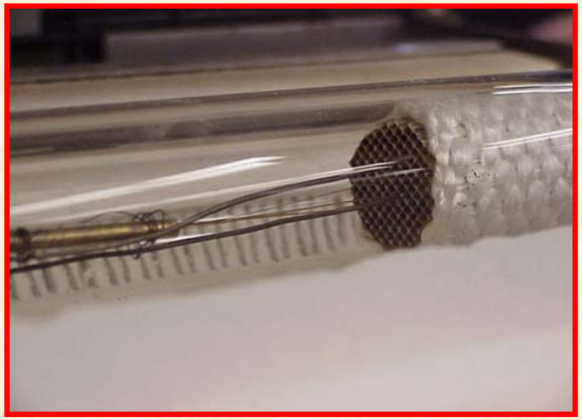
- Significantly different LNT performance data are often obtained under the same conditions by different labs
  cf. John Hoard, 8th CLEERS Workshop
- Different catalyst sizes can be used at different labs
  - Required by each lab. reactor specification
  - Suspected as an origin of LNT performance disparity
  - But existing theory rules out performance dependence on length at a given space velocity
- Length effect issue needs to be addressed
  - To refine CLEERS LNT characterization protocol
  - To develop models

Our approach: well-controlled bench reactor evaluation of core samples



SpaciMS:
Spatially-Resolved Capillary Inlet Mass Spectrometer





Magnetic sector mass spectrometer

- Capable of quantifying various species including H_2
- Better temporal resolution than conventional analyzers

Multiple capillary inlets allow *in-situ* spatially resolved measurements

Minimally invasive

- Sample rate ~10 μL/min
- probe diameter 185 μm

Test Matrix

Compare 1”, 2”, 3” LNT cores at an identical space velocity: 30000 h^{-1}

Cycling Type	Mode	Time	Gas Composition
Long	**Lean**	**15 min**	**300 ppm NO, 10% O_2**
	Rich	**10 min**	**0.2 (or 0.5)% H_2**
Short	**Lean**	**56 s**	**300 ppm NO, 10% O_2**
	Rich	**4 s**	**1 (or 2)% H_2**

- All experiments included 5% CO_2, 5% H_2O and balance N_2
- Temperature: 200, 300, and 400 °C
- Gas analysis:
  - NO/NO_x: chemiluminescence detectors
  - NO_2/N_2O/NH_3/CO/CO_2/H_2O: FT-IR
  - SpaciMS: H_2

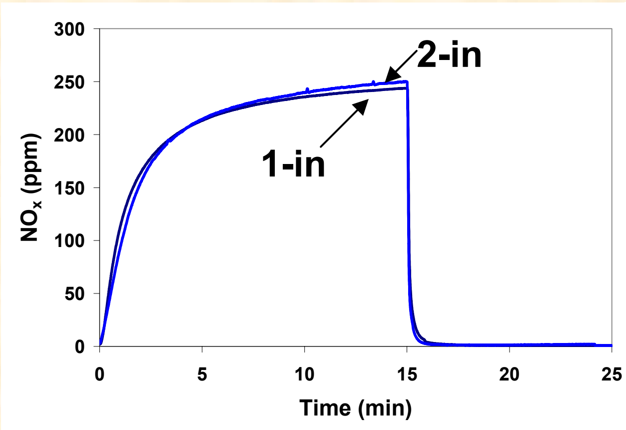
Three "identical" 7/8" OD x 1" long cores selected & used as building blocks

- Cores made from a 200 cpsi cordierite brick washcoated w/ $Pt/K/Al_2O_3$ (EmeraChem)
- Sample-to-sample variation made direct comparison of cores w/ different lengths challenging
- Three 1" cores w/ similar performance were selected and used as building blocks:
  - 1-in core=1 x 1" (evaluation completed)
  - 2-in core=2 x 1" (evaluation completed)
  - 3-in core=3 x 1" (evaluation in progress)

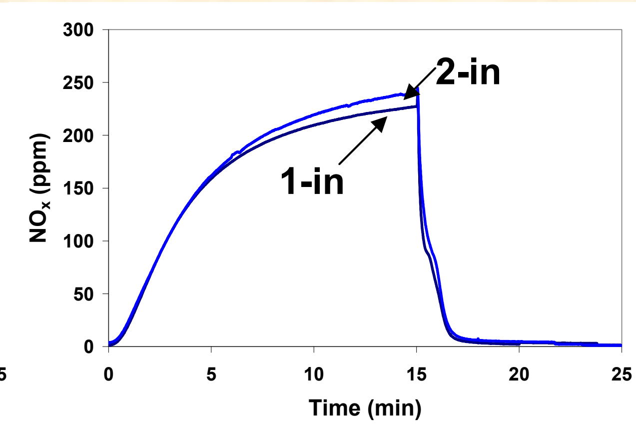
Long Cycling Experiments

Long cycling performance not affected by LNT length: NO_x profiles

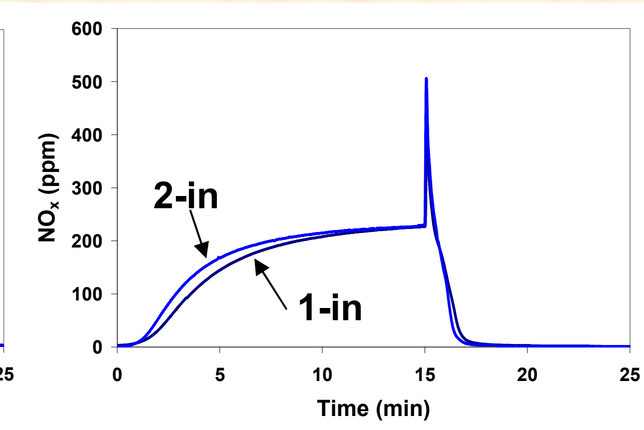
0.2% H_2 at 200 °C



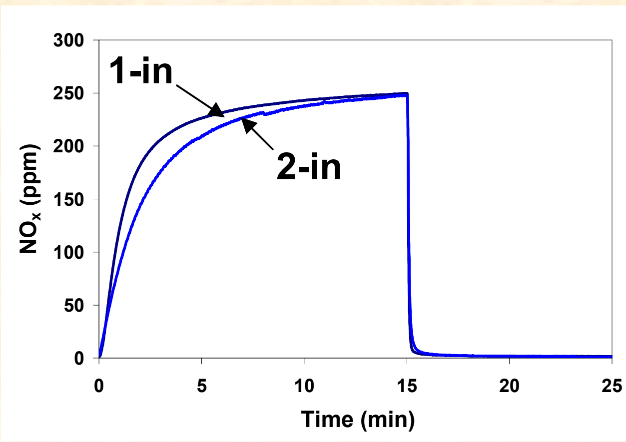
0.2% H_2 at 300 °C



0.2% H_2 at 400 °C



0.5% H_2 at 200 °C



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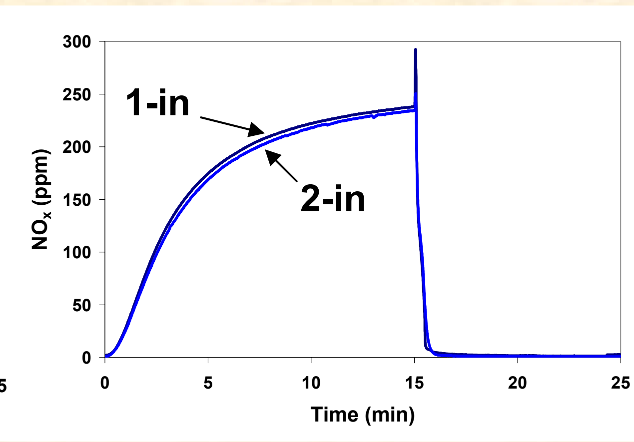

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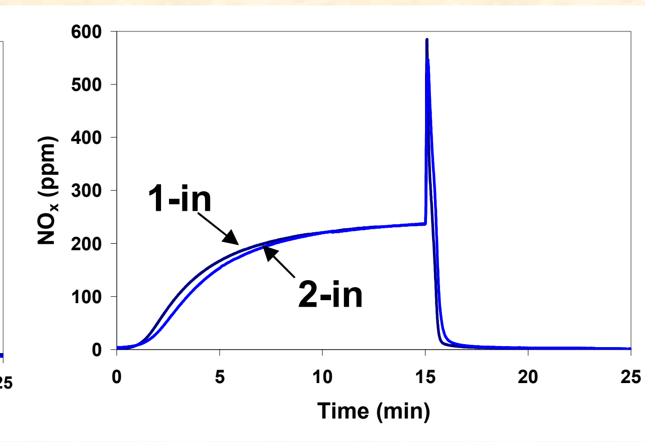
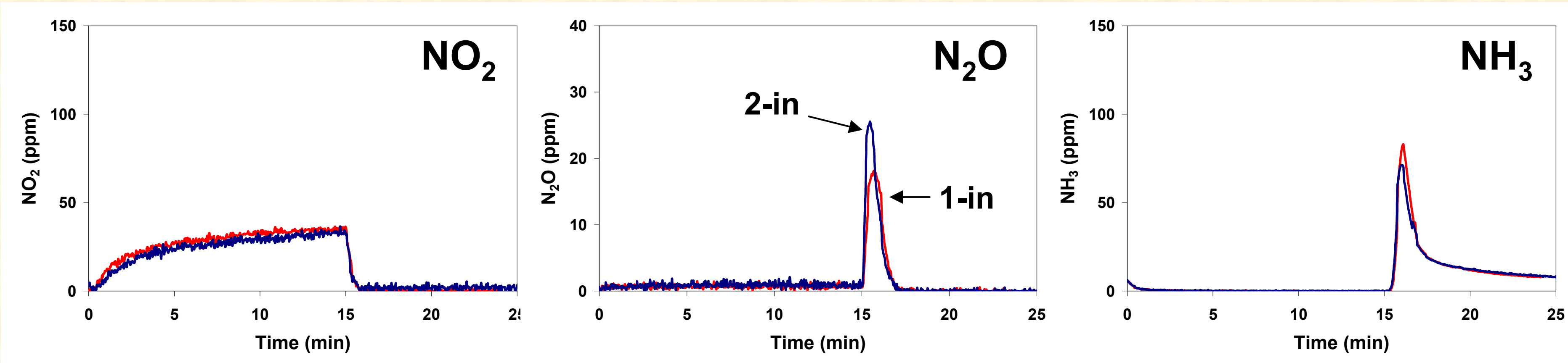
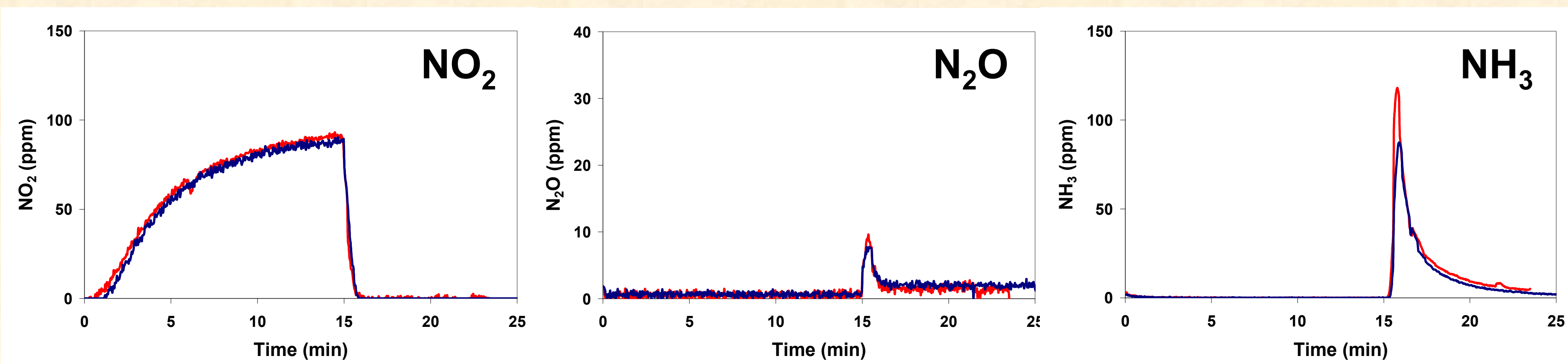


Long cycling performance not affected by LNT length: NO_2, N_2O, NH_3 profiles

0.2% H_2 at 200 °C



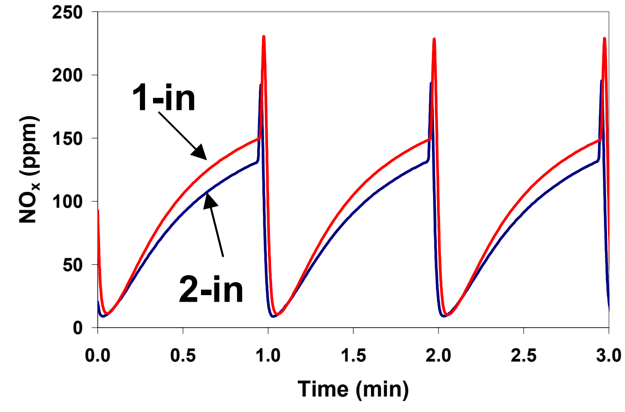
0.5% H_2 at 300 °C



Short Cycling Experiments

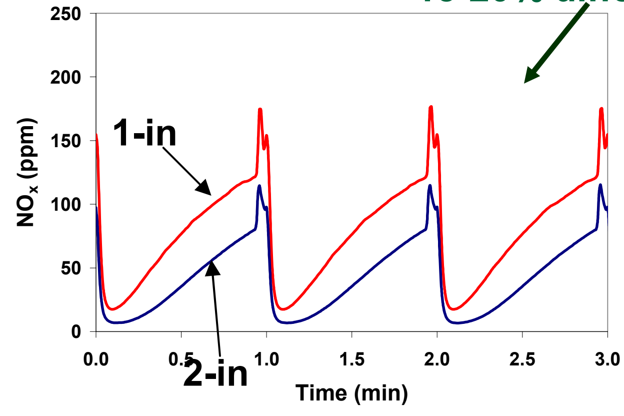
Longer sample performs better during short cycling w/ 1% H_2 reductant: NO_x profiles

1% H_2 at 200 °C

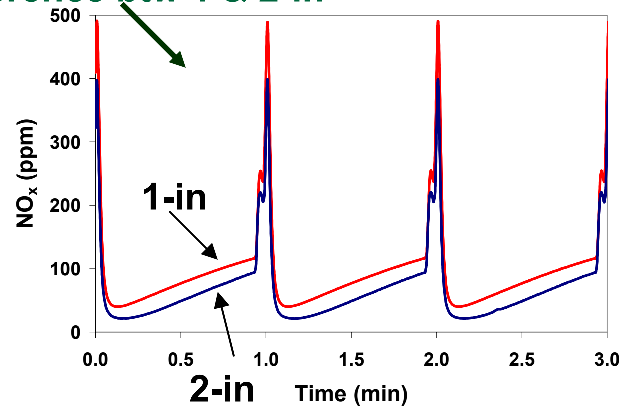


1% H_2 at 300 °C

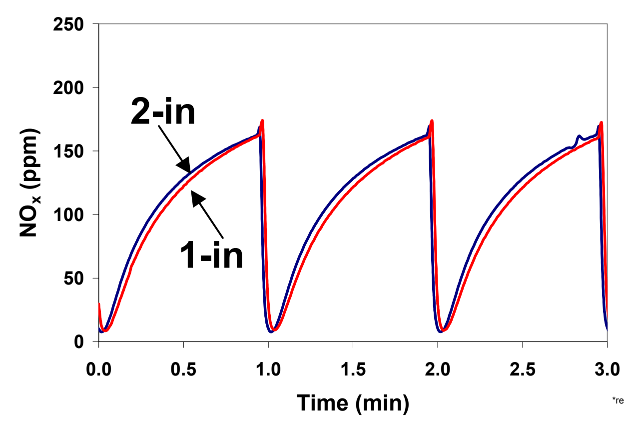
15-20% difference btw 1 & 2-in



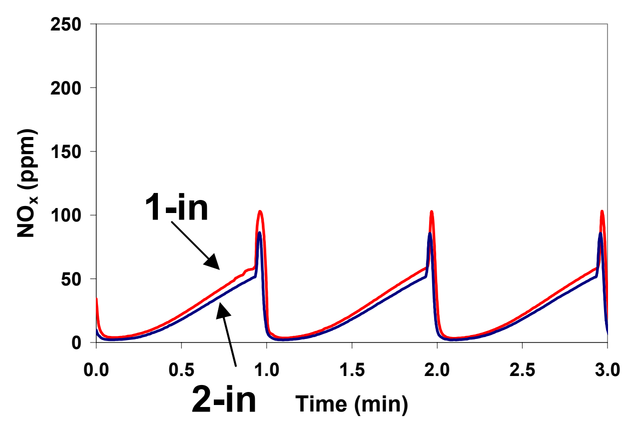
1% H_2 at 400 °C



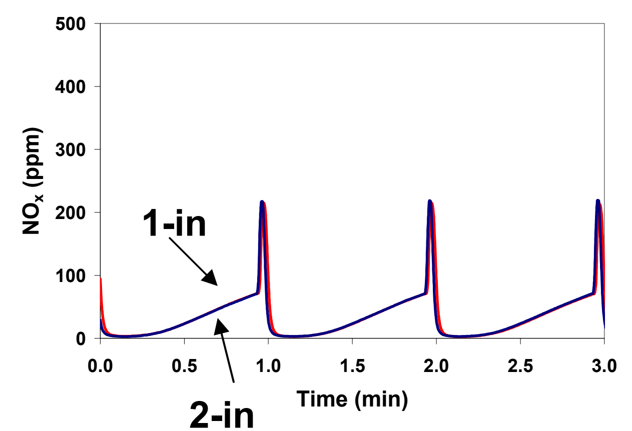
2% H_2 at 200 °C



2% H_2 at 300 °C

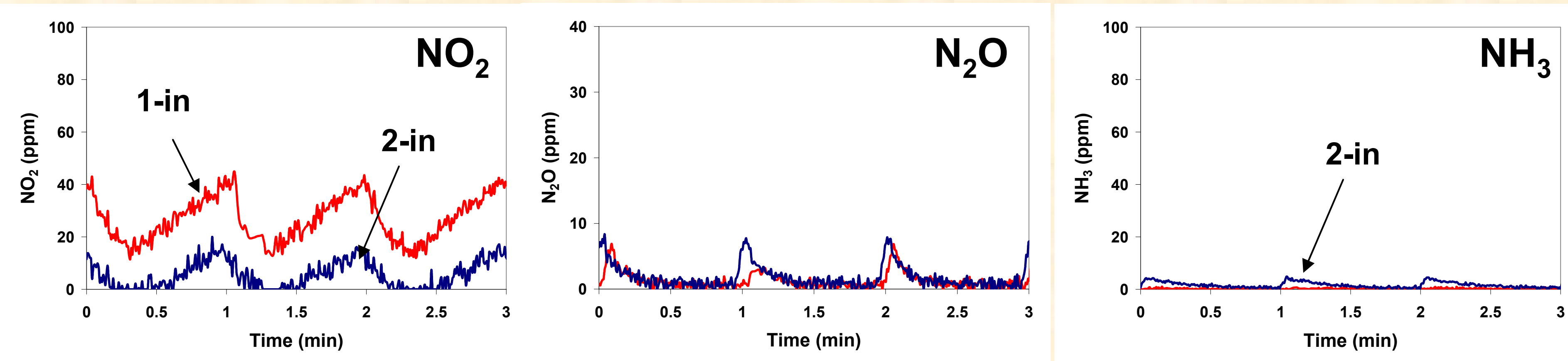


2% H_2 at 400 °C

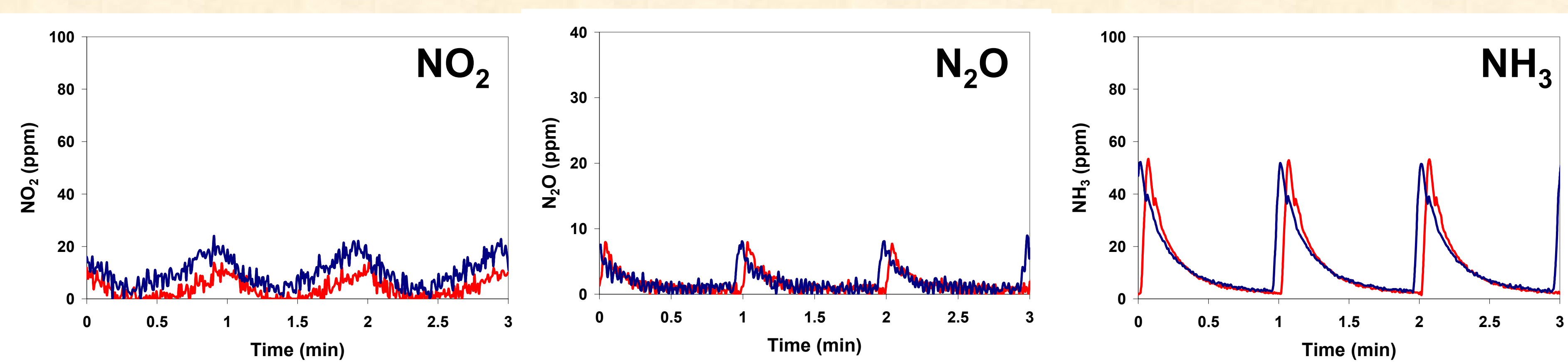


Longer sample performs better during short cycling w/ 1% H_2 reductant: NO_2, N_2O, NH_3 profiles

1% H_2 at 300 °C



2% H_2 at 300 °C



LNT Performance vs. Length: Summary

- **Performance of short cycling with full regen and long cycling not affected by monolith length**

  2 in = 1 in

- **Performance of short cycling with partial regen affected by monolith length**

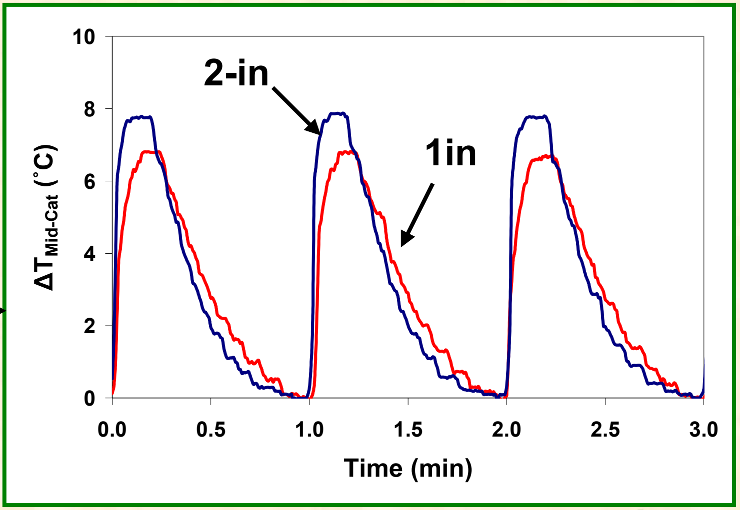
  2 in > 1 in

  What is going on here?

- **Little difference in T profiles observed**

  (indicating negligible thermal effect)

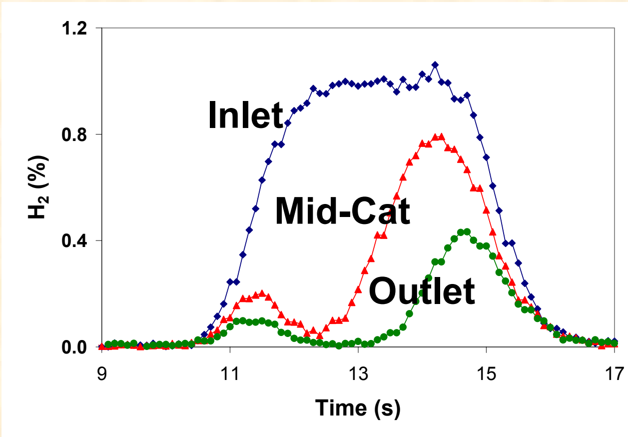
Comparison of $\Delta T_{Mid\text{-}Cat}$
Short cycling; 1% H_2; 300 ˚C
(Biggest performance difference observed)



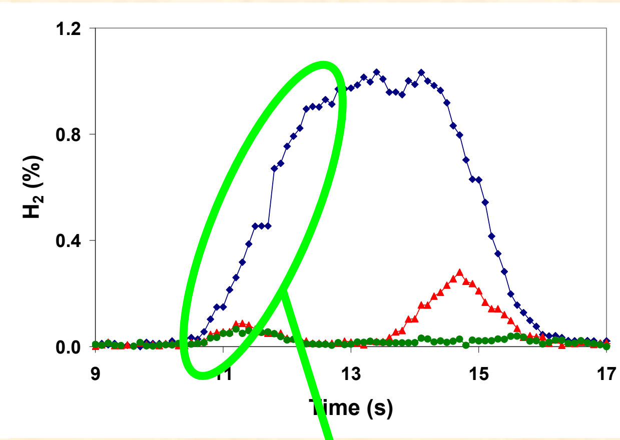
H_2 Consumption Trends During Short Cycling

Apparent H_2 consumption was similar or slightly higher for 1-in: contradicts performance trends

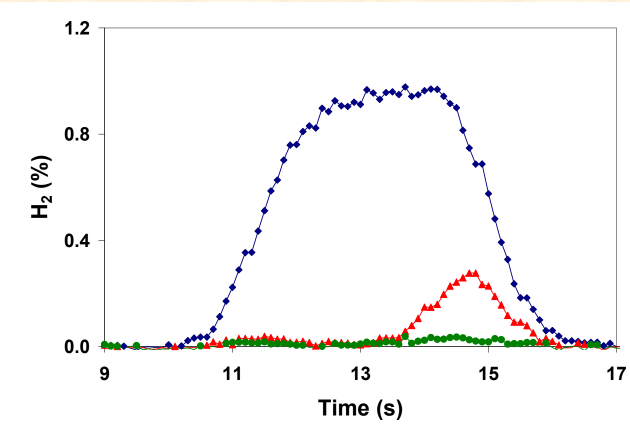
1% H_2 at 200 °C, 1-in



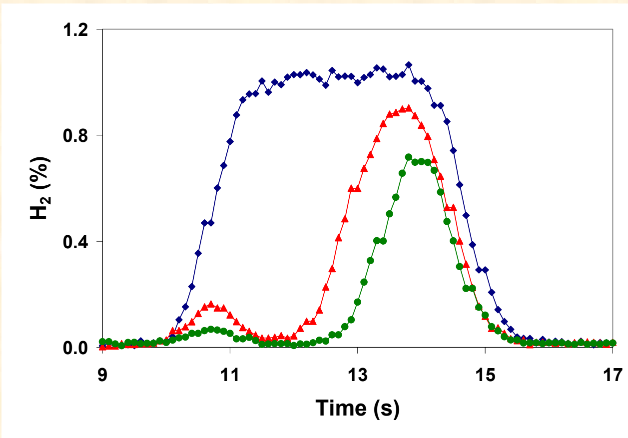
1% H_2 at 300 °C, 1-in



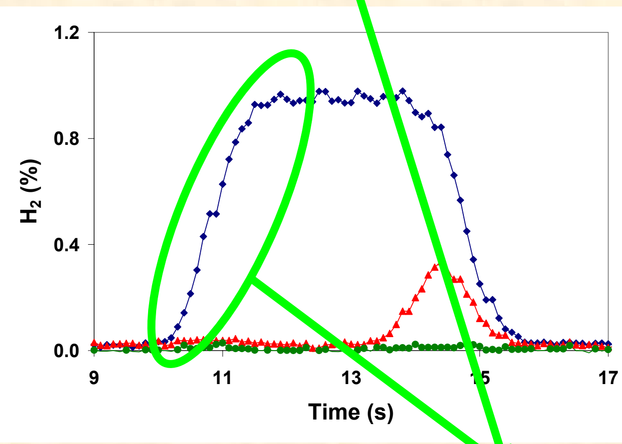
1% H_2 at 400 °C, 1-in



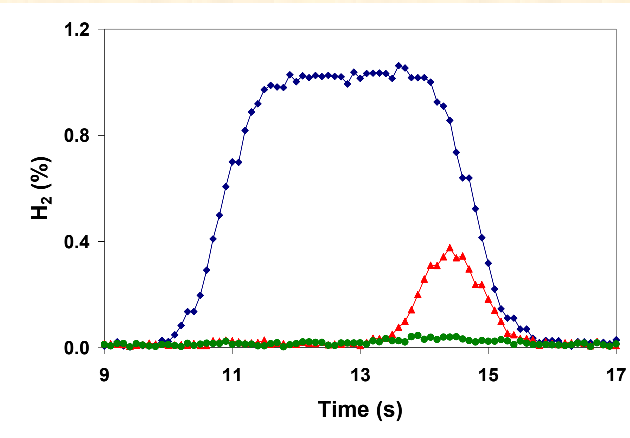
1% H_2 at 200 °C, 2-in



1% H_2 at 300 °C, 2-in

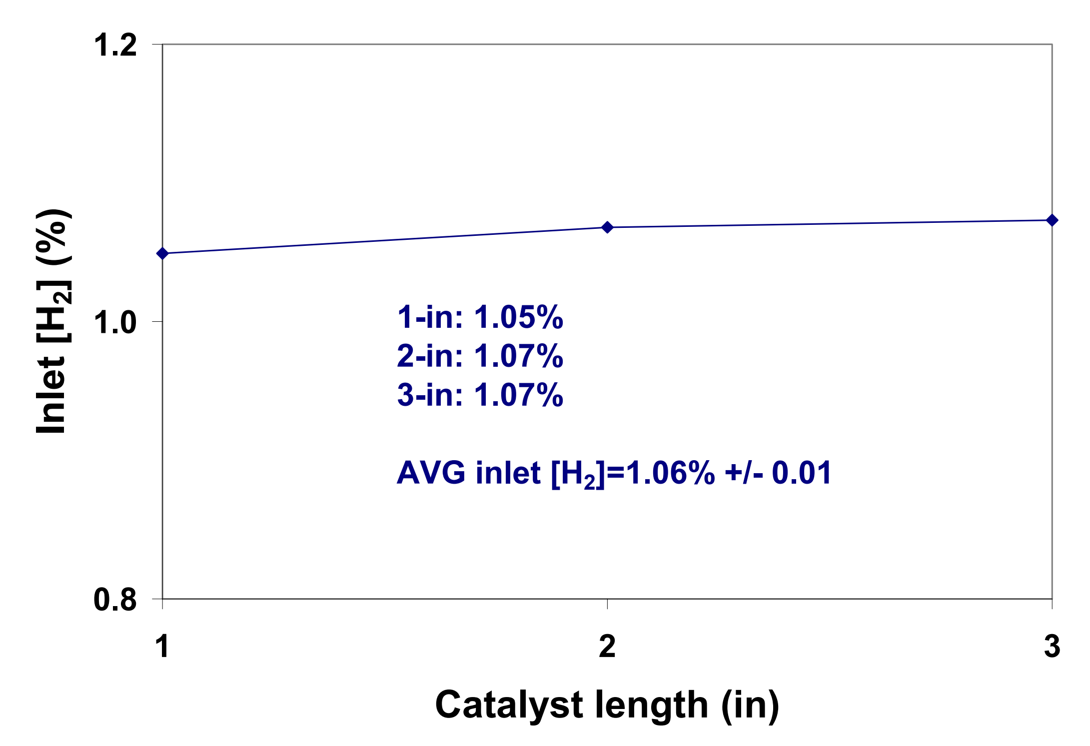


1% H_2 at 400 °C, 2-in



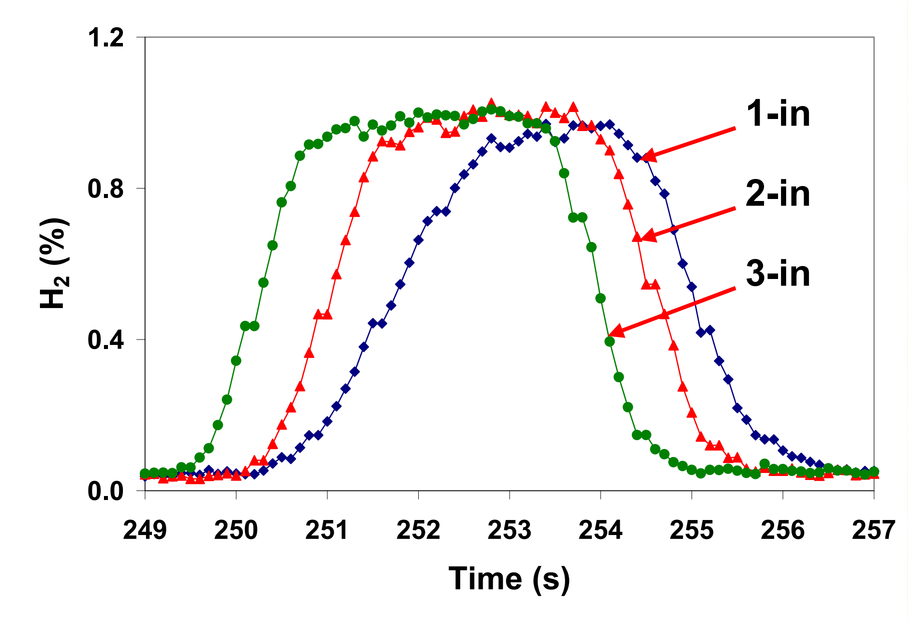
Was the actual inlet [H_2] lower for 1-in cases?

Without cycling, inlet H_2 levels were identical regardless of monolith length



- So, there was no $[H_2]$ variability due to different combinations of mass flow controllers
  - Different total flows required by different LNT lengths
- Then why inlet H_2 levels were different during cycling?

Different H_2 rise times during short cycling suggests different degrees of backmixing



- **Inlet [H_2]: 3-in > 2-in > 1-in**
  - 3-in: 3.68 %-s
  - 2-in: 3.63 %-s
  - 1-in: 3.33 %-s
- **Even for 3-in, H_2 level still lower than the commanded value ~4%-s**

- **1-in has longest transport time (switching valve to cat-in) and T10-90 rise time**
- **Varying T10-90 suggests different degrees of lean/rich front backmixing**
  - Can lead to H_2 + O_2 reactions to different extents
  - Resulting in different levels of H_2 loss

Experiments performed to investigate lean/rich front backmixing

Normal short cycling versus **Short cycling w/ neutral purge**

Lean	56 s	10% O_2 5% CO_2, 5% H_2O, bal. N_2
Rich	4 s	1% H_2 5% CO_2, 5% H_2O, bal. N_2

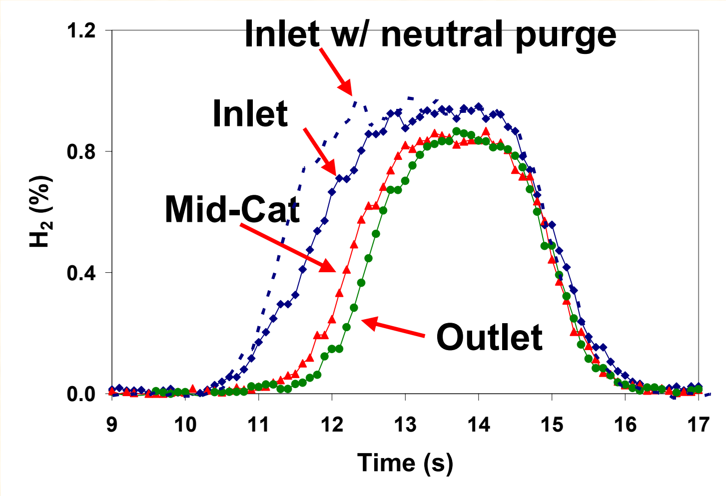
Lean	56 s	10% O_2 5% CO_2, 5% H_2O, bal. N_2
Purge	10 s	5% CO_2, 5% H_2O, bal. N_2
Rich	4 s	1% H_2 5% CO_2, 5% H_2O, bal. N_2

1-in core; SV=30000 h^{-1}, 400 °C

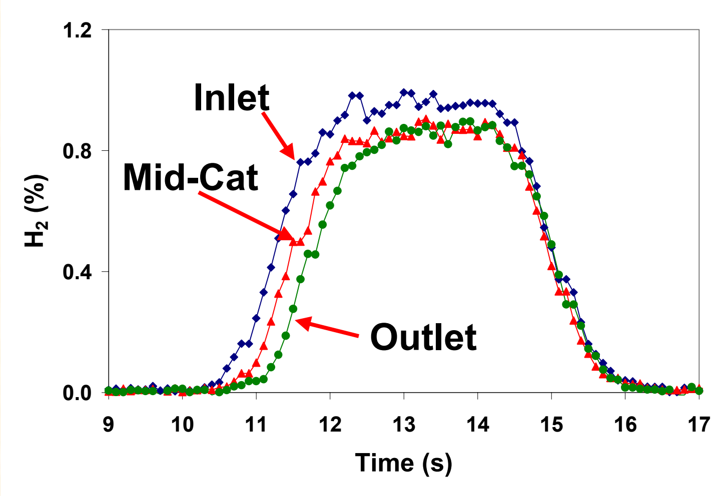
- If lean/rich front backmixing does occur, neutral purge bwn lean/rich switching should give higher inlet H_2
- Inlet, mid-cat, outlet H_2 concentrations were measured via SpaciMS and compared

Neutral purge bwn lean/rich switching did increase significantly inlet H_2

Without neutral purge



With neutral purge

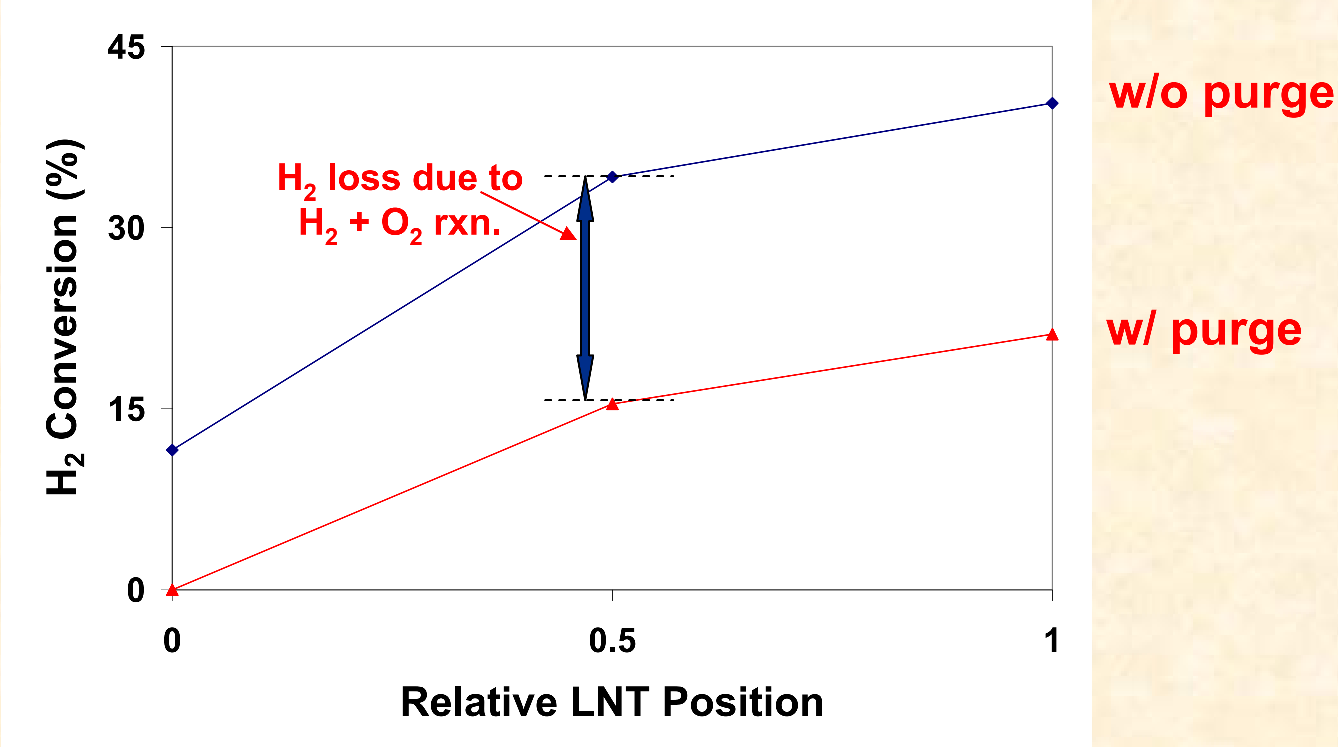


- Neutral purge also decreased H2 consumption inside the 1st half of LNT
- It clearly evidences H_2 loss due to gas-phase and catalytic oxidation by O_2

before LNT **in the 1st half of LNT**

- Same amount of H_2 consumed inside the 2nd half

Comparing conversions based on inlet H_2 w/ neutral purge clearly shows H_2 loss due to O_2



- Significantly higher H_2 consumption before and inside 1st half LNT
- Same H_2 consumption in the 2nd half LNT: by only surface O
- Without purge, ~19% of H_2 lost before and in the front portion of 1-in LNT

Conclusions

- No significant length effect observed on $Pt/K/Al_2O_3$ during long cycling or short cycling with full regeneration
- Significant monolith "length effect" on LNT performance during short cycling with partial regeneration
  - The longer the sample, the better the performance
- Observed "length effect" seems to come from different degrees of lean/rich front axial backmixing at different linear velocities
  - The lower the linear velocity (i.e. shorter LNT), the higher the backmixing
- Higher backmixing resulted in a higher reductant loss via oxidation by O_2
  - Implication in fuel economy and modeling
  - Need to incorporate backmixing effect into model
- Backmixing could explain in part lab-to-lab discrepancy
  - Different degrees of backmixing depending on bench reactor switching valve/gas delivery system specification
  - In addition to other factors: temperature, degreening/pretreatment
- We plan to extend our study to a commercial formulation
  - Umicore GDI LNT used by CLEERS LNT Focus Group
  - To explore other possible "length effects" (e.g., effect of axial 'gaps', flow disturbances in monolith)
  - Due to oxygen storage capacity and higher cell density etc.

Acknowledgements

- DOE Office of FreedomCAR & Vehicle Technologies
- EmeraChem
- Prof. Bill Epling of Univ. of Waterloo
- Colleagues at Fuels, Engines, and Emissions Research Center (FEERC) of Oak Ridge Nat'l Lab