Effect of Length on LNT Performance

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10th DOE Crosscut Workshop on Lean Emissions Reduction Simulation

May 2, 2007

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

- **Conventional census rules out performance dependence on length at a given space velocity**
  - **Reacting system is governed by residence time (reciprocal of space velocity) and mass transfer coefficient**

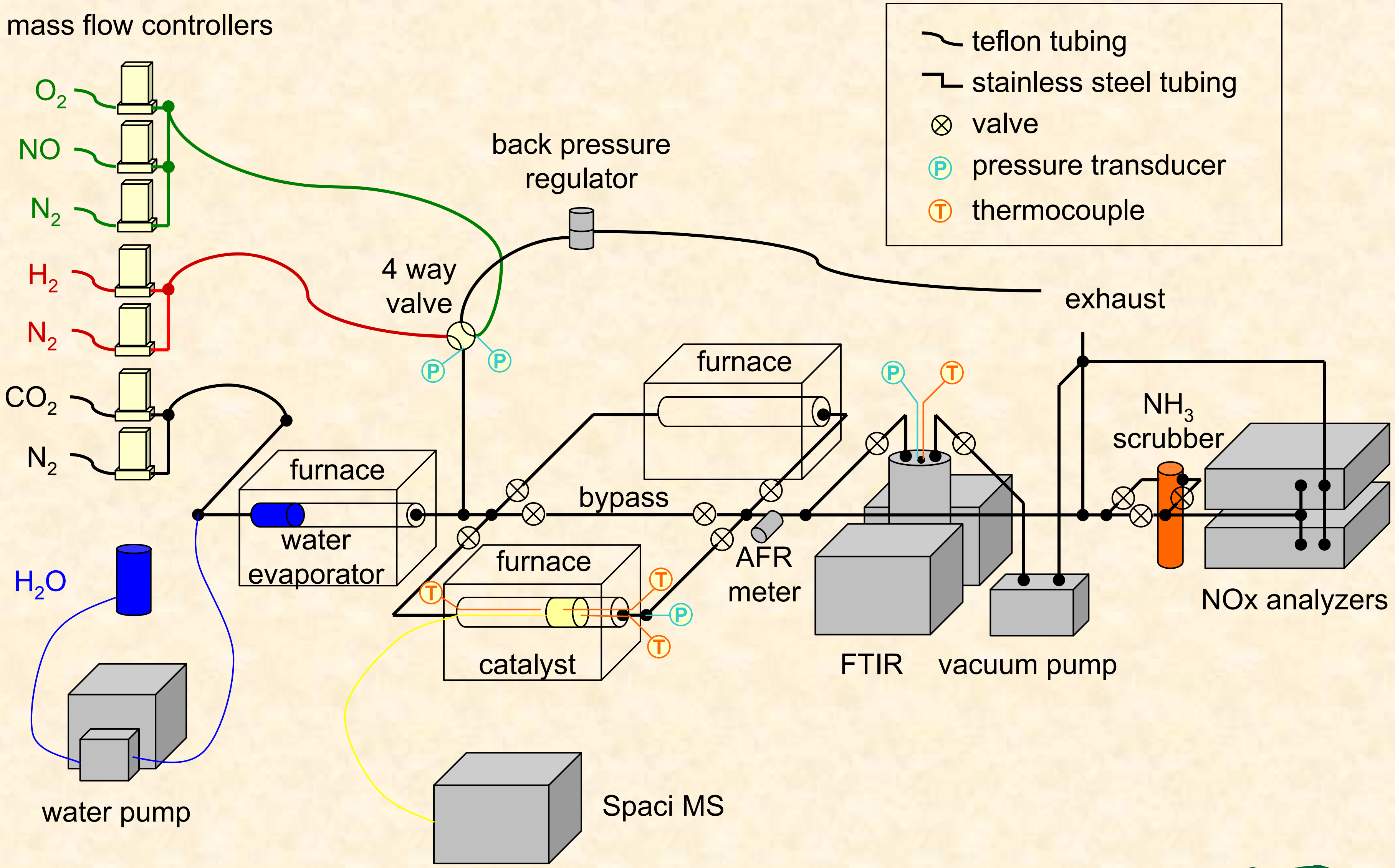
$$-\frac{\partial C_A^*}{\partial z^*} - \tau\, k_{m,A}\, a_c\,(C_A^* - C_{As}^*) = \frac{\partial C_A^*}{\partial t^*} \qquad C_A^* = 1 \text{ at } z^*=0 \qquad \frac{\partial C_A^*}{\partial z^*} = 0 \text{ at } z^*=1$$

  - **Mass transfer coefficient is constant in a fully-developed laminar flow**

- **Significant difference in LNT performance data are often obtained under the same conditions by different labs (cf. John Hoard, 8th CLEERS Workshop)**
  - **Different experimental catalyst sizes are used at different labs**
  - **No standard reactor size**
  - **Suspected as the culprit of LNT performance disparity**

- **Length effect issue needs to be addressed**
  - **To compare data from different sources**
  - **To develop commercial design criteria**
  - **To develop models**

Approach: evaluation of core samples using well-controlled bench reactor



Two LNTs of different formulation and physical properties were evaluated

- **$SCONO_x$**
  - EmeraChem LNT used in the power generating industry
  - 200 cpsi cordierite brick washcoated with Pt/K/γ-Al_2O_3
- **Umicore**
  - Umicore GDI LNT used by CLEERS LNT Focus Group
  - 625 cpsi cordierite brick washcoated with Pt, Pd, Rh, Ba, CeO_2, ZrO_2, γ-Al_2O_3 and etc.

Samples of 7/8'' OD and 1'', 2'' and 3'' long were evaluated at SV=30,000 h^{-1} using long and short cycles

Long-cycle Experiments:

- **SCONO$_x$**

Mode	Time	Gas Composition
Lean	15 min	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	10 min	**0.2% or 0.5% H_2**, 5% H_2O, 5% CO_2, balance N_2
Temperatures: 200, 300 and 400°C		

- **Umicore**

Mode	Time	Gas Composition
Lean	15 min	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	10 min	**0.4% H_2**, 5% H_2O, 5% CO_2, balance N_2
Temperatures: 230, 325 and 500°C		

- **Gas Analysis:**
  - NO/NO$_x$ (chemiluminescence detectors)
  - NO_2/N_2O/NH_3/CO/CO_2/H_2O (FTIR)

Samples of 7/8'' OD and 1'', 2'' and 3'' long were evaluated at SV=30,000 h^{-1} using long and short cycles

Short-cycle Experiments:

- **$SCONO_x$**

Mode	Time	Gas Composition
Lean	56 s	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	4 s	**1% or 2% H_2**, 5% H_2O, 5% CO_2, balance N_2
Temperatures: 200, 300 and 400°C		

- **Umicore**

Mode	Time	Gas Composition
Lean	60 s	300 ppm NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	5 s	**1.4% or 3.4% H_2**, 5% H_2O, 5% CO_2, balance N_2
Temperatures: 230, 325 and 500°C		

- **Gas Analysis:**
  - NO/NOx (chemiluminescence detectors)
  - $NO_2/N_2O/NH_3/CO/CO_2/H_2O$ (FTIR)
  - H_2 (SpaciMS)

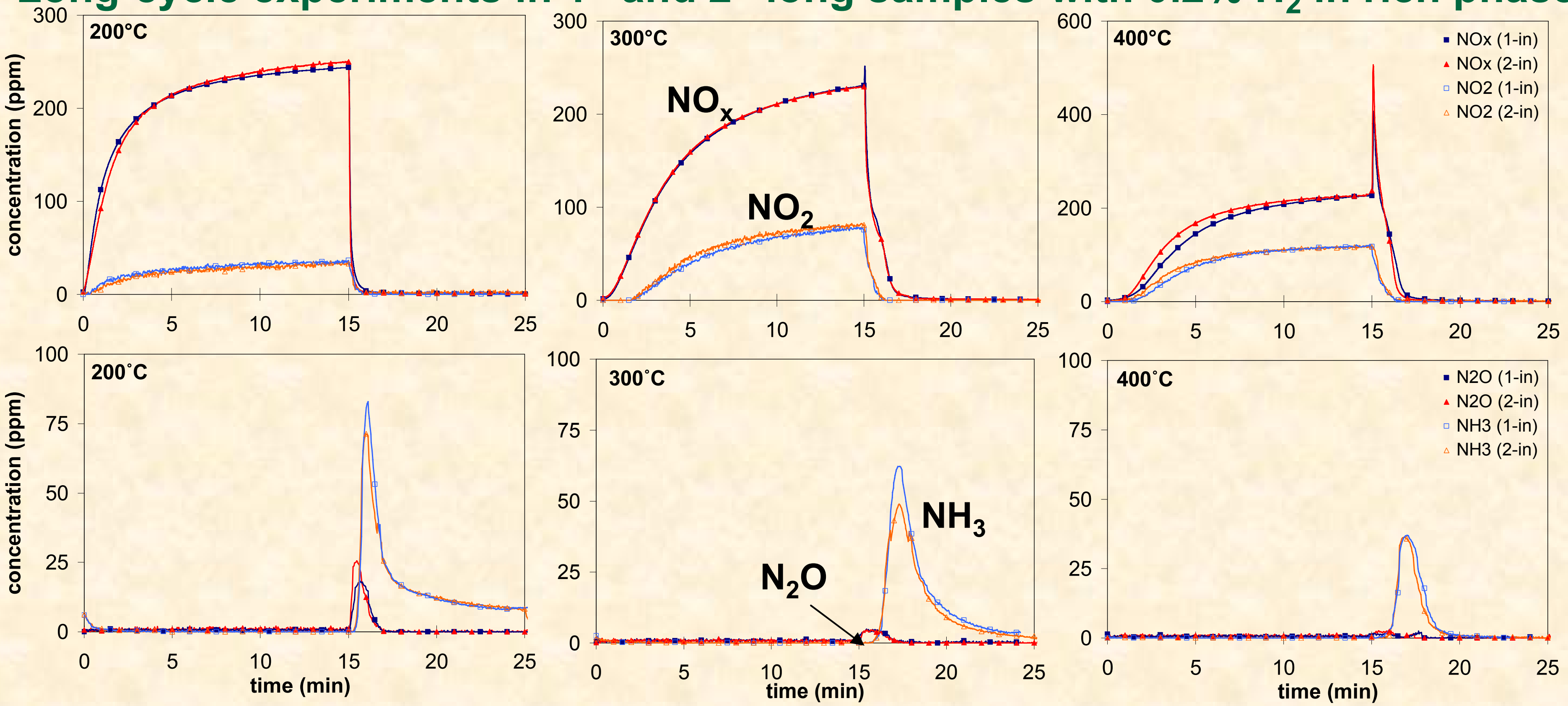
$SCONO_x$

Three “identical” 7/8” OD x 1’’ long cores were selected as building blocks

- **To evaluate and compare performance of 1’’, 2’’ and 3’’ long samples**
- **Experimental artifacts needed to be addressed for meaningful comparison**
  - **Sample-to-sample variation**
  - **Effect of channel misalignment and “discontinuity” on catalyst performance**
  - **Develop “degreening” protocol for obtaining reproducible data of catalyst activity**

Performance of $SCONO_x$ is not affected by sample's length in long-cycle experiments

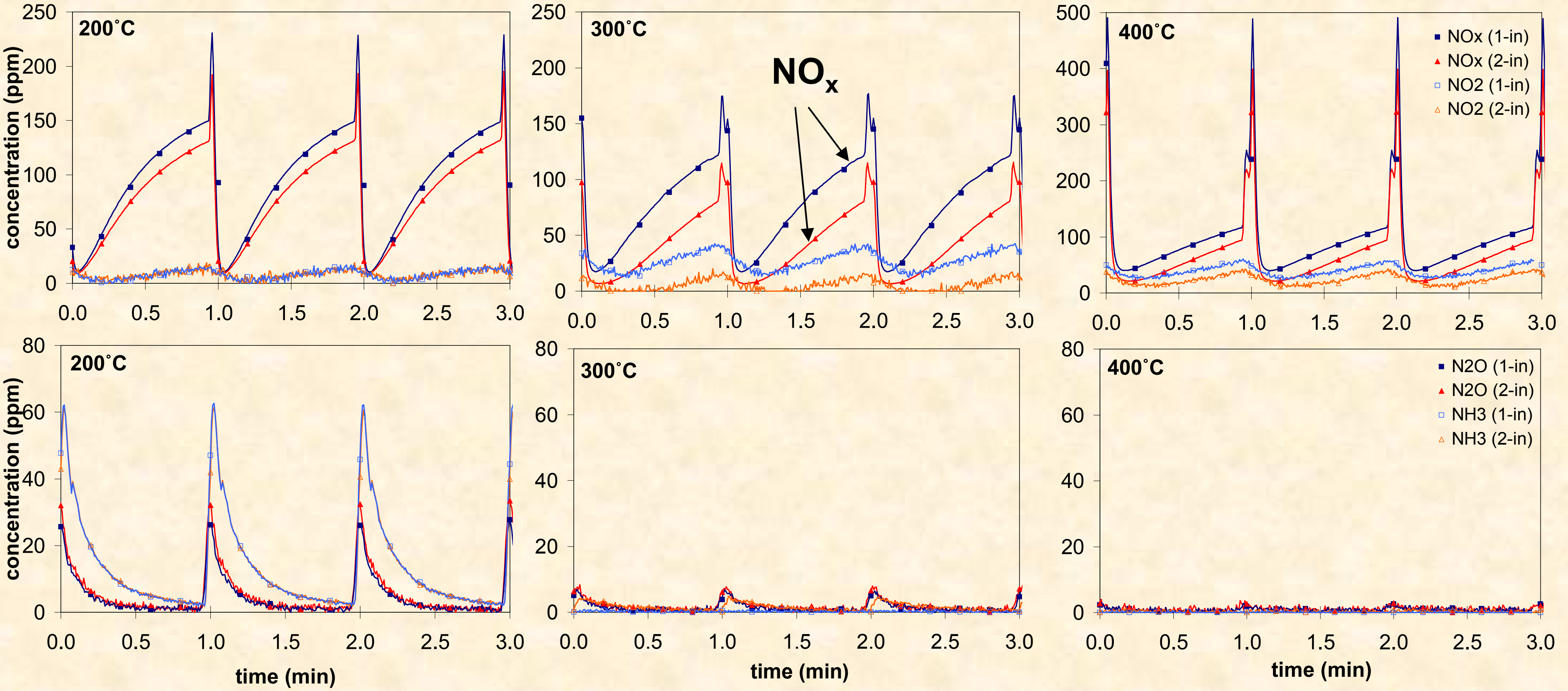
Long-cycle experiments in 1" and 2" long samples with 0.2% H_2 in rich phase



NOx conversion efficiencies

Length \ T	200°C	300°C	400°C
1''	21.5%	36.0%	33.2%
2''	24.5%	36.5%	33.1%

Performance of $SCONO_x$ is affected by sample's length in short-cycle experiments with partial regeneration (1% H_2)

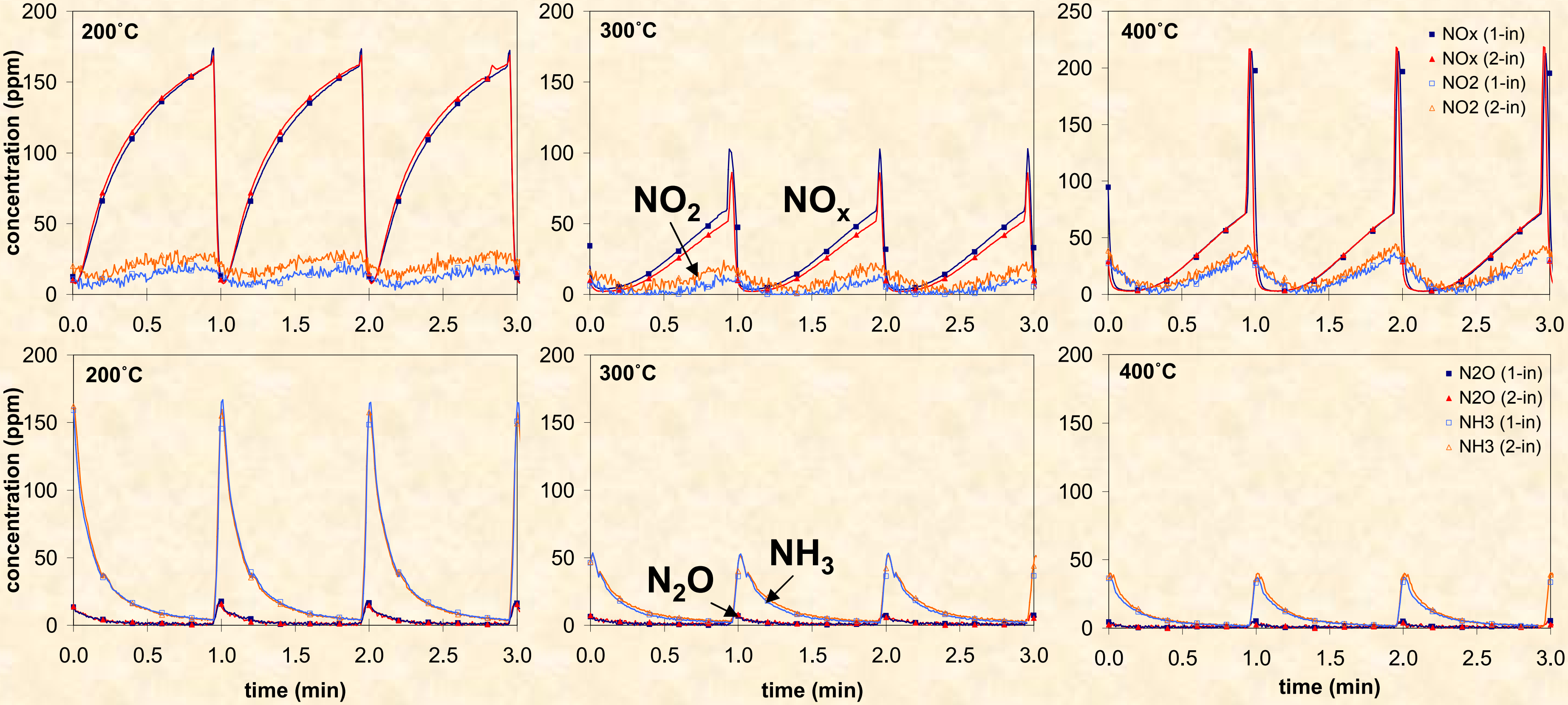


- Largest difference of 15% in NO_x conversion is at 300°C
- Longer the sample better the performance

NOx conversion efficiencies

Length \ T	200°C	300°C	400°C
1''	61.1%	68.7%	61.1%
2''	67.4%	83.6%	73.8%

Performance of $SCONO_x$ is not affected by sample's length in short-cycle experiments with full regeneration (2% H_2)

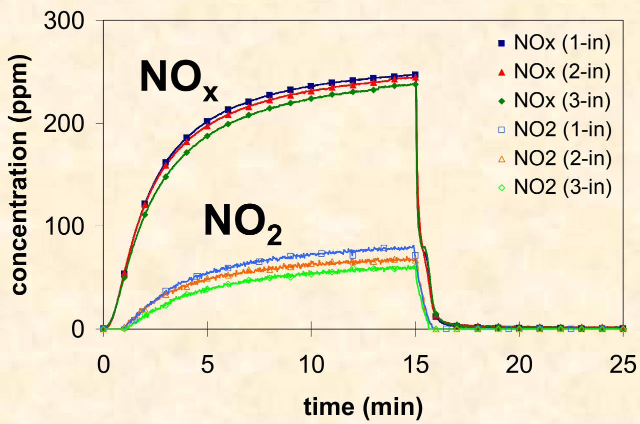


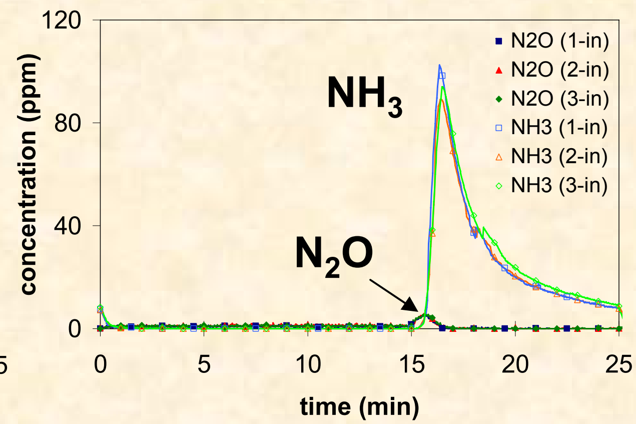
NOx conversion efficiencies

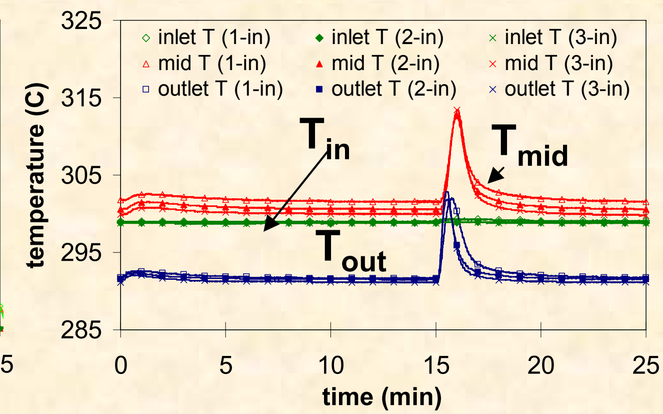
Length \ T	200°C	300°C	400°C
1''	58.5%	89.2%	86.0%
2''	57.5%	91.0%	86.6%

Trend was further confirmed with 1", 2" and 3" long samples: performance in long cycling is not affected by sample's length

Long-cycle experiments in 1", 2" and 3" long samples at 300°C with 0.2% H_2 in rich phase





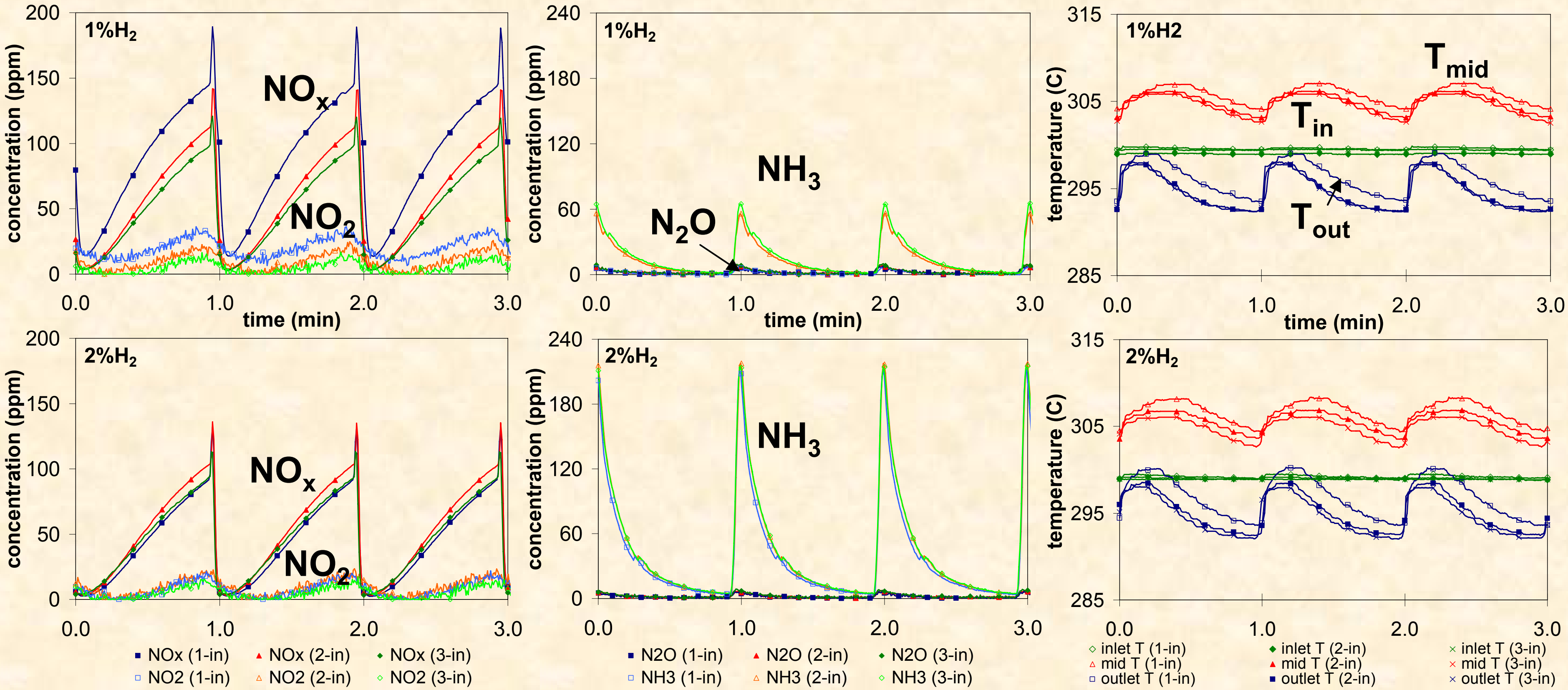


Observed difference is within experimental uncertainty

NOx conversion efficiencies

Length \ T	300°C
1"	25.4%
2"	26.4%
3"	29.1%

Trend was further confirmed with 1”, 2” and 3” long samples: performance in short cycling is affected by sample’s length with 1% but not with 2% H_2 at 300°C



With 1% H_2:

2” > 1” by 11%

3” ≈ 2”

NOx conversion efficiencies

Length \ C	1% H2	2% H2
1’’	65.7%	82.1%
2’’	77.1%	79.5%
3’’	80.5%	81.7%

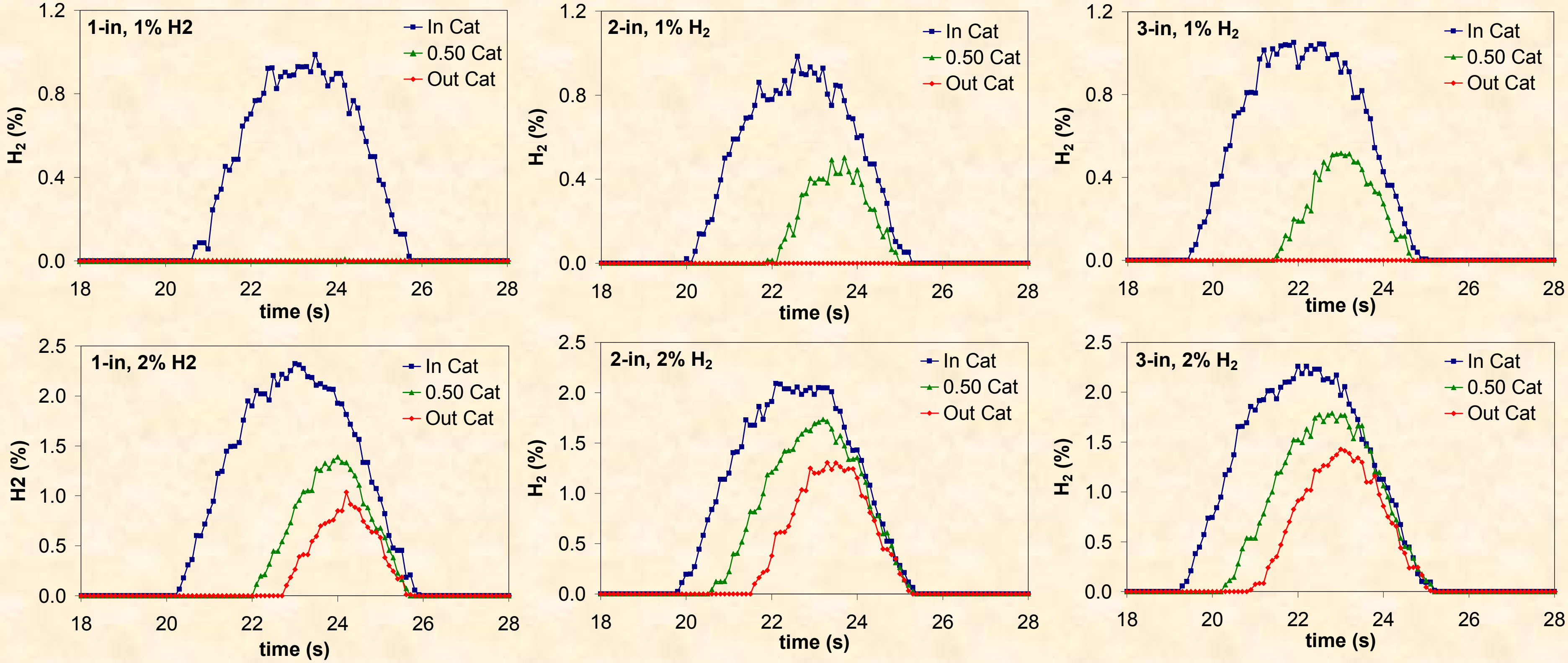
SCONO$_x$ Performance vs. Length: Summary

- **Performance in short-cycle experiments with full regeneration (2% H_2) and in long-cycle experiments is not affected by monolith length**
  - **3 in = 2 in = 1 in**
- **Performance in short-cycle experiments with partial regeneration (1% H_2) is affected by monolith length**
  - **2 in > 1 in & 3 in = 2 in**
- **Little difference in temperature profiles is observed: negligible thermal effect**

H_2 Consumption Trends in Short-Cycle Experiments at 300°C $SCONO_x$ (measured with SpaciMS)

More H_2 is consumed in 1'' than in 2'' and 3'' long samples

Short-cycle experiments with 1% and 2% H_2 at 300°C

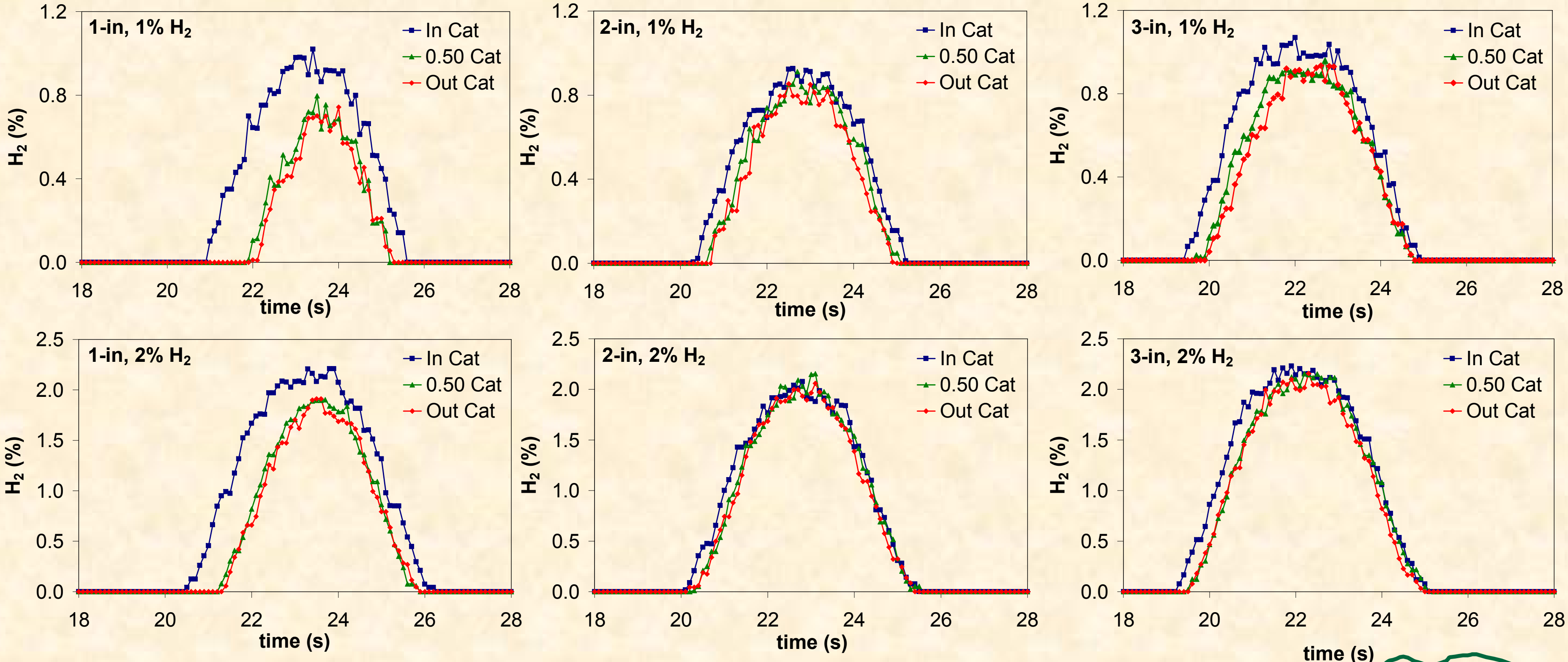


- **With 1% H_2, 100% is consumed in first half of 1'' vs. 75% in 2'' and 3''**
- **With 2% H_2, 80% is consumed in 1'' vs. 60% in 2'' and 3''**

Same trend in OSC experiments: more H_2 is consumed in 1'' than in 2'' and 3'' long samples

Short-cycle experiments without NO in the lean phase

Mode	Time	Gas Composition
Lean	56 s	0% NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Rich	4 s	**1% or 2% H_2**, 5% H_2O, 5% CO_2, balance N_2

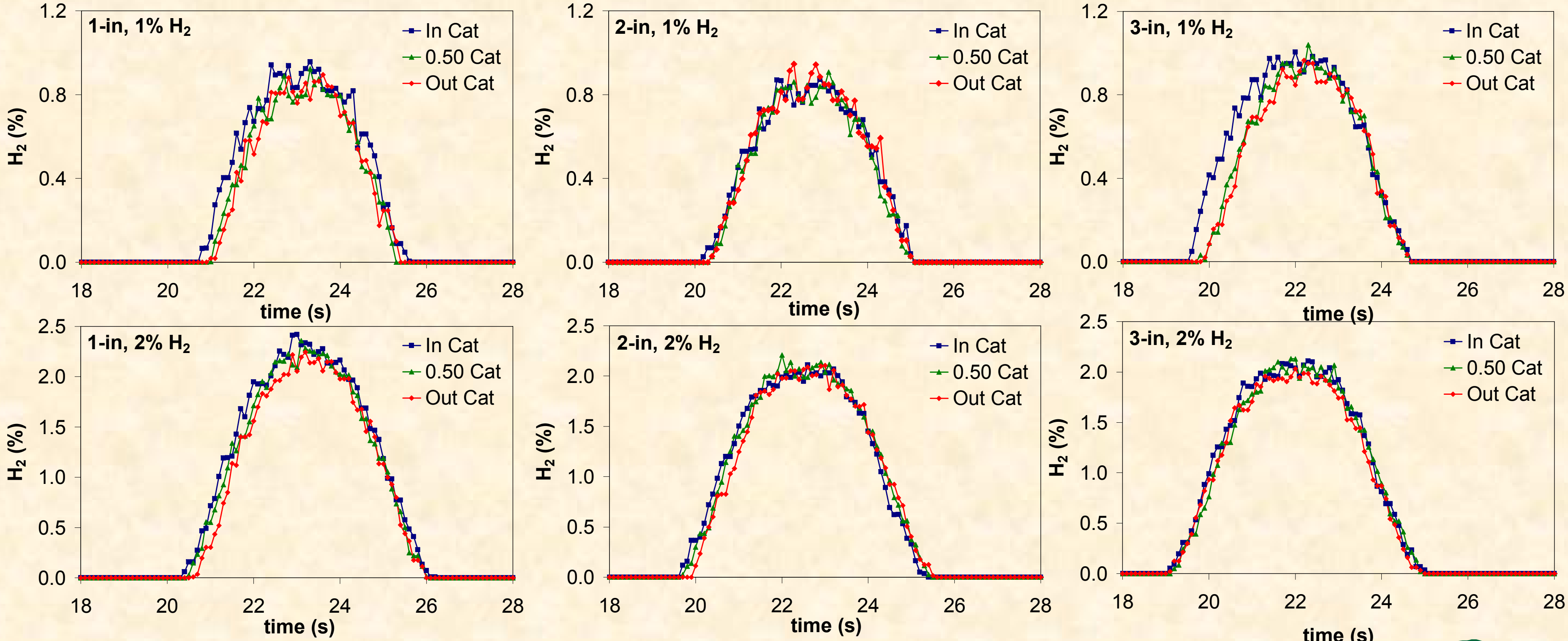


Lean/rich front back-mixing may contribute to significant reductant loss and in turn affects NO_x conversion efficiency

- **With 1% H_2, 50% of H_2 is consumed in the front half of 1'' long sample compared to 18% in 2'' and 3''**
- **Different H_2 consumption in OSC experiments indicates other mechanisms for H_2 consumption might occur in addition to reaction with surface O_2**
  - **Catalytic reaction between H_2 and O_2 at the interface between the lean and rich phases; the extent of which depends on the degree of mixing at the lean/rich interface**
  - **Higher back-mixing → higher H_2 consumption → less amount of H_2 available for reducing NO_x → lower NO_x conversion**
  - **Similar H_2 consumption in 2'' and 3'' indicates lesser degree of back-mixing with increasing flow rate (at a fixed SV and catalyst diameter, i.e., gas velocity or flow rate increases with increasing length)**

Difference in H_2 consumption trends between 1”, 2” and 3” disappears with neutral purge: evidence of different degree of back-mixing

Mode	Time	Gas Composition
Lean	56 s	0% NO, 10% O_2, 5% H_2O, 5% CO_2, balance N_2
Purge	10 s	5% H_2O, 5% CO_2, balance N_2
Rich	4 s	**1% or 2% H_2**, 5% H_2O, 5% CO_2, balance N_2



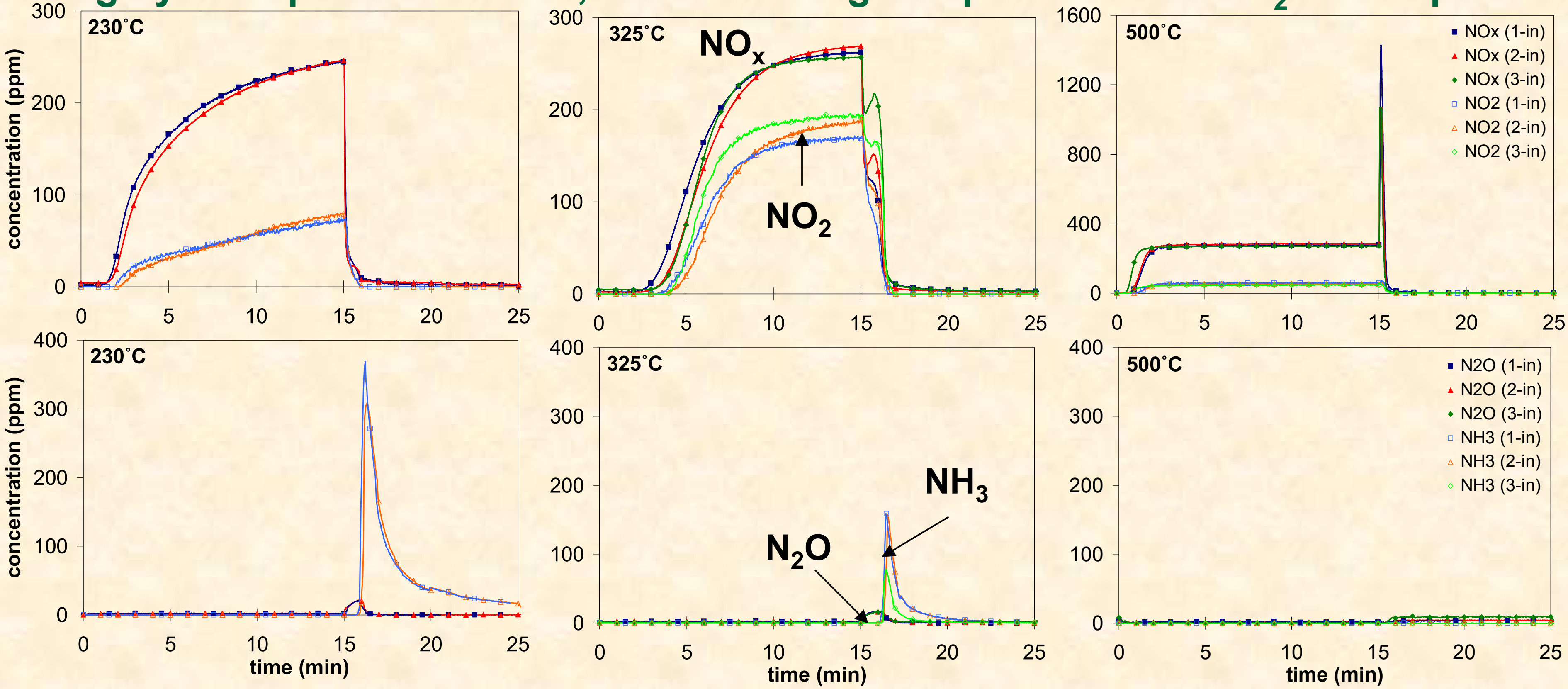
Back-mixing is responsible for differences in NO_x conversion between 1”, 2” and 3” long samples as a result of H_2 loss

- **In 1” long sample, ~35% of H_2 is consumed by the catalytic oxidation at the lean/rich interface, compared to ~ 10% in longer samples, resulting in a reduction of 15% in NO_x conversion in short-cycle experiments with 1% H_2**
- **If 2.5 moles of H_2 are required to reduce 1 mole of inlet NO, 25-30% less availability of H_2 would result in 10 to 14% decrease in NO_x conversion, which is consistent with experimental data**
  - $K_2CO_3 + 2NO + 1.5O_2 \rightarrow 2KNO_3 + CO_2$
  - $2KNO_3 + 5H_2 + CO_2 \rightarrow K_2CO_3 + N_2 + 5H_2O$

Umicore

Performance of Umicore is not affected by sample's length in long-cycle experiments

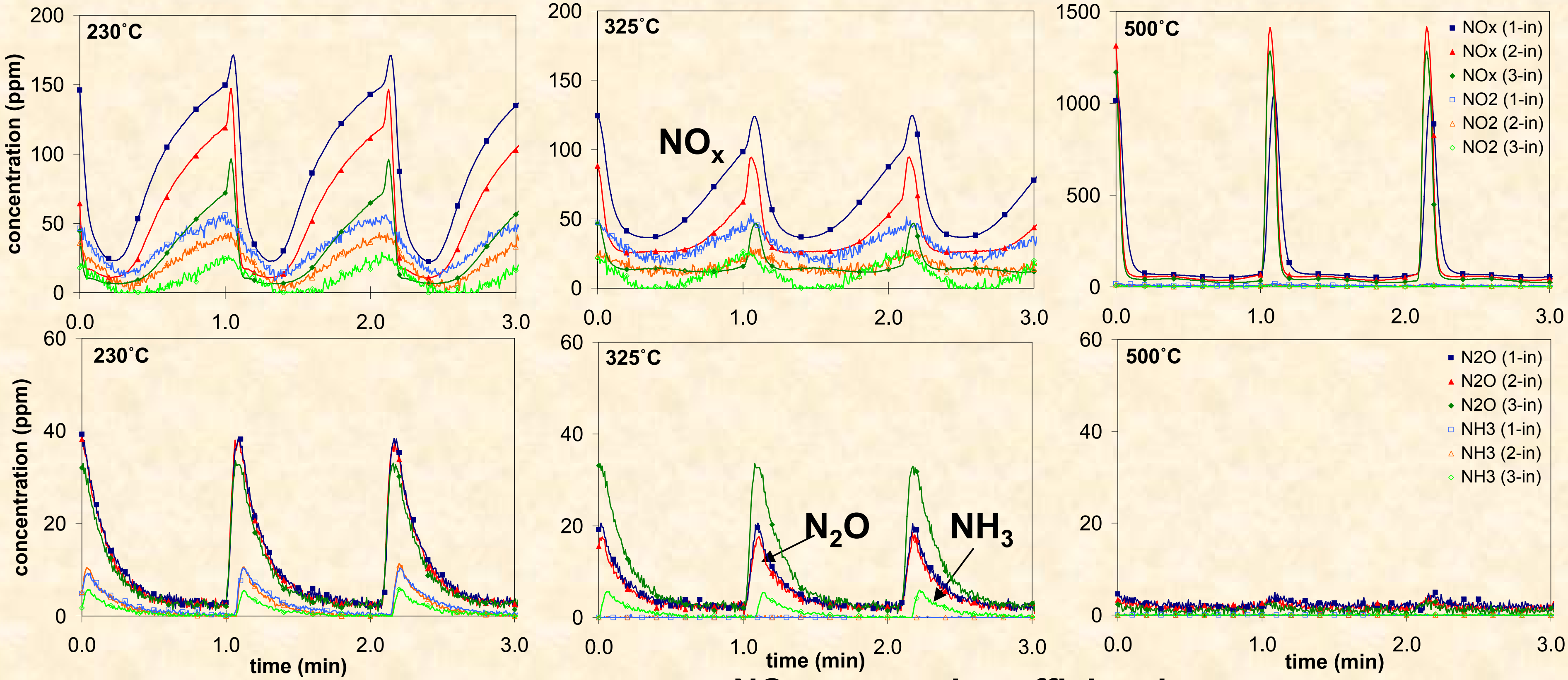
Long-cycle experiments in 1", 2" and 3" long samples with 0.4% H_2 in rich phase



NOx conversion efficiencies

Length \ T	230°C	325°C	500°C
1''	36.6%	36.5%	1.6%
2''	40.7%	40.8%	1.9%
3''	--	35.8%	1.8%

Performance of Umicore is affected by sample's length in short-cycle experiments with partial regeneration (1.4% H_2)

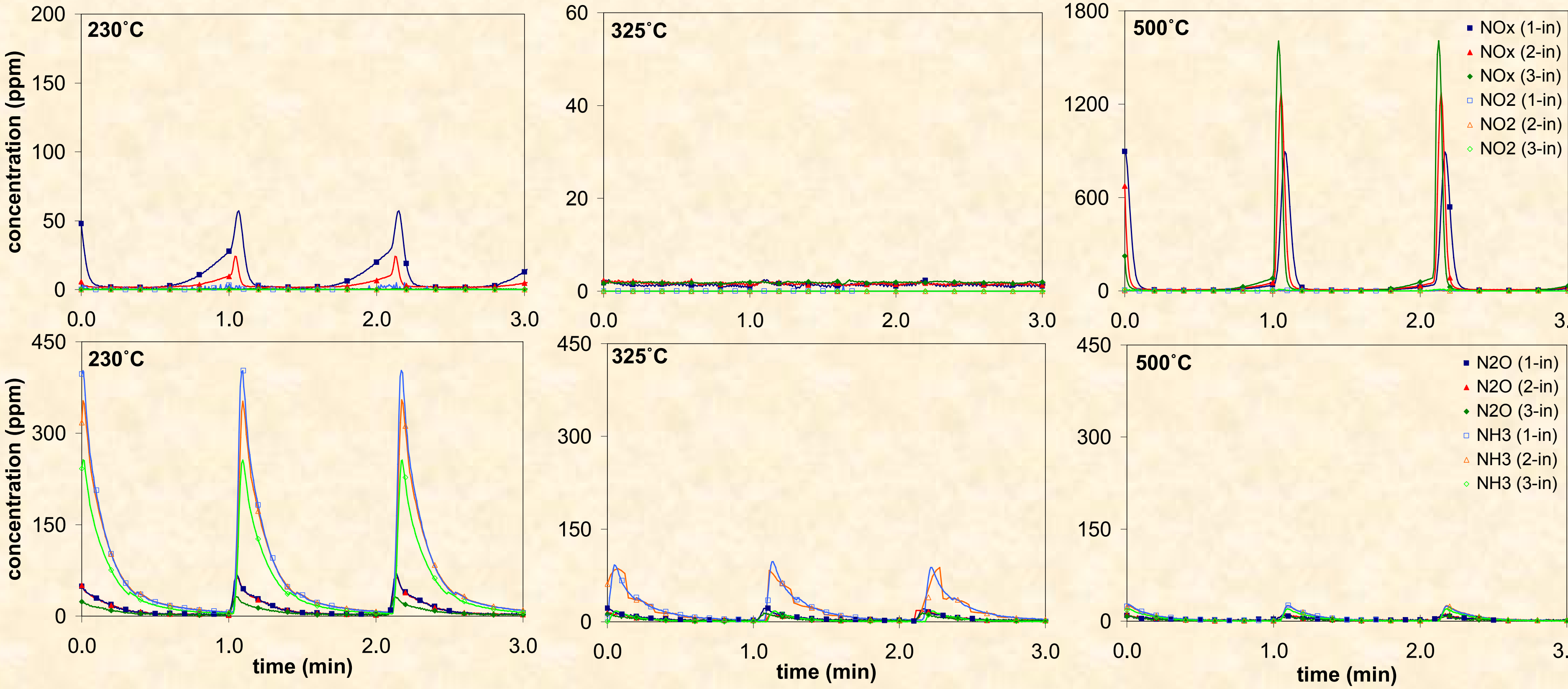


At 325°C
2" > 1" by 10%
3" > 2" by 8%

NOx conversion efficiencies

Length \ T	230°C	325°C	500°C
1''	64.3%	75.3%	43.0%
2''	76.9%	85.1%	45.1%
3''	86.4%	93.1%	49.1%

Performance of Umicore is not affected by sample's length in short-cycle experiments with full regeneration (3.4% H_2)



Length \ T	230°C	325°C	500°C
1''	96.0%	99.5%	72.9%
2''	98.5%	99.4%	71.3%
3''	99.8%	99.2%	62.9%

Umicore Performance vs. Length: Summary

- **Performance in short-cycle experiments with full regeneration (3.4% H_2) and in long-cycle experiments is not affected by monolith length as in the case of $SCONO_x$**

  3 in = 2 in = 1 in

- **Performance in short-cycle experiments with partial regeneration (1.4% H_2) is affected by monolith length**

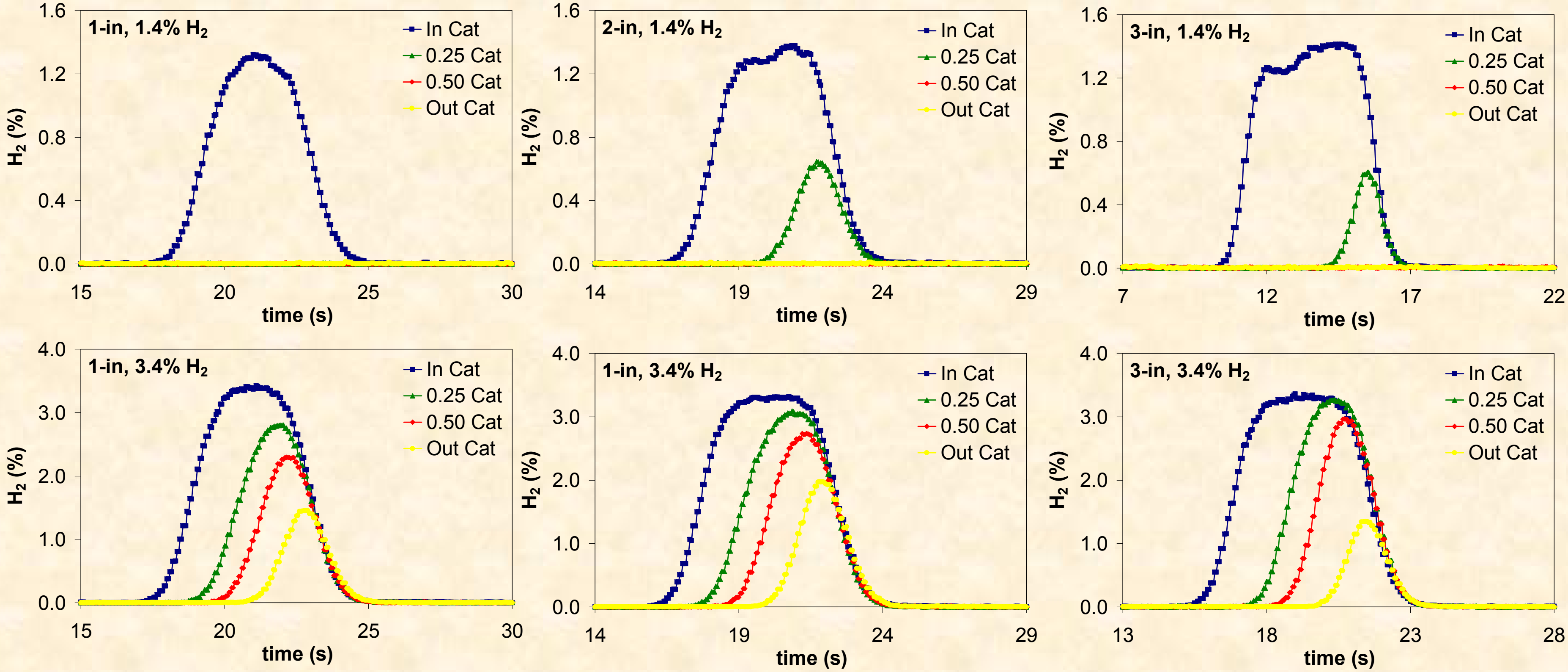
  3 in > 2 in > 1 in

- **Little difference in temperature profiles is observed: negligible thermal effect**

H_2 Consumption Trends in Short-Cycle Experiments Umicore (measured with SpaciMS)

More H_2 is consumed in shorter sample

Short-cycle experiments at 325°C with 1.4% & 3.4% H_2 in rich phase



- **With 1.4% H_2, 100% is consumed in first quarter of 1'' vs. 77% in 2'' and 86% in 3''**

Back-mixing is responsible for differences in NO_x conversion between 1", 2" and 3" long samples as a result of H_2 loss

- **Different slopes in catalyst's inlet H_2 profiles suggest different degree of lean/rich front back-mixing which may contribute to significant reductant loss**
- **Average inlet H_2 is different between samples**
  - **1.4%: 1.02%, 1.20% and 1.25% in 1'', 2'' and 3'' long samples**
  - **3.4%: 2.89%, 3.22% and 3.23% in 1'', 2'' and 3'' long samples**
  - **Indicating H_2 consumption prior to the catalyst**
- **Back-mixing depends on catalyst's length or linear velocity**

Theoretical explanation of back-mixing

- **Back-mixing is attributed to axial diffusion of chemical species in gas mixture (transport = bulk flow + diffusion)**
- **Dimensionless form of fluid phase mole balance equation for each species for dispersion with reaction**

$$\frac{D_a}{U_z L}\frac{\partial^2 C_A^*}{\partial z^{*2}} - \frac{\partial C_A^*}{\partial z^*} - \frac{L}{U_z} k_{m,A} a_c (C_A^* - C_{As}^*) = \frac{\partial C_A^*}{\partial t^*}$$

$$\left(-\frac{D_a}{U_z L}\frac{\partial C_A^*}{\partial z^*} + \frac{\partial C_A^*}{\partial z^*}\right)_{0^-} = \left(-\frac{D_a}{U_z L}\frac{\partial C_A^*}{\partial z^*} + \frac{\partial C_A^*}{\partial z^*}\right)_{0^+} \quad \text{at } z^*=0$$

$$\frac{\partial C_A^*}{\partial z^*} = 0 \quad \text{at } z^*=1$$

  – **The dimensionless group D_a/U_zL, referred to as the reactor dispersion number, measures the extent of axial dispersion**

Conclusions

- **Similar results obtained from two LNT's with different formulations**
- **No significant length effect observed on $SCONO_x$ and Umicore in long and short-cycle experiments with full regeneration**
- **Significant monolith "length effect" on LNT performance in short-cycle experiments with partial regeneration**
  - **The longer the sample, the better the performance**
- **Observed "length effect" comes from different degrees of lean/rich front axial back-mixing at different linear velocities**
  - **The lower the linear velocity (i.e. shorter LNT), the higher the back-mixing**
- **Higher back-mixing results in a higher reductant loss via oxidation by O_2**
  - **Implication in fuel economy and modeling**
  - **Need to incorporate back-mixing effect into model**
- **Back-mixing could explain in part lab-to-lab discrepancy**
  - **Different degrees of back-mixing depending on bench reactor switching valve/gas delivery system specifications**
  - **In addition to other factors: degreening/pretreatment, sample-to-sample variation**

Acknowledgements

- DOE Office of FreedomCAR & Vehicle Technologies
- EmeraChem/Umicore
- Stuart Daw, Ke Nguyen, Jae-Soon Choi, Josh Pihl, Todd Toops
- Fuels, Engines, and Emissions Research (FEERC) group of Oak Ridge National Laboratory