Spatially-resolved *in situ* measurements of transient species breakthrough during low-temperature regeneration of a $Pt/K/Al_2O_3$ lean NO_x trap

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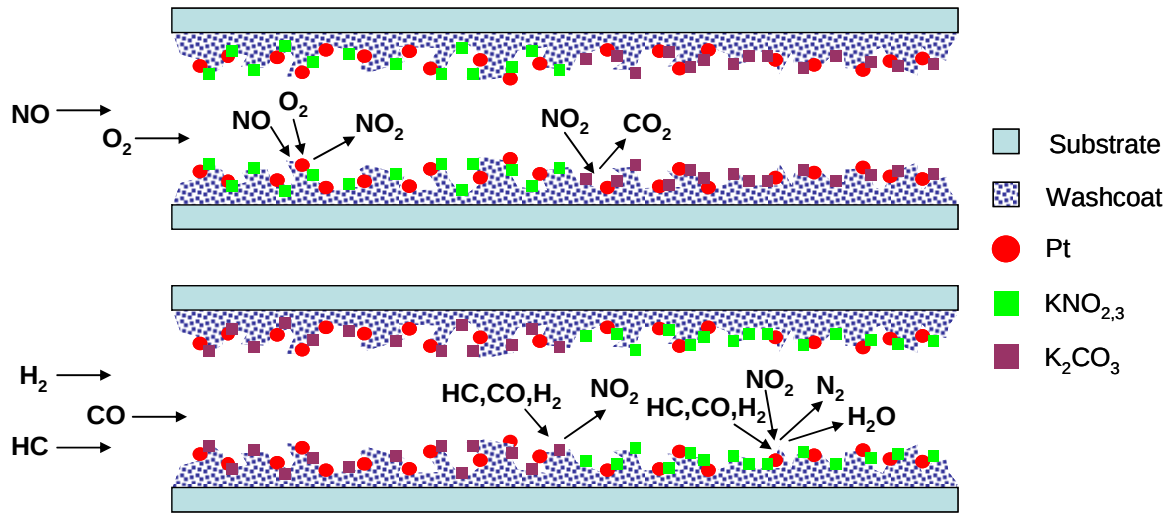
Lean NO_x Trap (LNT) Catalyst

- Proven potential for NO_x removal in fuel-lean diesel environments
  - **a.k.a. : NO_x Storage-Reduction (NSR) catalyst, NO_x Adsorber Catalyst (NAC)**
  - **3-way catalyst + NO_x storage material (alkali, alkaline-earth)**
  - **Cyclic operation: normal lean (storage)/short rich (release/reduction)**

Storage (lean)
30-120 s

Regeneration (rich)
1-10 s



- NSR catalyst system is inherently transient and integral
  - **Evaluation/understanding challenging**
  - **Need analytical tools with temporal and spatial resolution**

Improved understanding of LNT regeneration necessary

- Having clear understanding of chemistry/kinetics is essential for fuel-efficient LNT system implementation (model, LNT design, control)
- For example, relative efficacy and interaction of different reductants
- CO and H_2 are major reductants from certain "in-cylinder" regeneration
  - **CO and H_2 similarly effective except low T**
  - **Low T performance: issue relevant to cold start, small engines**
  - **What's the origin of similarity/difference of H_2 and CO?**

Objectives of this study

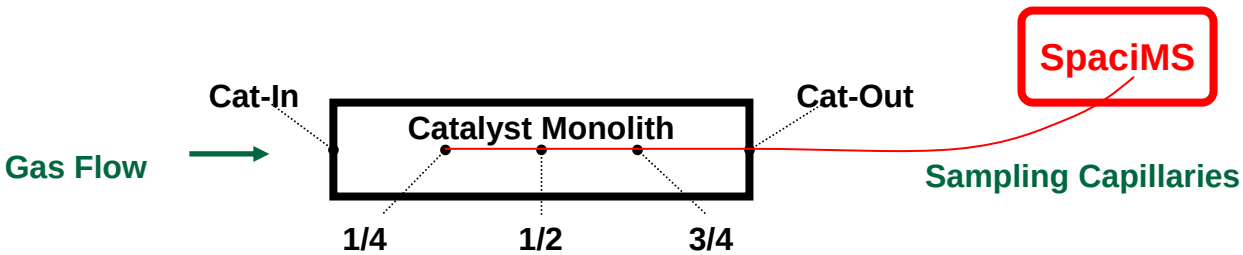
- Compare efficiency of H_2 and CO reductants
- Determine origin of poor CO performance at low T
- Relevance of water-gas shift reaction (CO as H_2 source?)

Approach

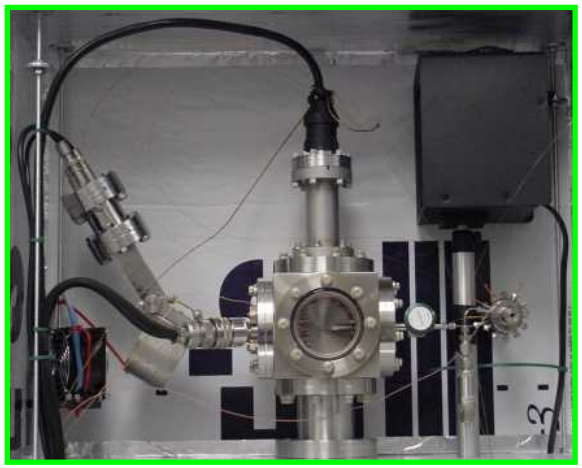
- **Model catalyst in "monolith form"**
  - **Simplified but representative ($Pt/K/Al_2O_3$)**

- **Well-defined bench reactor investigation**
  - **Controlled reaction conditions**
  - **Realistic conditions**

- **Intra-catalyst performance evaluation**
  - **Intra-channel speciation via SpaciMS**
  - **Spatial and temporal resolution**

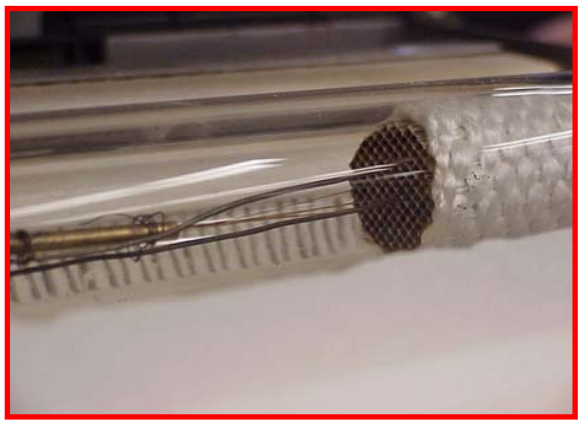


Intra-channel speciation via SpaciMS



SpaciMS: Spatially-resolved capillary inlet Mass Spectrometry

Magnetic sector mass spectrometer
capable of quantifying various species including H_2
higher time resolution than conventional analyzers



Multiple capillary inlets allow *in-situ* spatially resolved measurements
minimally invasive (sample rate ~10 μL/min, probe diameter 200 μm)

Reaction Conditions

- Space velocity: 25000 h^{-1}
- Temperature: 200, 300 °C

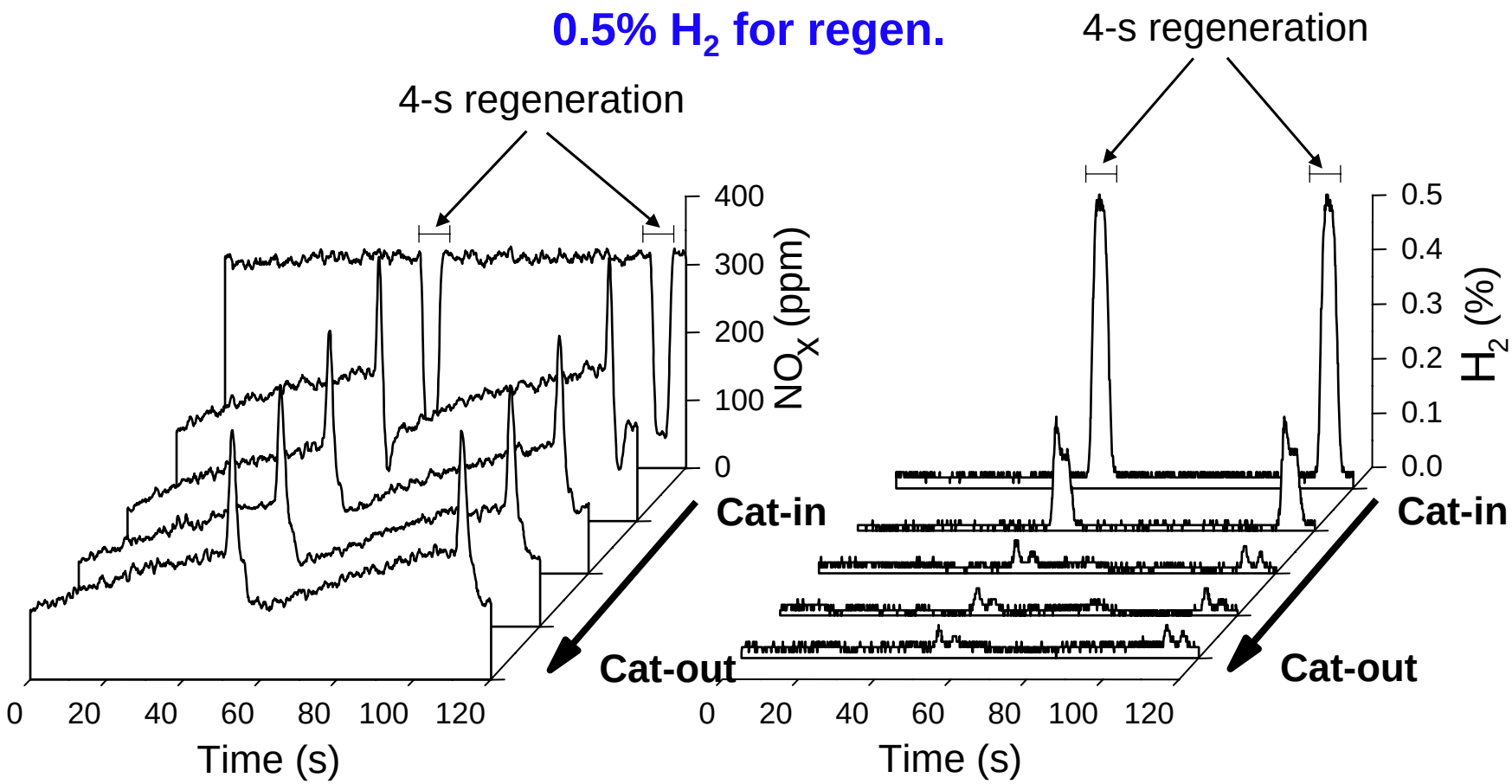
- Simulated exhausts:

Environment	Time	Gas Composition			
Lean (storage)	56 s	NO 300ppm	O_2 12%	H_2O 5%	N_2 balance
Rich (regeneration)	4 s	Reductant* 0.5%	O_2 0%	H_2O 5%	N_2 balance

* Pure H_2, Pure CO or equimolar H_2 + CO.

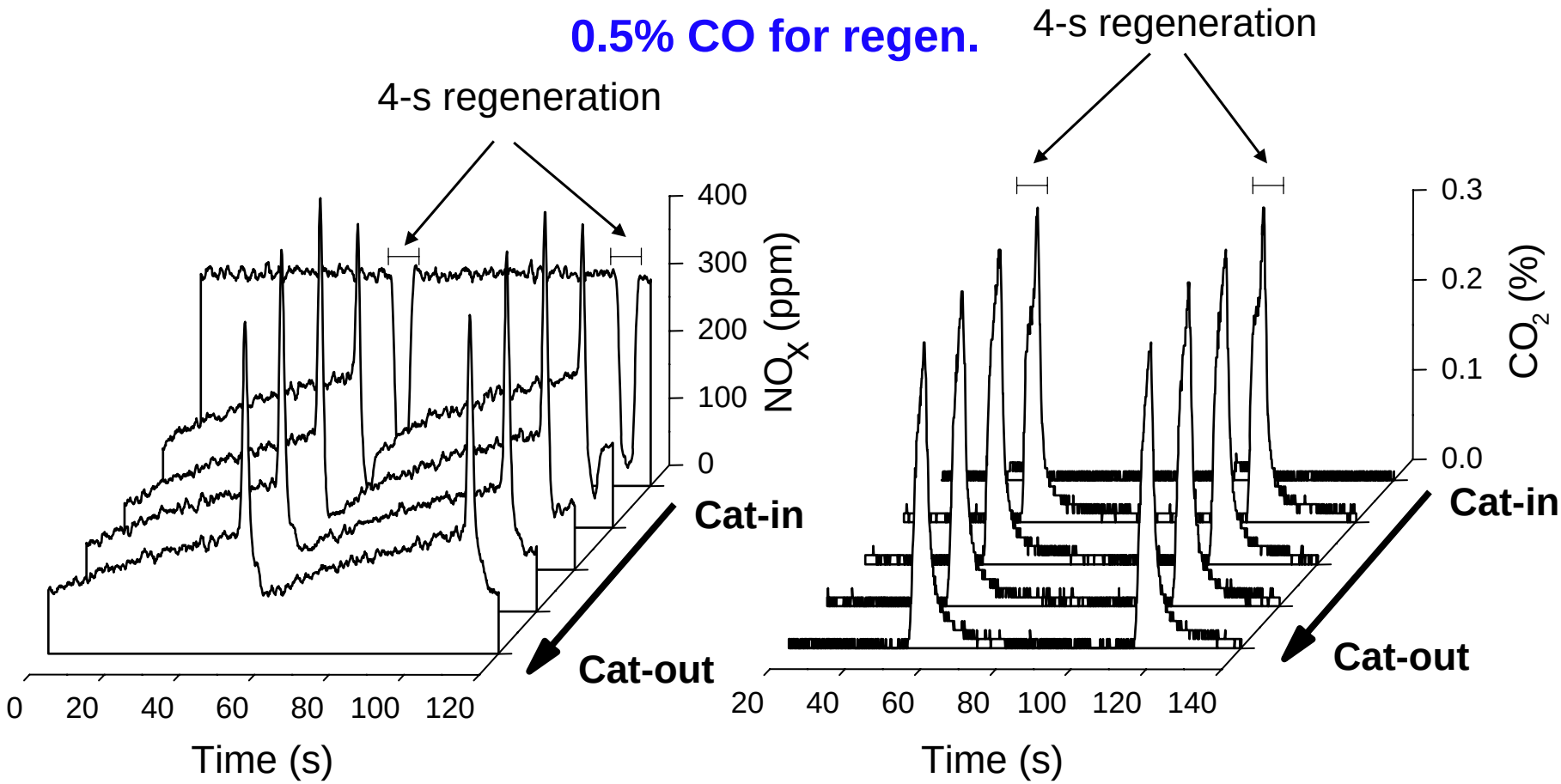
Regen. Performance Comparison at 300 °C

Intra-channel NO_x and H_2 Breakthrough Profiles



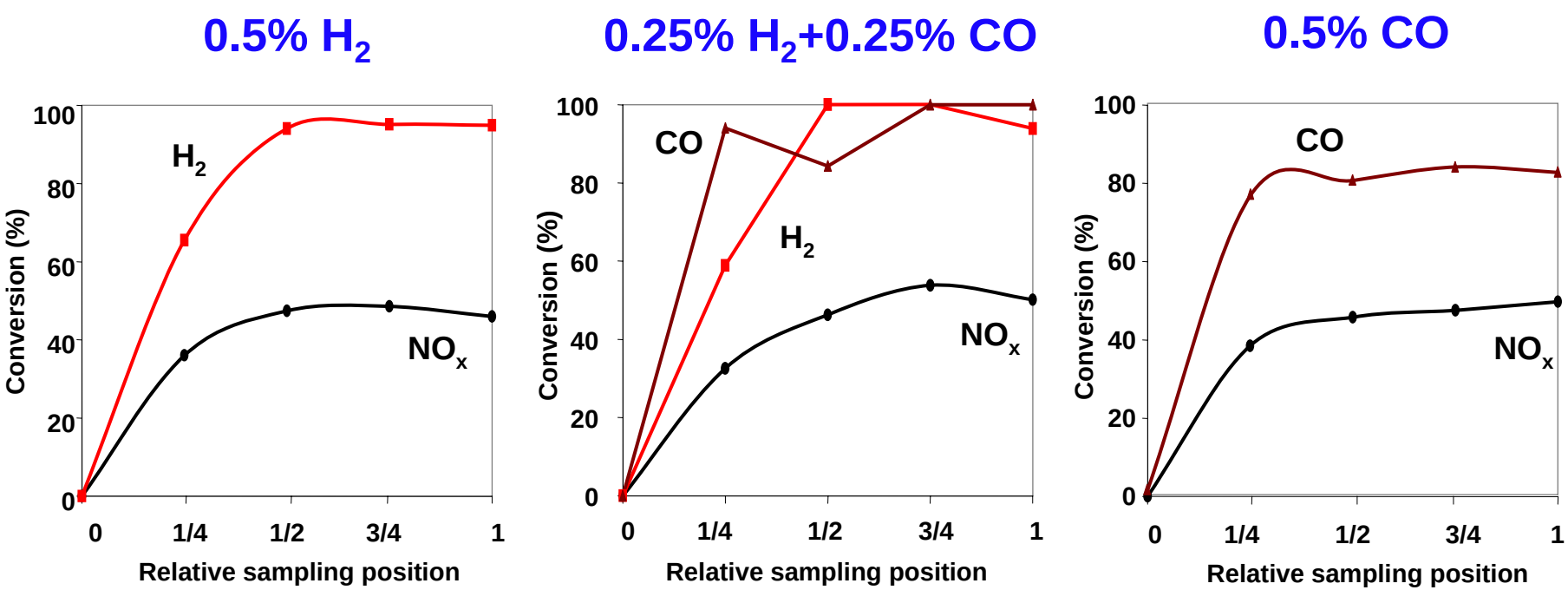
- **First half of LNT being used (partial regeneration under employed conditions)**
- **Complete H_2 consumption before ½ axial location**
- **No change in NO_x profiles after H_2 depletion (importance of reductant)**
- **Sharp NO_x breakthrough at regen. inception**

Intra-channel NO_x and CO_2 Breakthrough Profiles



- **Similar overall trend except higher NO_x peak at regen. inception**
- **CO_2 profiles give information about CO chemistry**

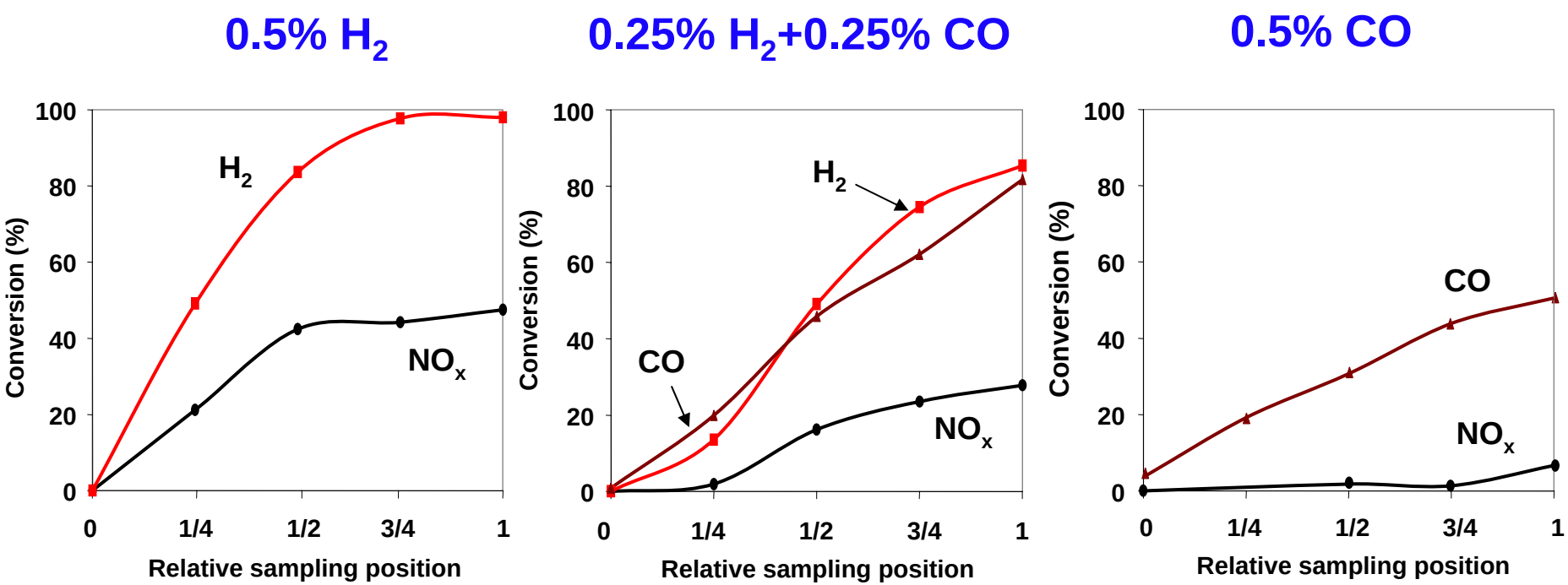
Three reductants show similar NO_x conversion efficiency at 300 °C



- Cycle-averaged conversion vs. LNT axial location
- All three reductants very effective
- Reductant consumed/NO removed=2.4
- CO consumption seems slightly faster than H_2 (not conclusive)

Regen. Performance Comparison at 200 °C

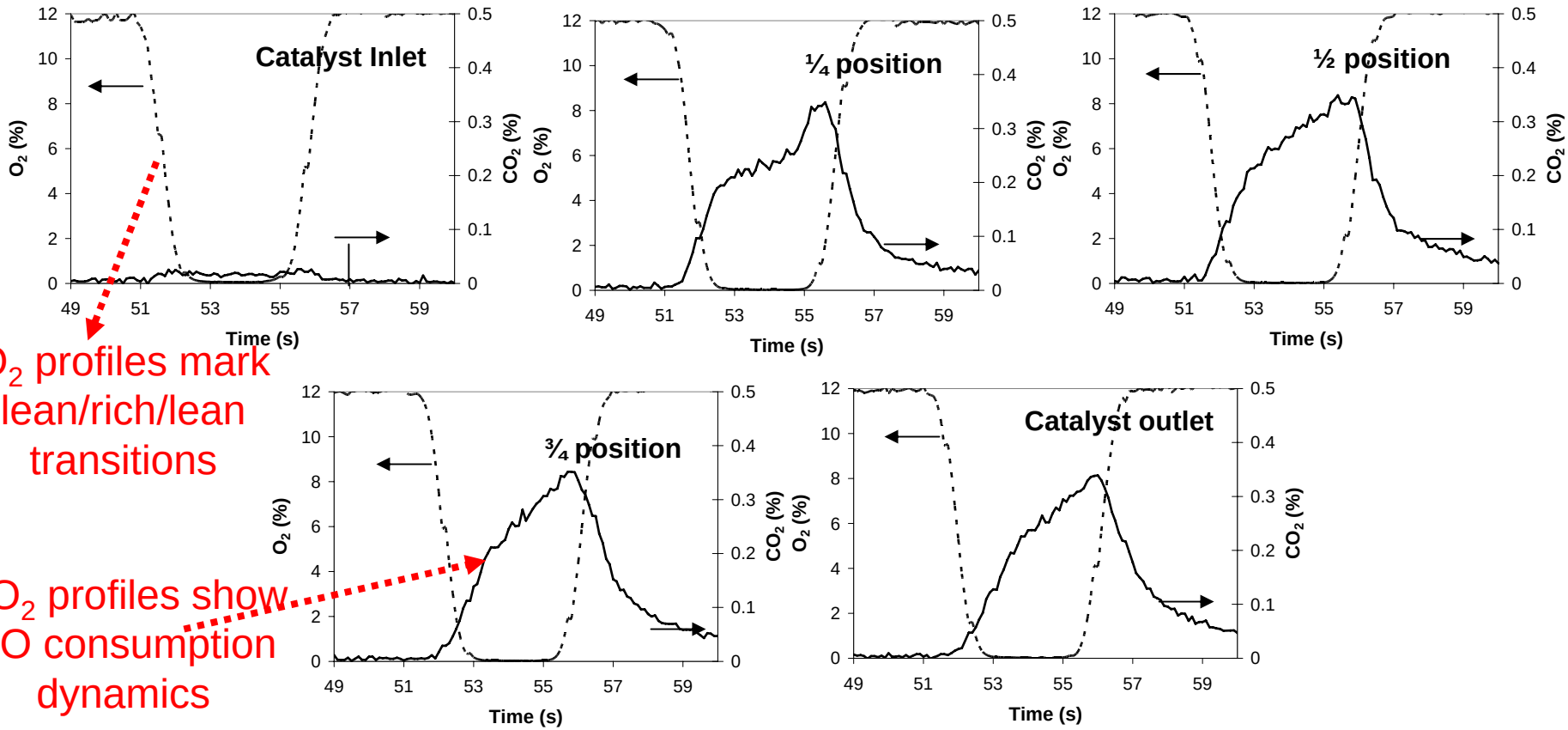
Increasing CO content decreases NO_x conversion at 200 °C



- For all three reductants, lower performance than at 300 °C
- Pure H_2 still performs well
- Inefficiency of pure CO is dramatic
- Intermediate efficiency of H_2 and CO mixture

Origin of Low CO Regen Efficiency at 200 °C Compared to 300 °C

Effective CO consumption over the entire regen. times at 300 °C

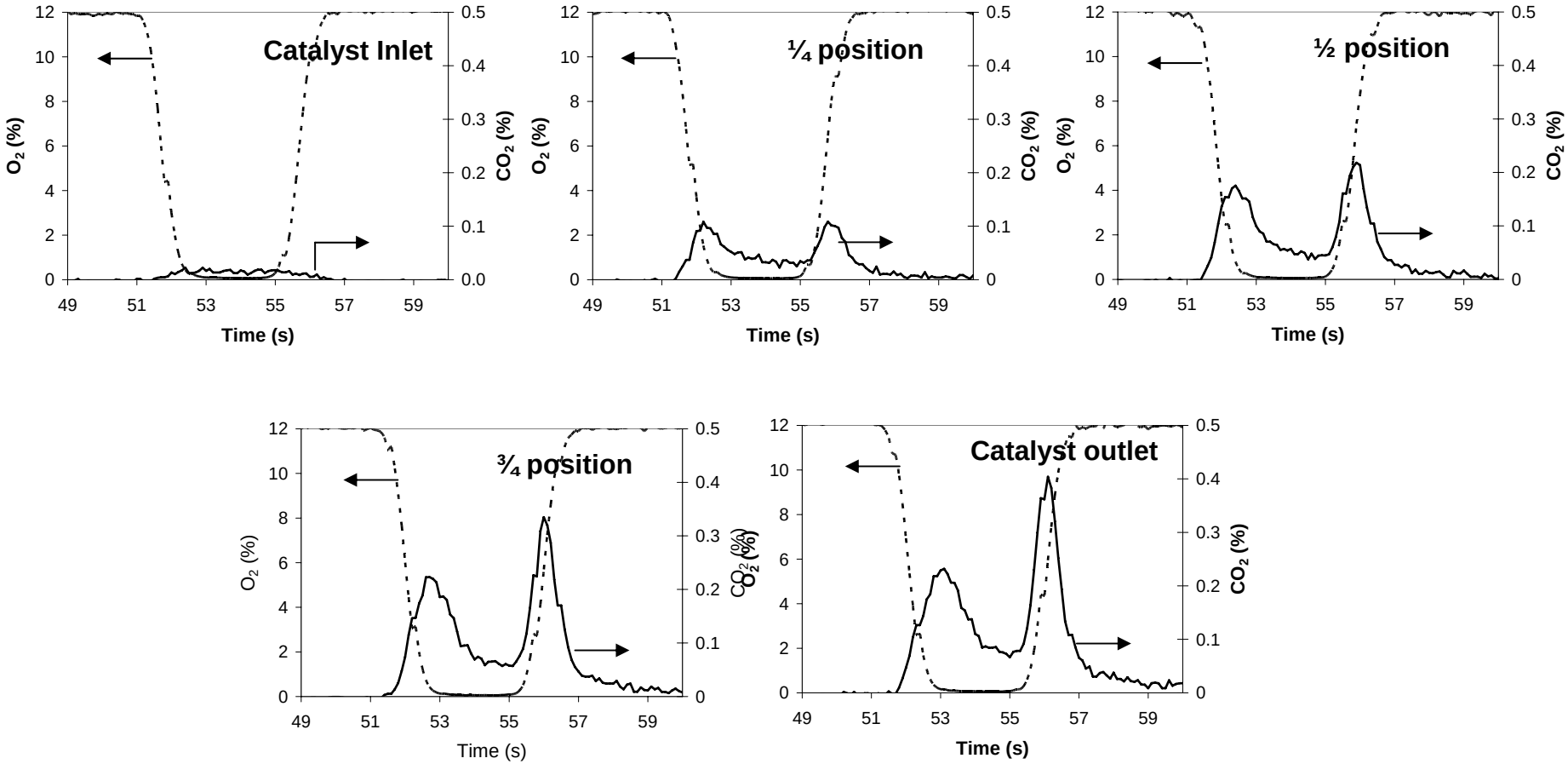


O_2 profiles mark lean/rich/lean transitions

CO_2 profiles show CO consumption dynamics

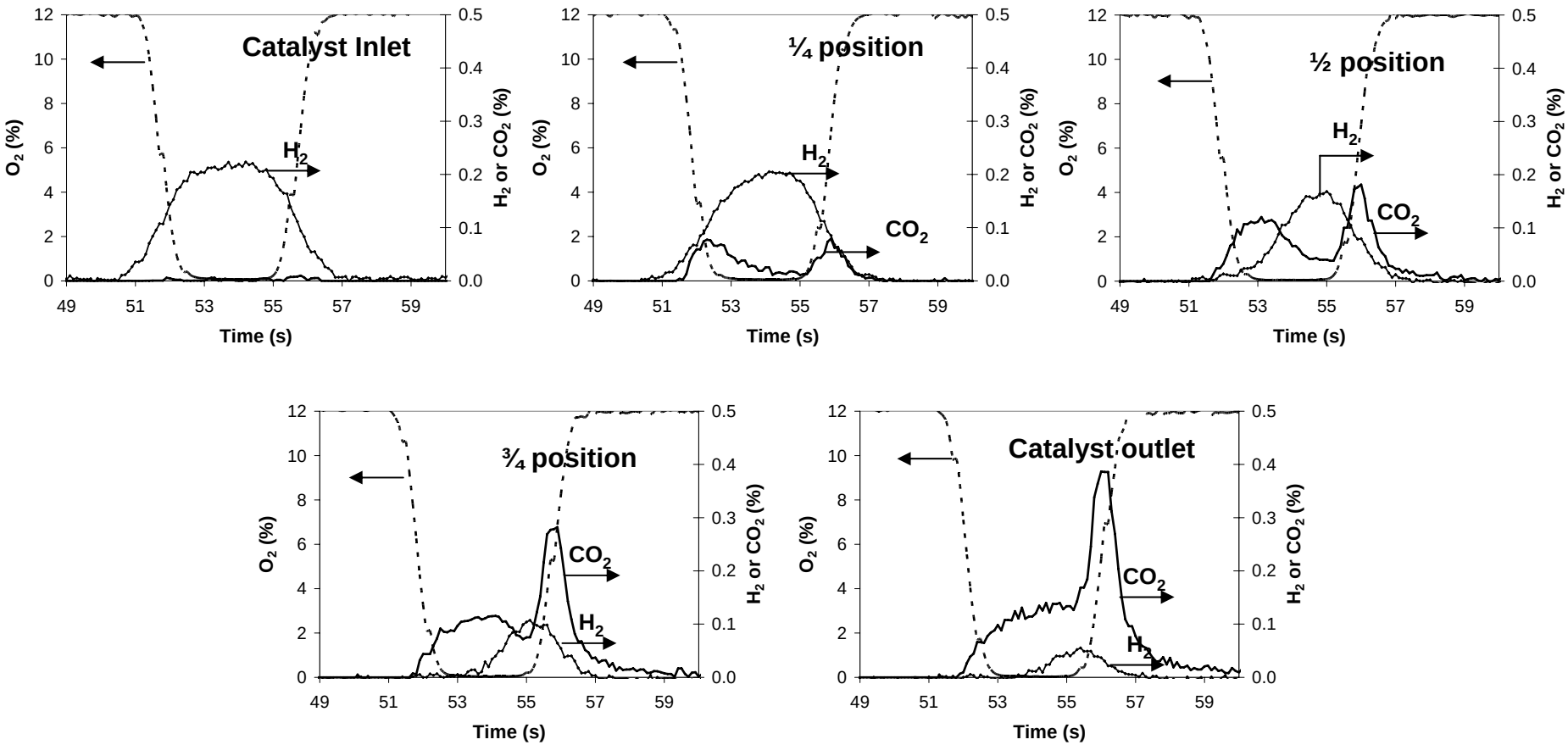
- **Near complete CO consumption by ½ position**
- **CO_2 adsorption/desorption dynamics observed**

Strong CO adsorption on Pt at 200 °C: "CO self poisoning"



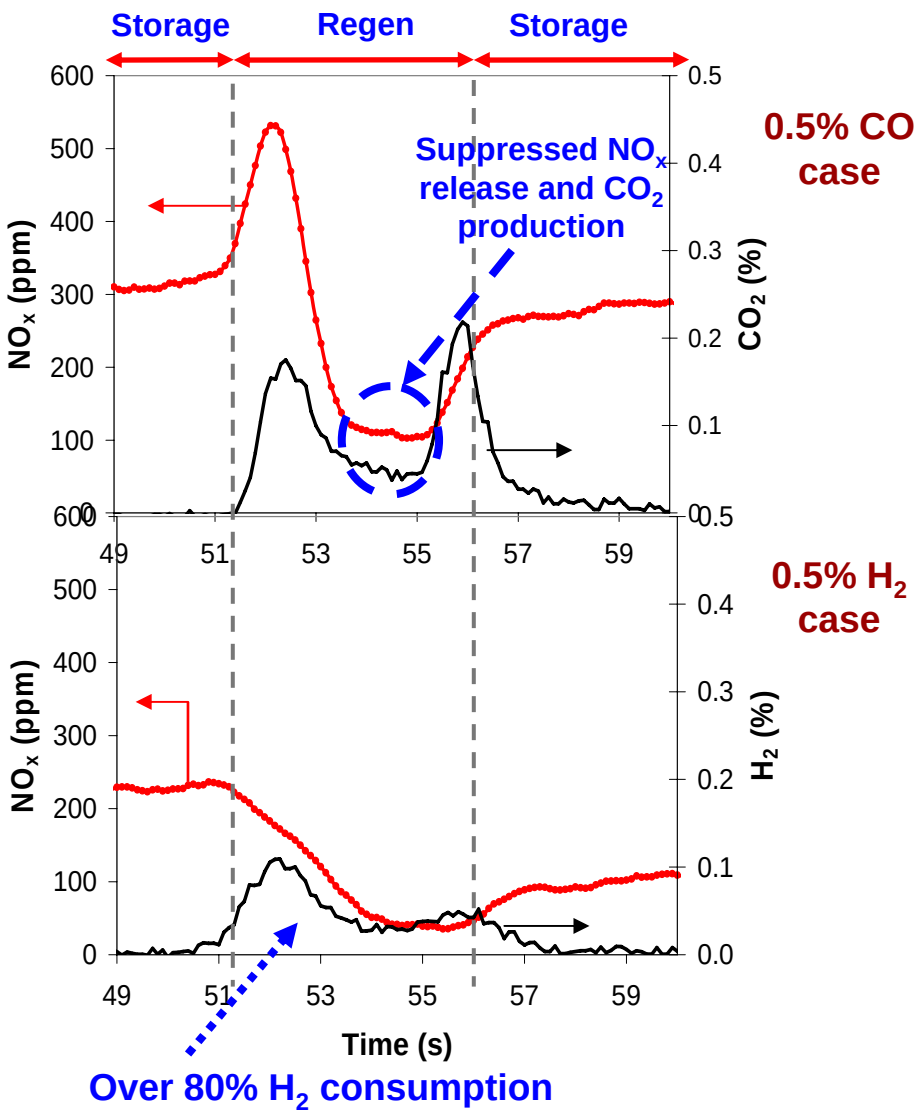
- **Bi-modal CO_2 dynamics (high > low > high reaction-rate branches)**
- **Initial CO oxidation by surface oxygen & NO_x**
- **Rxn. suppressed w/ Pt surface dominated by CO at mid regen. times**
- **Upon switching back to lean, surface CO is scavenged by gas-phase O_2**

CO also inhibits H_2 utilization at 200 °C



- **Again, bi-modal CO_2 dynamics**
- **H_2 consumption lower at late regen times**

CO-poisoning of Pt prevents efficient NO_x release & reduction



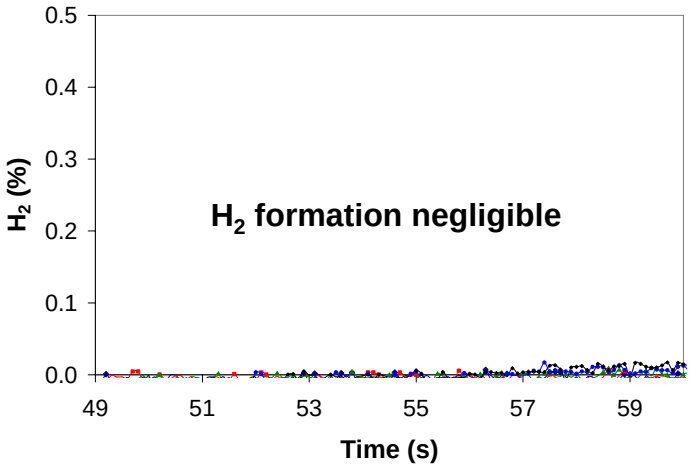
- NO_x, CO_2, H_2 profiles at ½ LNT at 200 °C
- Indicates importance of reductant activation for NO_x release

Contribution of Water-Gas Shift to Observed Similarity/Difference between H_2 and CO?

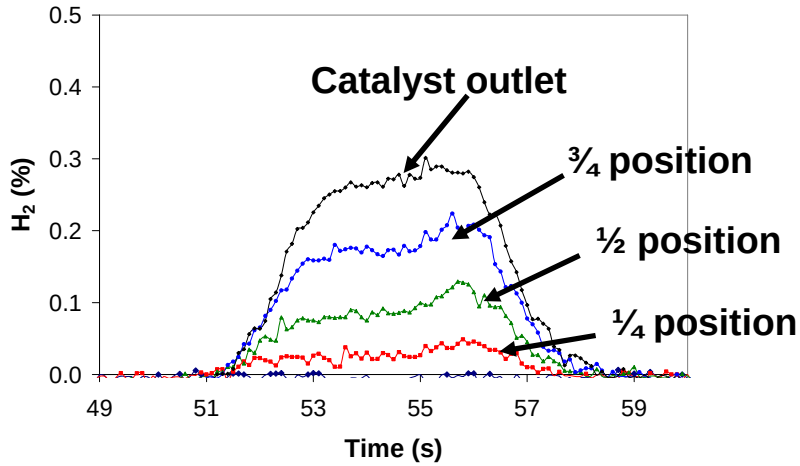
Direct contribution of water-gas shift appears to be limited

56 s: 5% H_2O + N_2 vs. 4 s: 0.5% CO + 5% H_2O + N_2

200 °C



300 °C



- **Even under O_2 and NO_x-free condition, progression of WGS is slow i.e., less than 10% of CO conversion via WGS at ¼ LNT at 300 °C**
  cf. Almost 100% CO conversion during LNT regen. at ¼ LNT
- **Under practical gas composition, CO conversion via WGS will be even significantly lower**
  Surface oxygen; gas-phase O_2; gas-phase CO_2; NO_x

Conclusions

- **Time-resolved in situ intra-channel speciation clarified relative efficiency of H_2 and CO in $Pt/K/Al_2O_3$ LNT regeneration**
- **H_2, H_2/CO, CO similarly efficient at 300 °C**
  - **Reductant/NO_x removed=2.4**
- **H_2 much better reductant compared to CO at 200 °C**
  - **Higher the H_2 content, better the regen efficiency**
- **CO-poisoning of Pt sites responsible for low performance at 200 °C**
  - **CO also inhibits H_2 access to Pt sites in the case of H_2/CO**
- **Reductant activation necessary for LNT regen at 200 and 300 °C**
- **CO acts as a direct reductant of NO_x**
  - **Water-gas shift contribution as H_2 source appears limited**

Future Work

- Other reductants concentrations and ratios
- Different analytical tools: DRIFTS, isotopic labeling
- Different LNT formulations