Spatiotemporal Distribution of NO_x Storage: a Factor Controlling NH_3 and N_2O Selectivities over a Commercial LNT Catalyst

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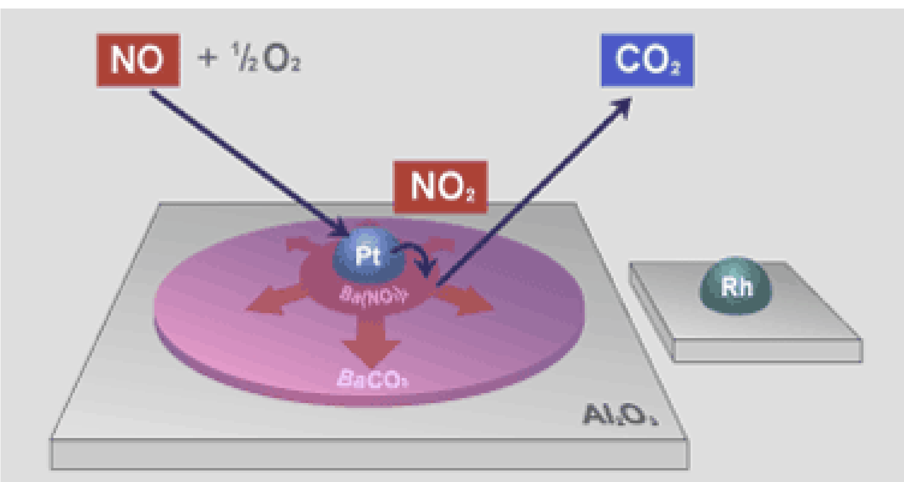
17th DEER Conference
October 5, 2011
Detroit, MI

Lean NO_x traps remove NO_x from lean-burn engine exhausts in cyclic lean/rich operation

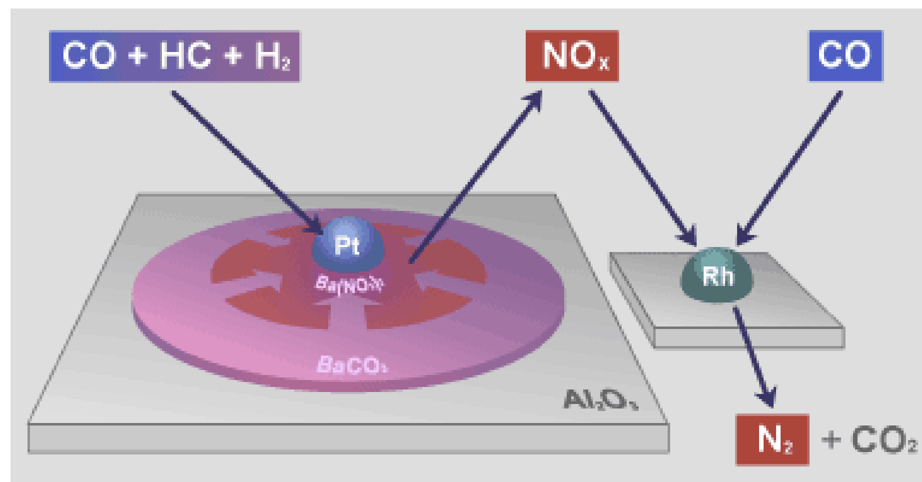
LNT = 3-way catalyst + NO_x storage material

Pt, Pd, Rh, Al_2O_3, CeO_2 *Ba, K*

Lean environment (long interval)
NO_x storage

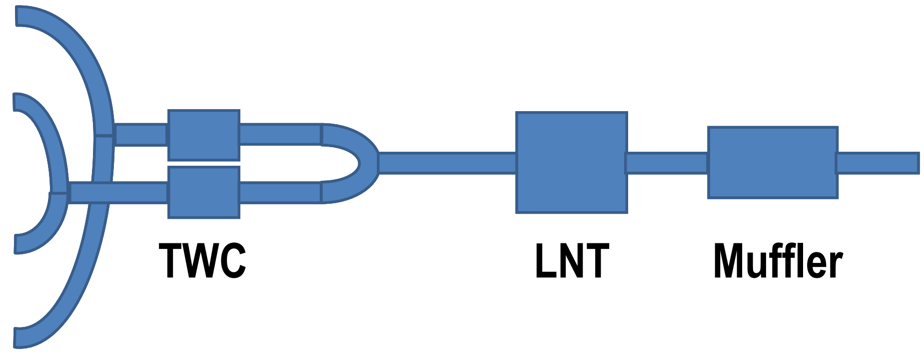


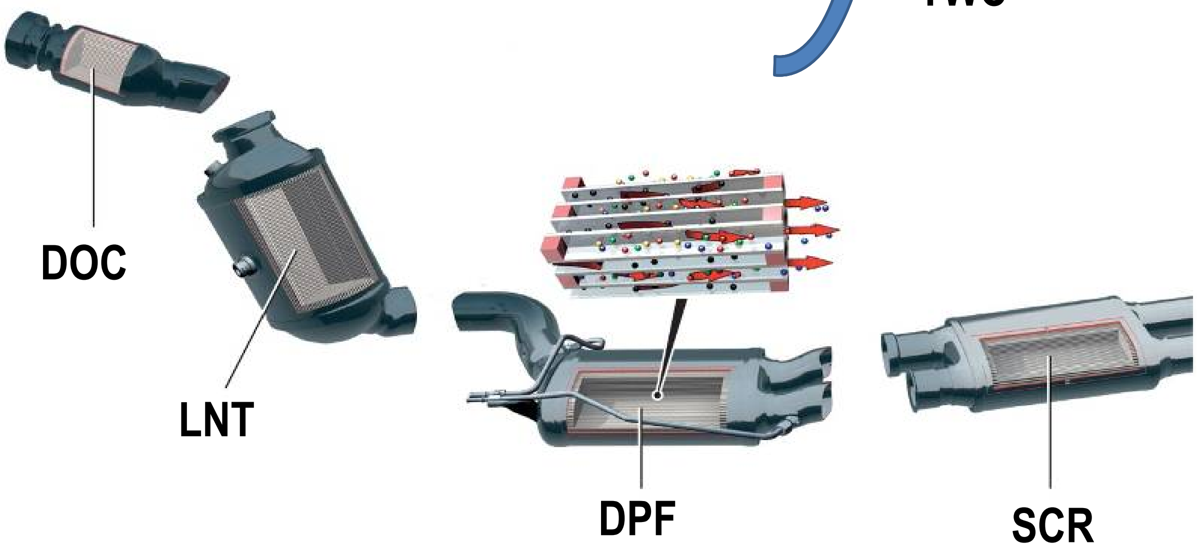
Rich environment (short interval)
NO_x release & reduction



Commercialized variants of LNTs

Lean gasoline (TWC + LNT)





Diesel (LNT+SCR)

Diesel (LNT)

LNT catalysts represent non-urea aftertreatment option for lean engines:
no need for urea storage & delivery systems

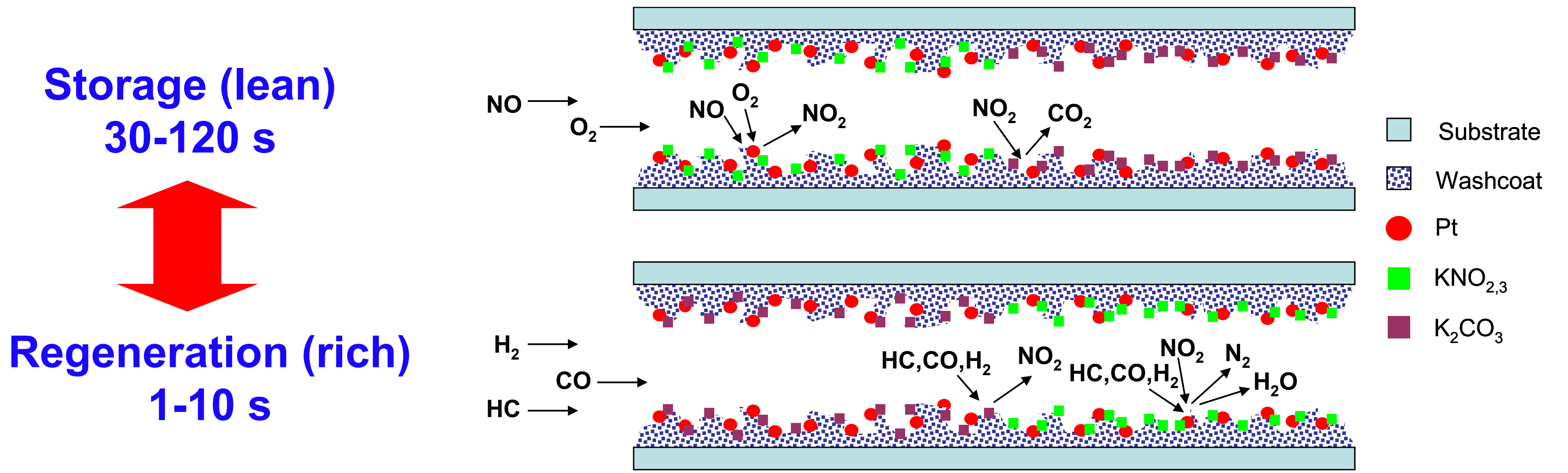
Technical barriers

- Fuel penalty
  - Regeneration & desulfation
- Cost
  - High cost of platinum group metals
- Durability
  - Large built-in catalyst margin
- Byproduct emissions
  - NH_3: useful in LNT+SCR application
  - N_2O: greenhouse gas to be controlled

Fundamental insights can enable more efficient and cost effective technology development

Understanding spatiotemporal distribution of reactions can lead to new insights

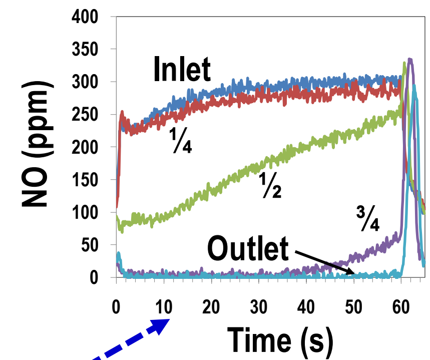
- LNT is an inherently transient & integral reactor
  - Transient chemistry evolves along the catalyst length

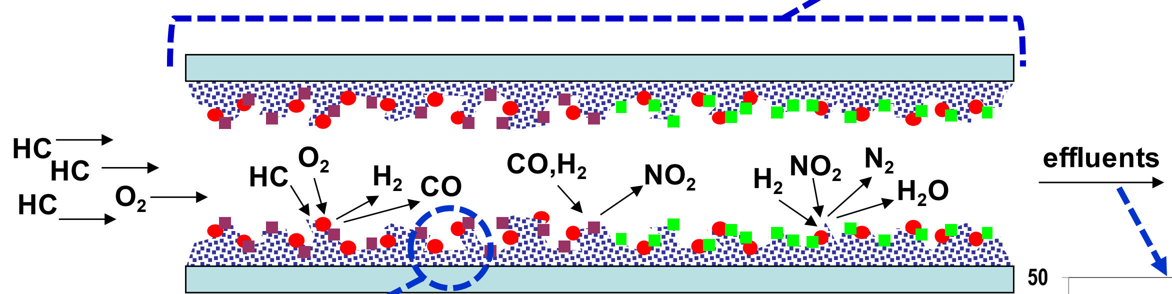


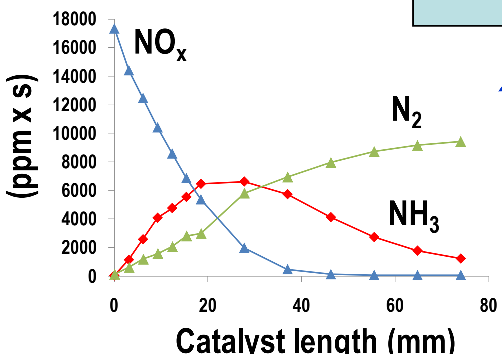
- Traditional, zero-dimensional (i.e., non-integral) consideration of reactions is not sufficient to describe relevant processes
  - Intermediate reductant roles of NH_3
  - Sulfation impact on catalyst performance

Objective: understand how spatiotemporal distribution of NO_x storage coupled with local chemistry affects NH_3 & N_2O selectivity

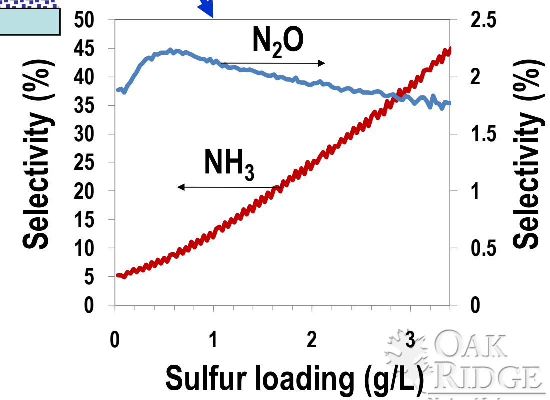
1. Major storage during lean phase
2. Readsorption during rich phase
3. Sulfation-induced storage displacement







NH_3 chemistry



Approach: controlled lab reactor study with spatiotemporally resolved analysis

- Commercial LNT:

– Pt/PdRh, Ba-based, oxygen storage capacity (OSC: Ce/Zr)

- Two types of experiments (base gas: 5% H_2O, 5% CO_2, N_2 balance)

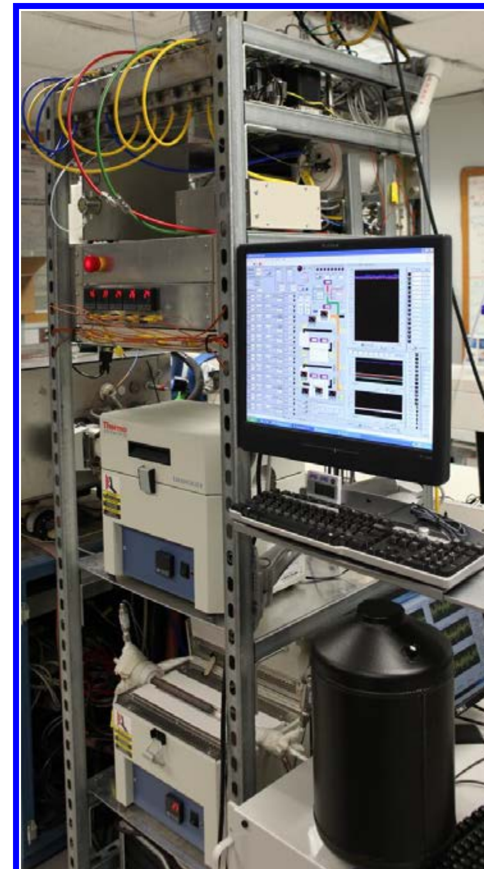
1. Lean/rich cycling (with or without sulfation)
    - Lean (60 s): 300 ppm NO, 10% O_2
    - Rich (5 s): 3.4% H_2
2. Transient response

– Initial LNT surface: oxidized or nitrated

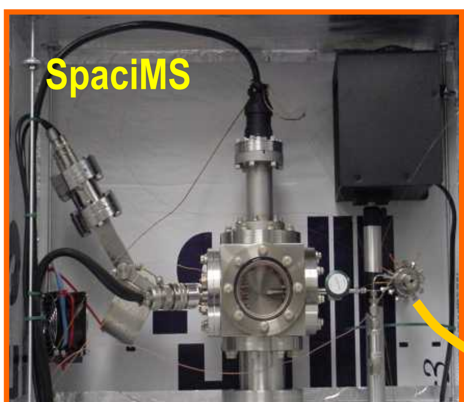
– NH_3 pulse input

- Spatiotemporal resolution of reactions

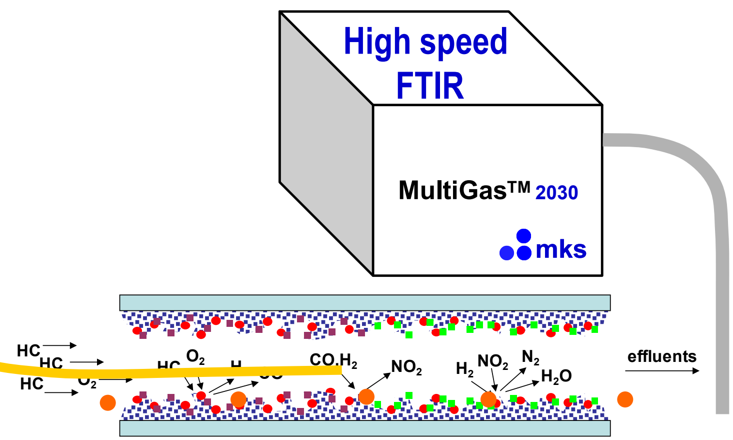
Bench reactor



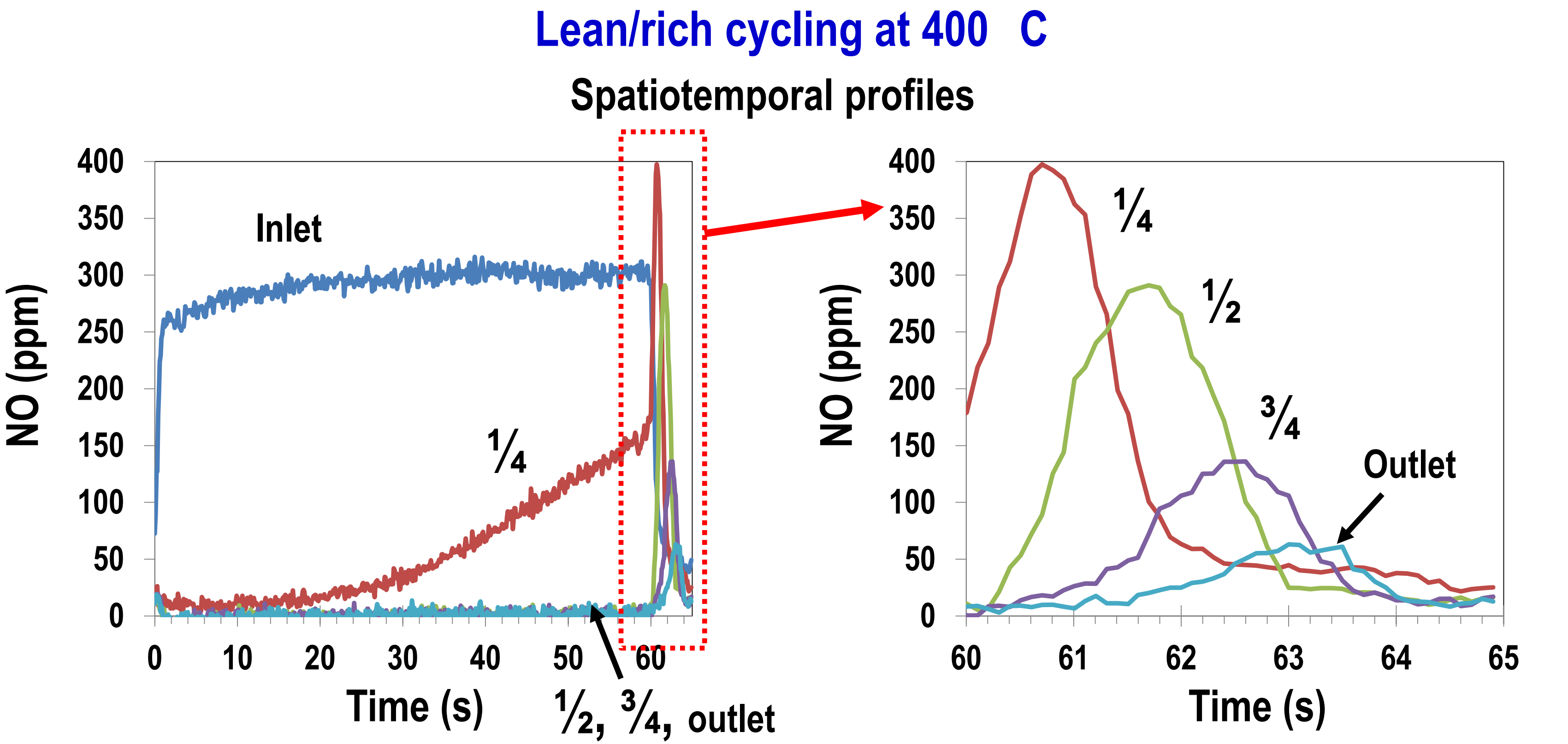
Inside catalyst



In catalyst effluents



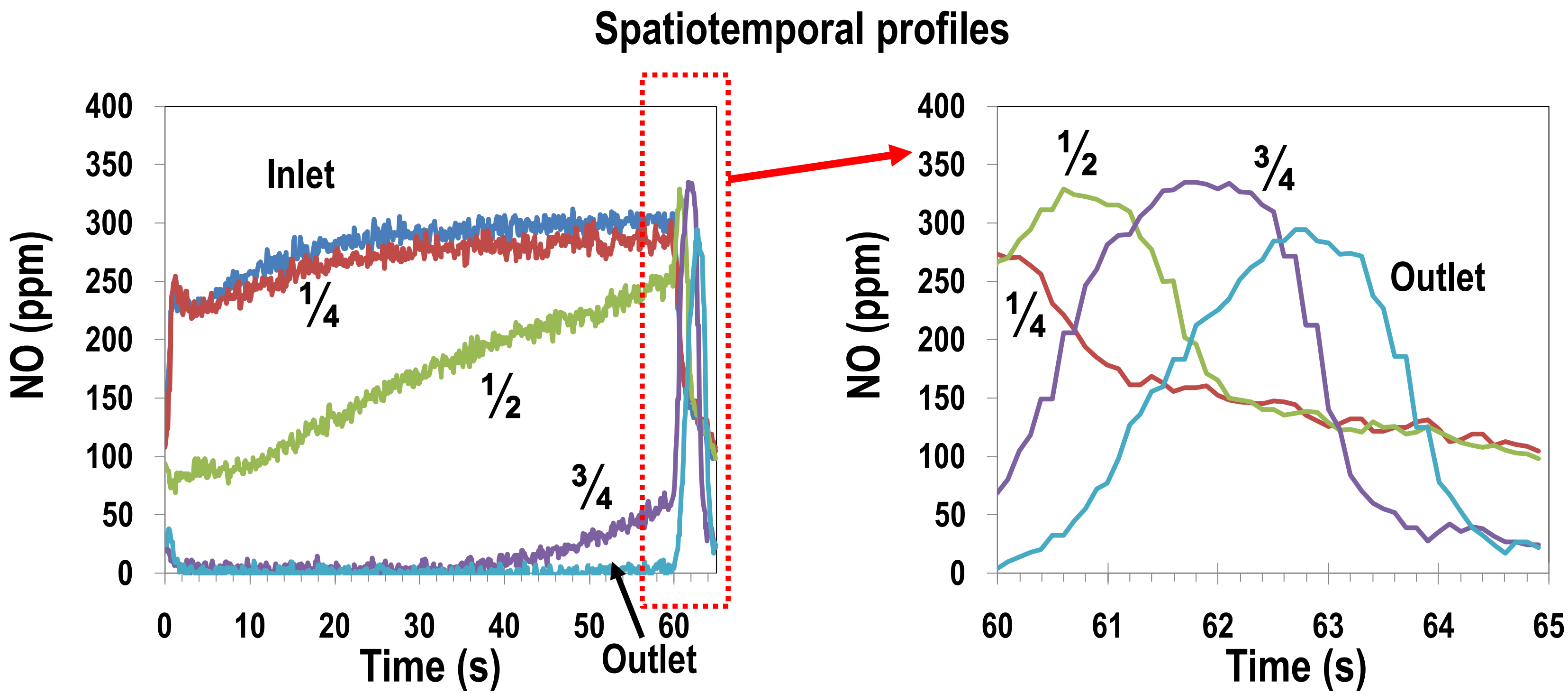
Upstream-slipped NO_x during regeneration can be re-adsorbed and reduced downstream



- Fraction of LNT sufficient for complete NO_x storage under optimal conditions
  - Complete lean-phase trapping of inflow NO_x in 1st half ("active NSR zone")
- Upstream-slipped rich-phase NO_x can be readsorbed & further reduced in 2nd half
  - Almost complete cycle averaged NO_x conversion

Sulfation axially displaces lean NO_x storage increasing rich NO_x slip

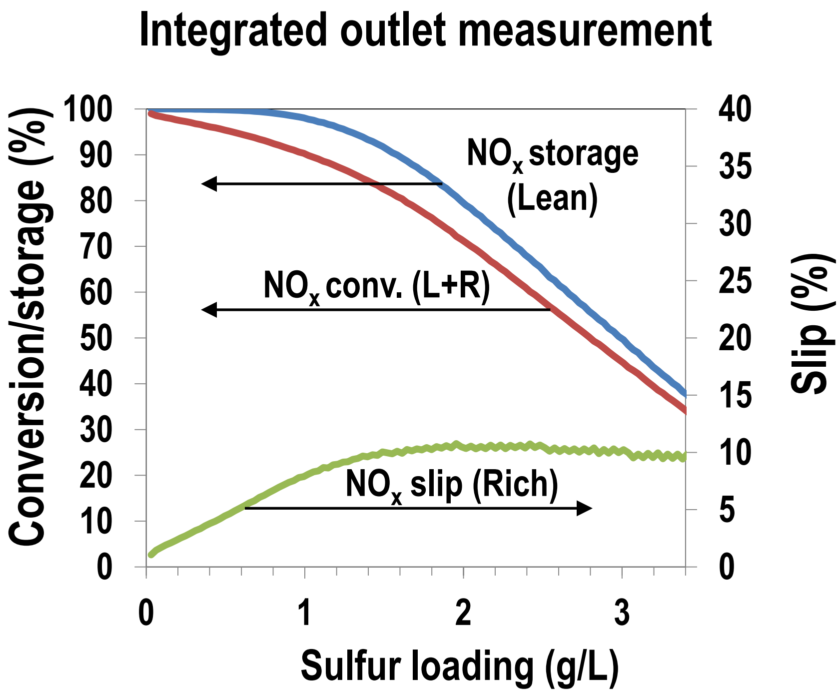
Lean/rich cycling at 400 C (after sulfation; 1.7 g/L)

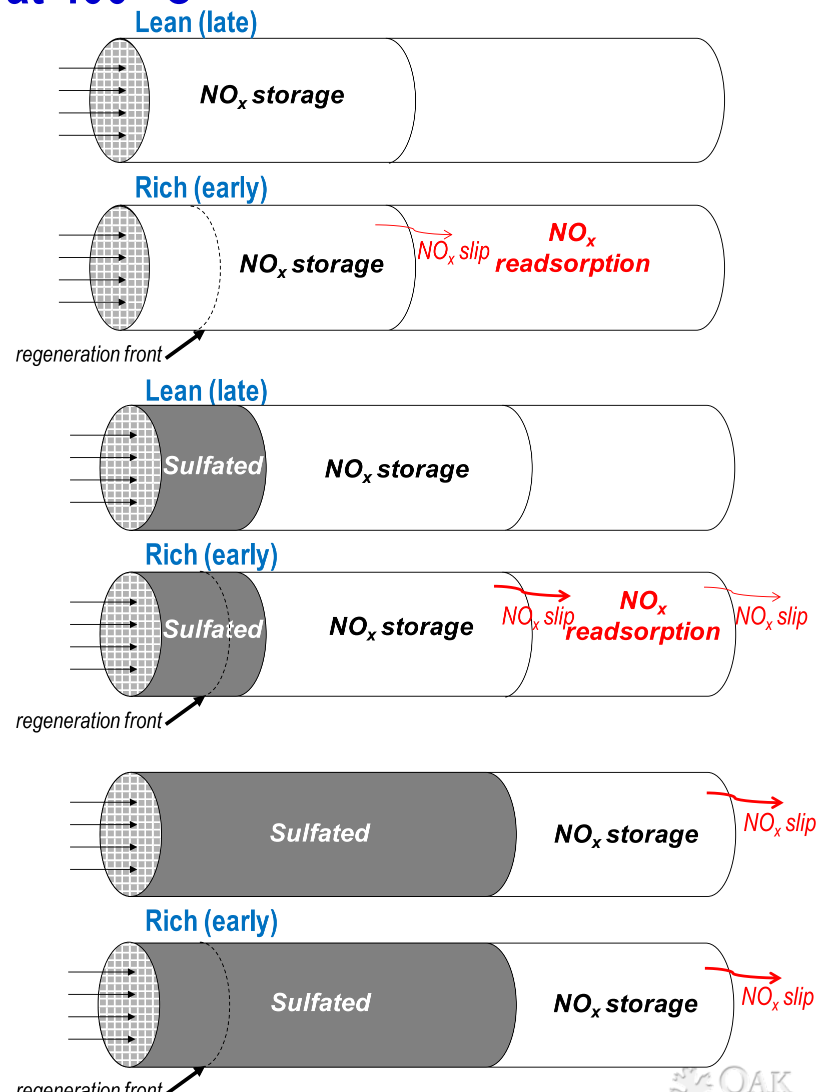


- Plug-like axial displacement of lean NO_x storage
  - Complete lean-phase trapping of inflow NO_x still maintained
- Earlier & greater rich-phase NO_x slip
  - Due to less downstream storage buffer
  - Significant rich-phase NO_x slip leading to a reduced cycle-averaged conversion

Sulfation-induced axial redistribution explains decreasing NO_x conversion pattern

Lean/rich cycling at 400 C

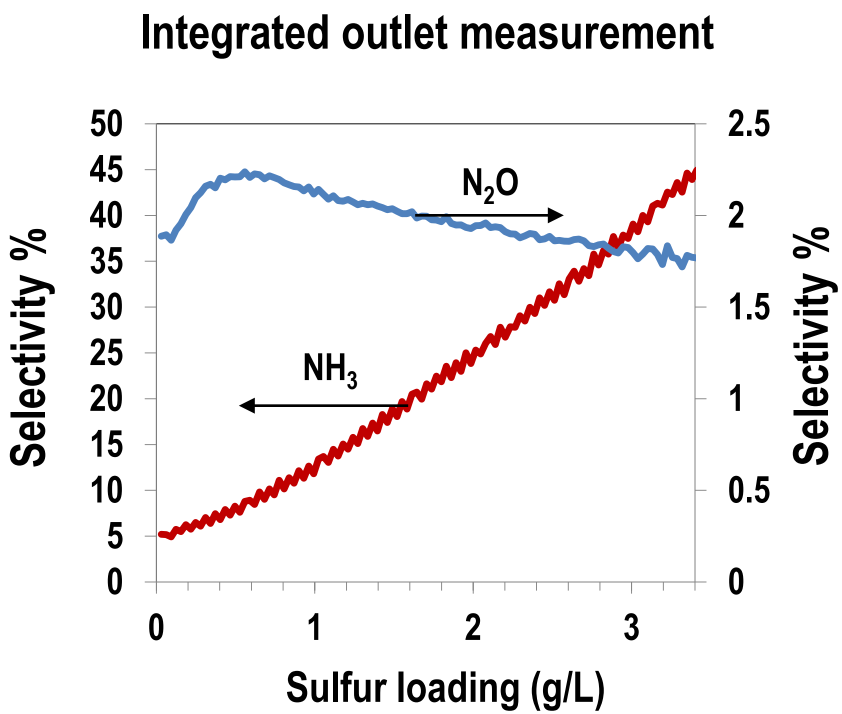


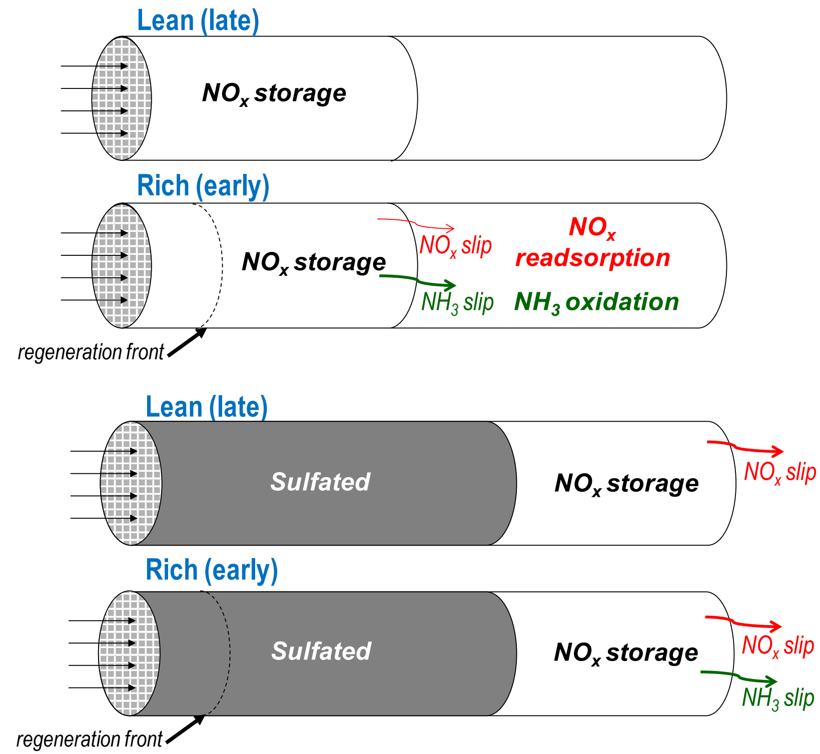


- < ~1 g S, conversion increasingly limited by rich NO_x slip
  - Continuous decrease in readsorption
- > 1 g S, accelerated decrease due to insufficient storage capacity

Sulfation-induced axial redistribution explains increasing NH_3 selectivity

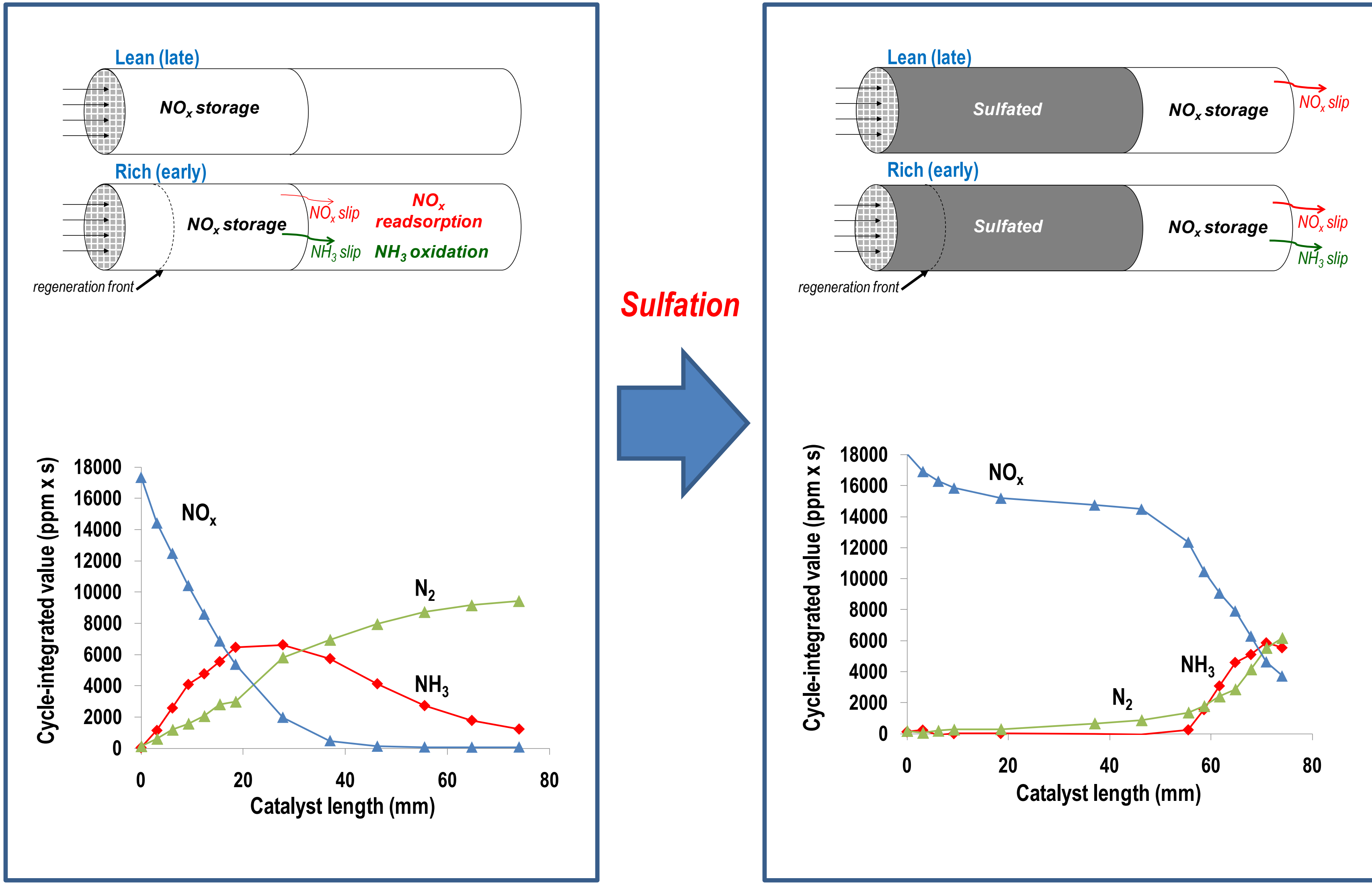
Lean/rich cycling at 400 C





- Significant increase in NH_3 selectivity (9-fold increase)
  - Shortening of OSC-only zone: less NH_3 reaction with OSC
- Minor change in N_2O selectivity (initial increase followed by continuous decrease)

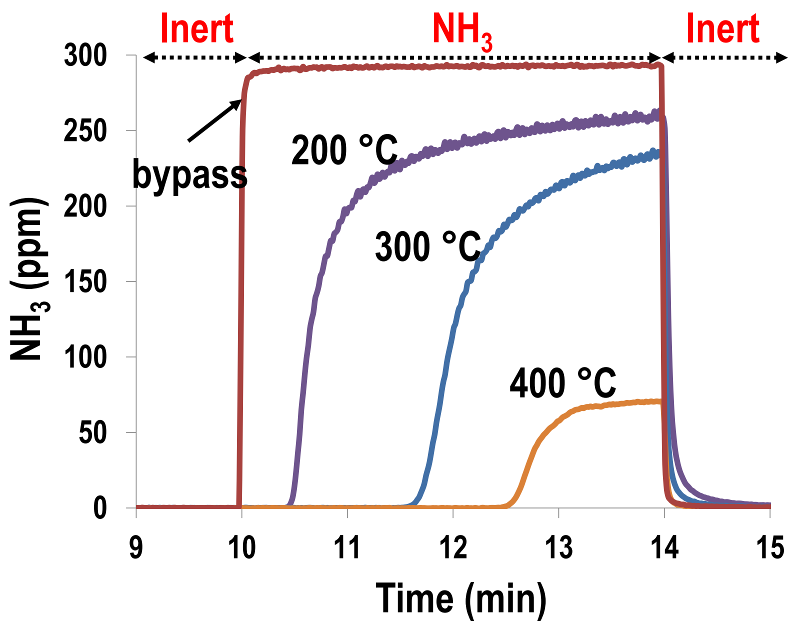
Direct intra-catalyst measurements confirm the link between NO_x distribution & NH_3

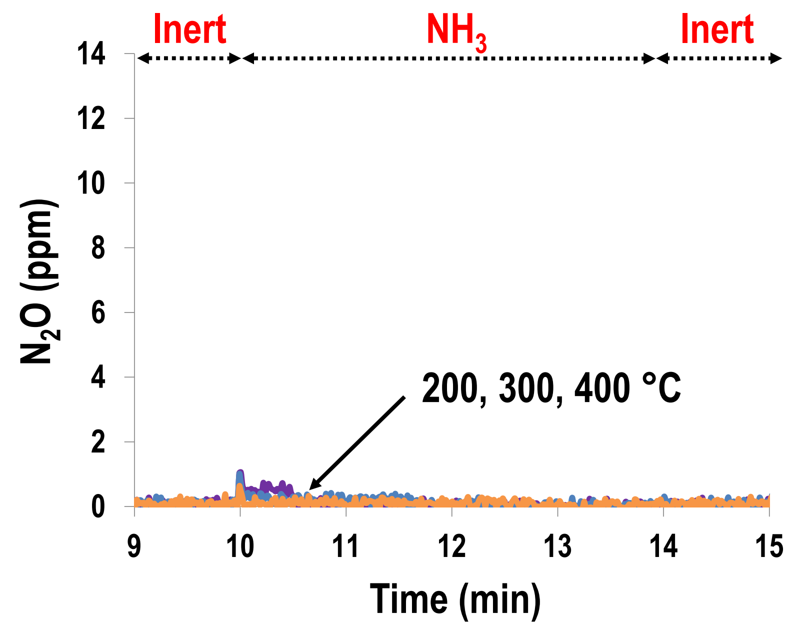


NH_3 reduction of surface oxygen does not lead to N_2O formation

Transient response experiment : NH_3 pulse input

LNT pre-oxidized with O_2 followed by inert purge



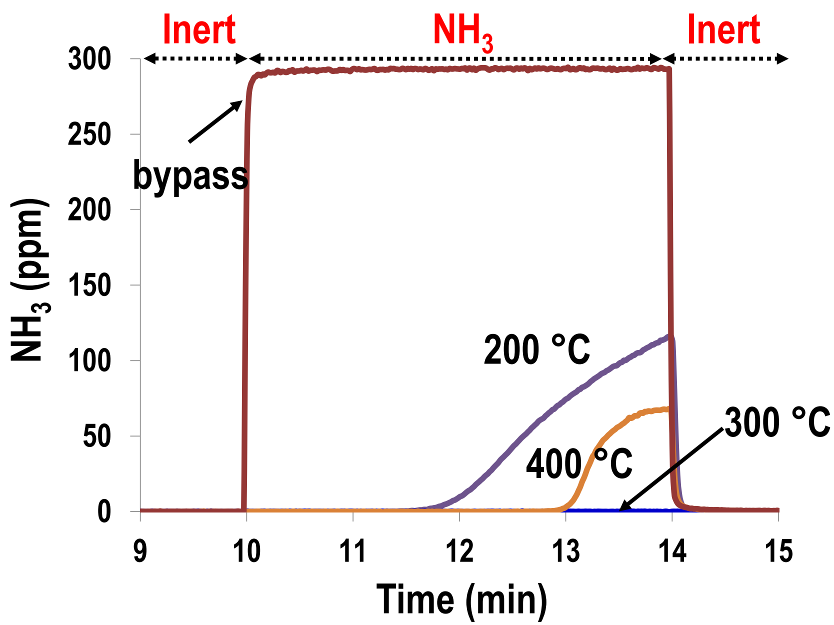


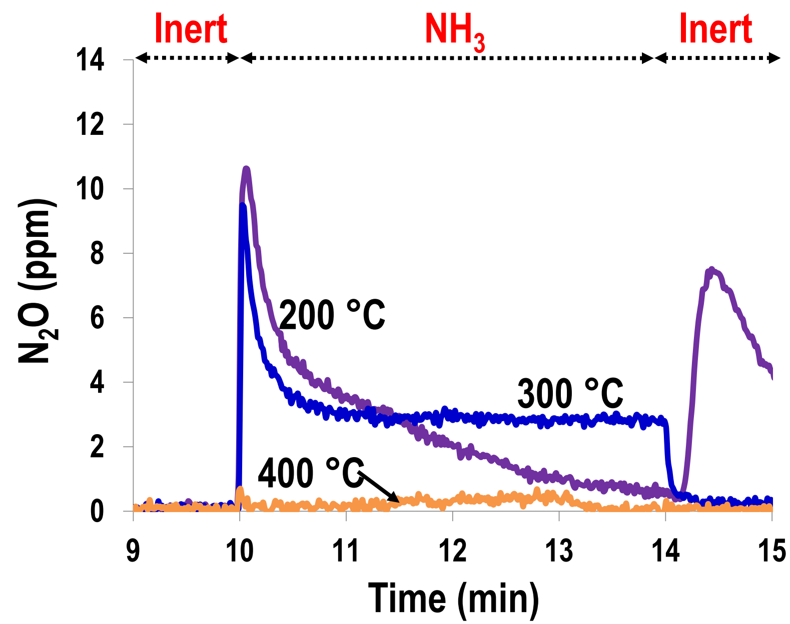
- NH_3 reduction of stored oxygen (CeO_2): efficient (plug-like front)
- Not a major contributor to N_2O formation
- Consistent with insignificant change in N_2O selectivity with sulfation
  - Despite 9-fold increase in NH_3 slip (i.e., less NH_3 reduction of OSC)

NH_3 reaction with stored NO_x leads to N_2O

Transient response experiment: NH_3 pulse input

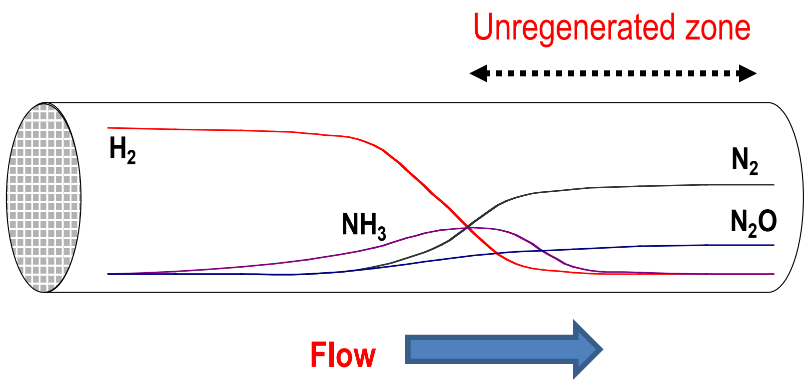
LNT pre-nitrated with 300 ppm NO_x + 10% O_2 followed by inert purge



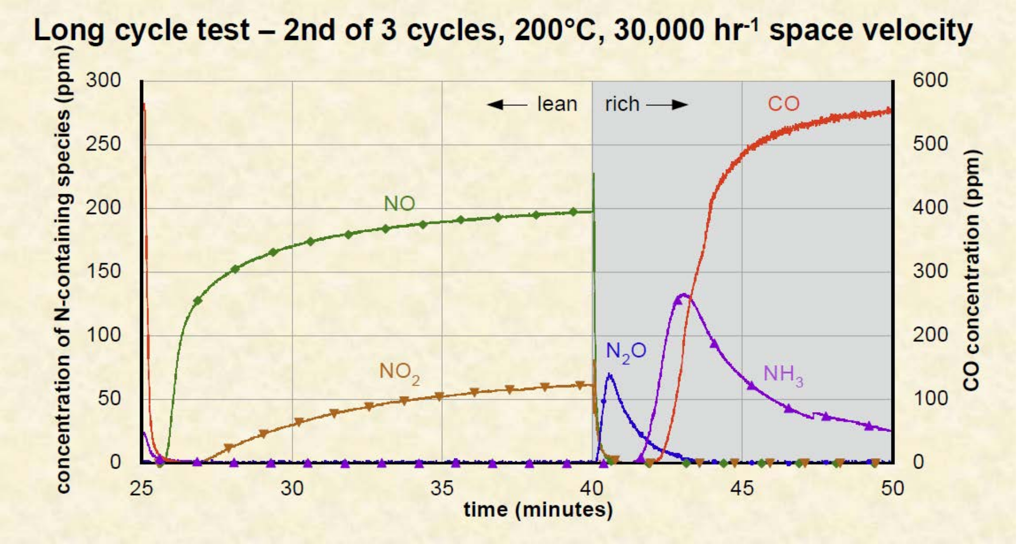


- NH_3 reduction of stored NO_x: efficient
- Major contributor to N_2O formation
- Consistent with insignificant change in N_2O selectivity with sulfation
  - Plug-like axial displacement of the active NSR zone (i.e., just location changes)

NH_3 reaction with stored NO_x relevant to LNT N_2O selectivity

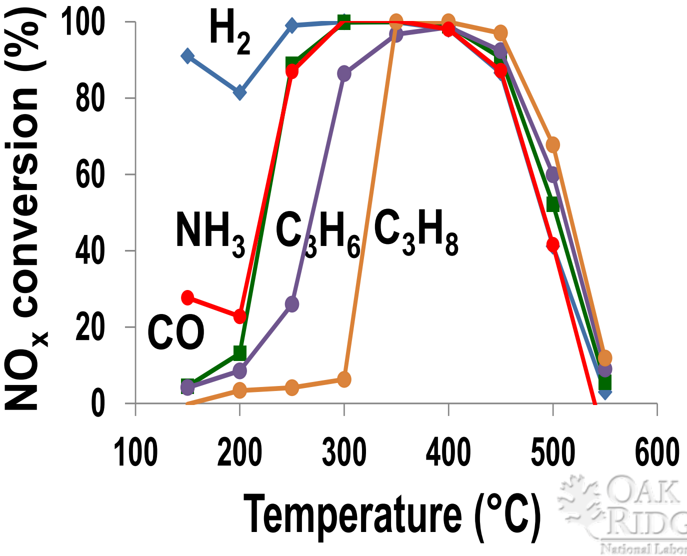


Pihl et al., SAE Technical Paper 2006-01-3441



- NH_3 reaches unregenerated zone earlier than H_2

  Partridge and Choi, Appl. Catal. B: Environ. 91 (2009) 144-151
- Due to lower regeneration efficiency of NH_3
- Co-presence of CO and HCs can further alter N_2O selectivity



Conclusions

- **Distribution of stored NO_x evolves continuously over space and time**
  - **Primary storage with inflow NO_x (lean)**
  - **Downstream readsorption of upstream-slipped NO_x (rich)**
  - **Sulfation-induced axial displacement of active NO_x storage (lean, rich)**
- **NH_3 byproduct plays intermediate reductant roles**
  - **NH_3 reduces efficiently stored oxygen (OSC) without N_2O formation**
  - **NH_3 reduces efficiently stored NO_x with N_2O formation**
- **Coupling of NO_x storage distribution with local chemistry is an important factor determining LNT performance trends**
  - **Example: sulfation impact**
    - Increased NO_x slips (both lean and rich)
    - Increased NH_3 selectivity
    - Minor change in N_2O selectivity
- **Insights can facilitate modeling and development efforts**

Acknowledgments

- Research sponsored by DOE, Vehicle Technologies Program
  - Program Managers: Ken Howden, Gurpreet Singh
- Catalyst from Umicore
  - Dr. Owen Bailey

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