N_2O Formation Pathways during the Regeneration of Lean NO_x Trap

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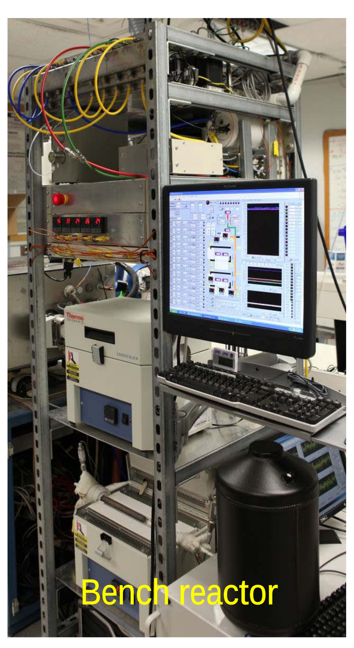
Motivation and Objective

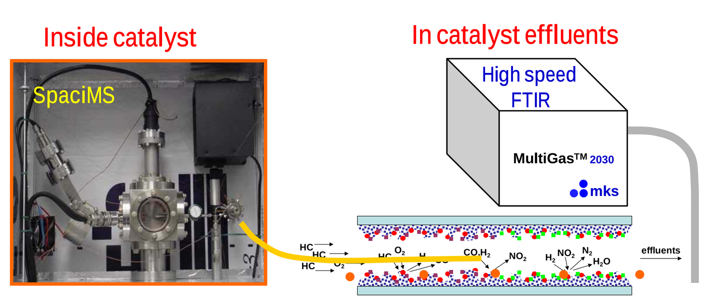
- Lean NO_x Traps (LNTs) are a leading candidate NO_x control technology for lean burn gasoline and light duty diesel
- Controlling N_2O emissions (a greenhouse gas) from LNT catalysts is important to meet future regulations such as CARB LEVIII
- Mechanisms of N_2O formation during LNT operation are not well understood and no predictive models are available
- We are investigating N_2O formation pathways during LNT regeneration and integrating them into a global kinetic model

Approach

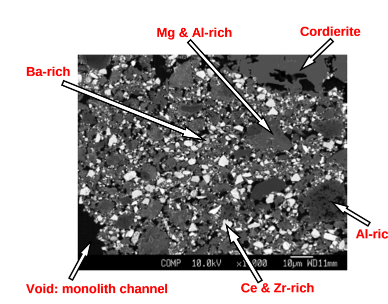
Experiments



- **Bench reactor evaluation**
  - *Reductant sweep*
  - *Temperature sweep*
  - *Short vs. long cycling*
- **Specialized measurements**
  - *SpaciMS*
  - *Transient response method*



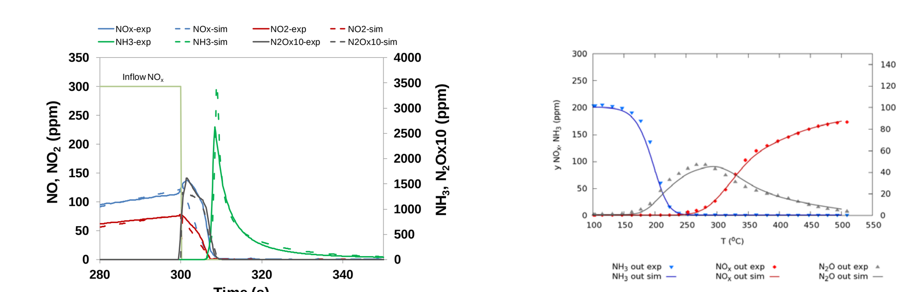
CLEERS reference LNT: Umicore, lean GDI



Domain	Composition
Ba-rich	Ba (high), Ce/Zr, Pt, Pd
Ce/Zr-rich	Ba (low), Ce/Zr, Pt, Pd
Al-rich	Al, Rh, Pd
Mg/Al-rich	Mg/Al, Pt, Ce

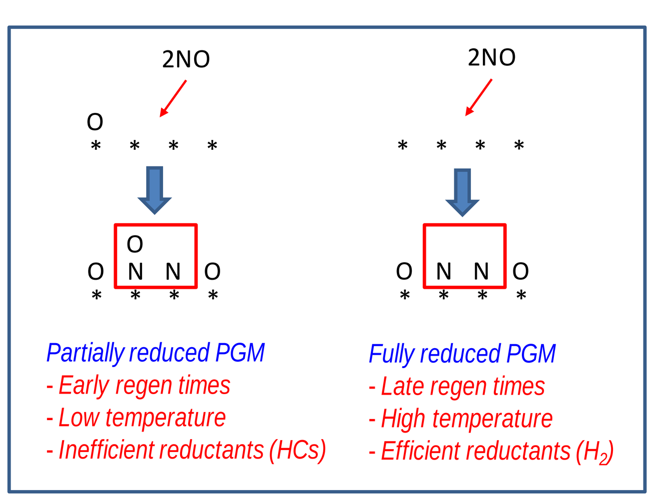
Modeling

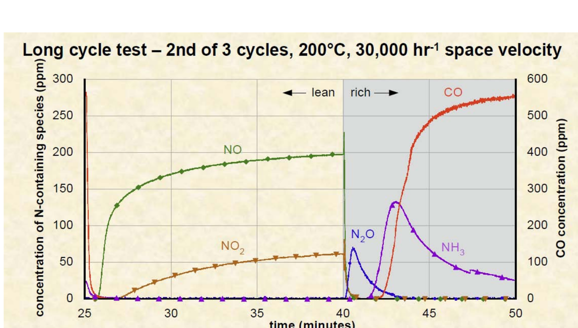
- **Global kinetic model**
- **Extend kinetics by integrating new findings**
  - *PGM redox state*
  - *Reduction of nitrates vs. oxygen storage capacity (OSC)*
- **Simulations guide experiments**

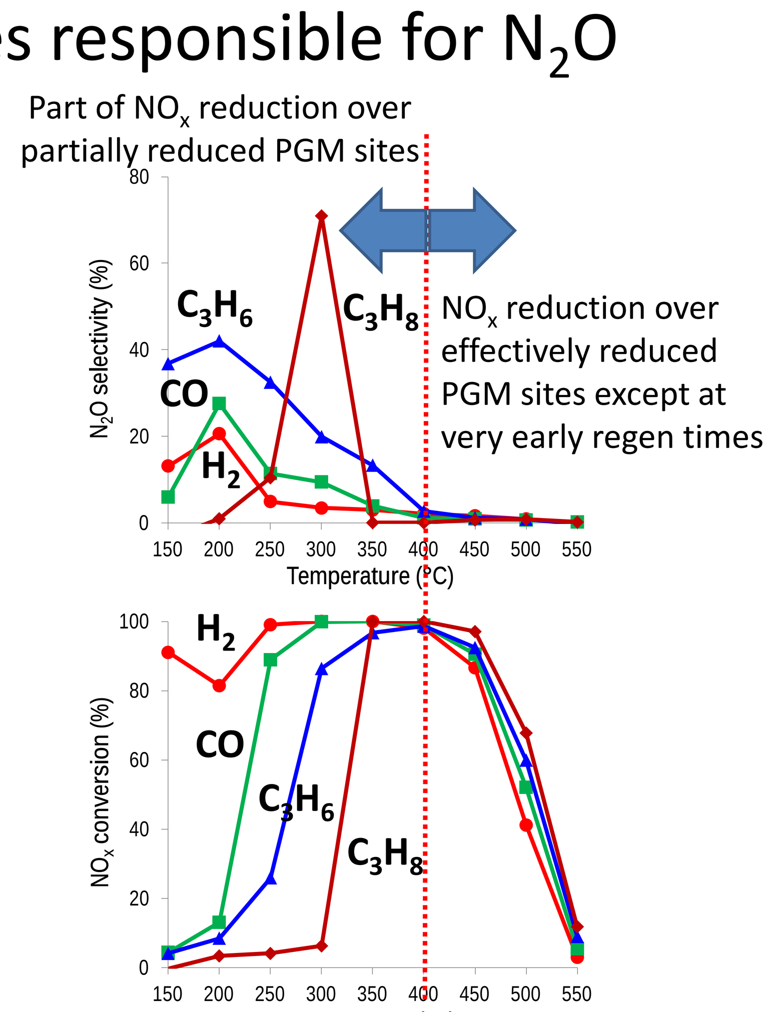


Redox States of Platinum Group Metal (PGM) Sites Determine Local N-Selectivity

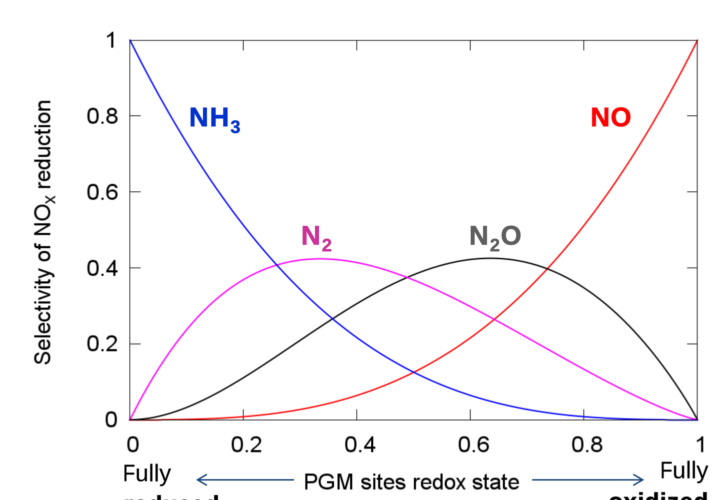
Partially reduced PGM sites responsible for N_2O







Approximation of local N-selectivity in dependence on PGM redox state

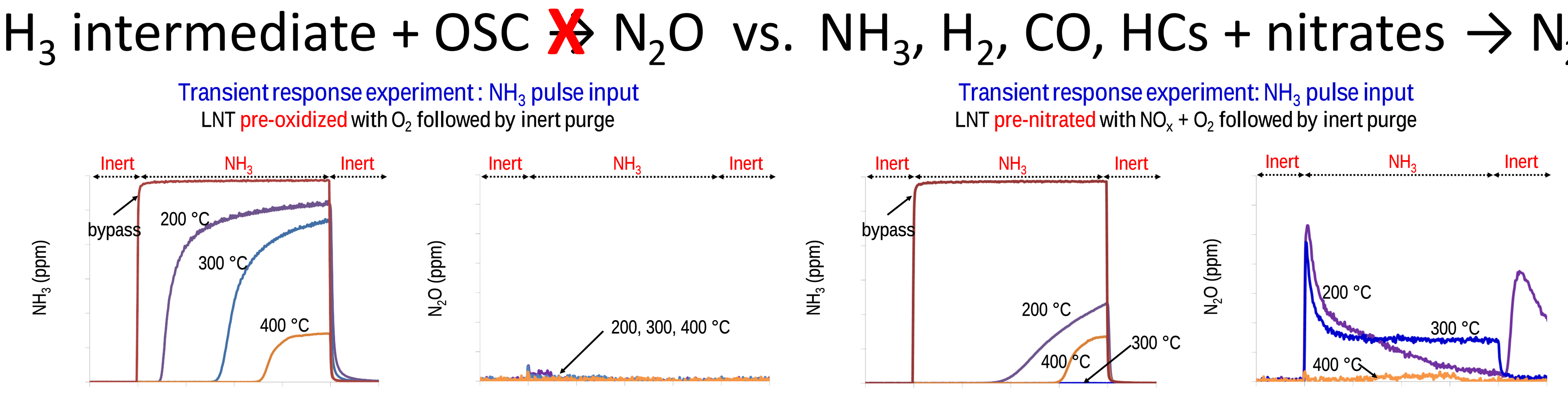


- Polynomial functions
- $S_{NO} + S_{N2O} + S_{N2} + S_{NH3} = 1.0$
- PGM redox state:

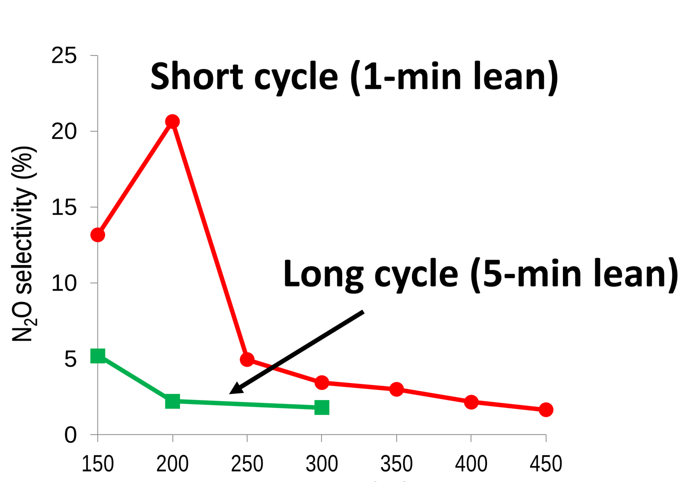
$$Pt + ½ O_2 \rightarrow Pt\text{-}O$$
$$Pt\text{-}O + CO \rightarrow Pt + CO_2$$
$$Pt\text{-}O + H_2 \rightarrow Pt + H_2O$$
$$Pt\text{-}O + 1/9\ C_3H_6 \rightarrow Pt + 1/3\ H_2O + 1/3\ CO_2$$

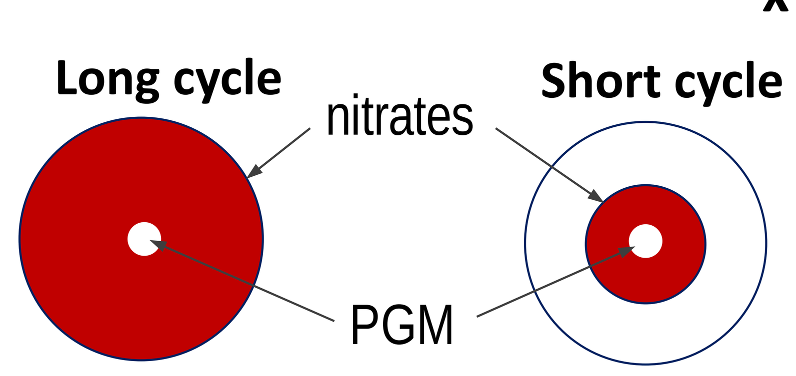
Reduction of Nitrates (not OSC) Leads to N_2O

NH_3 intermediate + OSC $\not\rightarrow$ N_2O vs. NH_3, H_2, CO, HCs + nitrates $\rightarrow$ N_2O

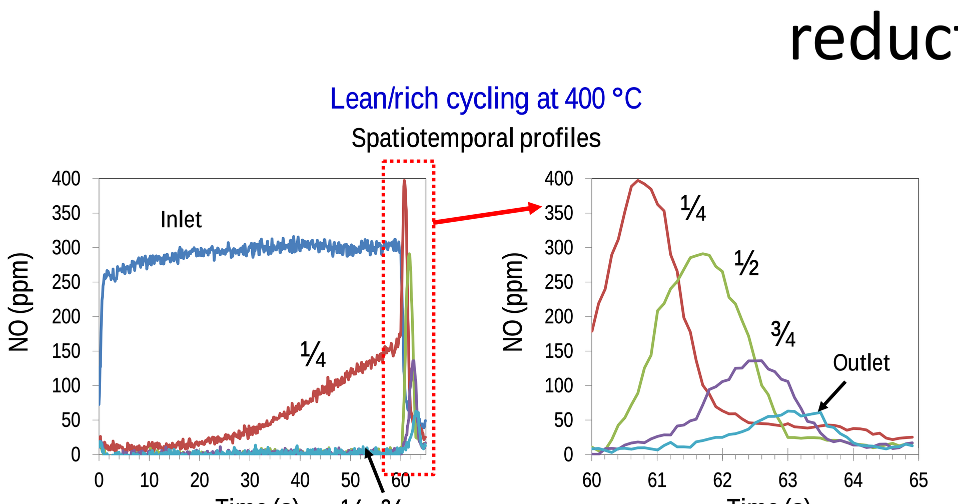


Spatiotemporal Distribution of Stored NO_x





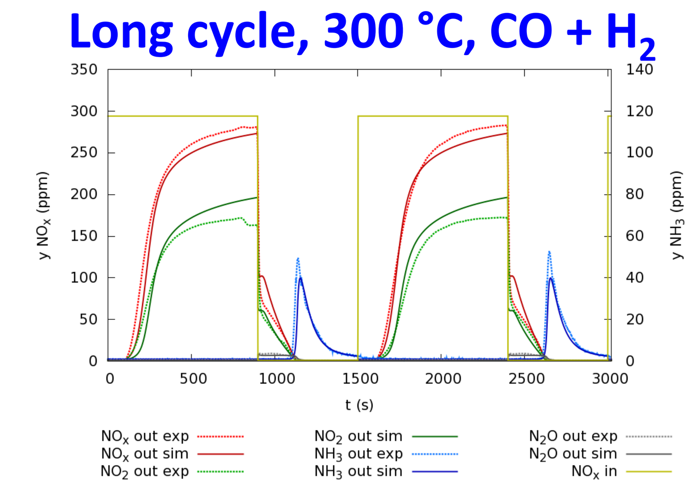
During short cycle, greater fraction of stored NO_x reduced before full reduction of PGM



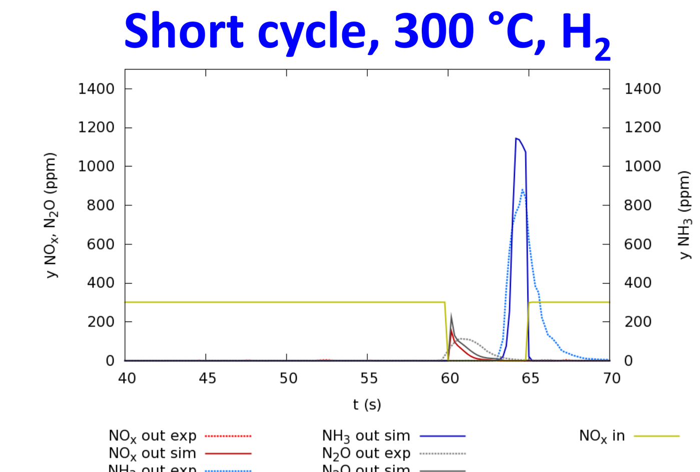
Downstream readsorption of released NO_x increases N_2O e.g., during short cycle at high T

Extended Kinetic Model Predicts N_2O Behavior over a Range of Conditions

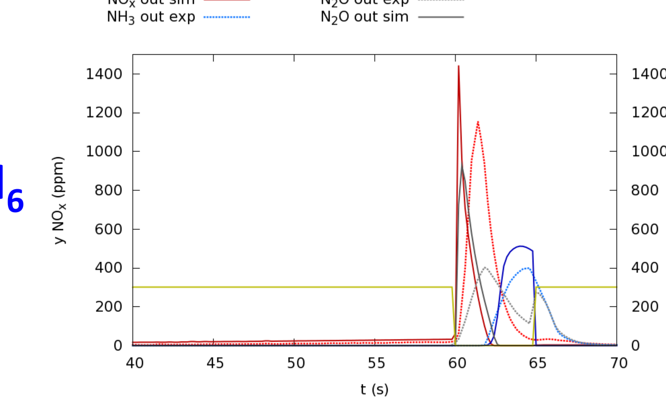
Long cycle, 300 °C, CO + H_2



Short cycle, 300 °C, H_2



Short cycle, 300 °C, C_3H_6



Conclusions

- Main source of N_2O is reduction of nitrates and not reduction of OSC with NH_3
- Local N-selectivity depends on PGM redox state: partially reduced sites $\rightarrow$ N_2O, N_2 vs. fully reduced sites $\rightarrow$ NH_3, N_2
- Local N-selectivity depends on amount and stability of stored NO_x: more stable nitrates $\rightarrow$ lower N_2O due to more NO_x being reduced on fully reduced PGM
- Axial redistribution of stored NO_x during regeneration contributes to the global N_2O selectivity
- Less effective reductants in rich mixture reach unregenerated region first (HCs > CO > NH_3 > H_2) $\rightarrow$ increased N_2O formation

Acknowledgements

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