Development of a global kinetic model for a commercial Lean NOx Trap based on laboratory measurements

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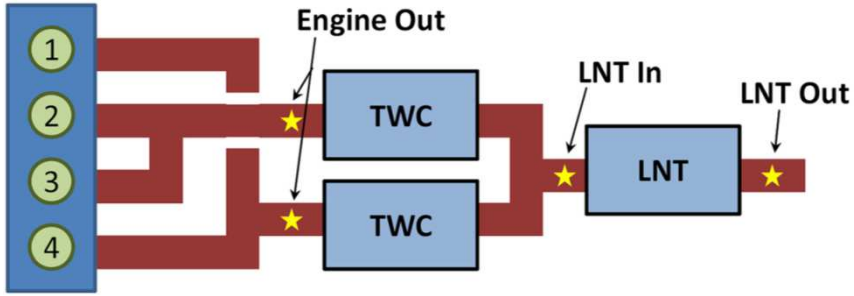
Outline

- Background
  - BMW LNT
  - CLEERS LNT Protocol
- Review Past Results
- NOx Storage Model
- NOx Reduction Model
- Conclusions

Background

- ORNL purchased a MY2008 BMW 1-series 120i lean gasoline engine vehicle with a N43B20 2.0-liter, 4-cylinder engine with direct injection
- The vehicle was characterized on a chassis dynamometer
- Engine measurement results are available on the CLEERS database
- A core from the LNT was made available for ORNL laboratory testing
- <u>Preliminary modeling results were shown at the 2013 workshop</u>



Lean Gasoline Engine Reductant Chemistry During Lean NOx Trap Regeneration

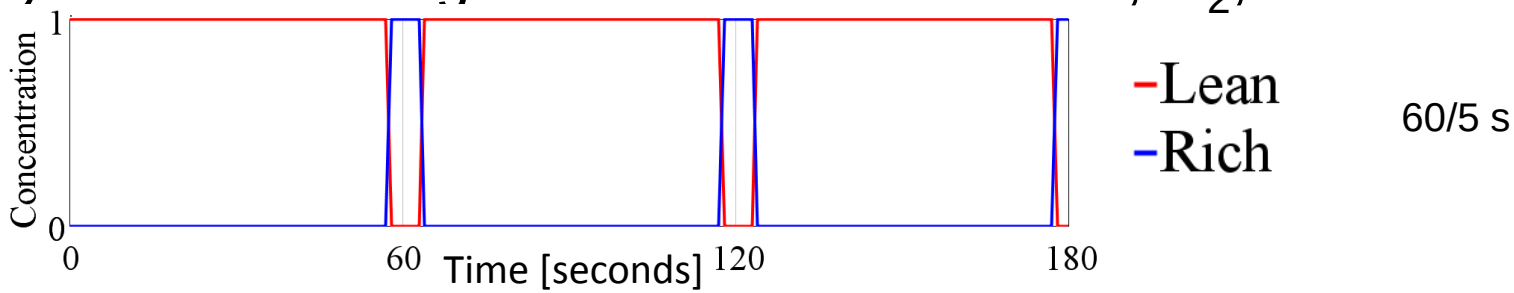
James E. Parks, Vitaly Prikhodko, William Partridge, Jae-Soon Choi, Kevin Norman, Shean Huff and Paul Chambon
Oak Ridge National Laboratory

SAE, 2010-01-2267

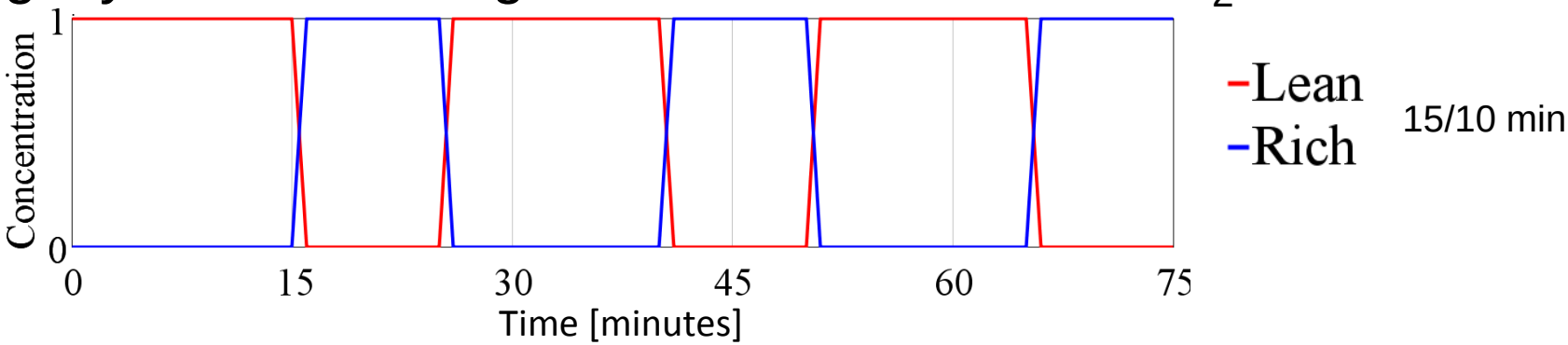
CLEERS LNT Protocol

http://cleers.org/focus_groups/private/Lean-NOx/files/1113847174LNTmap_7_18_05.pdf

- Oxygen storage and reduction via CO, H_2
- Short-Cycle NOx storage and reduction via CO, H_2, HC



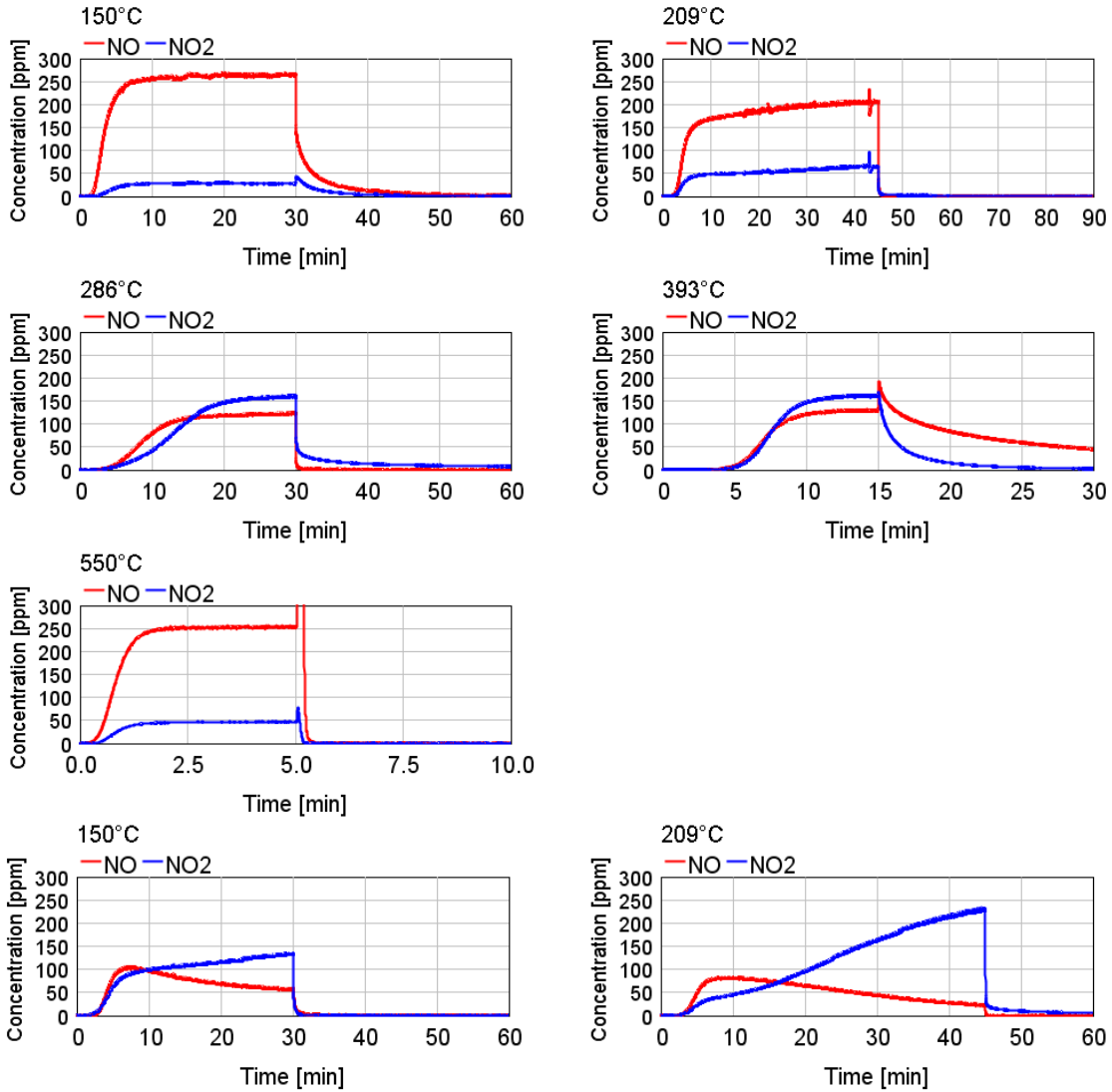
- Long-Cycle NOx storage and reduction via CO, H_2, HC



- Constant temperatures of 150, 209, 286, 393, 550°C
- Measured outlet data includes NO, NO_2, CO, N_2O, NH_3, O_2, H_2

Recap: NOx Storage Experiments

- Measurements available for 7 different cases

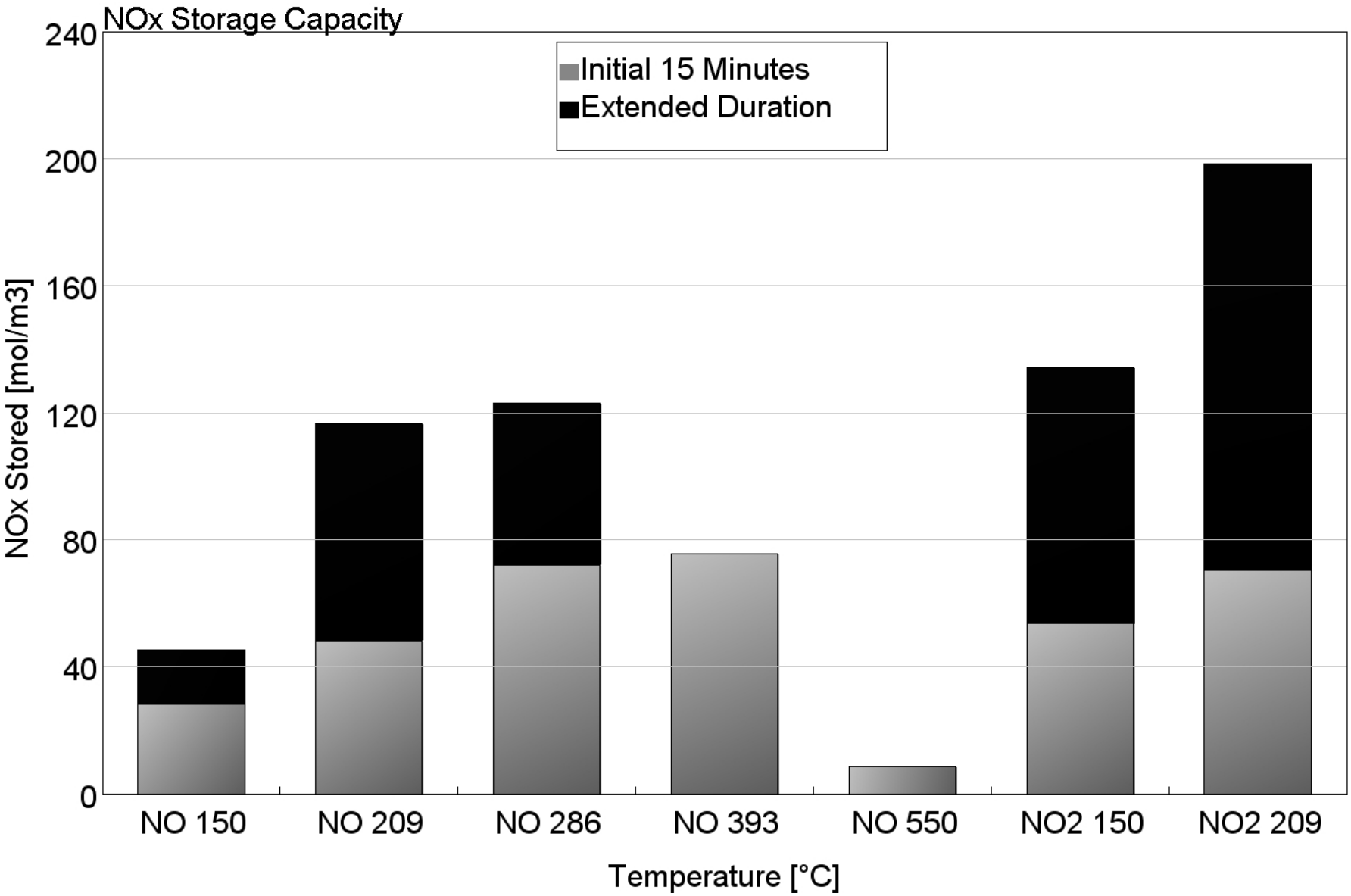


Variation with temperature of the NO and NO2 storage indicates the complexity of the storage mechanism

300 ppm NO

300 ppm NO_2

NOx Storage Capacity



Recap: NOx Storage – NO_2 Feed Experiments

- Three-step disproportion needed to match peak NO outlet concentration at 150°C for largest density site

$$BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO$$

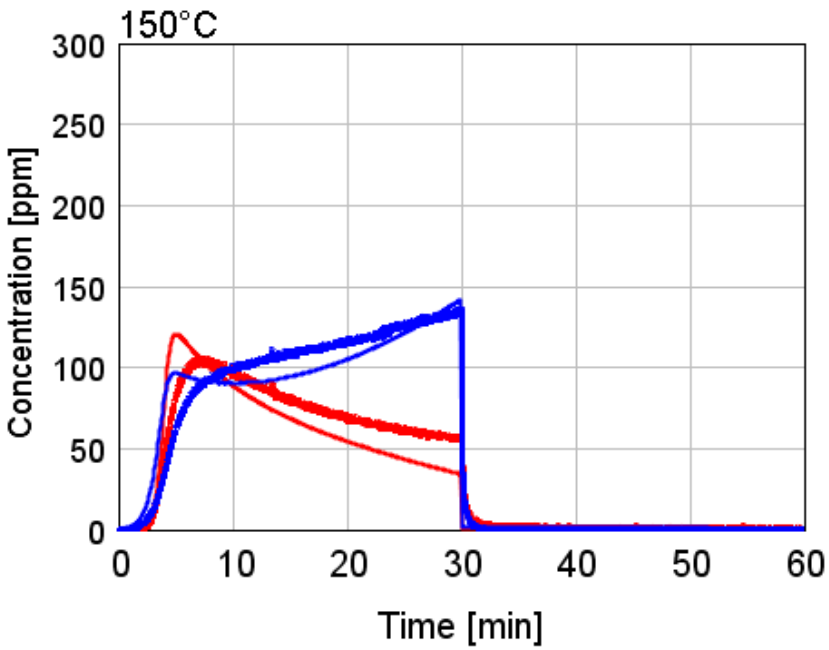
$$BaO + NO_2 \rightarrow BaO - NO_2$$

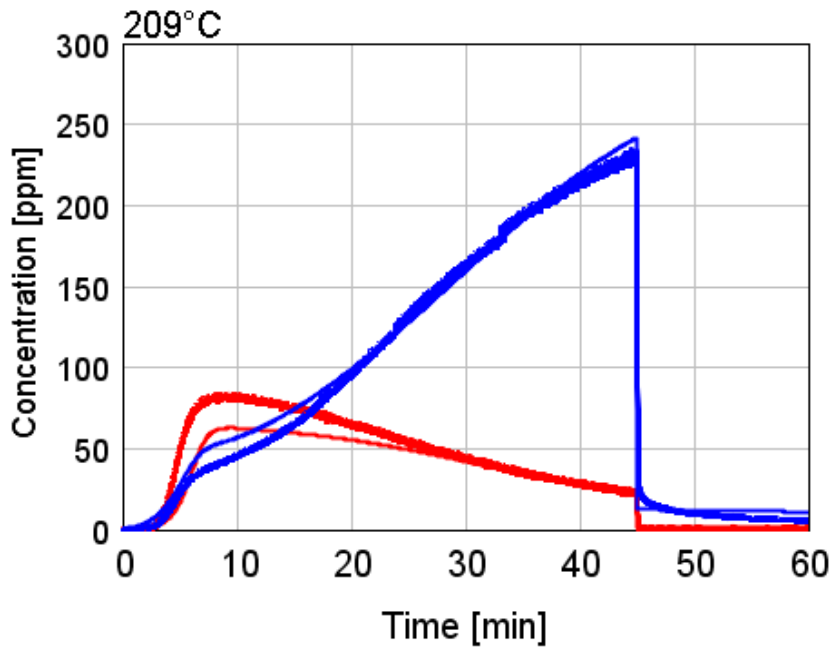
$$BaO - NO_2 \rightarrow BaO_2 + NO$$

$$BaO_2 + 2NO_2 \rightarrow Ba(NO_3)_2$$

rate-limited at low temperature

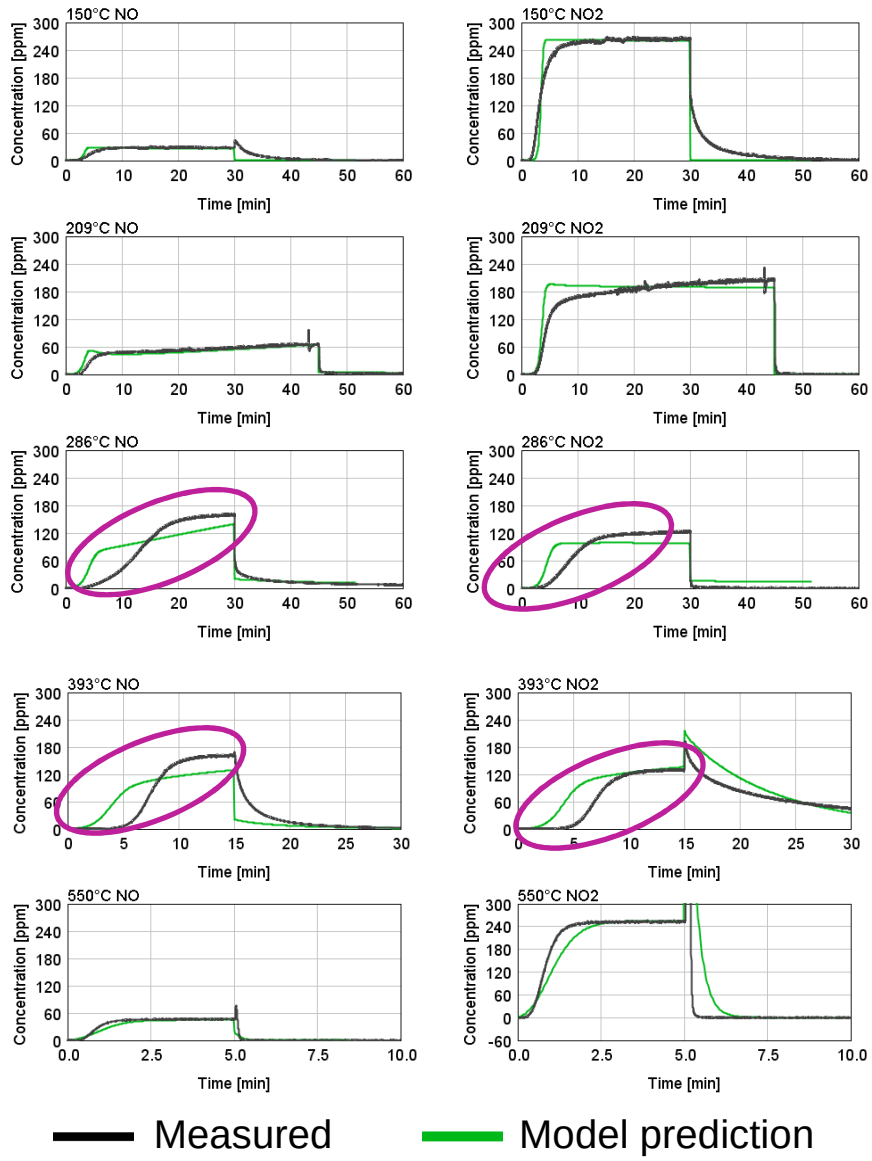
- Additional site needed to describe storage needed for delayed NO breakthrough





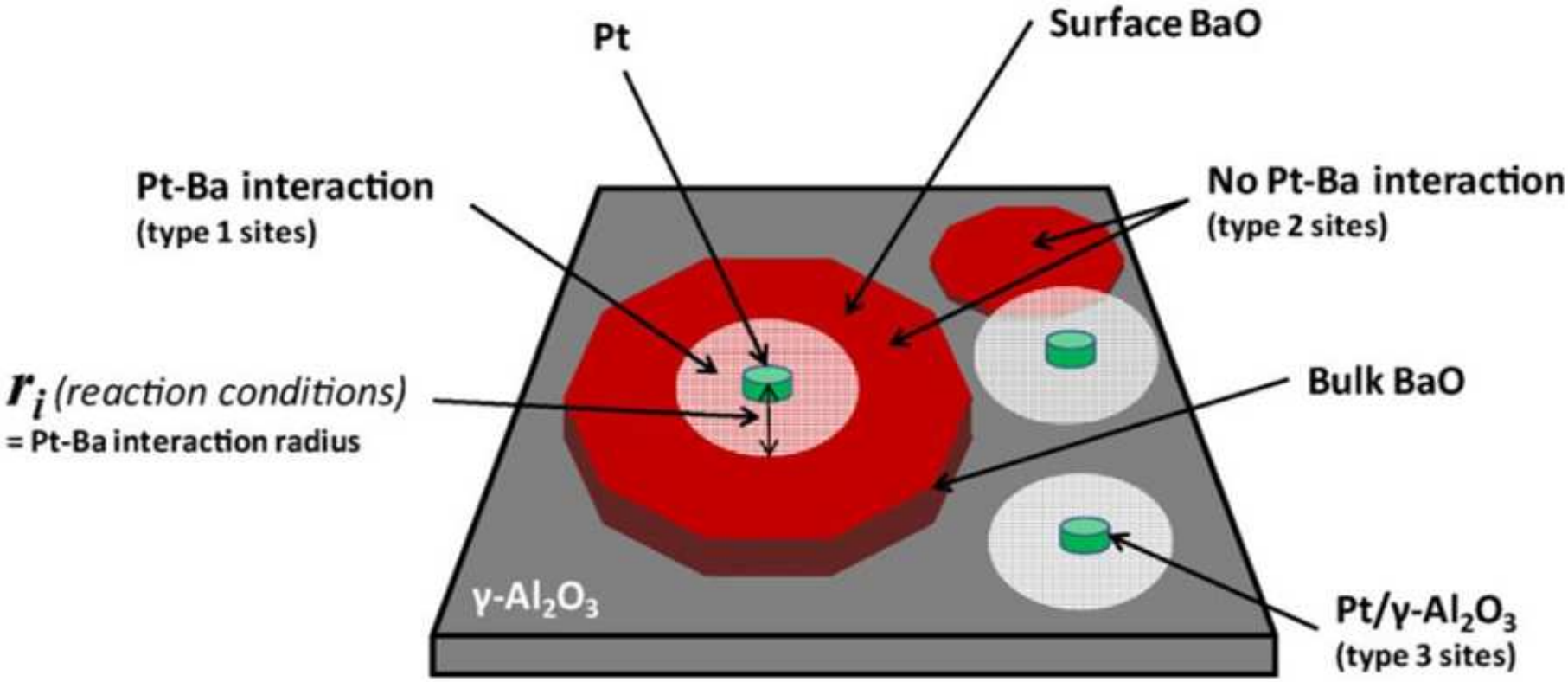
Recap: NOx Storage– NO Feed Experiments

- Typical mechanism
  - Two storage sites
  - Storage + release of both NO and NO_2
  - Retains satisfactory results with NO_2 experiments
- Additional work needed
  - Release at 150°C
  - Breakthroughs at 286°C and 393°C
- Data explicitly points to a required third storage site



Precedence for 3-Site Storage Mechanism

S.S. Chaugule et al. / Catalysis Today 151 (2010) 291–303 -Figure 11



NOx Storage Mechanism

$$Ba^{I}O + 2NO + 1.5O_2 \rightarrow Ba^{I}(NO_3)_2$$

$$Ba^{I}(NO_3)_2 \rightarrow Ba^{I}O + 2NO_2 + 0.5O_2$$

$$\boxed{Ba^{I}O + 3NO_2 \rightarrow Ba^{I}(NO_3)_2 + NO}$$

***3-step detailed disproportion**

$$Ba^{III}O + 2NO + 1.5O_2 \leftrightarrow Ba^{III}(NO_3)_2$$

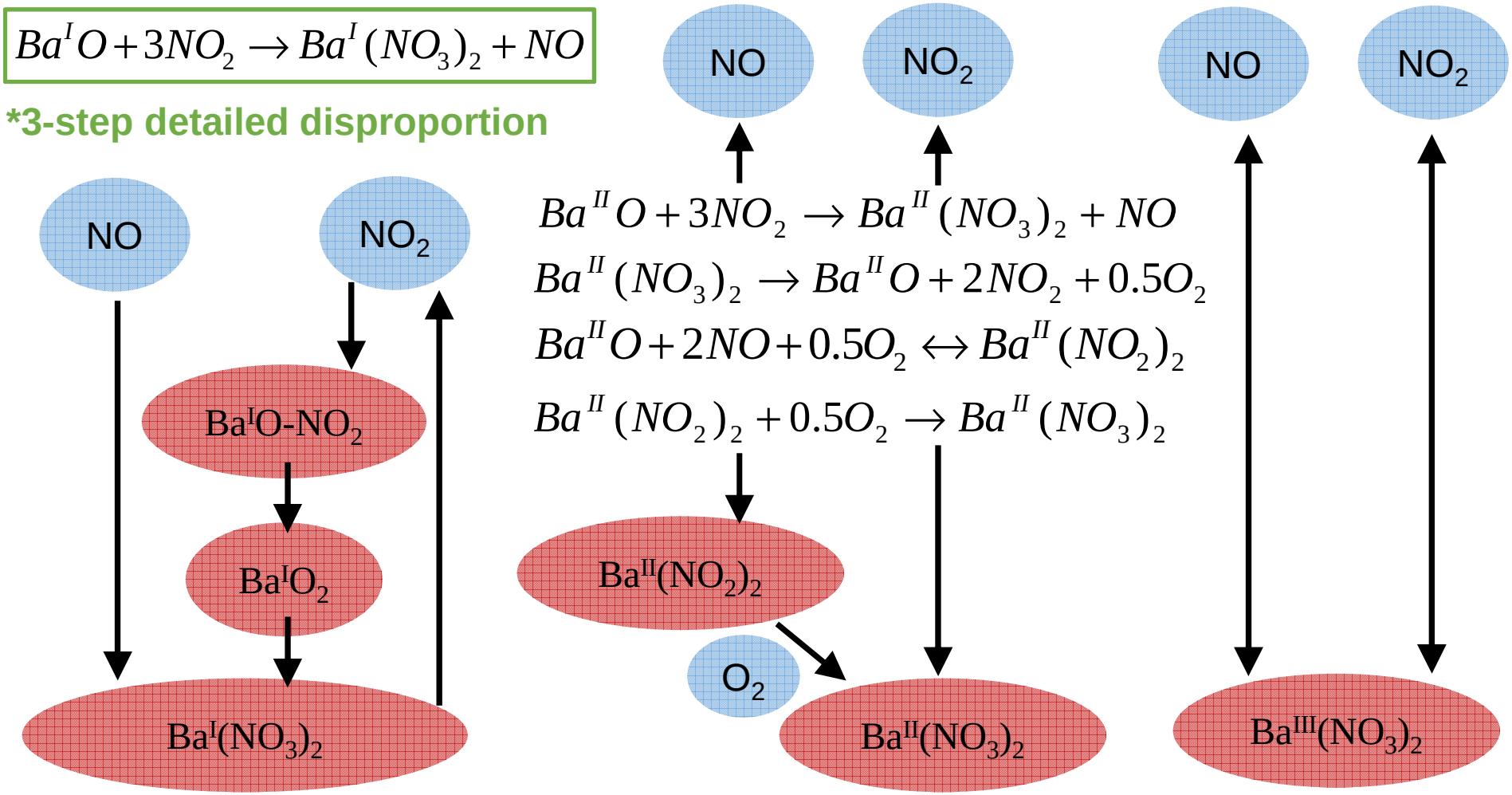
$$Ba^{III}O + 2NO_2 + 0.5O_2 \leftrightarrow Ba^{III}(NO_3)_2$$

$$Ba^{II}O + 3NO_2 \rightarrow Ba^{II}(NO_3)_2 + NO$$

$$Ba^{II}(NO_3)_2 \rightarrow Ba^{II}O + 2NO_2 + 0.5O_2$$

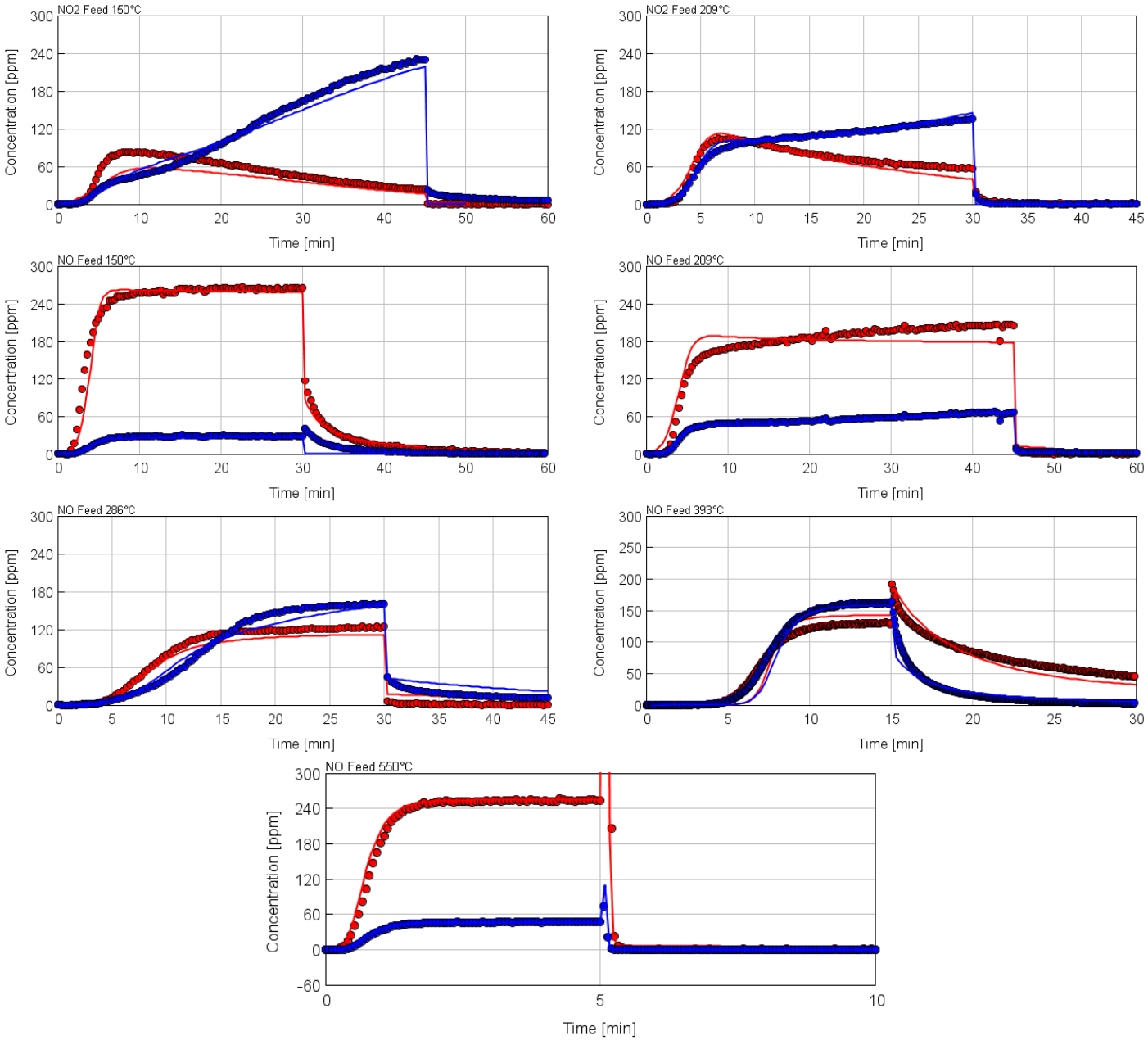
$$Ba^{II}O + 2NO + 0.5O_2 \leftrightarrow Ba^{II}(NO_2)_2$$

$$Ba^{II}(NO_2)_2 + 0.5O_2 \rightarrow Ba^{II}(NO_3)_2$$



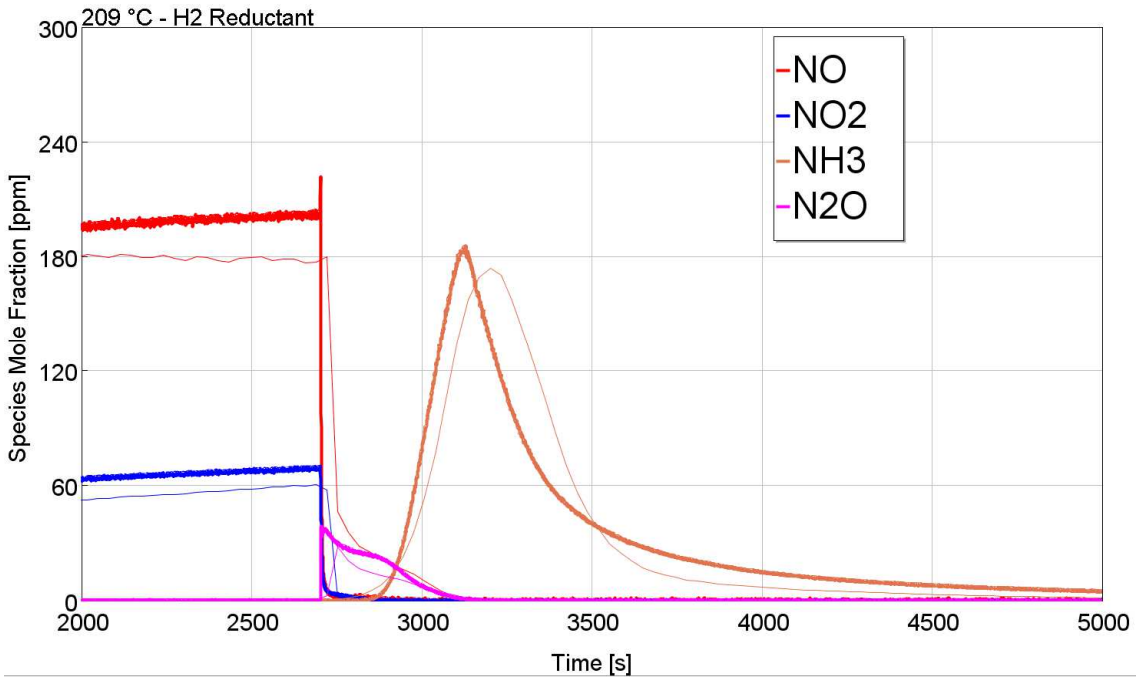
60 mol/m^3 Ba^{I} 14 mol/m^3 Ba^{II} 16 mol/m^3 Ba^{III}

NOx Storage Results

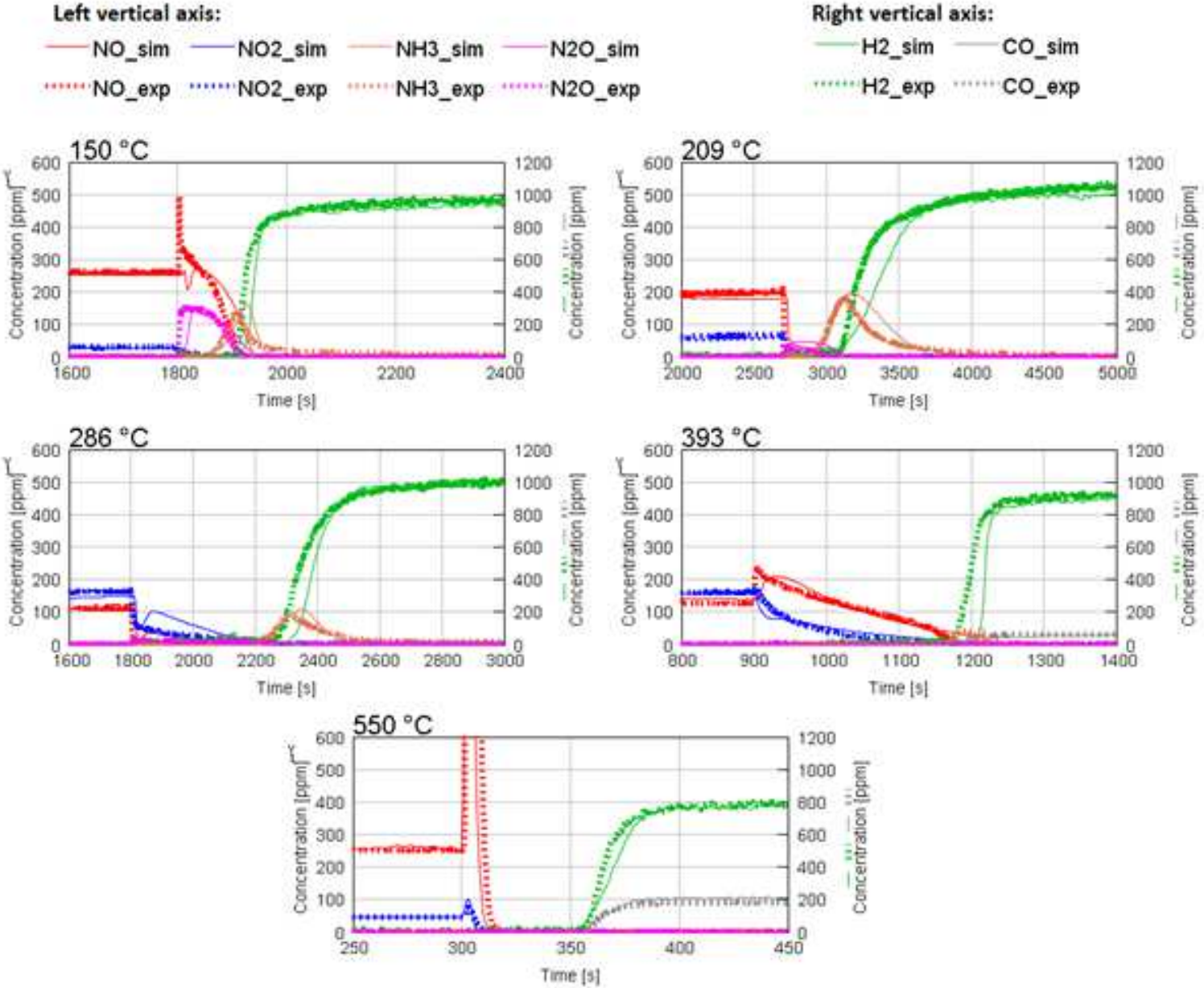


NOx Reduction via CO, H_2, C_3H_6

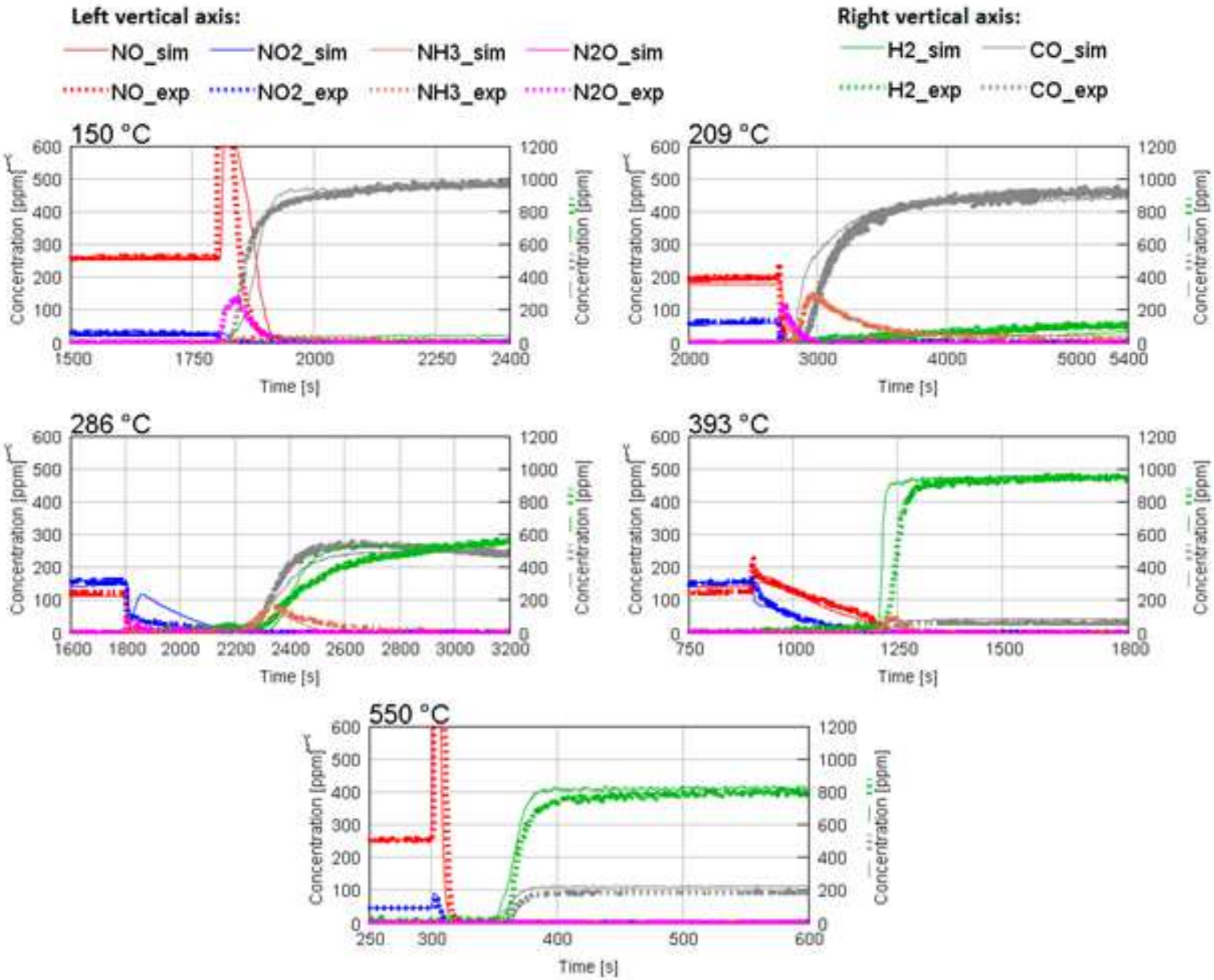
- When feeding CO and C_3H_6 as reductants, H_2 is still a primary cleanser of stored NOx after being generated from WGS and SRR, respectively
- NH_3 production occurs at lower temperatures and correlates to larger H_2 presence, as confirmed by others
- Model captures effect of NH_3 breakthrough after disappearance of N_2O



H_2 Reduction Mechanism Development



CO Reduction Mechanism Development



Conclusions

- A three site model is needed to adequately simulate the NOx storage
  - It is a physical approximation of the microkinetic conceptual model of Chaugule et al. (2010)

- Storage experiments show that the LNT procotol needs to be modified to achieve storage saturation in some long cycle measurements

- A full mechanism has been developed and implemented in GT-SUITE, including oxygen storage and NOx reduction steps

- A manuscript is in preparation for submission and will contain all site densities and kinetics parameters