Mechanism Development for the Simulation of LNT Lean/Rich Cycling

Richard S. Larson
Sandia National Laboratories, Livermore, CA

Kalyana Chakravarthy, Josh A. Pihl, and C. Stuart Daw
Oak Ridge National Laboratory, Knoxville, TN

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Overall objective

Develop an elementary surface reaction mechanism, complete with values for the kinetic parameters, that accounts for the observed product distribution from a lean NOx trap during both steady state and cyclical operation and under various conditions of temperature and inlet gas composition.

Basic approach

- Assemble tentative mechanisms for both precious metal (regeneration) and oxide (storage) sites, using reactions from literature together with additional hypothesized steps.
- Infer kinetic parameters for regeneration mechanism by matching product distributions from steady flow temperature ramp experiments done at ORNL.
  - Use Chemkin PLUG code to simulate (pseudo-) steady flow of reactant mixture through a catalyst monolith channel; temporarily discard storage mechanism.
  - Use Sandia APPSPACK code to carry out optimization.
  - Apply thermodynamic constraints to kinetic parameters in order to ensure complete consistency.

Basic approach (continued)

- **Infer kinetic parameters for storage mechanism by matching product distributions from cycling experiments done at ORNL.**
  - **Use new Chemkin-based transient plug flow code to simulate inherently unsteady storage/regeneration processes.**
  - **Incorporate thermodynamic constraints on kinetic parameters in storage mechanism.**
  - **Use regeneration parameters previously determined (ideally) or allow adjustments and reconsider temperature ramp data.**

Recent accomplishments

- **Formulated and implemented a complete set of thermodynamic constraints (all reactions treated as reversible with mass action kinetics).**

- **Completed construction of regeneration mechanism and optimization of kinetic parameters (72 adjustable, 96 total).**

- **Implemented a rate constant cap in order to alleviate mathematical stiffness.**

- **Verified thermodynamic consistency of regeneration mechanism via comparison of kinetic (tube flow) and equilibrium calculations.**

Recent accomplishments (continued)

- **Identified several instances of steady state multiplicity in simulations of temperature ramp experiments.**

- **Initiated simulation of complete storage/regeneration cycles with combined mechanism.**

Summary of “final” regeneration mechanism

- **10 gas phase species: O2, NO, NO2, CO, H2, CO2, N2, H2O, N2O, NH3**
- **13 surface species on precious metal (nominally platinum) sites: *(PT), O(PT), NO(PT), NO2(PT), CO(PT), H(PT), N(PT), OH(PT), H2O(PT), NH(PT), NH2(PT), NCO(PT), NH3(PT)**
- **No homogeneous gas phase reactions**
- **24 surface reactions, all of them reversible (in principle; five are found to be effectively irreversible)**

The reaction set includes many adsorption/ desorptions (some dissociative) …

O2 + 2 *(PT) = 2O(PT)

NO + *(PT) = NO(PT)

NO2 + *(PT) = NO2(PT)

CO + *(PT) = CO(PT)

H2 + 2 *(PT) = 2H(PT)

H2O + *(PT) = H2O(PT)

NH3 + *(PT) = NH3(PT)

2N(PT) = N2 + 2 *(PT)

CO(PT) + O(PT) = CO2 + 2 *(PT)

… and surface decomposition/recombinations.

NO2(PT) + *(PT) = NO(PT) + O(PT)

NO(PT) + *(PT) = N(PT) + O(PT)

H2O(PT) + *(PT) = H(PT) + OH(PT)

OH(PT) + *(PT) = H(PT) + O(PT)

NH(PT) + *(PT) = N(PT) + H(PT)

NH2(PT) + *(PT) = NH(PT) + H(PT)

NH3(PT) + *(PT) = NH2(PT) + H(PT)

Indirect reduction with CO can take place via two distinct pathways.

Hydrogen production via a water-gas shift reaction:

$$H_2O(PT) + CO(PT) = 2H(PT) + CO_2$$

Reaction of water with an isocyanate intermediate:

$$N(PT) + CO = NCO(PT)$$

$$NCO(PT) + H_2O(PT) = NH_2(PT) + CO_2 + *(PT)$$

The remaining reactions can be categorized as atom transfers.

$N_2O + H(PT) = N_2 + OH(PT)$

$2NO(PT) = N_2O + O(PT) + *(PT)$

$NO_2(PT) + CO(PT) = NO(PT) + CO_2 + *(PT)$

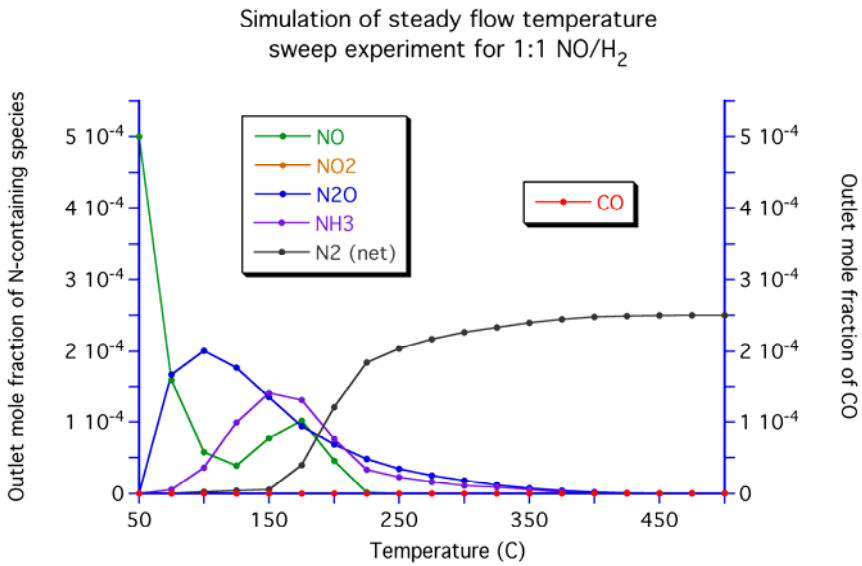
$NO(PT) + NH_2(PT) = N_2O + 2H(PT)$

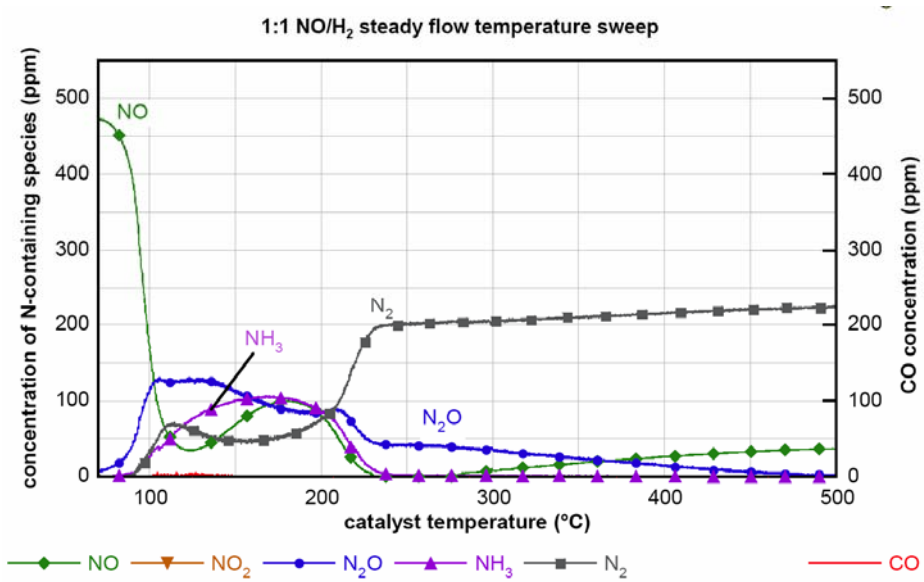
$NH_3(PT) + O(PT) = NH_2(PT) + OH(PT)$

Recap of steady flow experiments (ORNL)

- 21 separate runs with inlet compositions involving NO/H2, NO/CO, NO2/H2, NO2/CO, N2O/H2, N2O/CO, NH3/O2, NH3/NO, NH3, H2, or CO
- 5% H2O, 5% CO2, N2 carrier gas in all runs
- Temperature ramped from below 100 C to 500 C at 5 C/min
- Space velocity 100,000/hr
- Commercially available Umicore GDI LNT catalyst
- Chemiluminescent analyzers for NO and total NOx; FTIR for CO, NH3, and N2O; net N2 by difference

For a stoichiometric NO/H2 feed, nearly all features are reproduced accurately.





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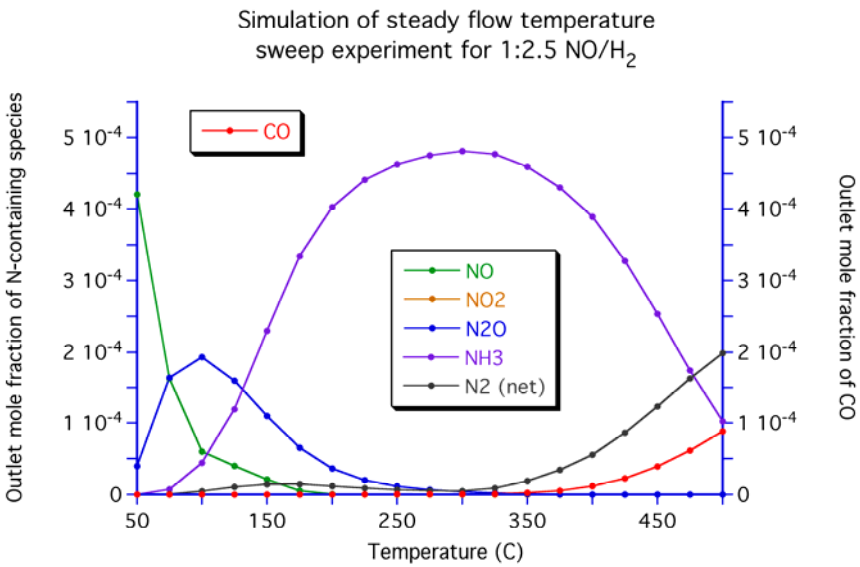
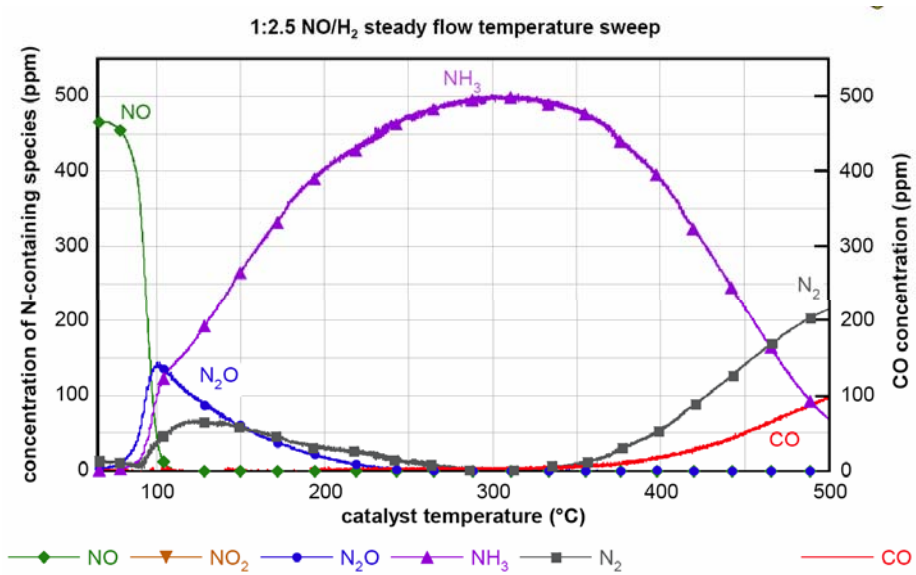
For NO with excess H2, the onset temperature for NH3 formation is now reproduced quite well.





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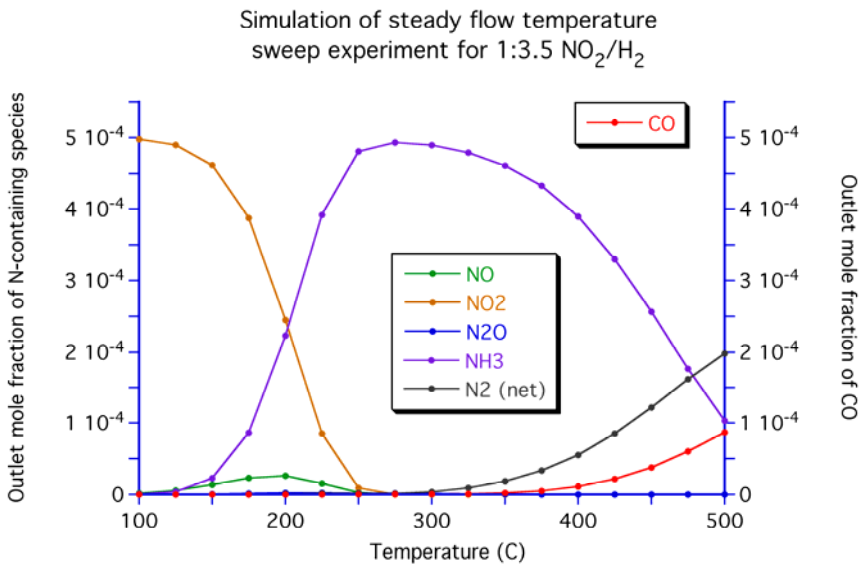
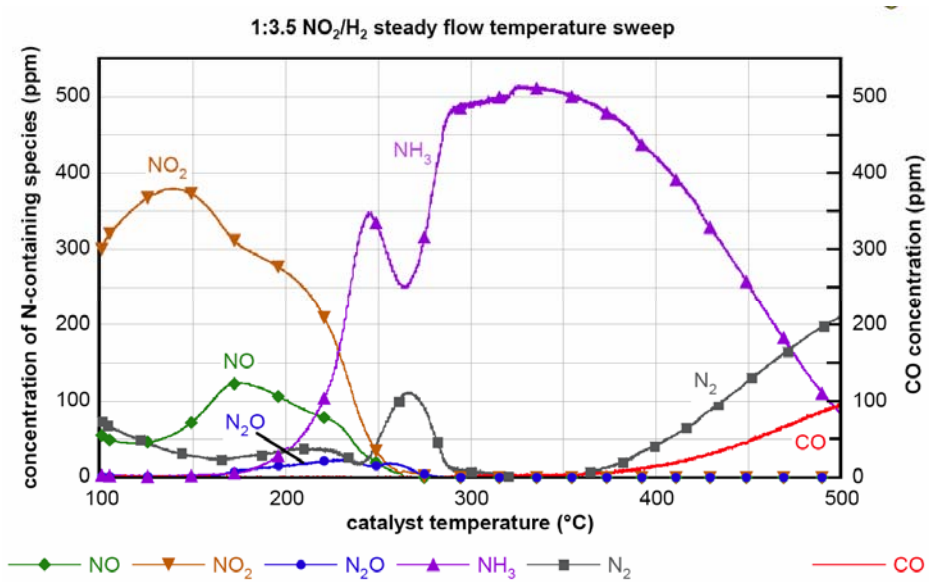
Reduction of NO2 by H2 is now simulated significantly better than before.





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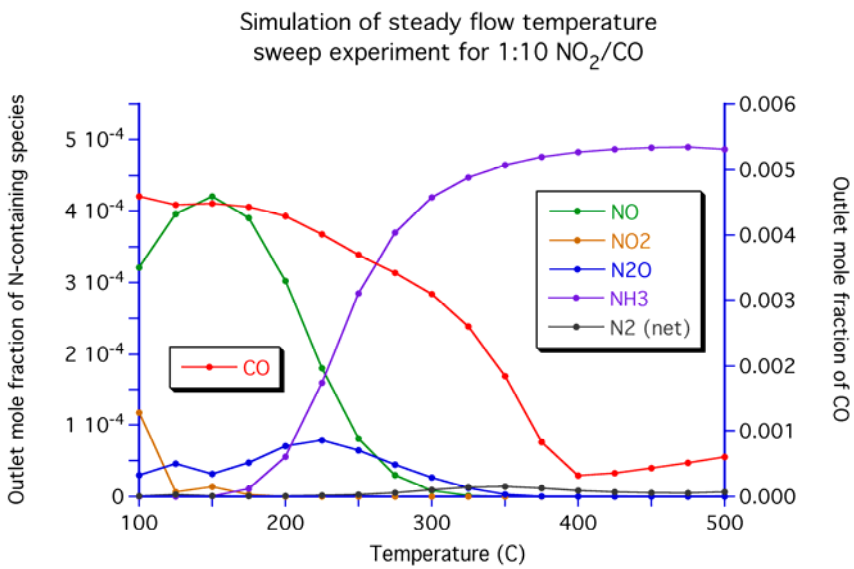
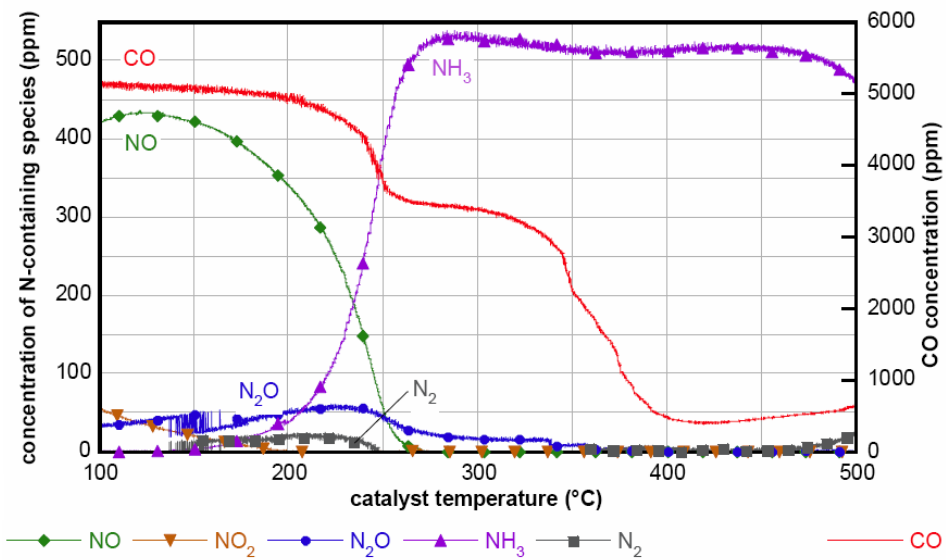
For 1:10 NO2/CO, the observed two-step drop in CO is mostly smoothed out by the model.





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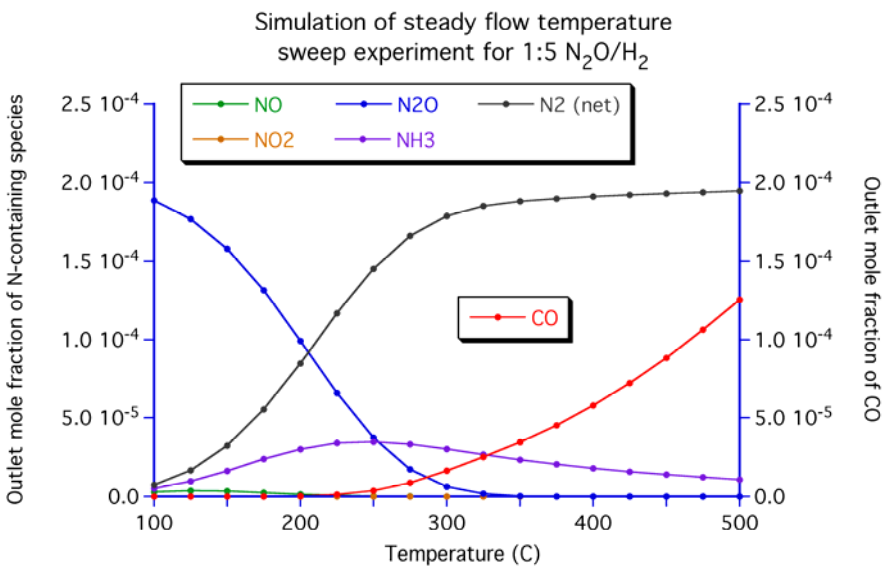
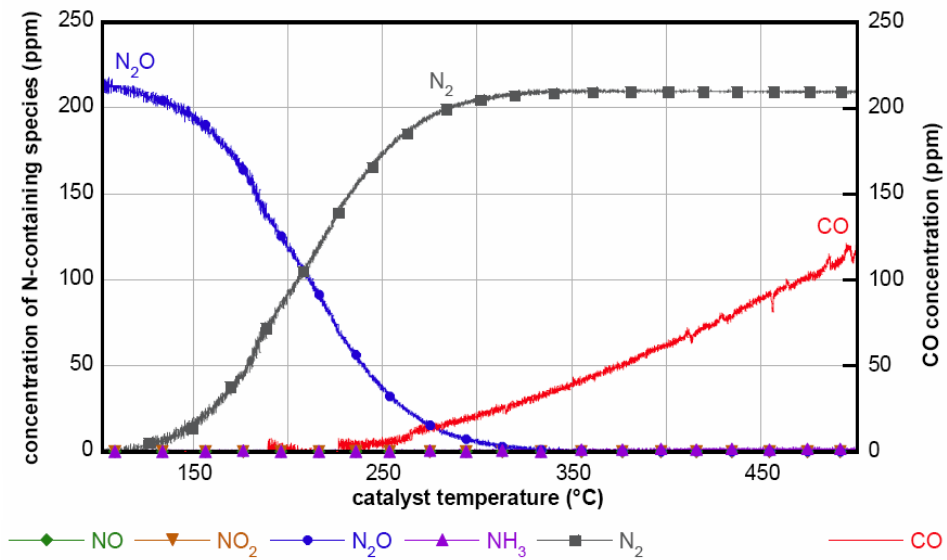
For reduction of N2O with a large excess of H2, the model predicts some NH3 formation.





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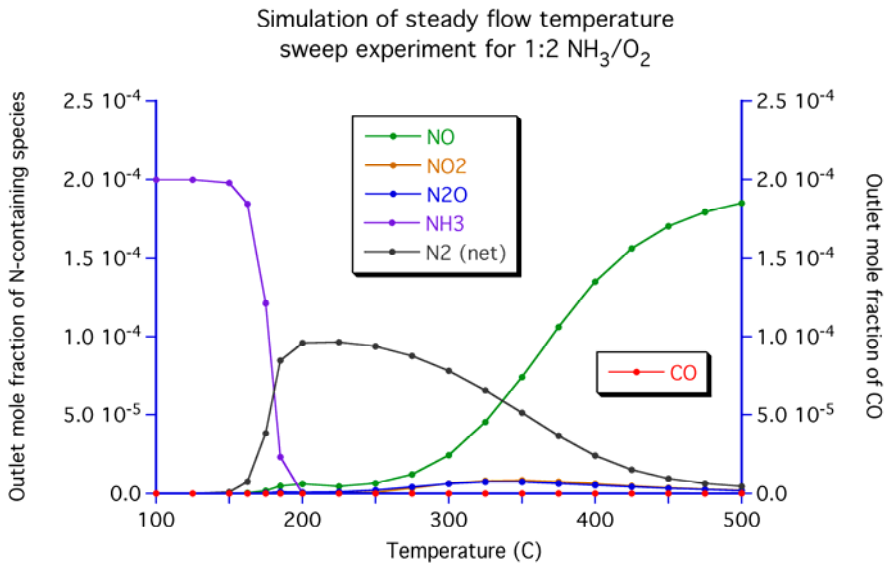
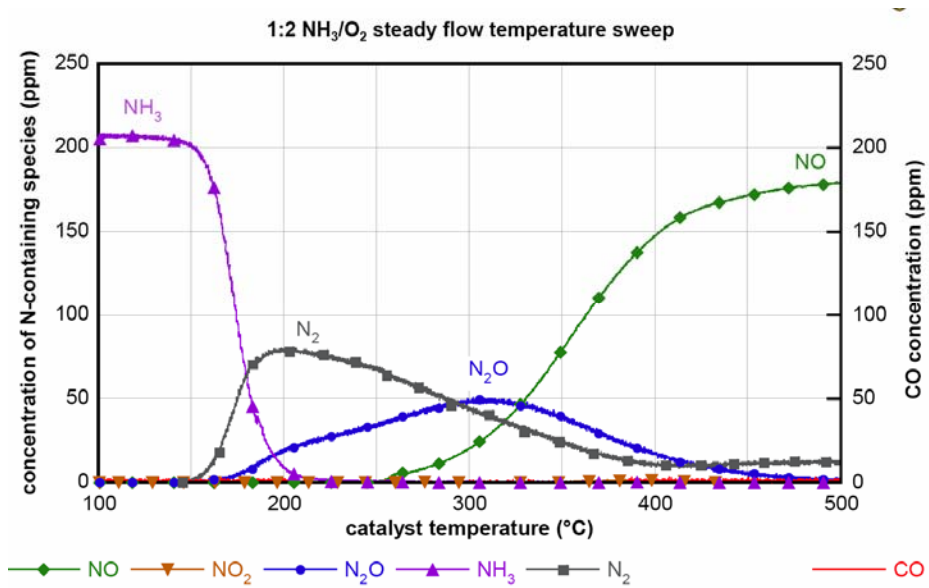
In direct oxidation of NH3 by O2, production of N2O tends to be seriously underpredicted.





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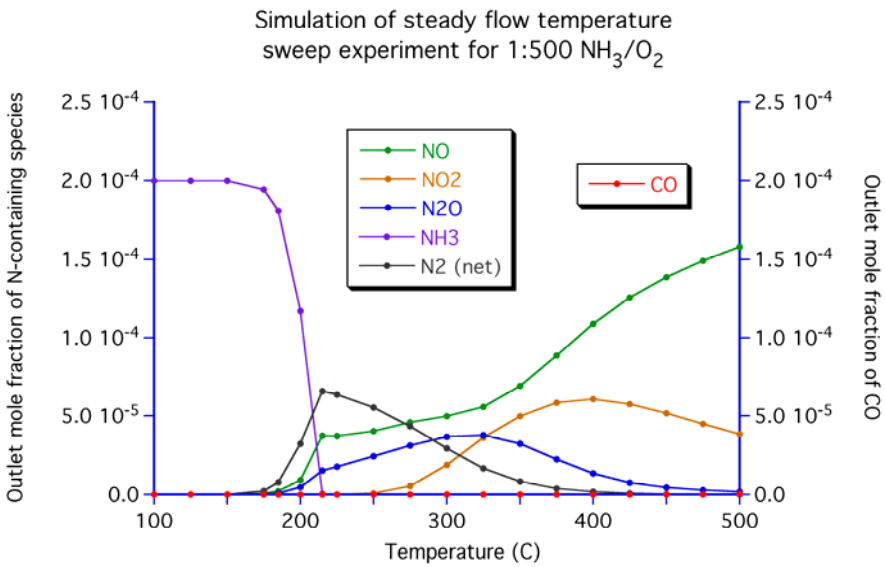
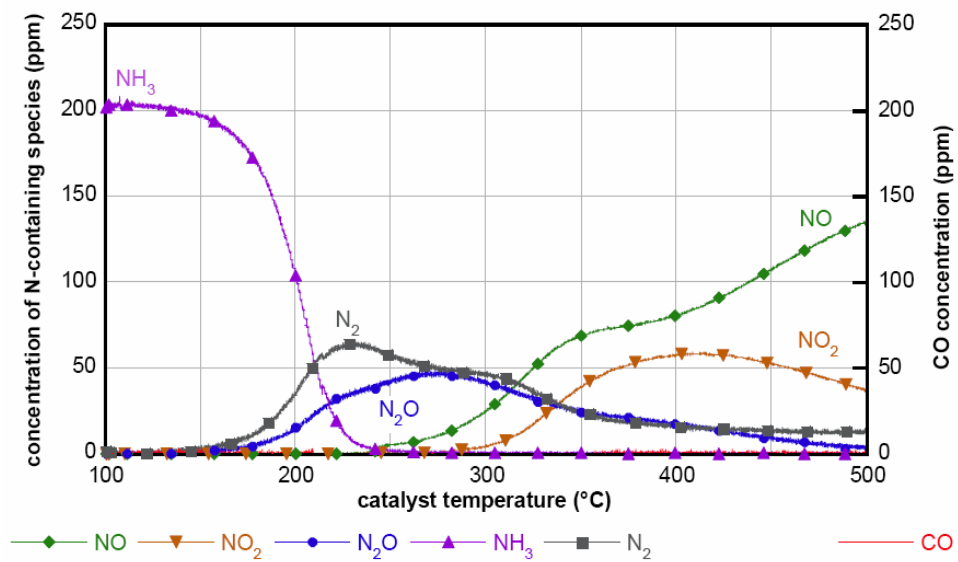
Oxidation of NH3 by a large excess of O2 is handled better, but NO appears too early.





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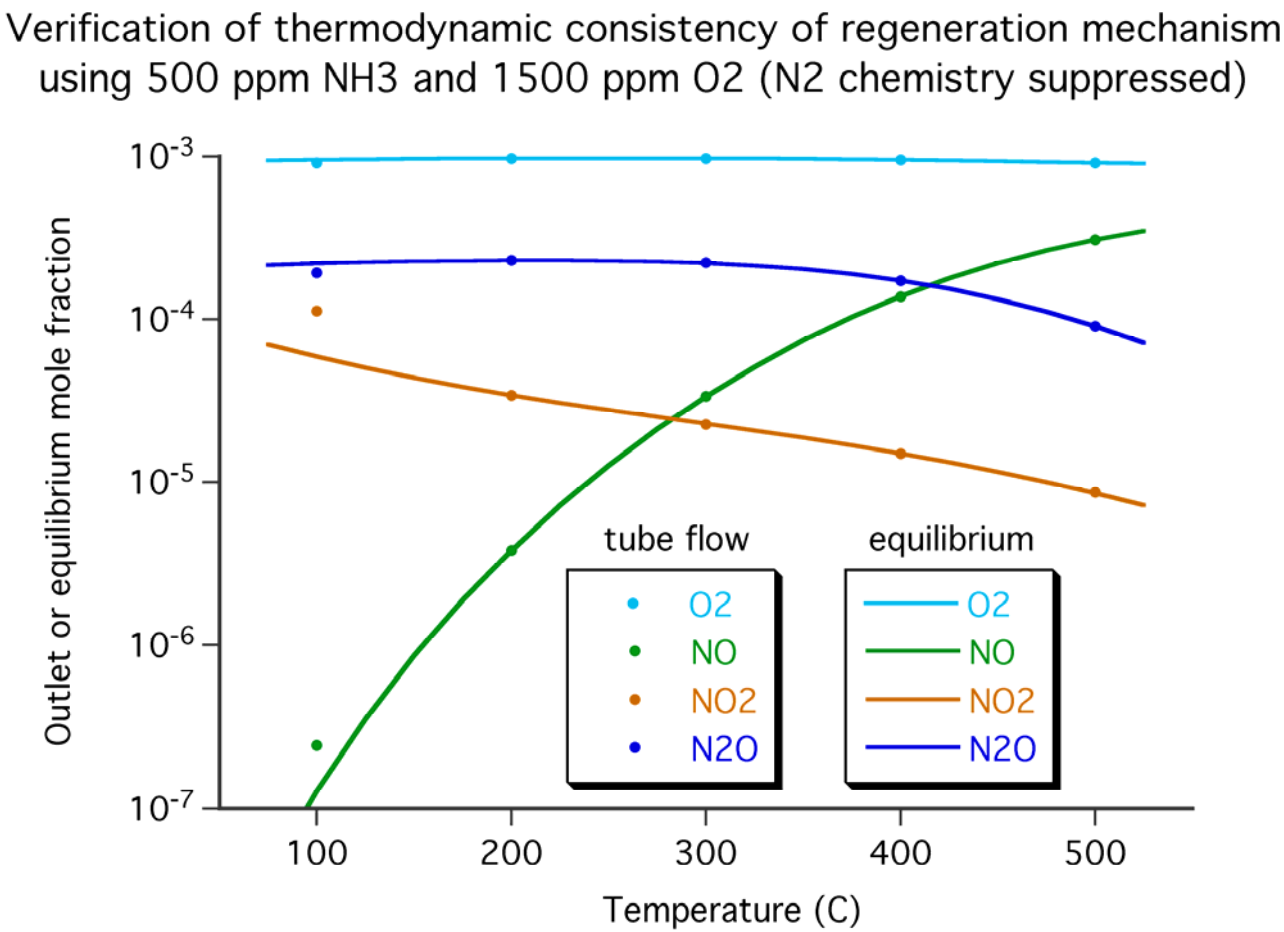
Thermodynamic consistency has been verified via infinite residence time tube flow simulations.



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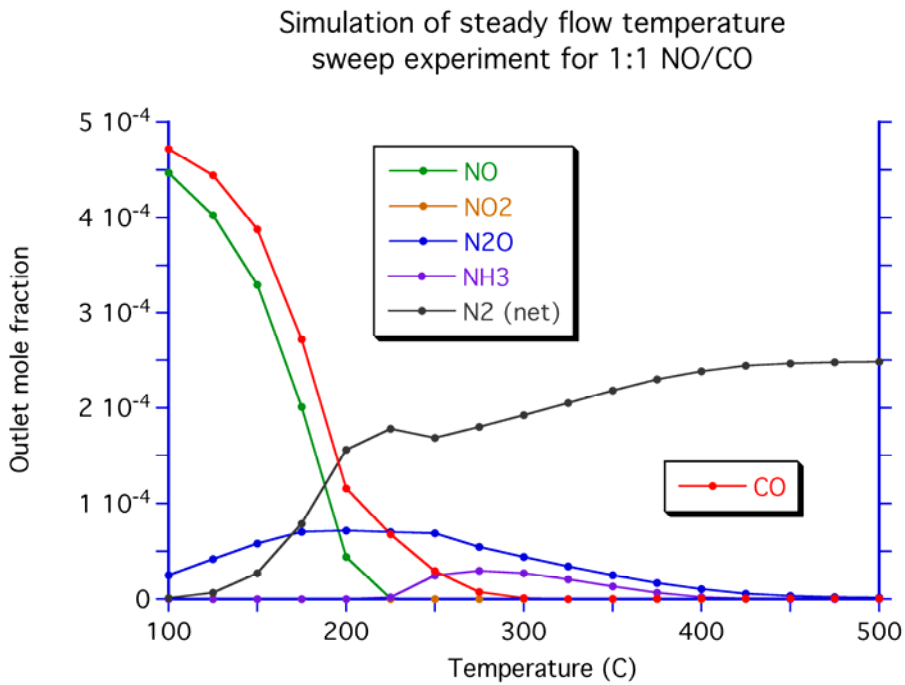
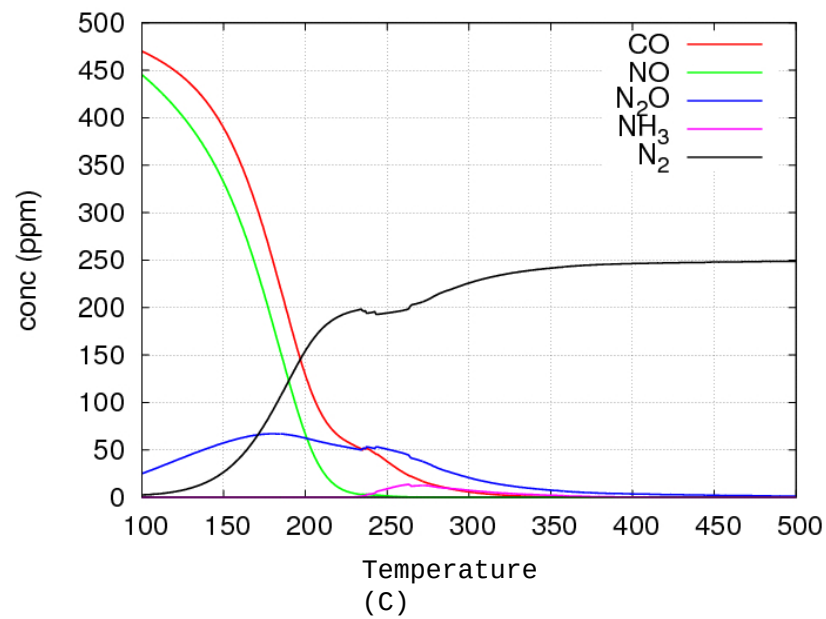
Transient simulations confirm that the temperature ramps can *generally* be treated as pseudo-steady.

pseudo-steady



transient



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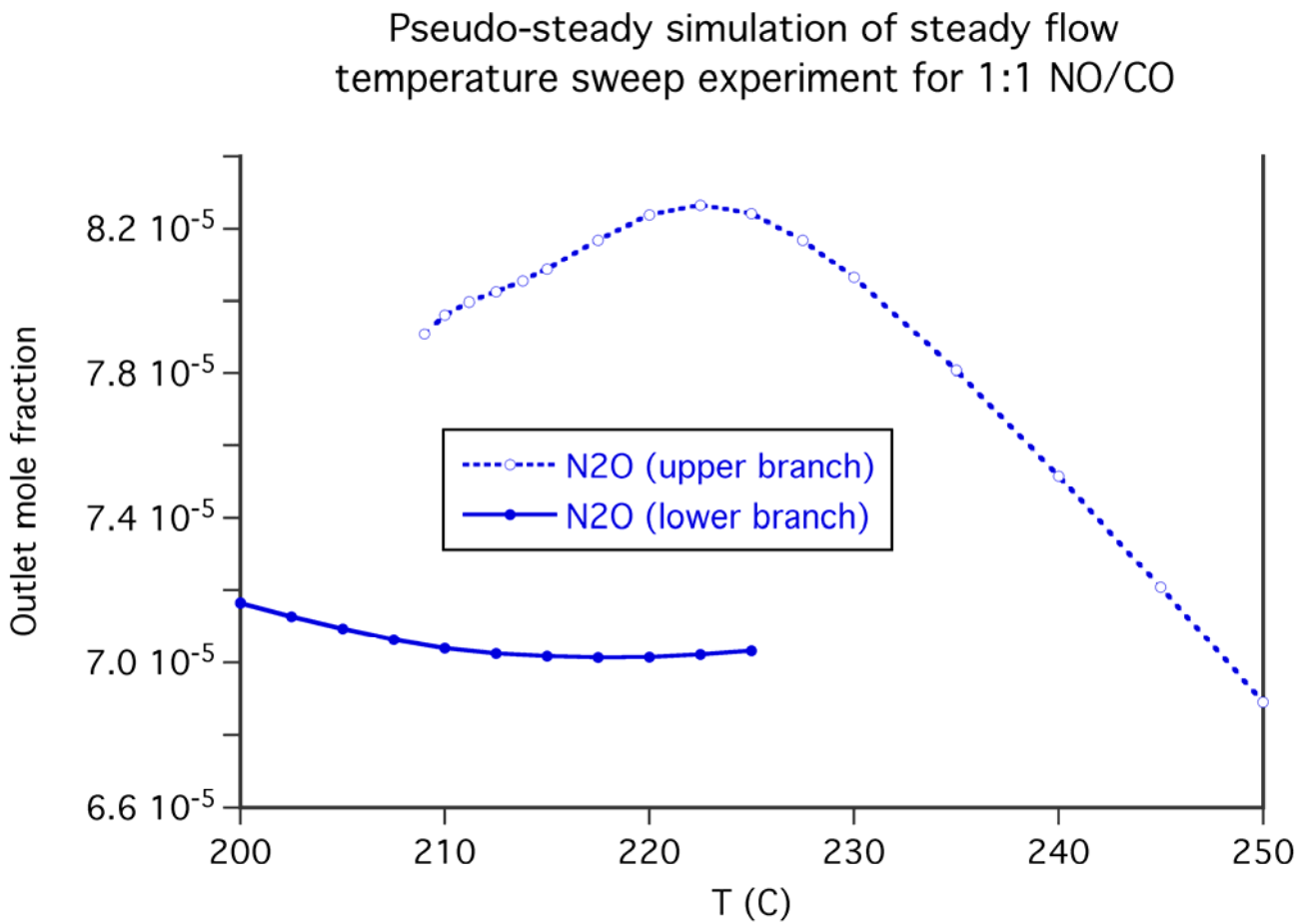
The complexity of the mechanism causes multiple steady states to occur locally, generally at low T.



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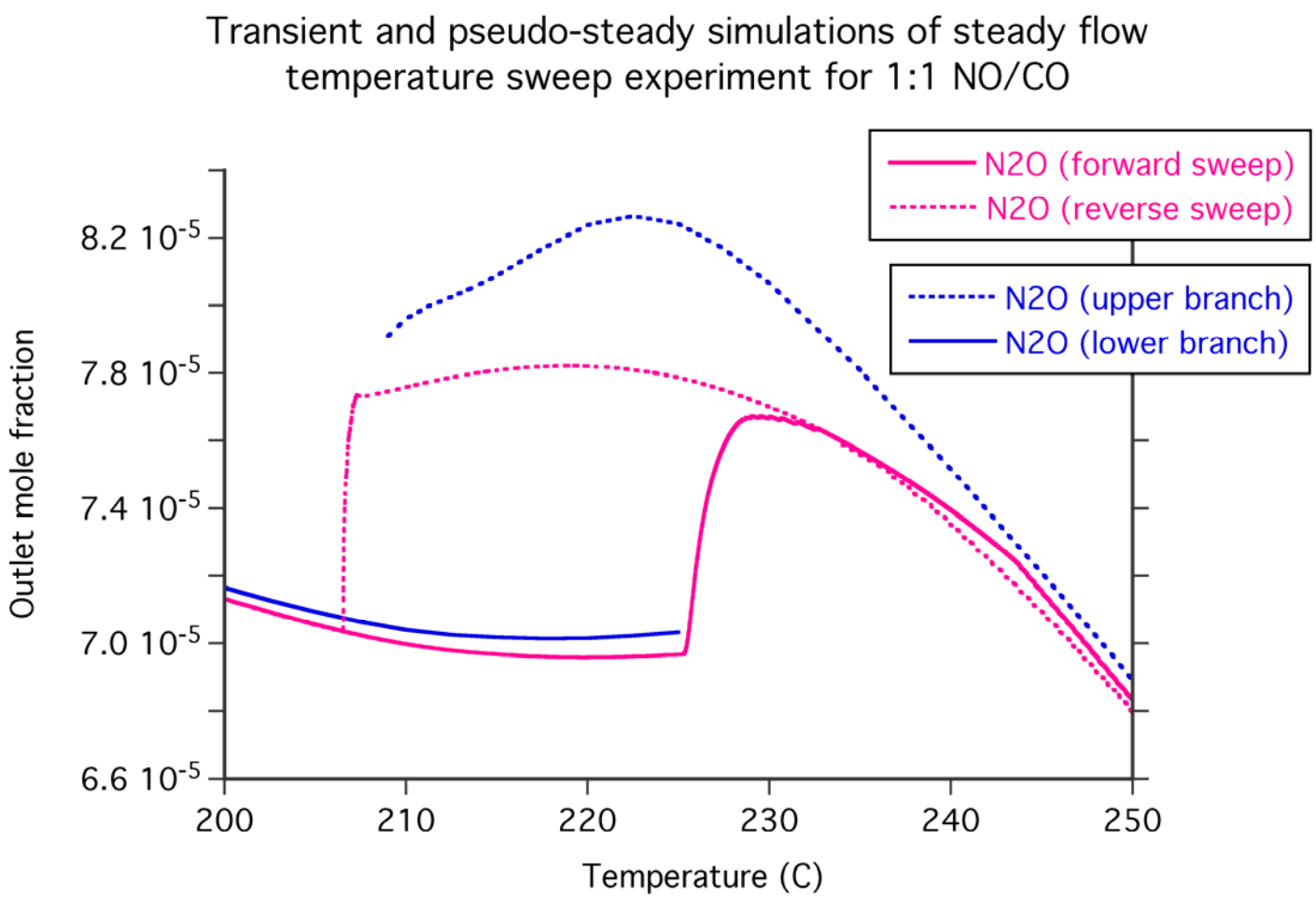
Fully transient simulations show local non-pseudo-steady behavior and hysteresis.



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The regeneration mechanism has been augmented with reactions occurring on storage sites.

$NO_2 + *(BAO) = NO_2(BAO)$

$NO_2 + NO_2(BAO) = NO + NO_3(BAO)$

$O_2 + 2\,*(BAO) = 2O(BAO)$

$NO + O(BAO) = NO_2(BAO)$

$NO_2 + O(BAO) = NO_3(BAO)$

$CO_2 + O(BAO) = CO_3(BAO)$

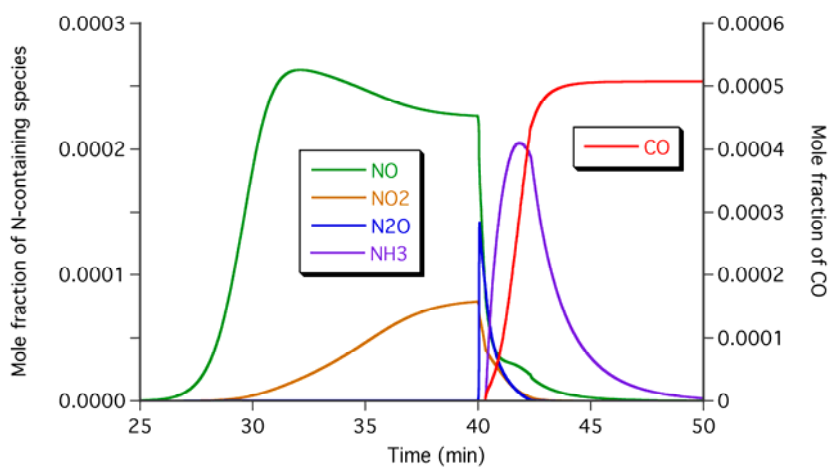
$NO + CO_3(BAO) = NO_2(BAO) + CO_2$

$NO_2 + CO_3(BAO) = NO_3(BAO) + CO_2$

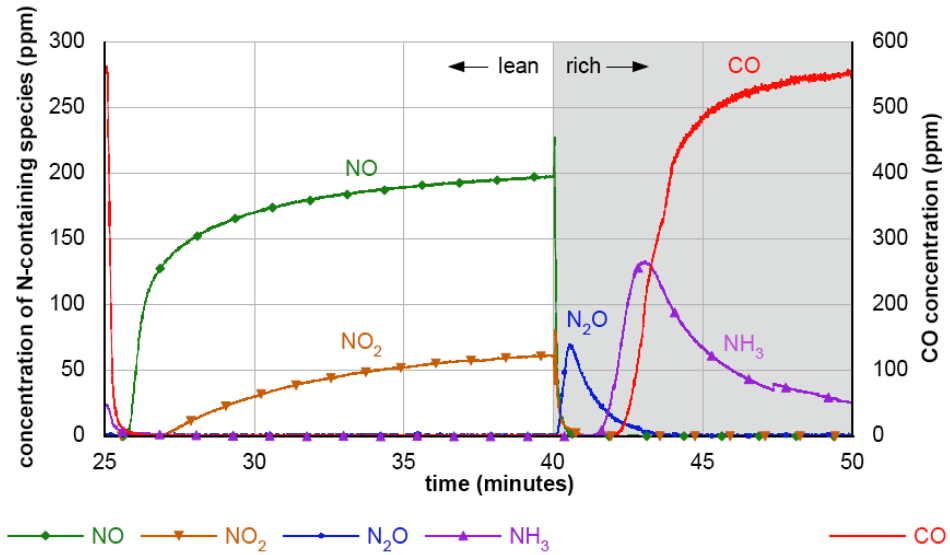
$NO_2(PT) + *(BAO) = NO_2(BAO) + *(PT)$

Preliminary cycle simulations with the combined mechanism show the correct qualitative behavior.

simulation



experiment



Long cycle test on Umicore catalyst at 200 C and 30000/hr space velocity;

15 min lean (300 ppm NO, 10% O2), 10 min rich (625 ppm CO, 375 ppm H2)

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Conclusions and future directions

- A robust, thermodynamically consistent mechanism for LNT regeneration has been developed.
- The mechanism tends to underestimate N2O production during NH3 oxidation and overestimate NH3 production during N2O reduction.
- Multiple steady states can occur and appear to be the result of parallel paths for reduction of NOx by CO.
- The proposed storage mechanism seems promising, but much work on parameter estimation (at least) is needed.
- Eventually, companion mechanisms for reduction by hydrocarbons and for sulfation/desulfation will be required.