Modeling Kinetics of NH3 and N2O Formation in Lean NOx Traps

Richard Larson
Sandia National Laboratories, Livermore, CA

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

Ninth CLEERS Workshop

Dearborn, MI

May 4, 2006

Sandia National Laboratories

ORNL

Principal 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 operating in the regeneration phase under various conditions of temperature and inlet gas composition.

Basic approach

- Assemble a tentative set of reaction steps and kinetic parameters for NOx reduction chemistry -- some from catalysis literature, others hypothesized.
- Use Chemkin PLUG code to simulate (pseudo-) steady state flow of reactant mixture through a monolith channel.
- Adjust kinetic parameters (pre-exponential factors and activation energies) to match product distributions from temperature ramp experiments done at Oak Ridge.
- Determine sensitivity of results to individual reactions and discard those found to be insignificant.

Basic approach (continued)

- Perform transient simulations for all cases in order to assess the validity of assuming pseudo-steady conditions.
- Apply thermodynamic constraints to reduced mechanism and re-optimize parameters to obtain a completely consistent set (in progress).

Features of current reaction mechanism

- 10 gas phase species: O_2, NO, NO_2, CO, H_2, CO_2, N_2, H_2O, N_2O, NH_3.
- 13 surface species on precious metal (nominally platinum) sites: S(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).
- 14 reversible and 15 irreversible surface reactions.
- N_2 appears strictly as a reaction product.
- N_2O reduction leads directly to N_2 (necessary to prevent NH_3 formation).

With one exception, the reversible reactions are all adsorption/desorptions …

$O_2 + 2S(PT) = 2O(PT)$

$NO + S(PT) = NO(PT)$

$NO_2 + S(PT) = NO_2(PT)$

$CO + S(PT) = CO(PT)$

$H_2 + 2S(PT) = 2H(PT)$

$H_2O + S(PT) = H_2O(PT)$

$NH_3 + S(PT) = NH_3(PT)$

… and decomposition/recombinations.

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

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

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

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

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

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

Reduction with CO can take place via two distinct pathways.

Hydrogen production via water-gas shift reaction:

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

Reaction of water with isocyanate intermediate:

$$N(PT) + CO \Rightarrow NCO(PT)$$

$$NCO(PT) + H_2O(PT) \Rightarrow NH_2(PT) + CO_2 + S(PT)$$

All other recombinations and atom transfers are treated as irreversible.

N2 formation:

2N(PT) => N2 + 2S(PT)

2NO(PT) => N2 + 2O(PT)

N2O + H(PT) => N2 + OH(PT)

N2O + CO(PT) => N2 + CO2 + S(PT)

N2O formation:

NO(PT) + N(PT) => N2O + 2S(PT)

2NO(PT) => N2O + O(PT) + S(PT)

NO(PT) + NH2(PT) => N2O + H2 + 2S(PT)

Irreversible reactions (continued)

Miscellaneous reactions:

NO2(PT) + CO(PT) => NO(PT) + CO2 + S(PT)

NH(PT) + O(PT) => NO(PT) + H(PT)

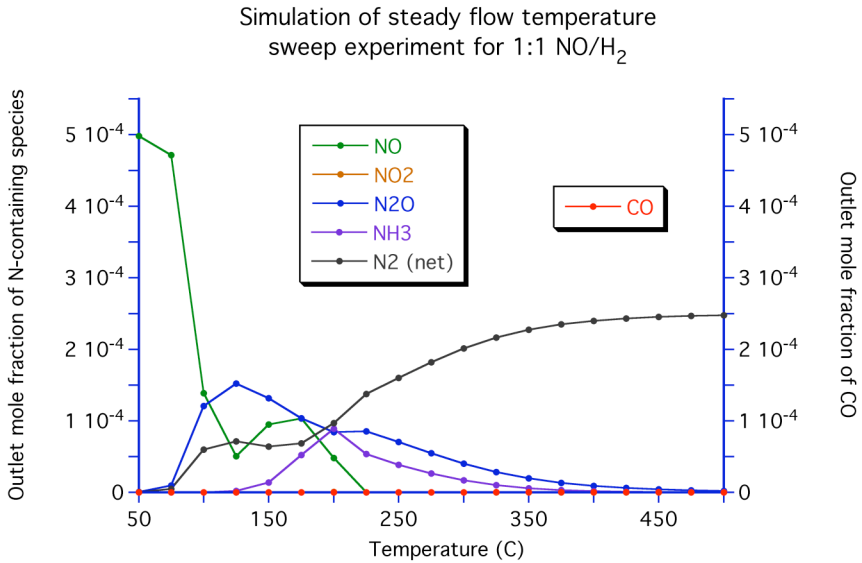
NH3(PT) + O(PT) => NH2(PT) + OH(PT)

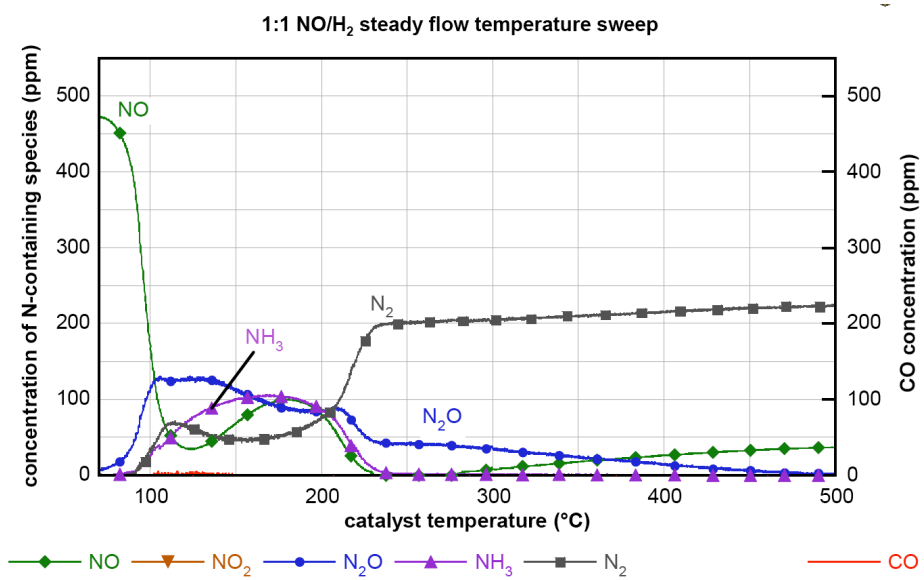
N2O + O(PT) => NO + NO(PT)

CO(PT) + O(PT) => CO2 + 2S(PT)

H(PT) + OH(PT) => H2O(PT) + S(PT)

For a stoichiometric (1:1) NO/H2 feed, the model shows N2O and NH3 formation at low T.

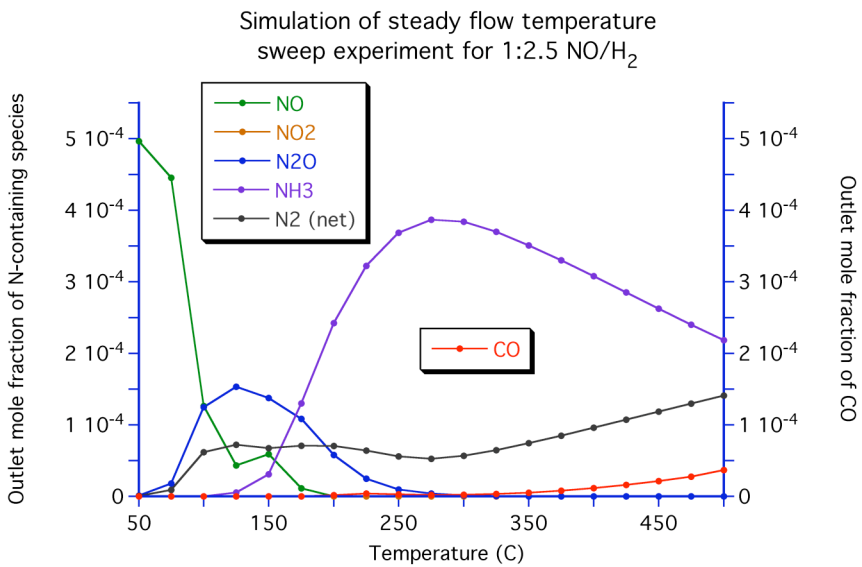


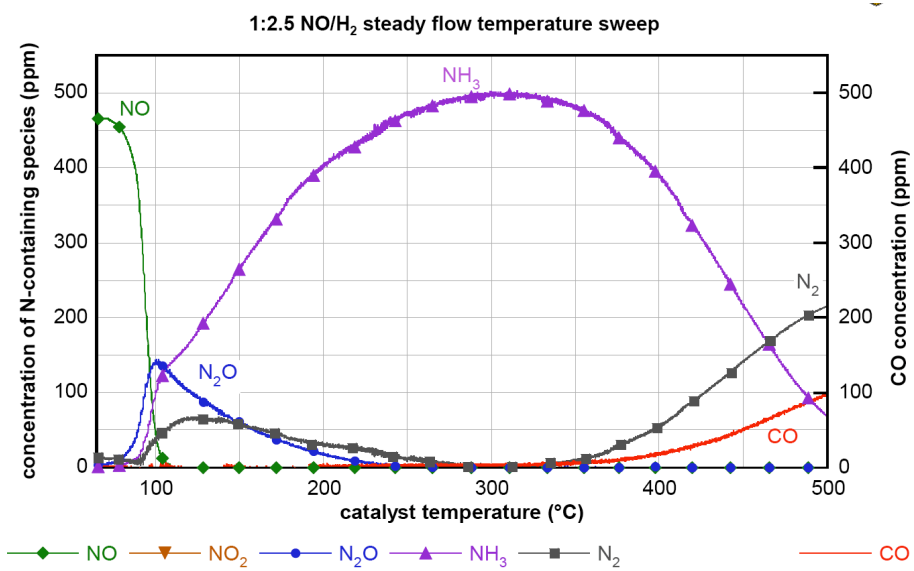


Sandia National Laboratories

ORNL

For NO with excess H2, the onset temperature for NH3 formation is somewhat too high.

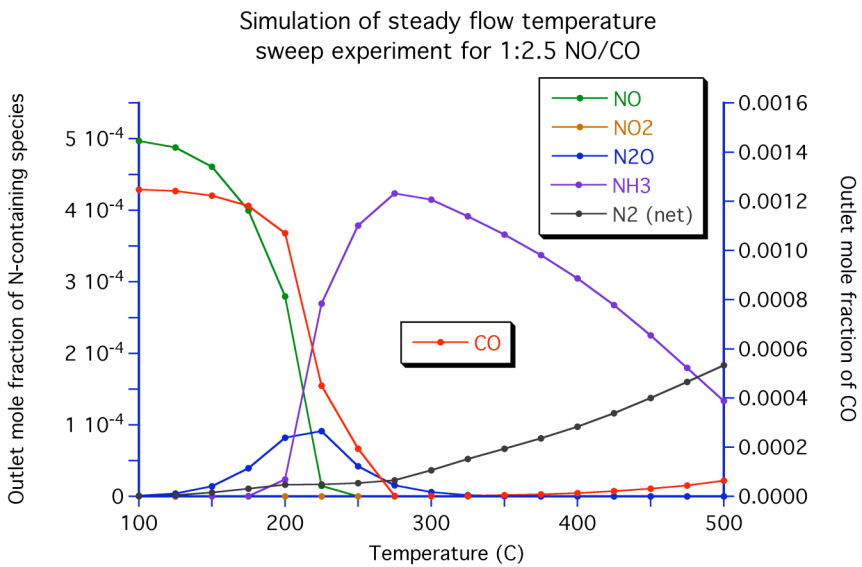


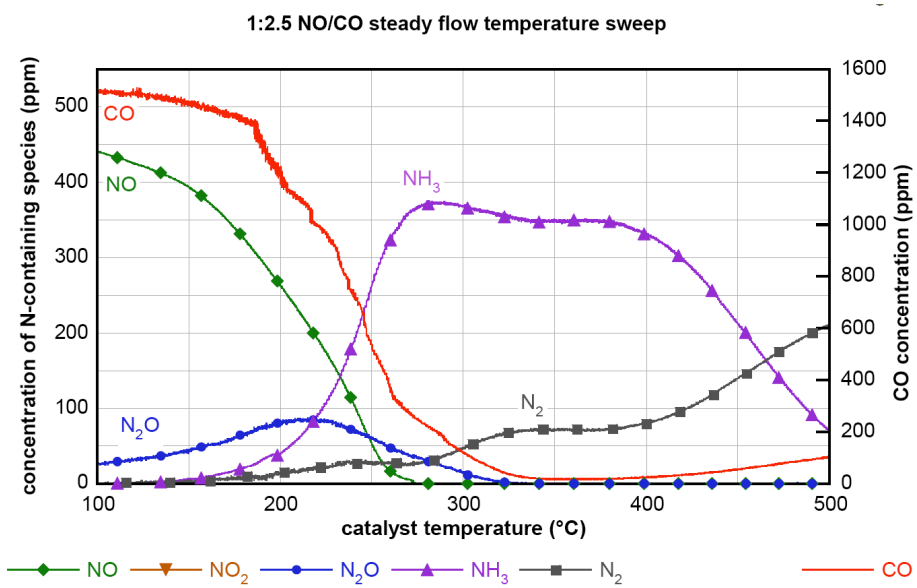


Sandia National Laboratories

ORNL

For NO with excess CO, the temperature at which NH3 appears is predicted more accurately.

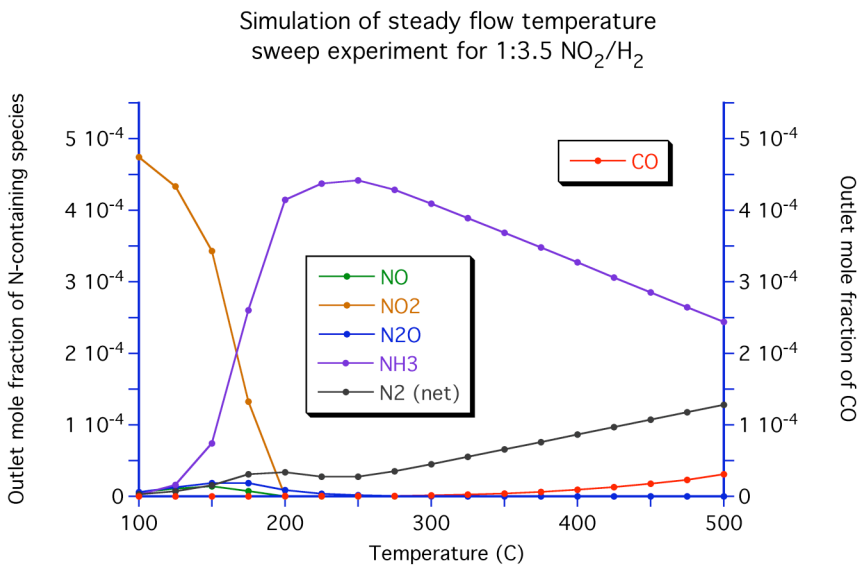


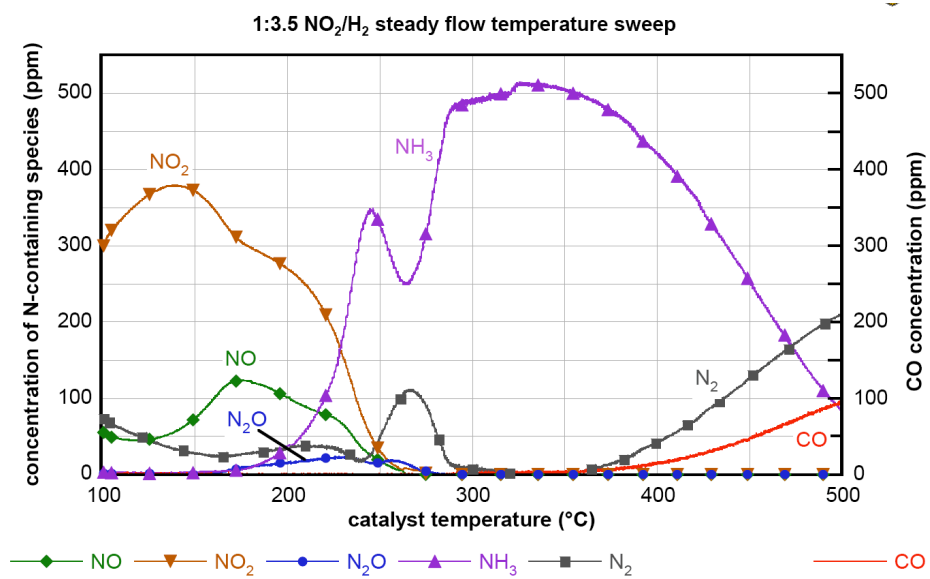


Sandia National Laboratories

ORNL

Reduction of NO2 by H2 is not reproduced well at low temperatures.

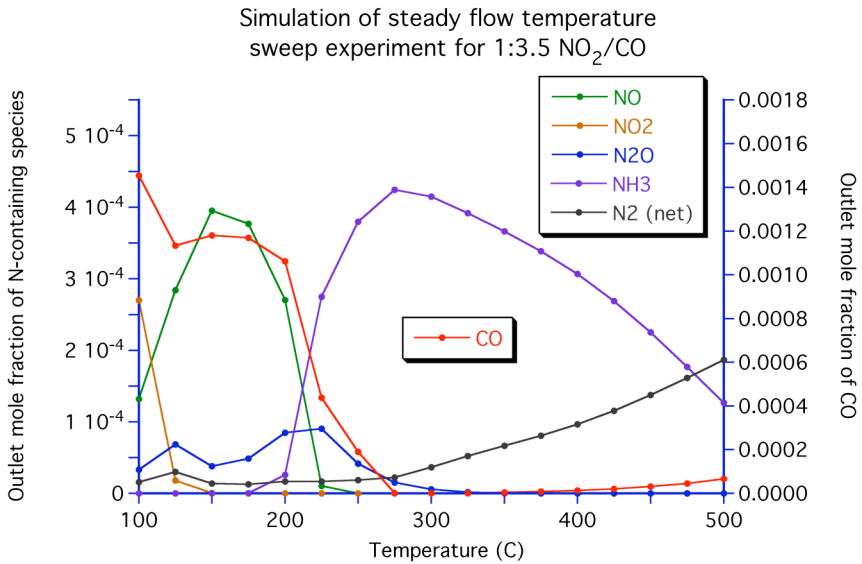


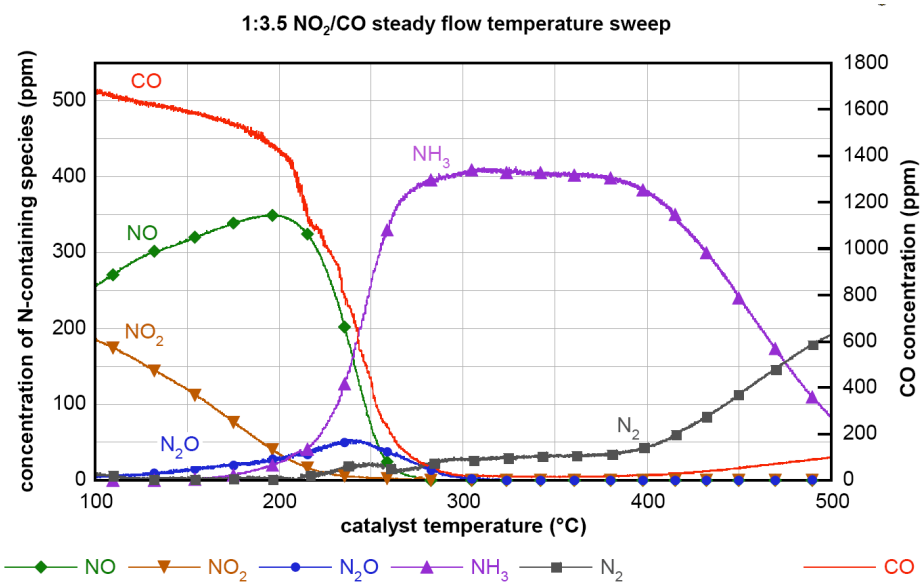


Sandia National Laboratories

ORNL

Reduction of NO2 by CO is simulated somewhat more successfully.

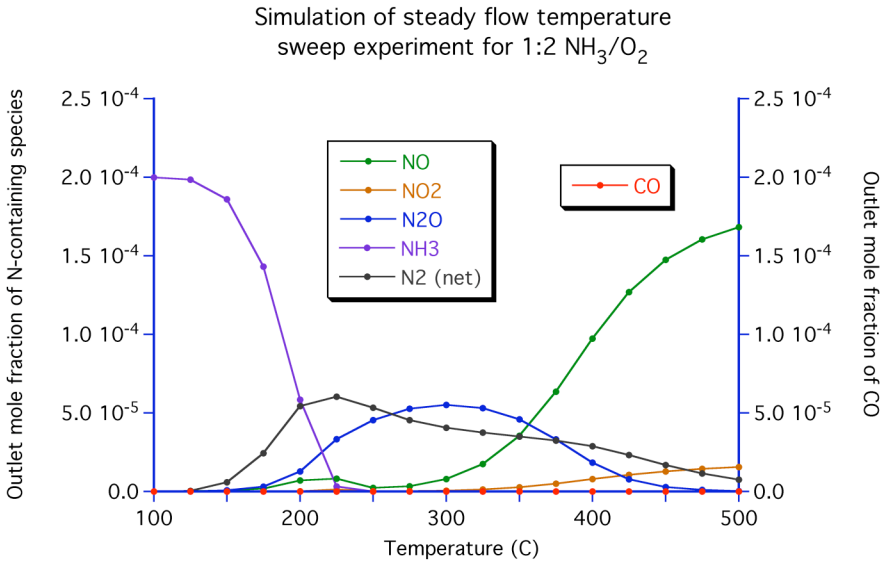


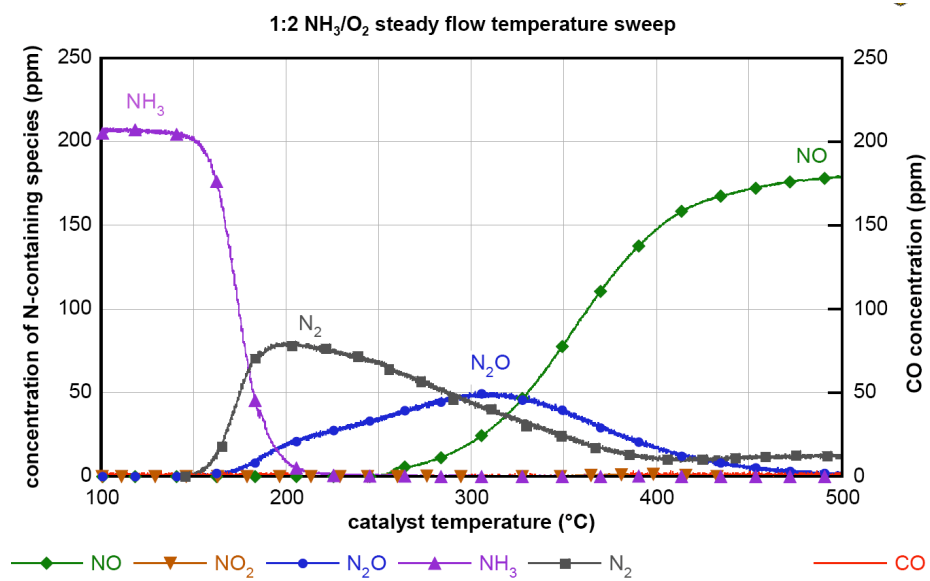


Sandia National Laboratories

ORNL

Simple oxidation of NH3 is accounted for quite accurately by the model …

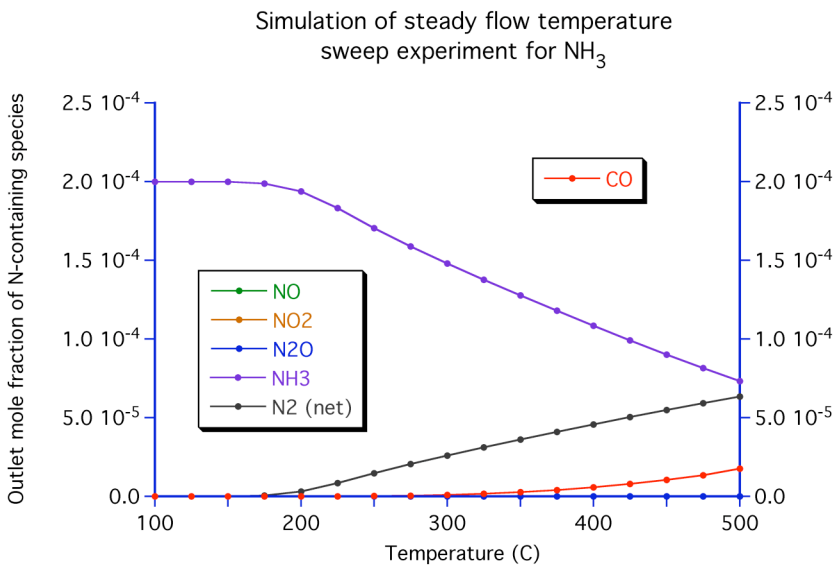


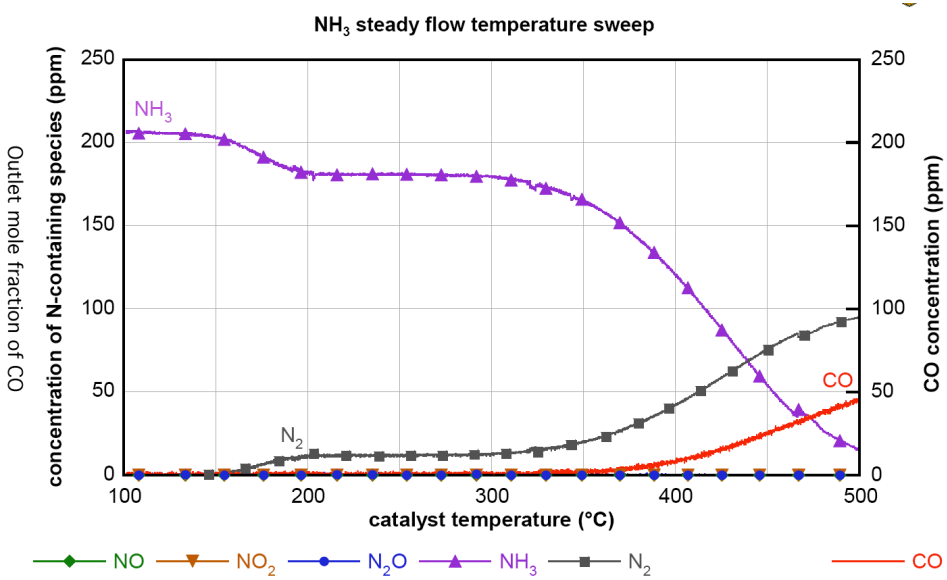


Sandia National Laboratories

ORNL

… and decomposition of NH3 is also simulated reasonably well.

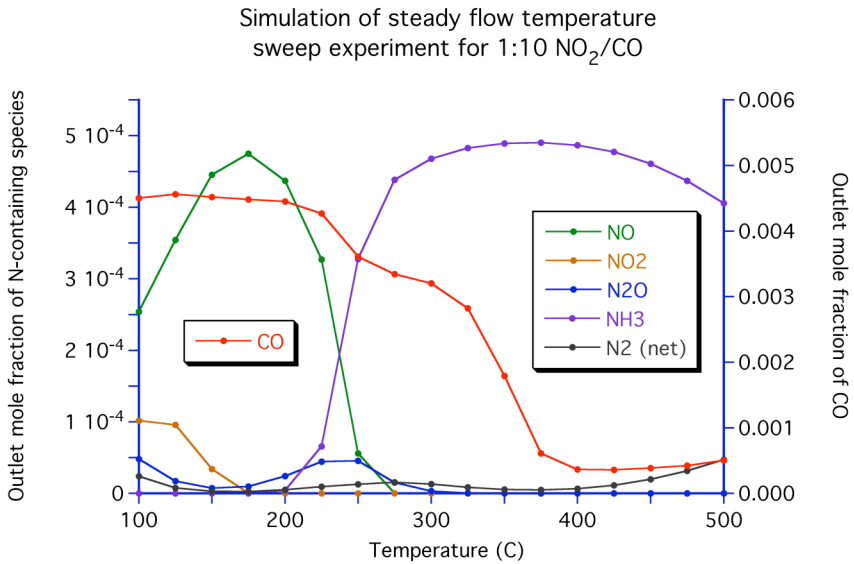


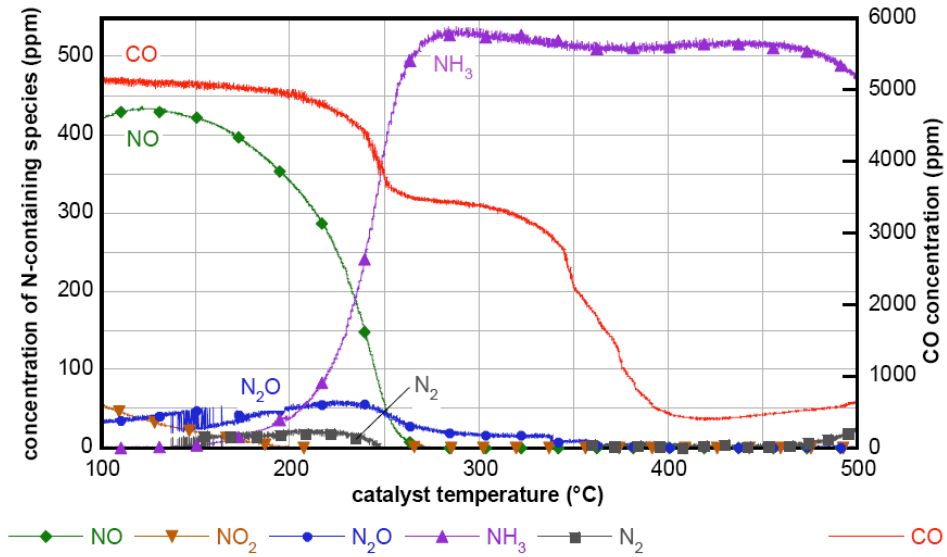


Sandia National Laboratories

ORNL

For 1:10 NO2/CO, the distinct two-step drop in CO is well reproduced by the model.

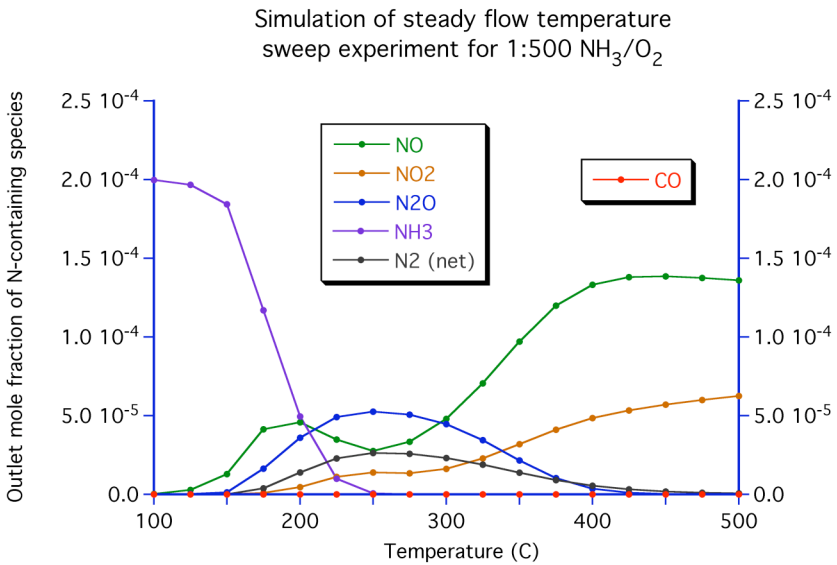


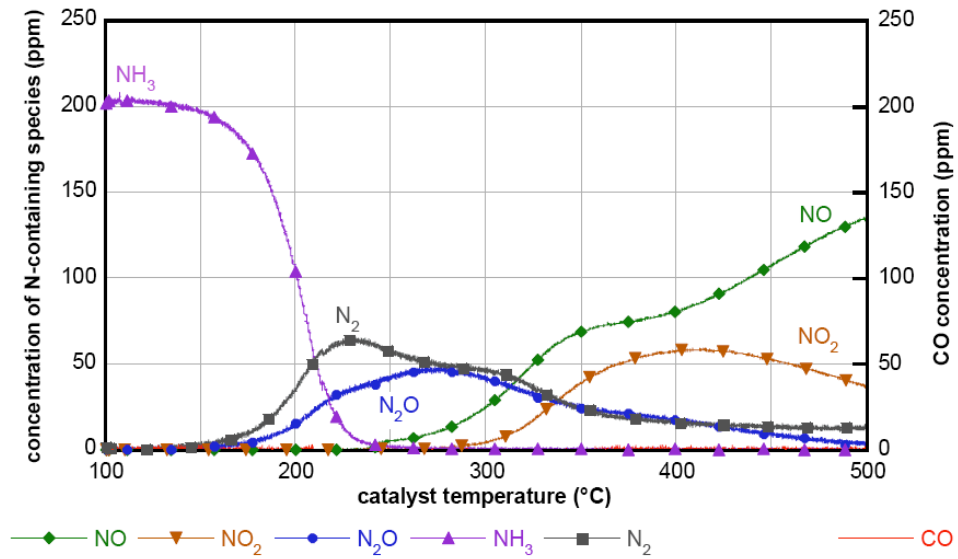


Sandia National Laboratories

ORNL

Oxidation of NH3 all the way to NO2 is accounted for semi-quantitatively.

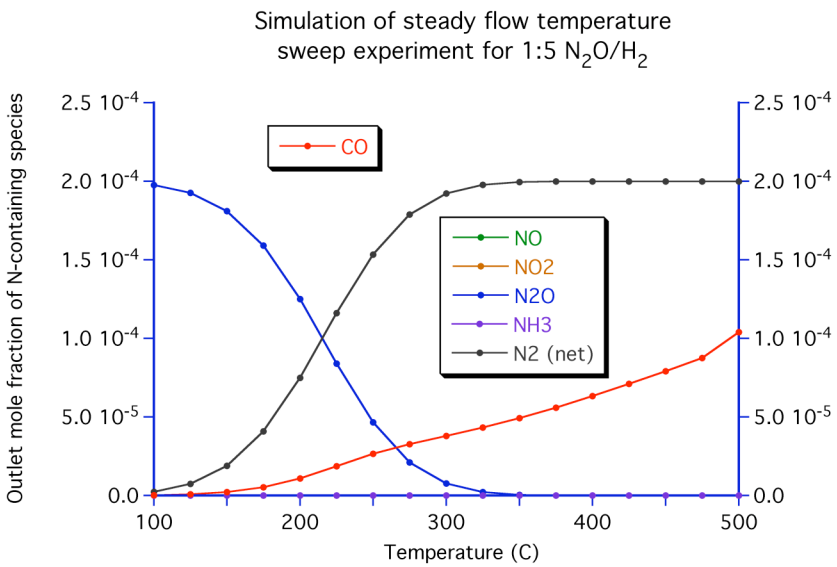


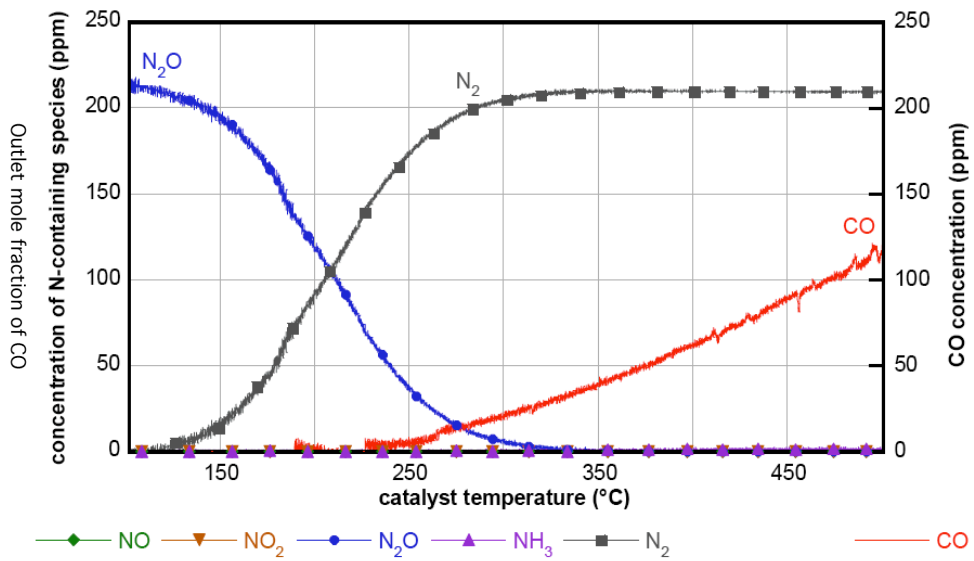


Sandia National Laboratories

ORNL

Reduction of N2O to N2, but not NH3, occurs even in the presence of a large excess of H2.

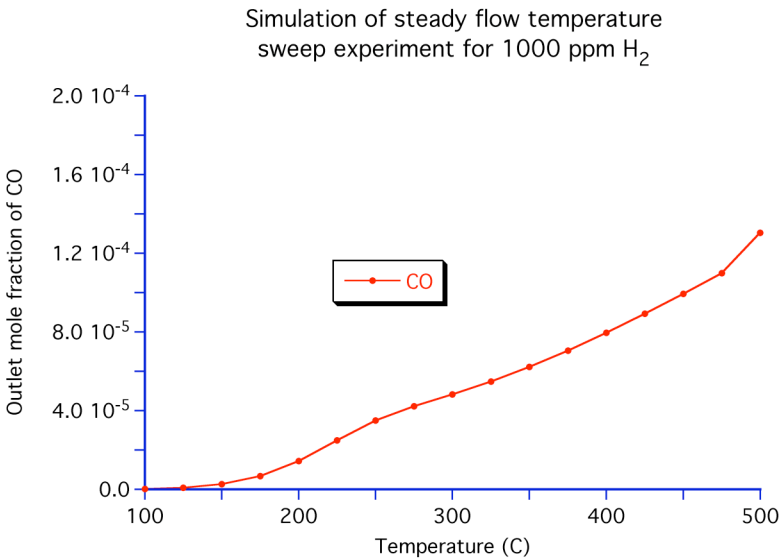


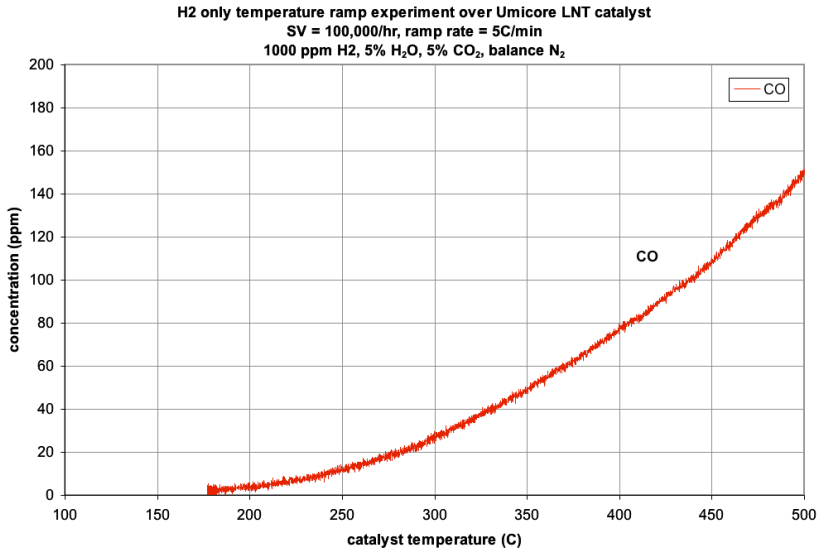


Sandia National Laboratories

ORNL

The water-gas shift reaction accounts for the observations whether the feed contains just H2 …

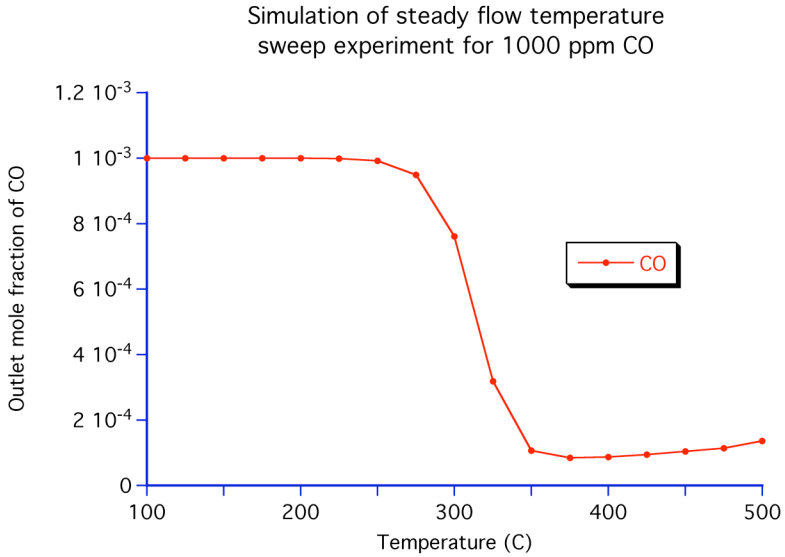


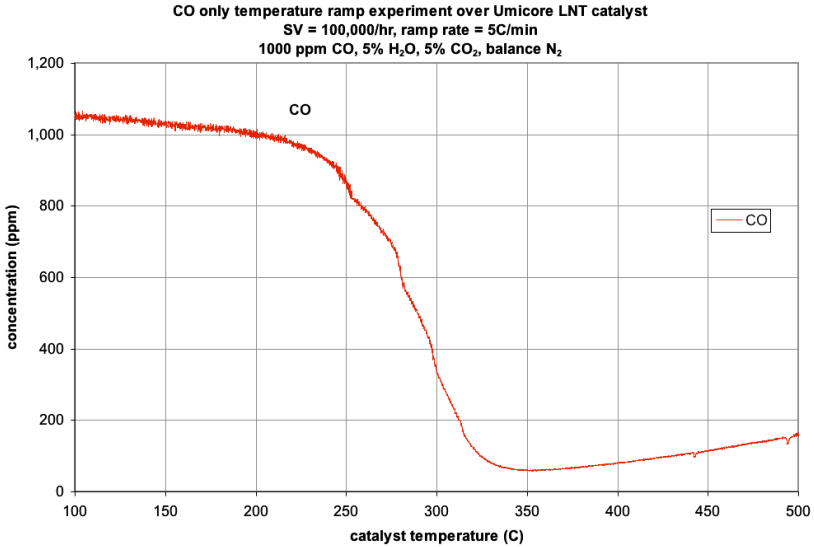


Sandia National Laboratories

ORNL

… or just CO.

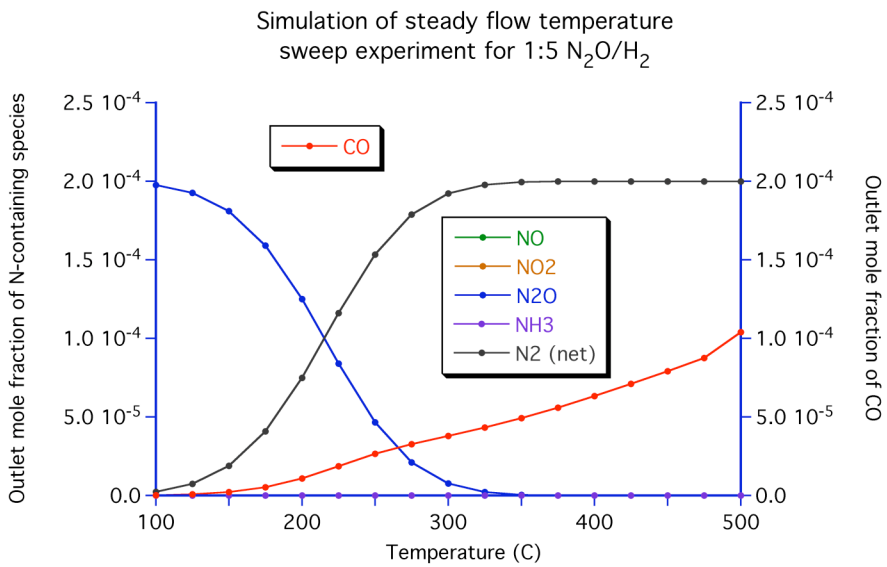


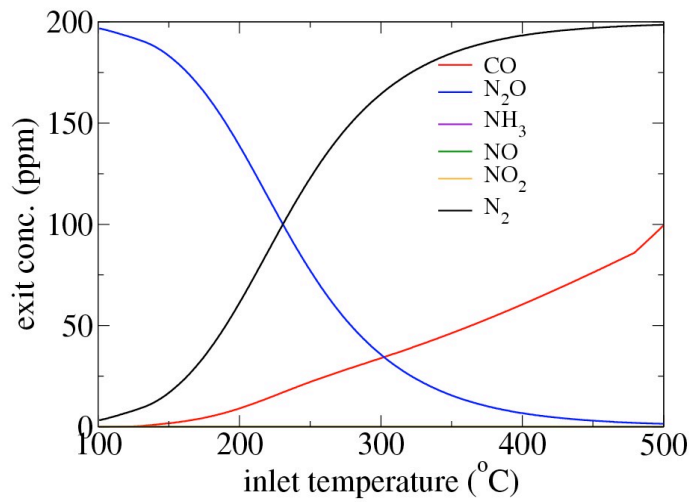


Sandia National Laboratories

ORNL

Even in the worst case, agreement between steady state and transient simulations is good.

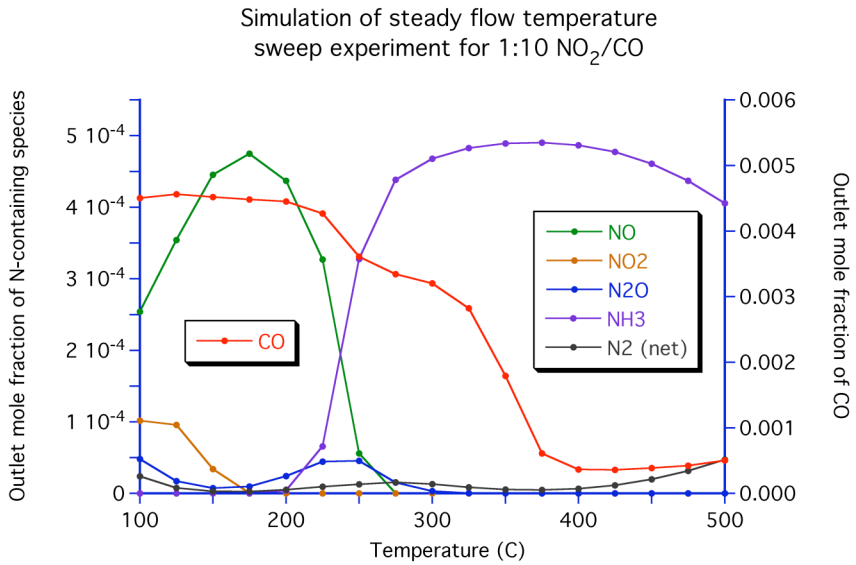


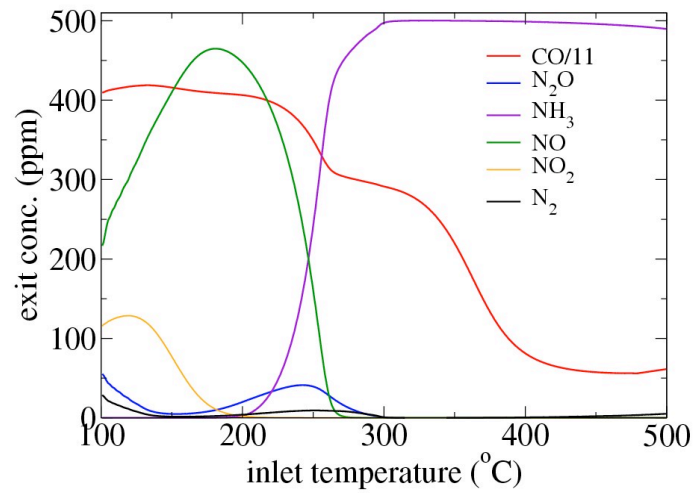


Sandia National Laboratories

ORNL

In most cases, differences between steady state and transient simulations are insignificant.





Sandia National Laboratories

ORNL

Observations and conclusions

- Regeneration chemistry in a lean NOx trap can be simulated with a reasonably compact elementary mechanism.
- The model tends to be least successful at low temperatures, especially with regard to NOx reduction by H2.
- Water-gas shift and isocyanate pathways are both needed to explain observed patterns of CO consumption.
- N2 formation appears to be irreversible, while N2O appears to be reduced directly to N2.
- The ORNL temperature ramp experiments approximate pseudo-steady state conditions very closely.

Future plans

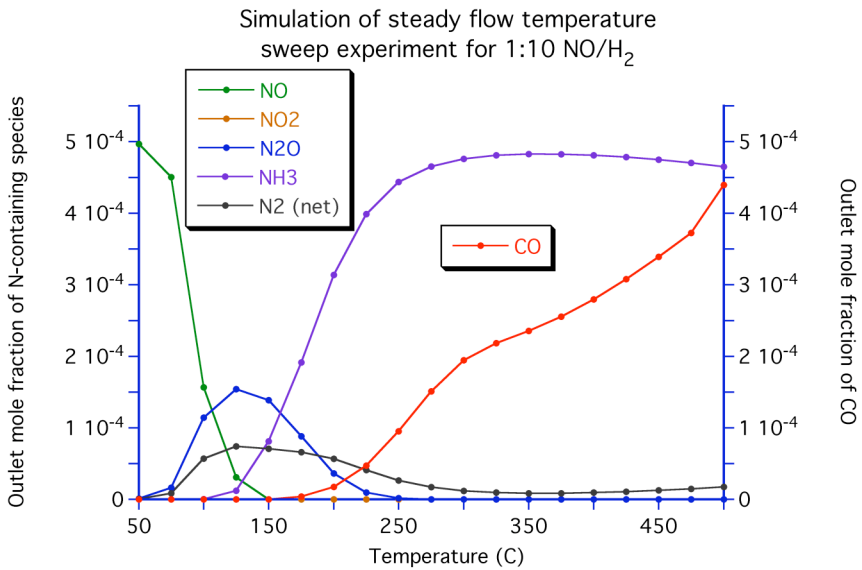
- Finish applying thermodynamic constraints to the mechanism, and investigate its equilibrium predictions.
- Introduce a physically-based value for the surface site density.
- Work with experimentalists to confirm the presence and chemical role of surface NCO.
- Demonstrate the behavior of the mechanism in a fully transient scenario.
- Begin the process of augmenting the mechanism with surface reactions taking place on storage (BaO) sites.

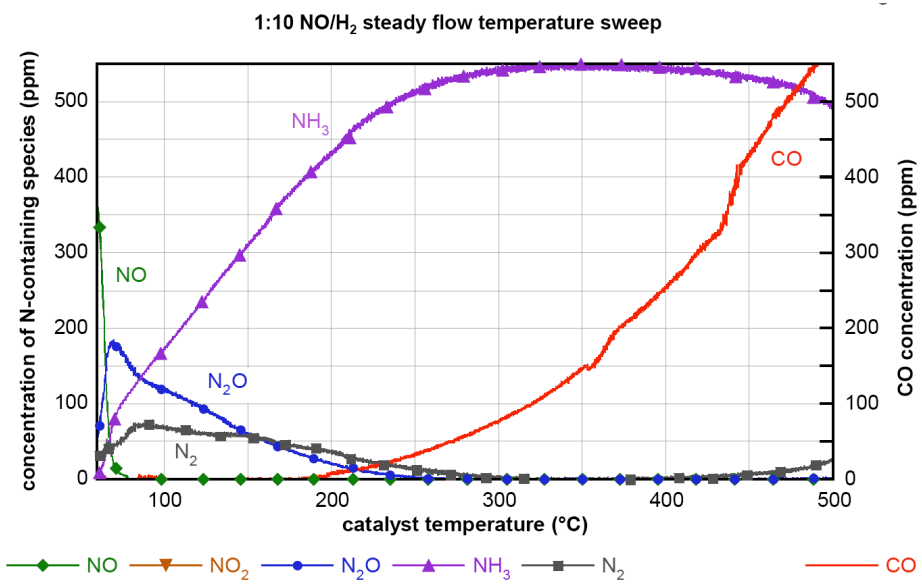
Extra Slides

Sandia National Laboratories

ORNL

1:10 NO/H2

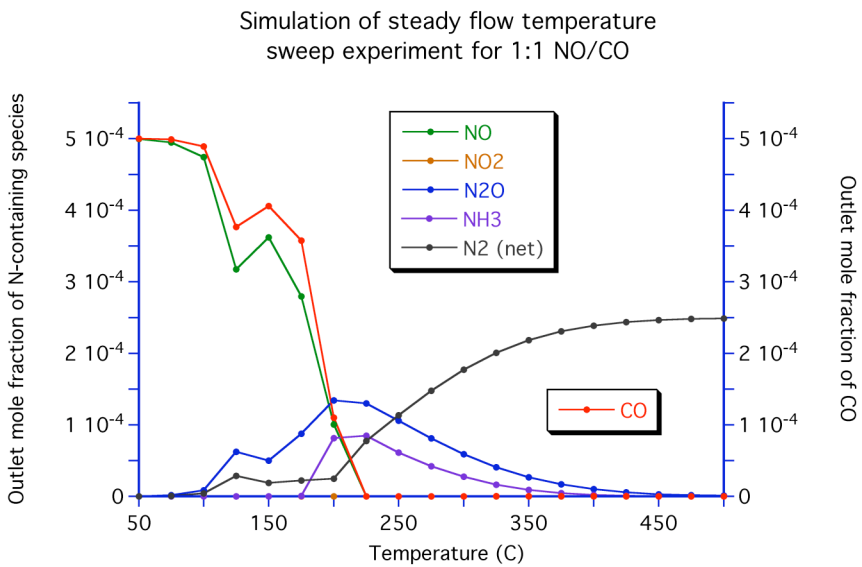


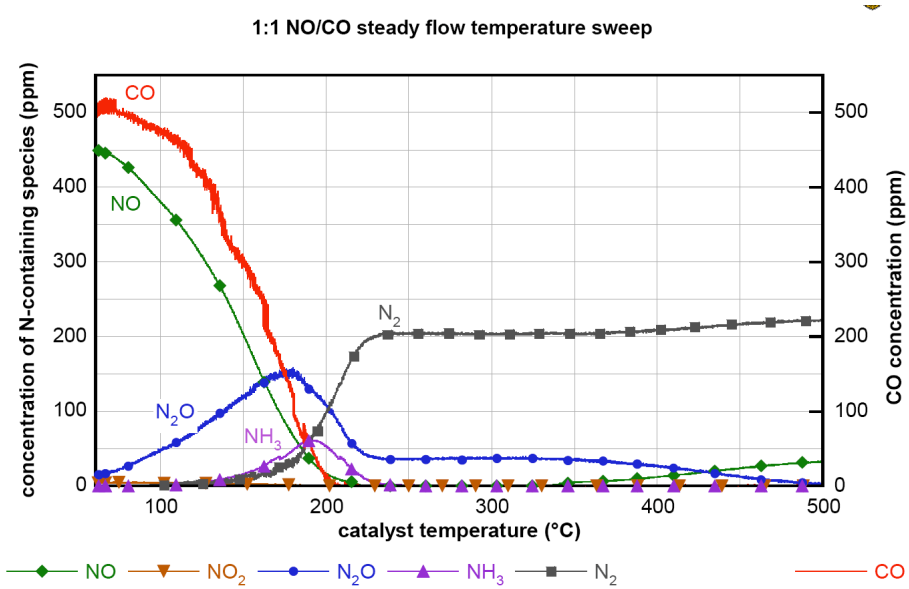


Sandia National Laboratories

ORNL

1:1 NO/CO

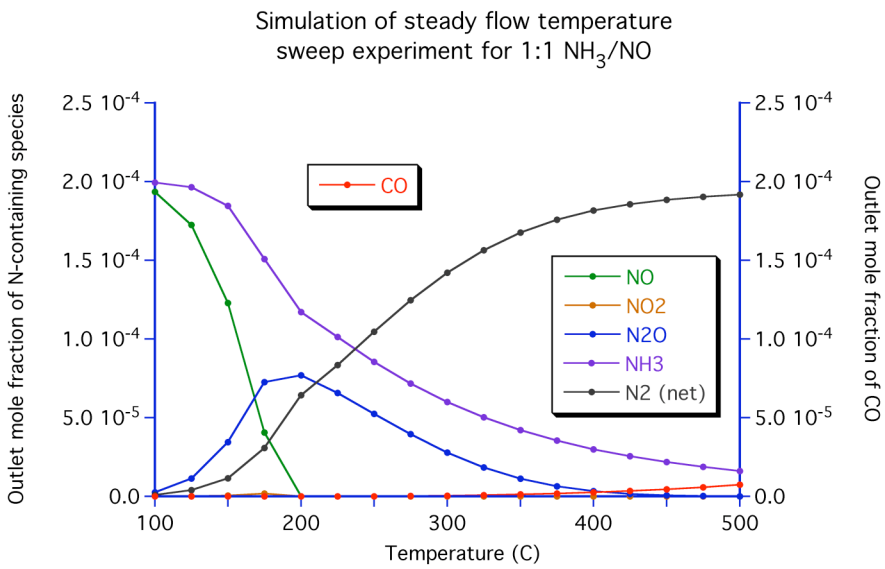


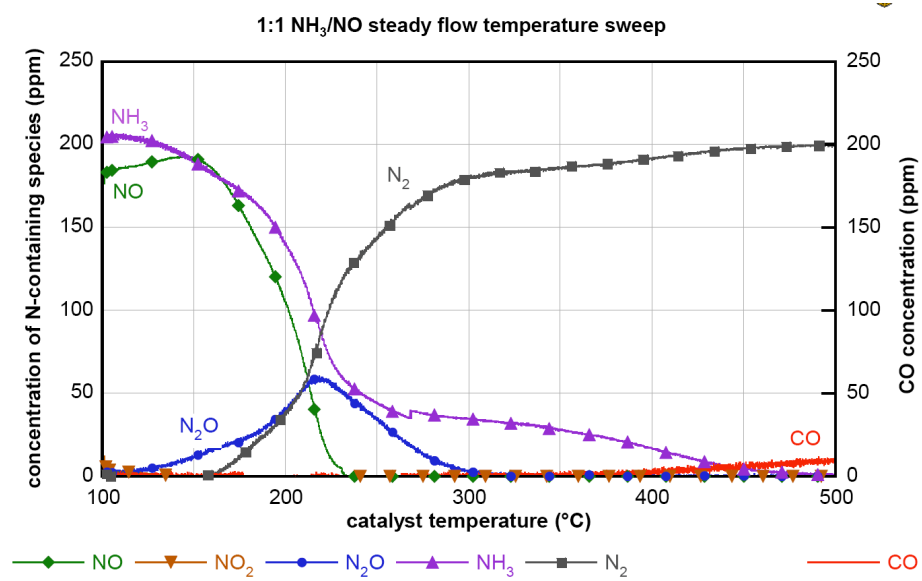


Sandia National Laboratories

ORNL

1:1 NH3/NO

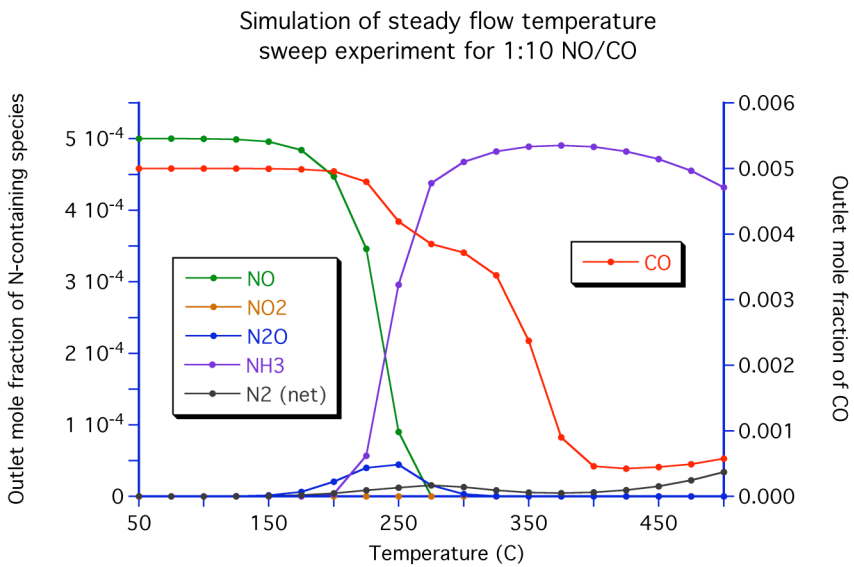


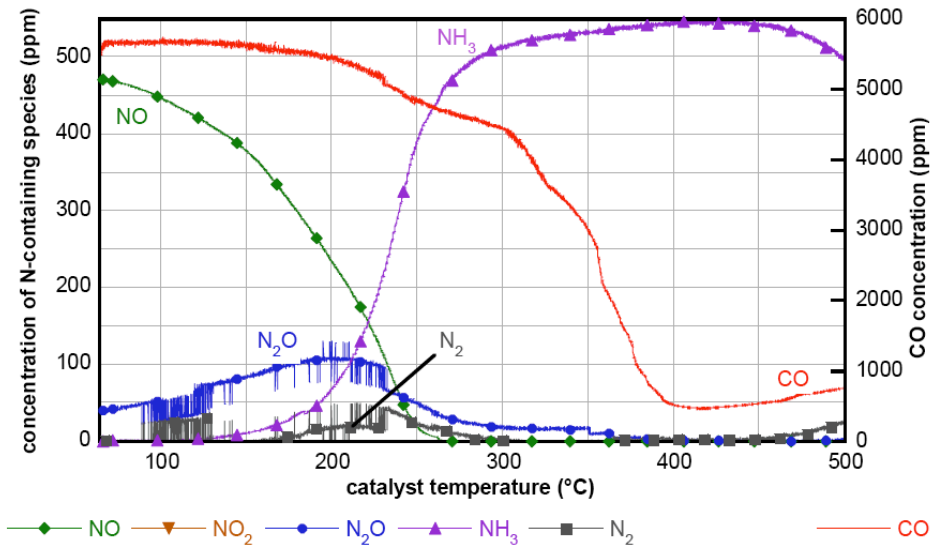


Sandia National Laboratories

ORNL

1:10 NO/CO

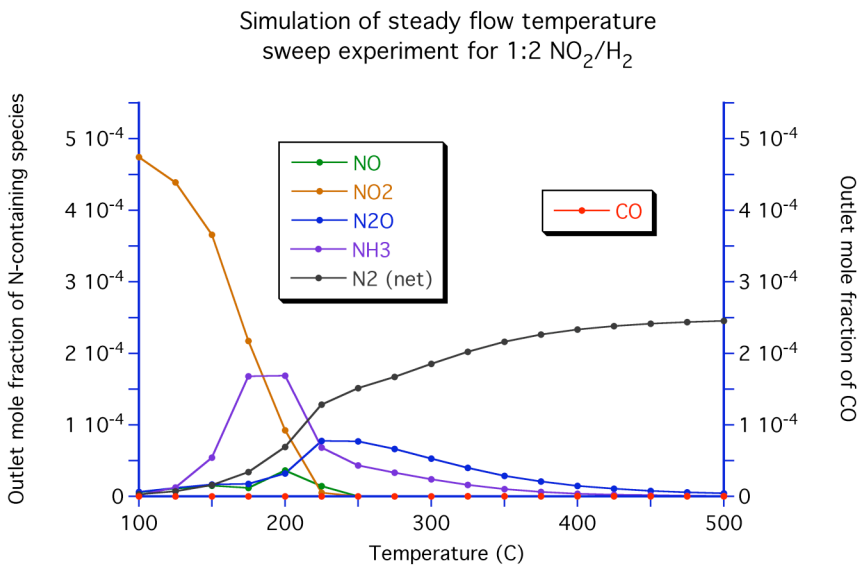


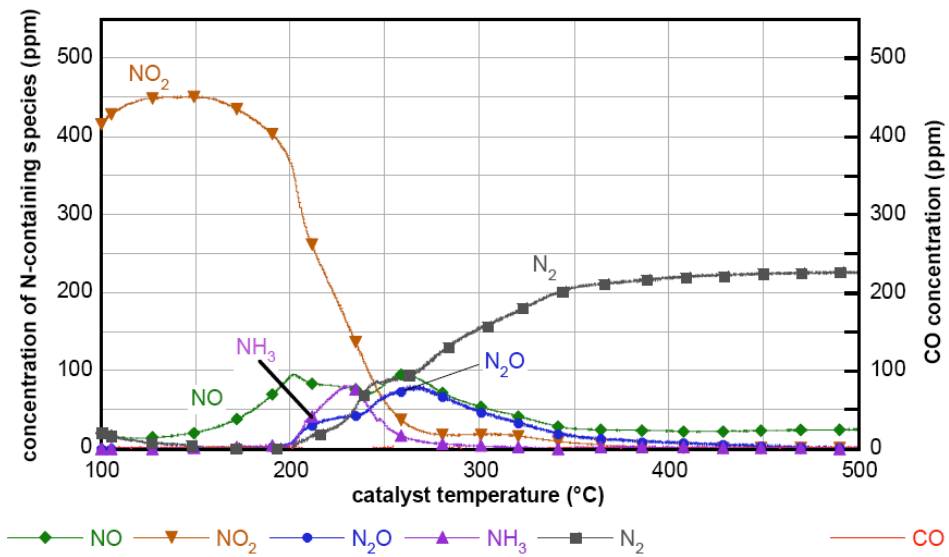


Sandia National Laboratories

ORNL

1:2 NO2/H2

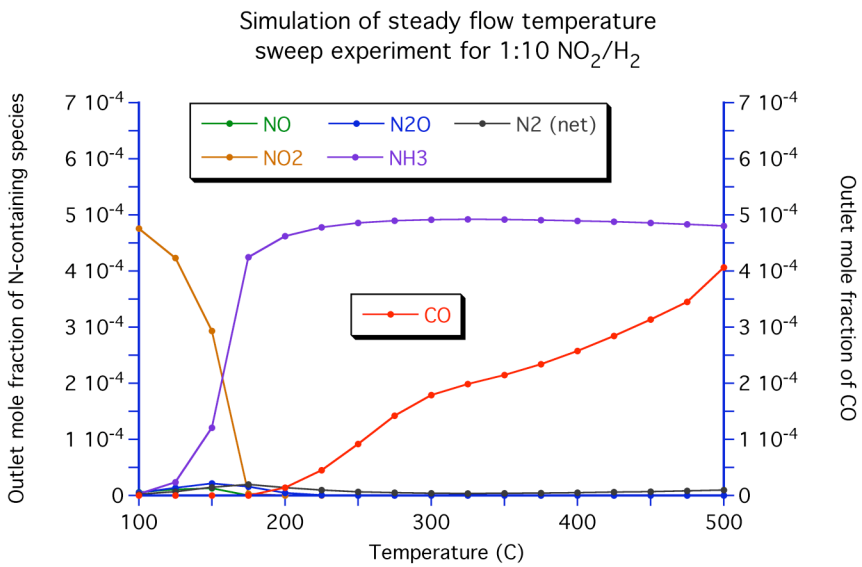


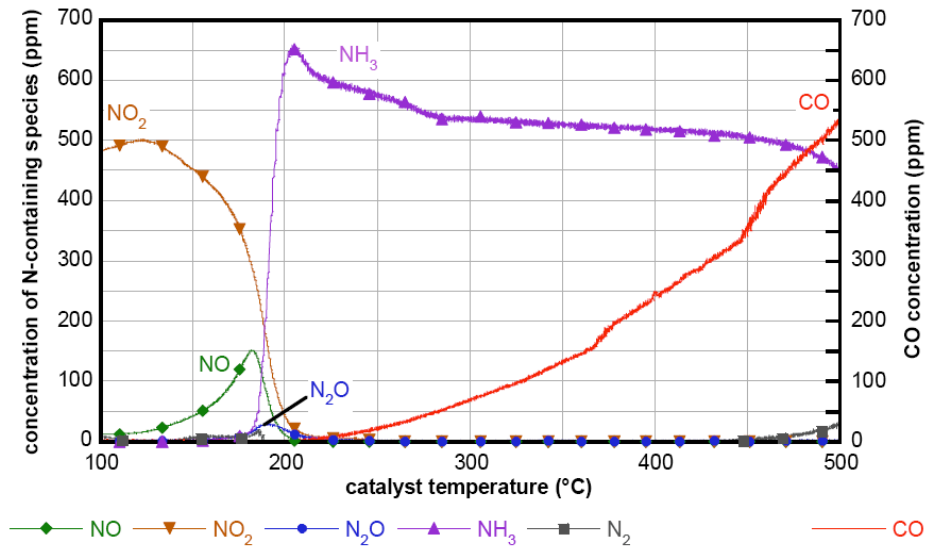


Sandia National Laboratories

ORNL

1:10 NO2/H2

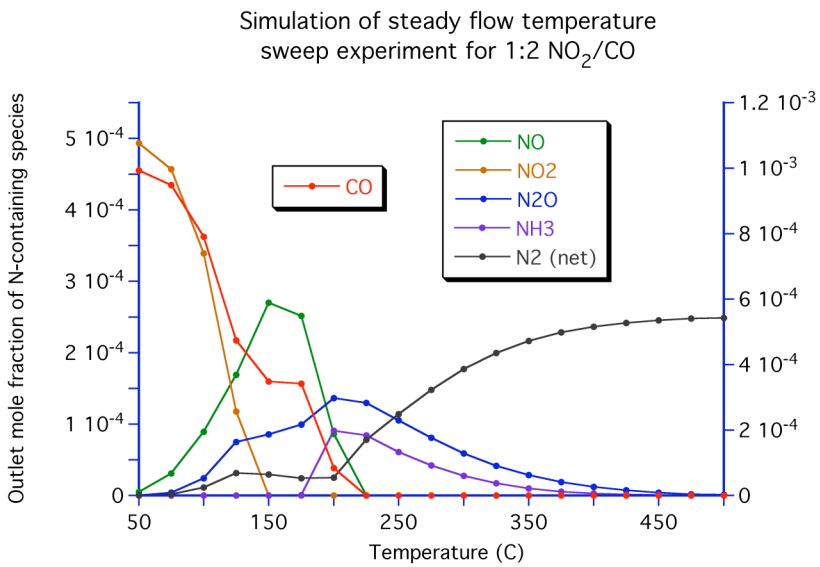


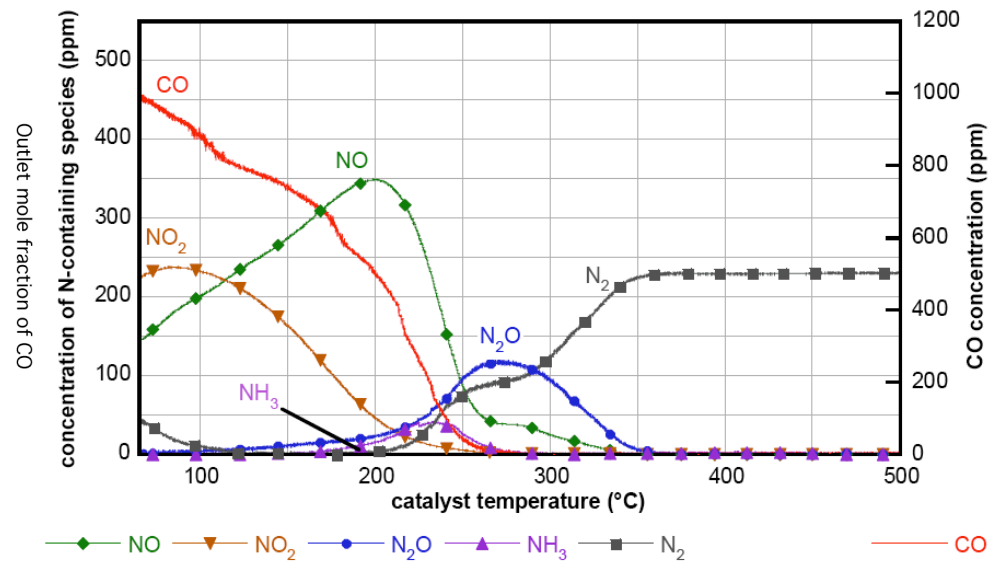


Sandia National Laboratories

ORNL

1:2 NO2/CO

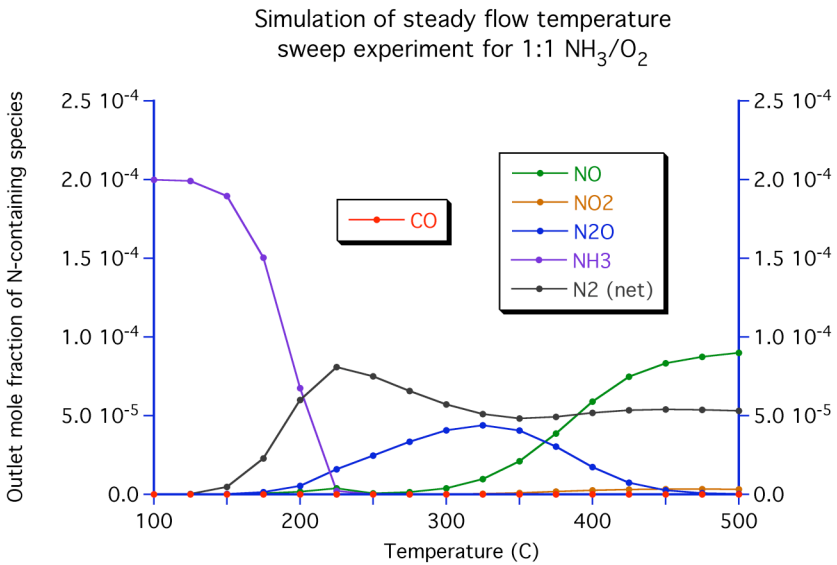


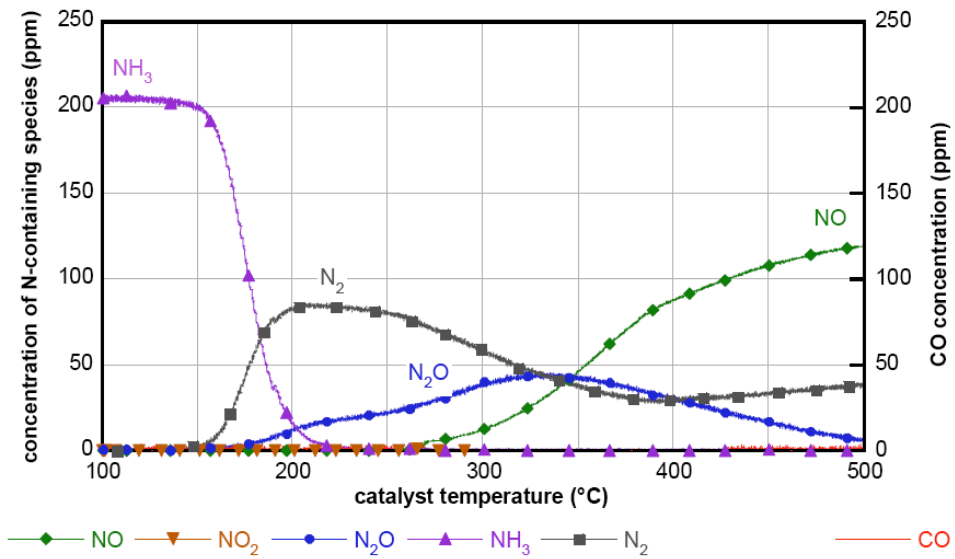


Sandia National Laboratories

ORNL

1:1 NH3/O2

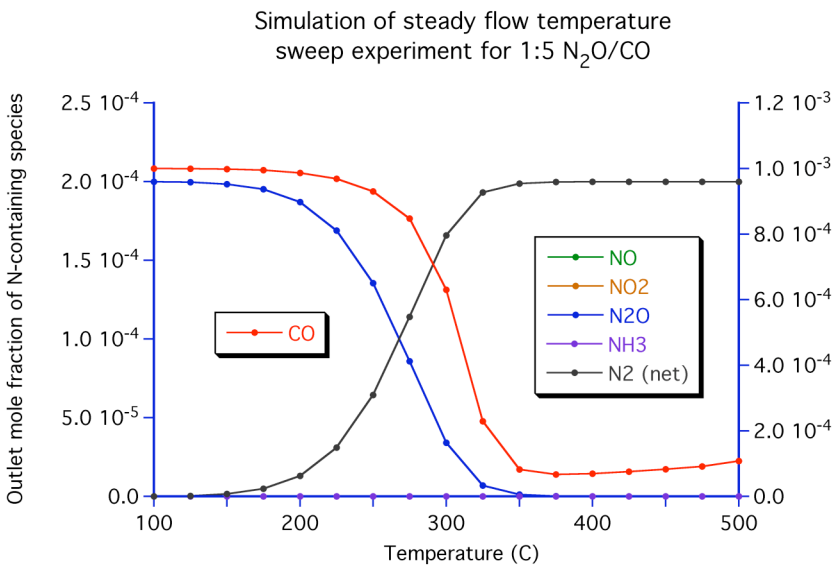


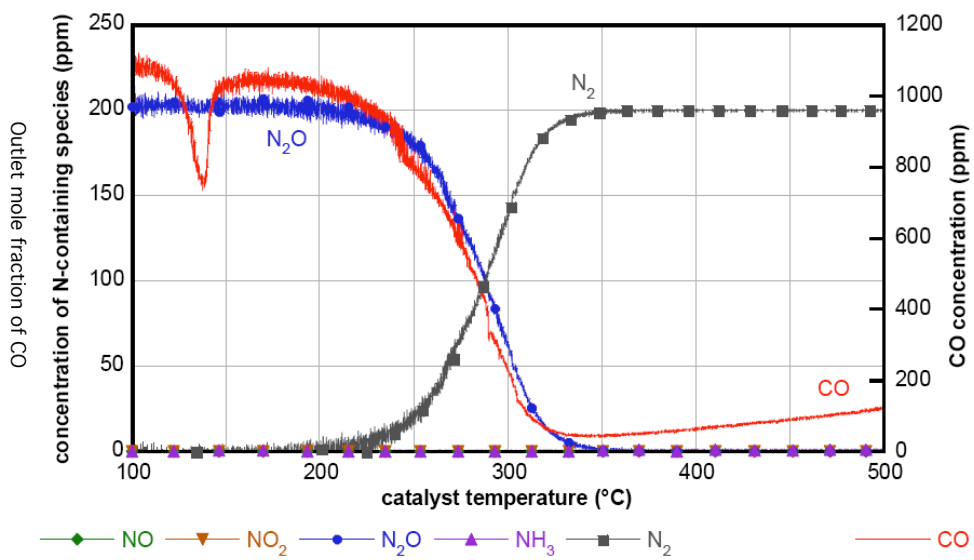


Sandia National Laboratories

ORNL

1:5 N2O/CO





Sandia National Laboratories

ORNL