Modeling the Regeneration Chemistry of Lean NOx Traps

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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.

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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: 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
- 17 reversible surface reactions
- 9 irreversible surface reactions

The reversible reactions consist mostly of adsorption/desorptions …

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

$NO + *(PT) = NO(PT)$

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

$CO + *(PT) = CO(PT)$

$H_2 + 2\,*(PT) = 2H(PT)$

$H_2O + *(PT) = H_2O(PT)$

$NH_3 + *(PT) = NH_3(PT)$

$N_2 + 2\,*(PT) = 2N(PT)$

… and decomposition/recombinations.

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

NO(PT) + *(PT) = N(PT) + O(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 water-gas shift reaction:

H2O(PT) + CO(PT) = 2H(PT) + CO2

Reaction of water with isocyanate intermediate:

N(PT) + CO = NCO(PT)

NCO(PT) + H2O(PT) => NH2(PT) + CO2 + *(PT)

Most remaining recombinations and atom transfers are treated as irreversible.

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

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

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

2NO(PT) = N2O + O(PT) + *(PT)

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

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

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

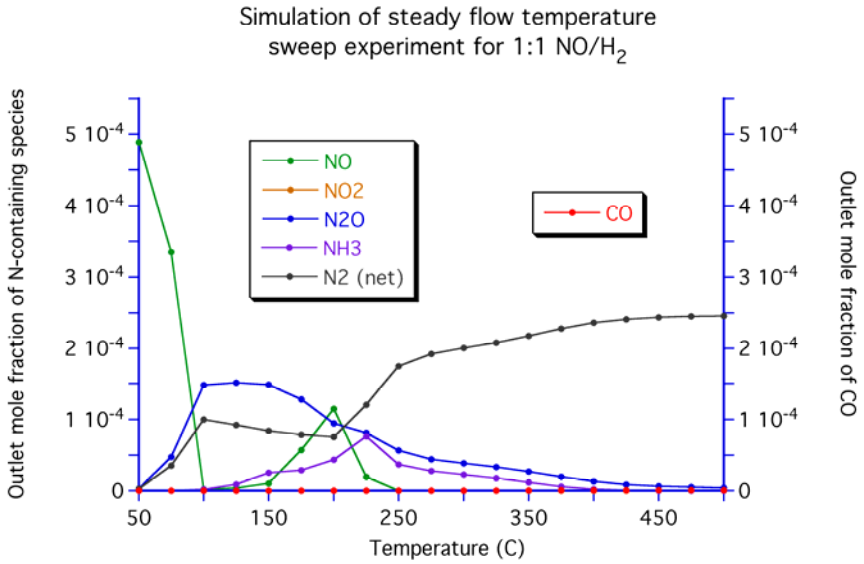
CO(PT) + O(PT) => CO2 + 2 *(PT)

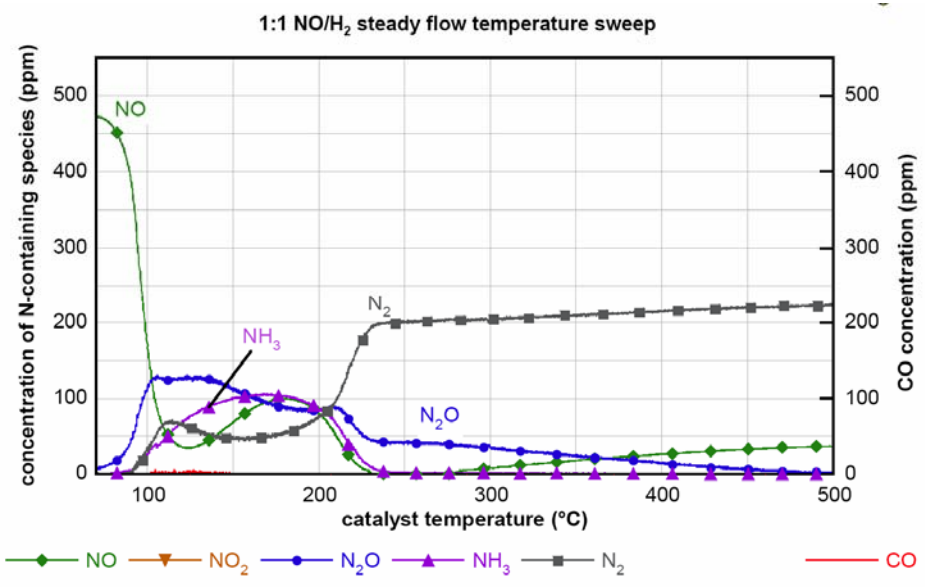
H(PT) + OH(PT) => H2O(PT) + *(PT)

Summary of experimental program

- 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, N2 formation is favored at high temperatures.





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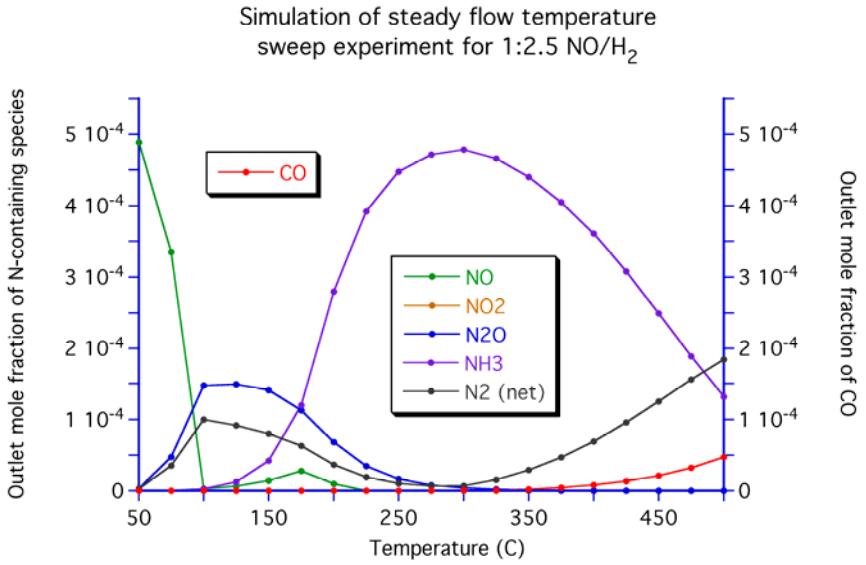
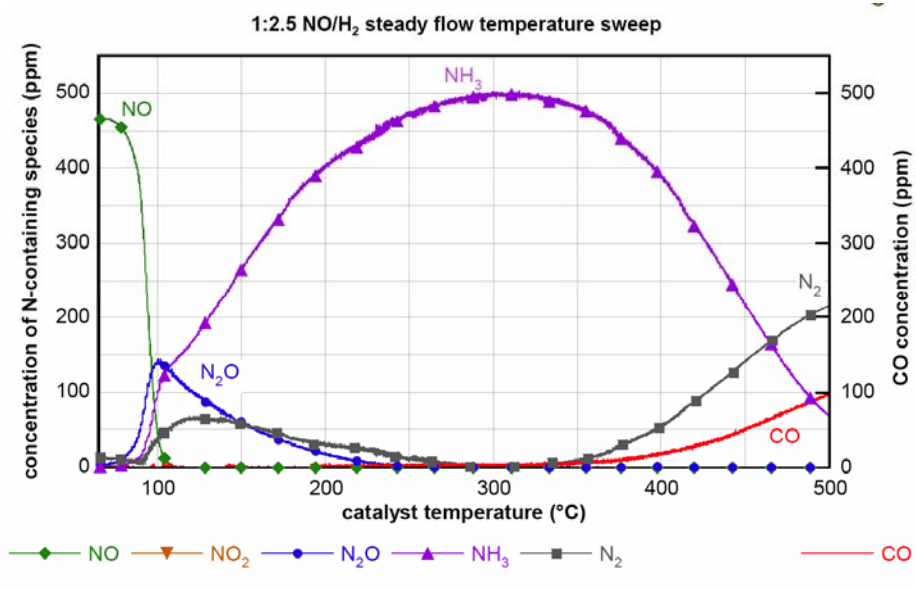
However, for NO with excess H2, large amounts of NH3 can be produced.





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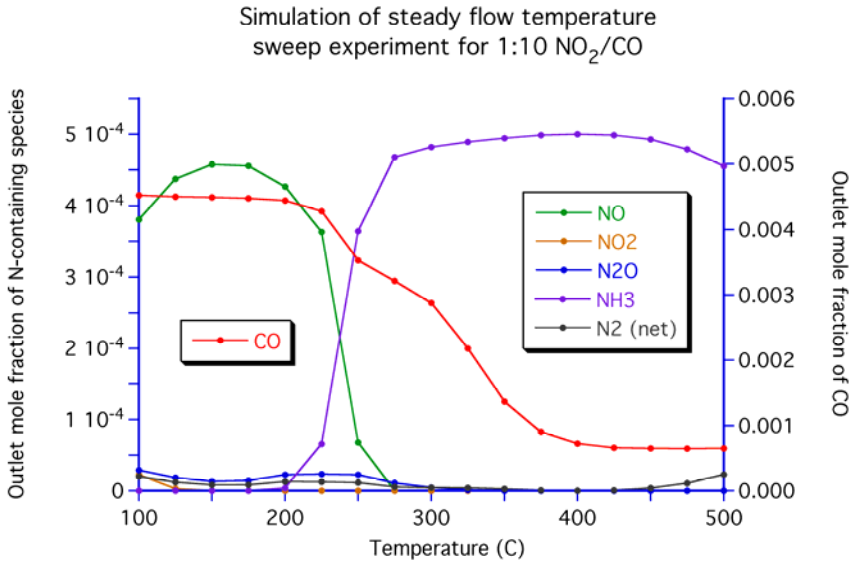
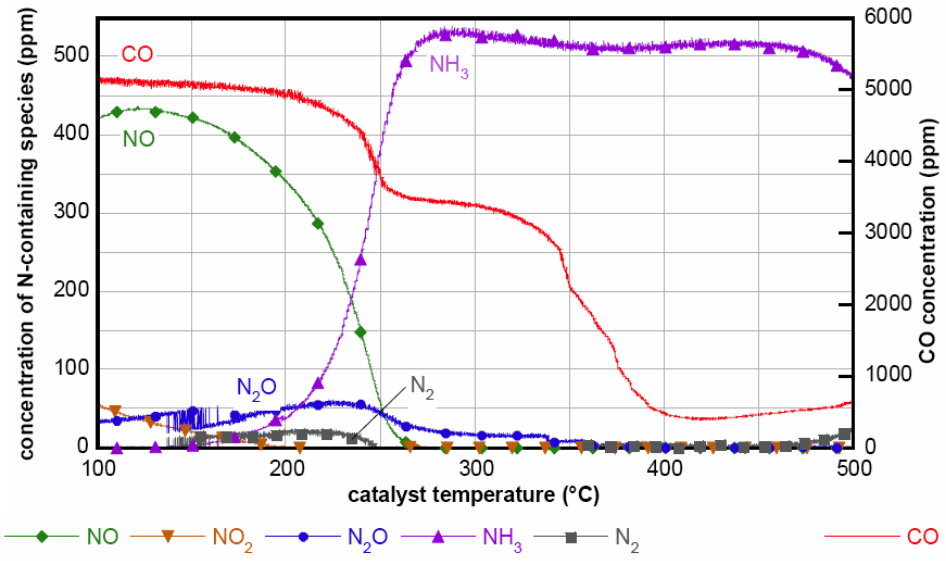
For 1:10 NO2/CO, a distinct two-step drop in CO is reasonably well reproduced by the model.





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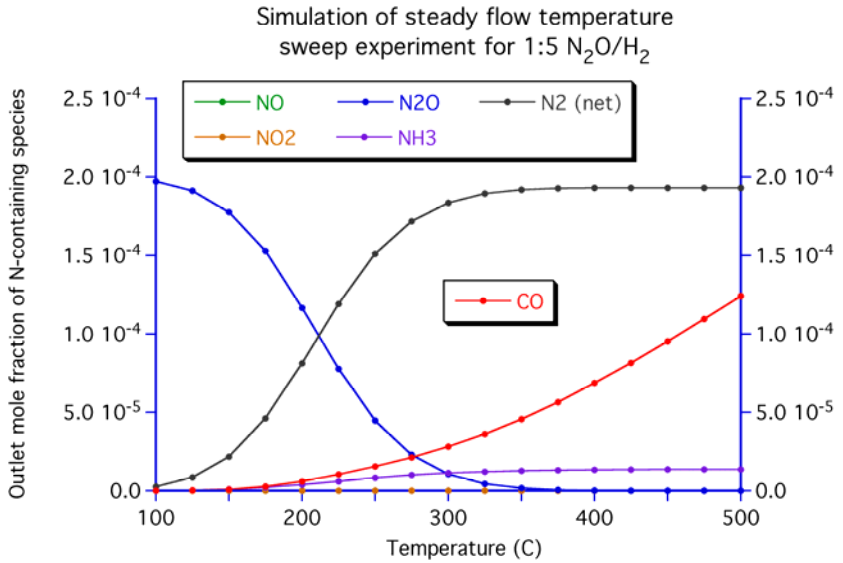
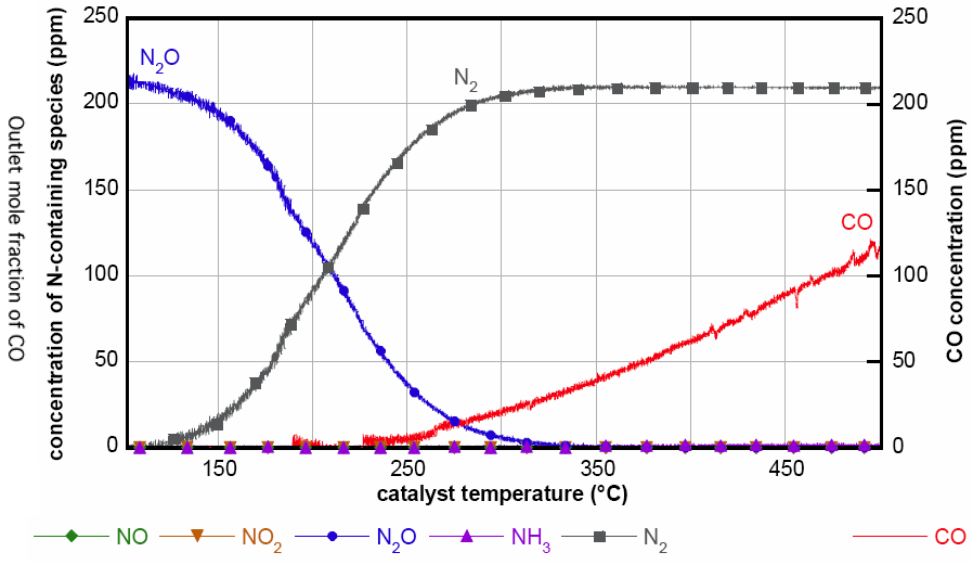
Even with a large excess of H2, reduction of N2O produces mostly N2 rather than NH3.





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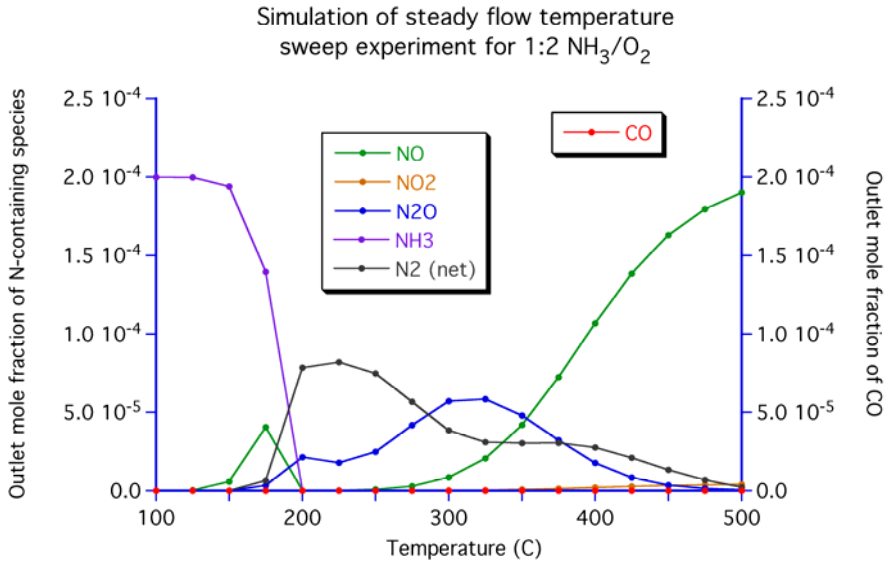
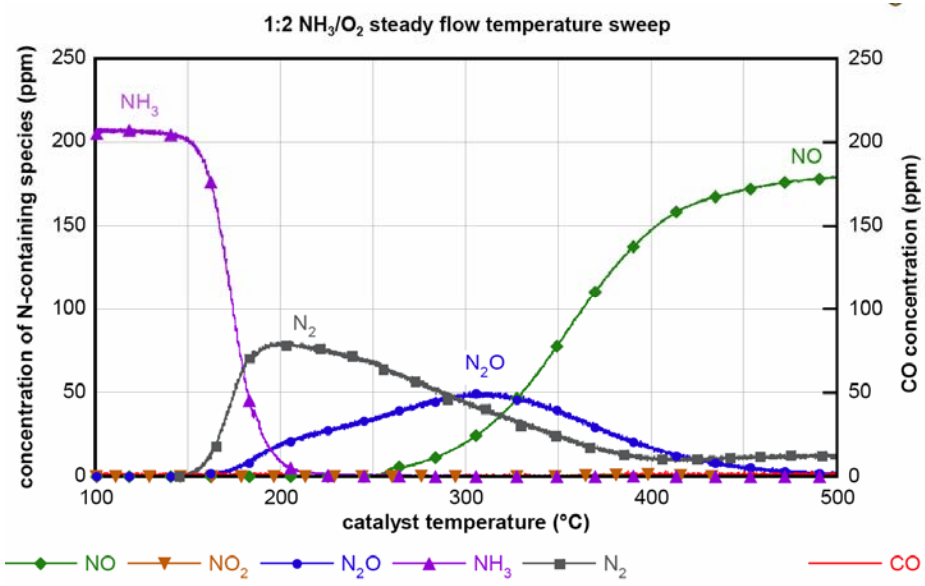
Direct oxidation of NH3 is accounted for quite accurately by the model.





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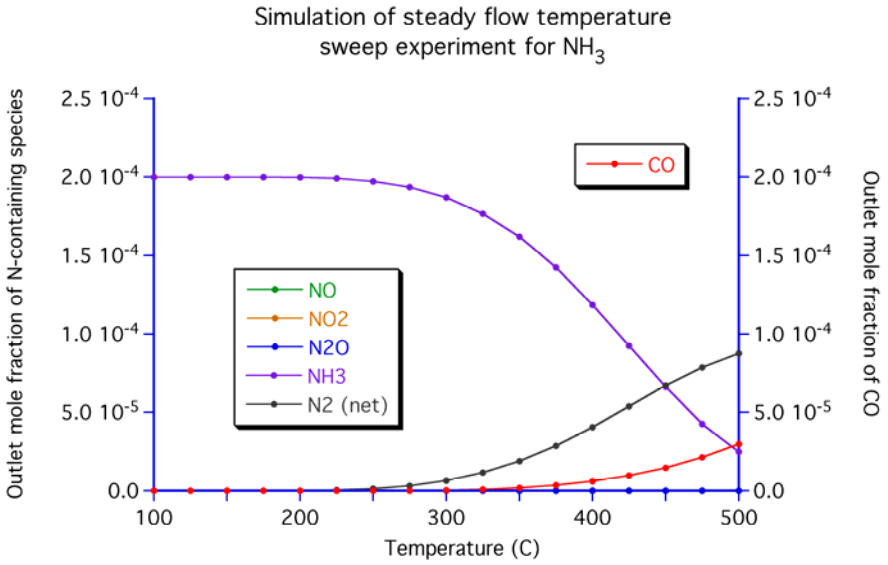
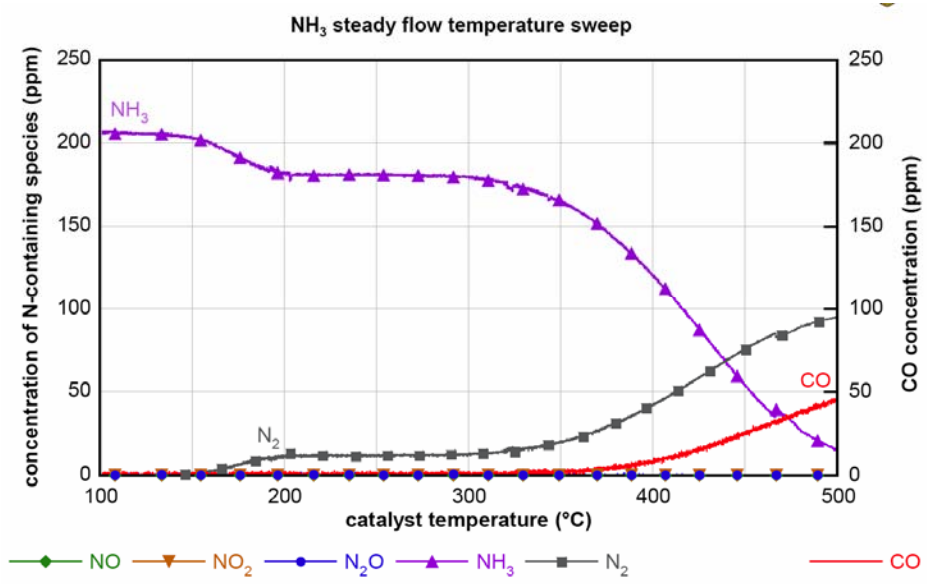
Simple decomposition of NH3 is also simulated successfully.





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Summary

- Regeneration chemistry in a lean NOx trap can be simulated with a reasonably compact elementary mechanism.
- Water-gas shift and isocyanate pathways are both needed to explain observed patterns of CO consumption.
- The next step is to apply formal thermodynamic constraints to the proposed mechanism.
- Eventually the regeneration mechanism must be augmented with surface reactions taking place on storage (BaO) sites.
- The combined storage/regeneration mechanism will allow the simulation of fully transient LNT cycles.

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