Microkinetic Modeling of Lean NOx Trap Storage and Regeneration

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Overall objective

Develop an elementary surface reaction mechanism, to be used in conjunction with an appropriate reacting flow model, that accounts for the observed product distribution from a lean NOx trap during cyclical operation under various conditions of temperature and inlet gas composition.

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Approach

- Assemble tentative mechanisms for precious metal (regeneration), baria (NOx storage), and ceria (oxygen storage) sites, using reactions from literature together with additional hypothesized steps.

- Infer tentative kinetic parameters for precious metal 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 mechanisms.
  - Use Sandia APPSPACK code to carry out optimization.
  - Apply thermodynamic constraints to kinetic parameters in order to ensure complete consistency.

Approach (continued)

- **Infer kinetic parameters for storage mechanisms by matching product distributions from cycling experiments done at ORNL.**
  - **Use Chemkin-based transient plug flow code, modified to account for washcoat diffusion and accumulation, to simulate unsteady storage/regeneration processes.**
  - **Incorporate thermodynamic constraints on kinetic parameters in storage mechanisms as well.**
  - **Initially use precious metal kinetic parameters determined from temperature ramp experiments.**
  - **Assess the improvement achievable by allowing previously determined precious metal parameters to vary.**

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Accomplishments

- **Completed construction of precious metal mechanism from temperature ramp experiments and published results in *Catalysis Today*.**

- **Assembled reaction sets for storage mechanisms and formulated corresponding thermodynamic constraints (all reactions treated as reversible with mass action kinetics).**

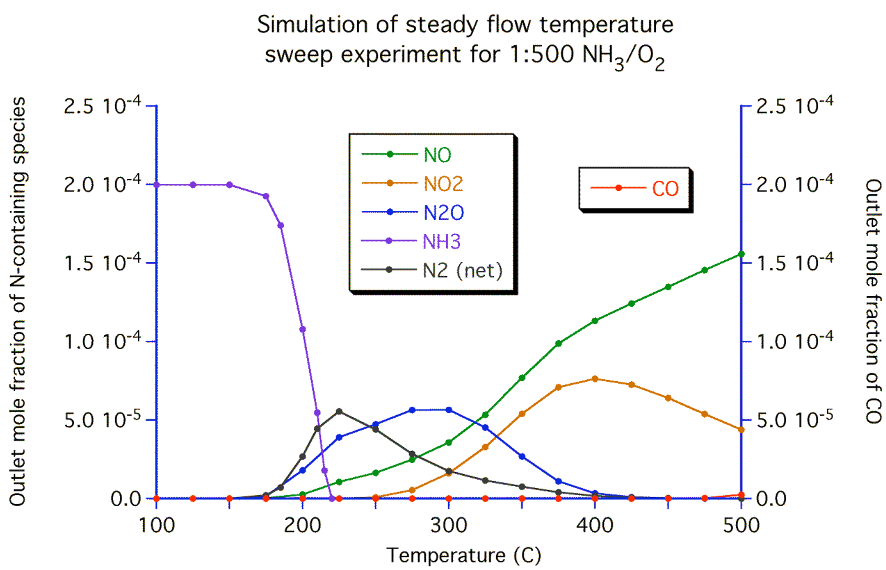
- **Modified transient plug flow code to account for washcoat diffusion and a finite capacity for "dissolved" gas while preserving one-dimensional nature.**

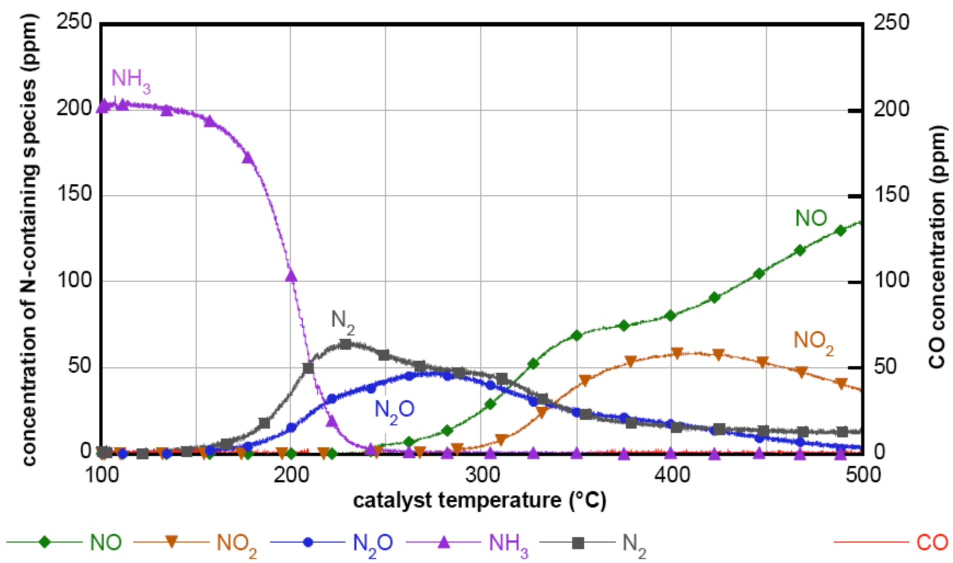
- **Inferred kinetic parameters for storage phases by fitting long cycle data, using both fixed and variable precious metal parameters.**

Recap of precious metal 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: V(PT), O(PT), NO(PT), NO_2(PT), CO(PT), H(PT), N(PT), OH(PT), H_2O(PT), NH(PT), NH_2(PT), NCO(PT), NH_3(PT)
- 28 surface reactions, all of them reversible (in principle; 10 are found to be effectively irreversible):
    - 5 simple adsorptions
    - 6 dissociative adsorptions
    - 7 surface decompositions
    - 7 surface atom transfers
    - water-gas shift reaction
    - isocyanate formation and hydrolysis

The PT mechanism can simulate temperature ramp experiments even under oxidizing conditions.





Summary of storage mechanisms

- 6 surface species on baria sites: V(BAO), NO2(BAO), NO3(BAO), O(BAO), BACO3, BA(OH)2
- “bulk” nitrate species BA(NO3)2
- 2 surface species on ceria sites: V(CERIA), O(CERIA)
- 18 reactions, all of them reversible (in principle; effective irreversibility yet to be determined):
    - adsorption of NO2 on vacant baria sites to give nitrite
    - oxidation of vacant baria sites by O2
    - reaction of oxidized sites with CO2, H2O, NO, NO2 to give carbonate, hydroxide, nitrite, nitrate

Storage reactions (continued)

- reaction of carbonate with H_2O, NO, NO_2 to give hydroxide, nitrite, nitrate
- reaction of hydroxide with NO, NO_2 to give nitrite, nitrate
- reaction of nitrite with NO_2 to give nitrate (disproportionation)
- surface oxidation of nitrite to nitrate by oxidized sites, carbonate, hydroxide
- spillover of nitrite to precious metal sites
- conversion of surface nitrate to bulk nitrate
- oxidation of vacant ceria sites by O_2

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Key features of reactor model

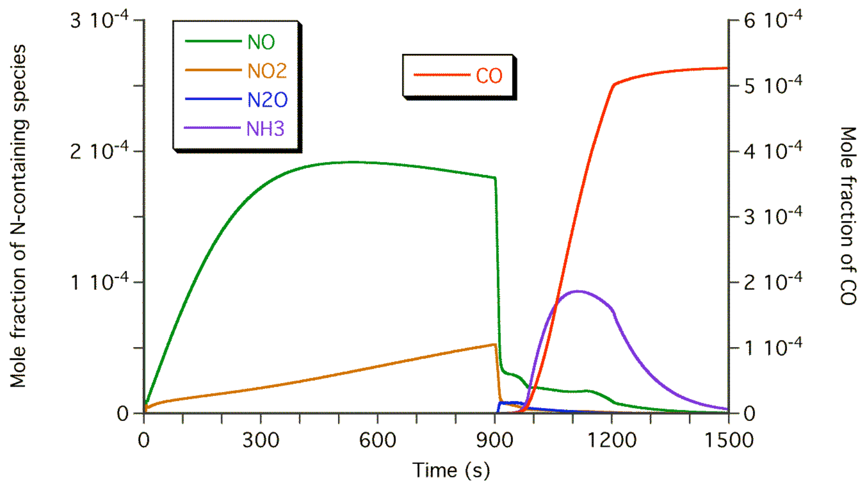
- Transient plug flow model for gas in monolith channel
- Transient lumped parameter model for species diffusing through washcoat (to preserve one-dimensionality)
- All reaction rates evaluated at washcoat concentrations
- Effective diffusion layer thickness and effective capacity for dissolved gas are adjustable parameters
- Measured axial temperature profiles (not quite isothermal) are used as inputs

Summary of long cycle experiments (ORNL)

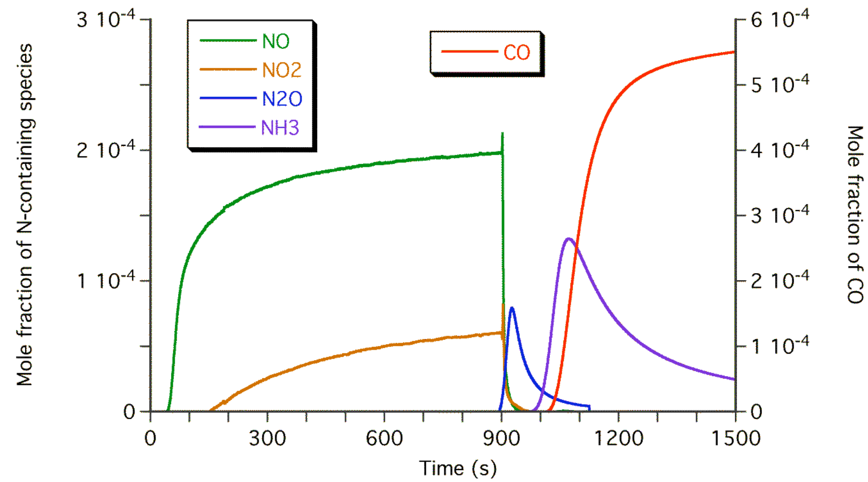
- Commercially available Umicore GDI LNT catalyst
- Space velocity 30,000/hr
- 15 min lean (300 ppm NO, 10% O_2)
- 10 min rich (625 ppm CO, 375 ppm H_2)
- 5% H_2O, 5% CO_2, N_2 carrier gas in all flows
- Reactor nearly isothermal at 200, 300, or 400 C
- Chemiluminescent analyzers for NO and total NOx; FTIR for CO, NH_3, and N_2O

At 200 C, fitting results using fixed PT parameters are largely correct qualitatively but could be better.

simulation



experiment



Outlet concentrations of gas-phase species during long storage/regeneration cycle at 200 C

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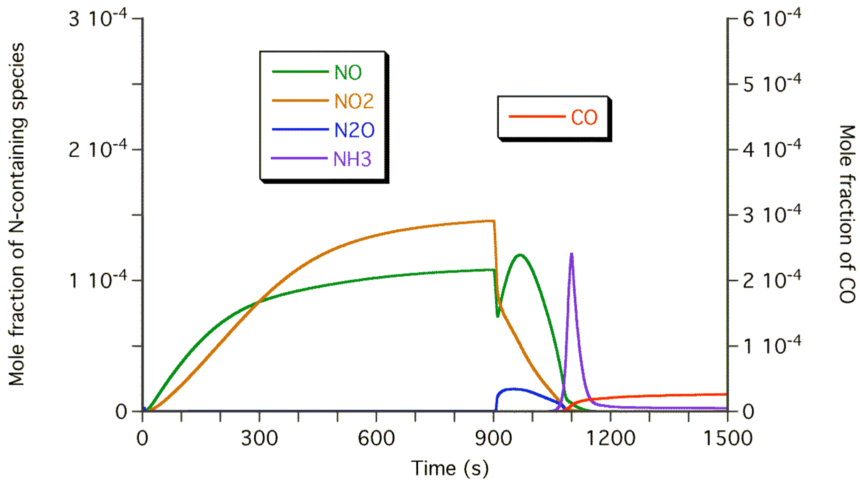
At 300 C, the simulation incorrectly predicts substantial NO slip during regeneration.

simulation



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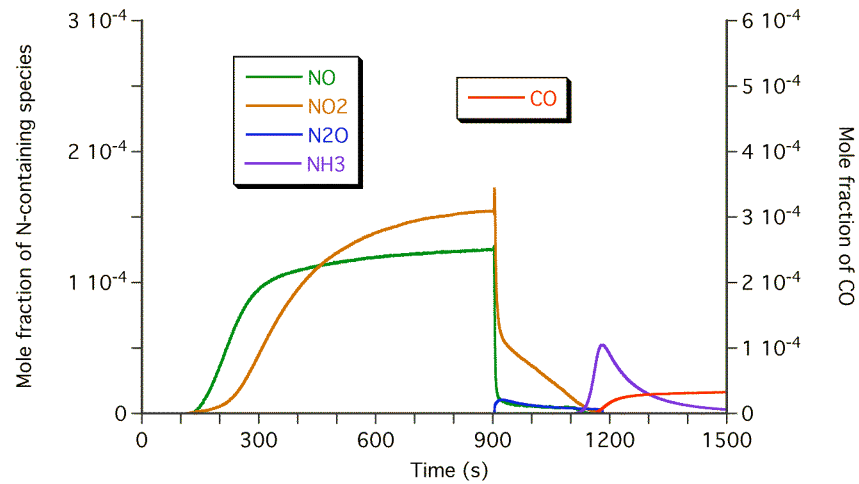

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 300 C

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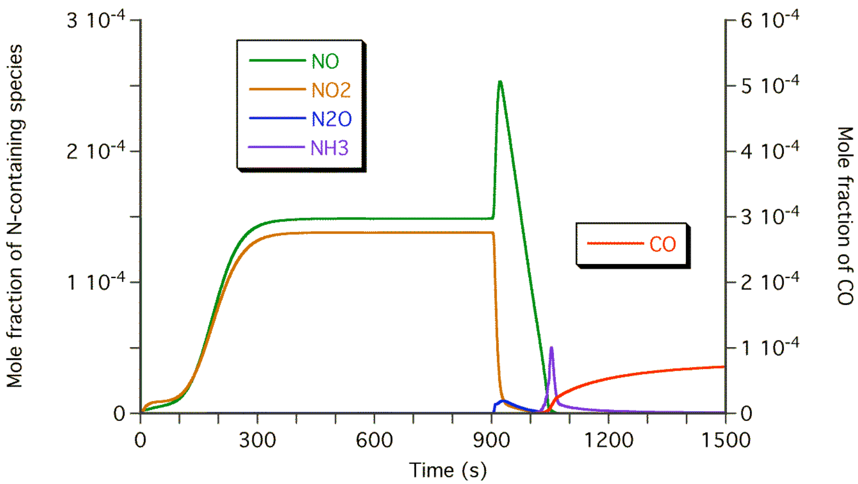
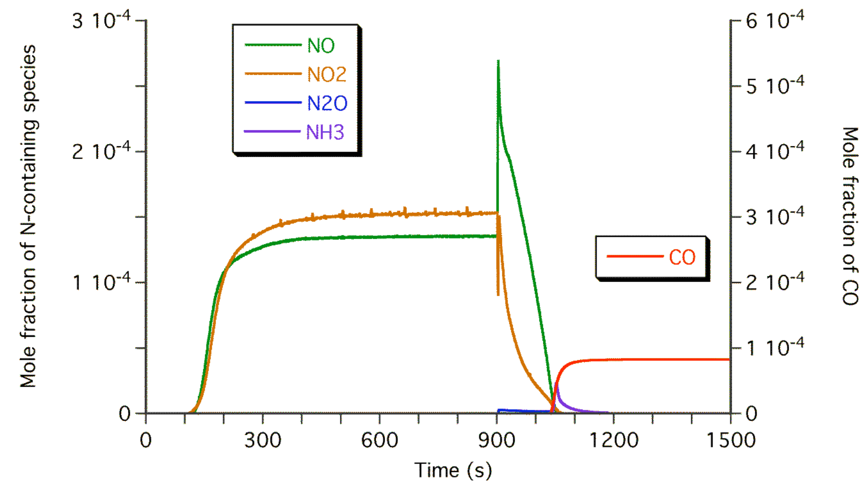
At 400 C, the predicted NO puff is actually observed and results are generally satisfactory.

simulation



experiment



Outlet concentrations of gas-phase species during long storage/regeneration cycle at 400 C

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At least four explanations for the deficiencies in the fits using fixed PT parameters are possible.

- **The precious metal mechanism alone, without storage reactions, may not be adequate to describe the chemistry in all of the temperature ramp experiments.**
- **The steady state plug flow reactor model, without washcoat diffusion, may not be adequate to describe the transport in the temperature ramp experiments.**
- **The description of transport, accumulation, and reaction within the washcoat in the transient plug flow model may be too simple to simulate the cycle experiments.**
- **The storage mechanisms used in simulating the cycle experiments may be incomplete or otherwise inadequate.**
- **At present the true explanation is not known.**

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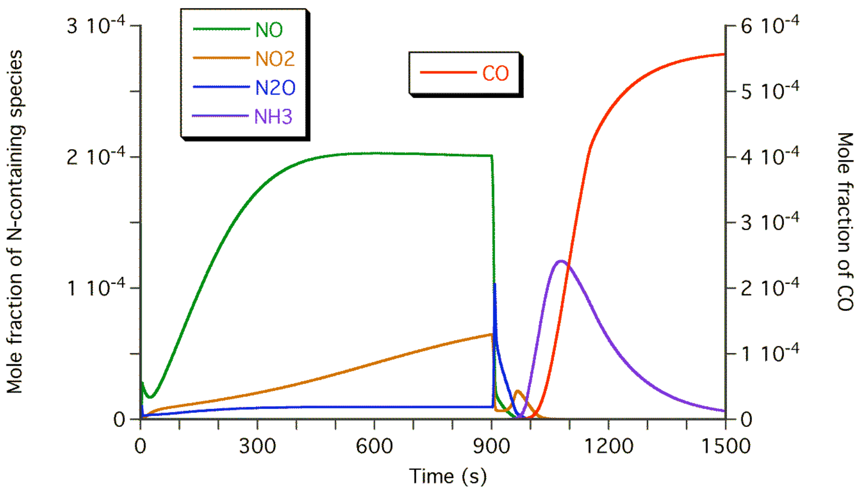
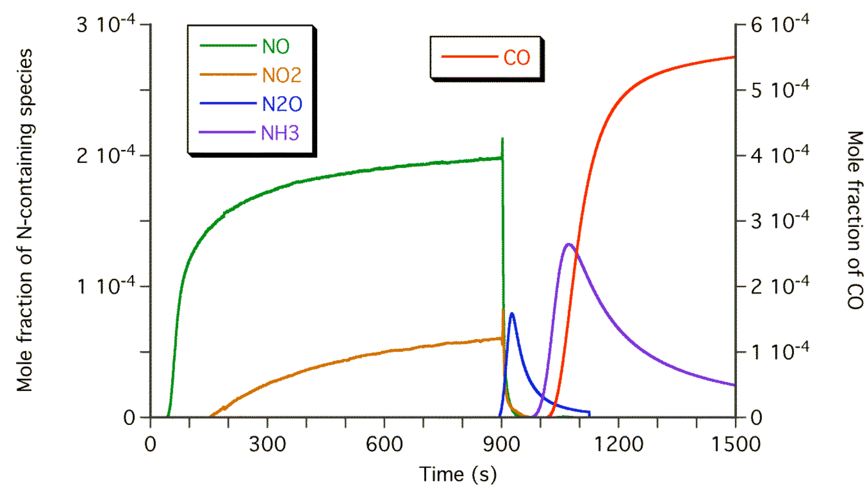
At 200 C, allowing the kinetic parameters in the PT reactions to vary does give significant improvement.

simulation



experiment



Outlet concentrations of gas-phase species during long storage/regeneration cycle at 200 C

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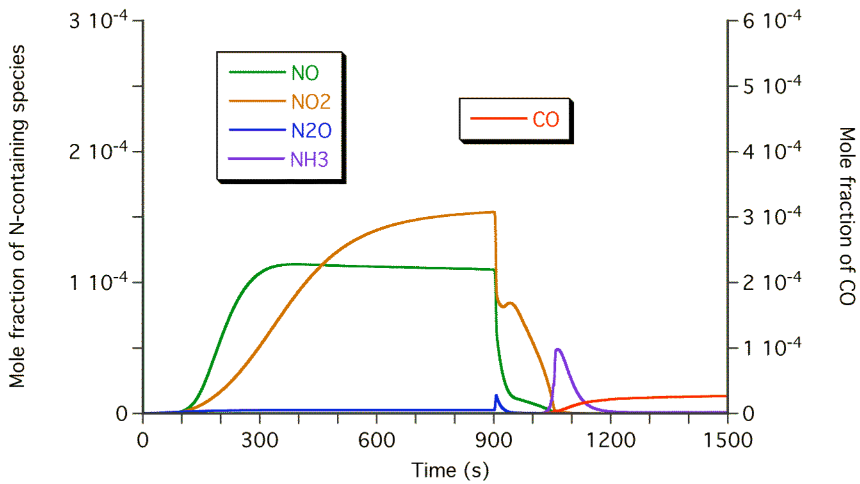
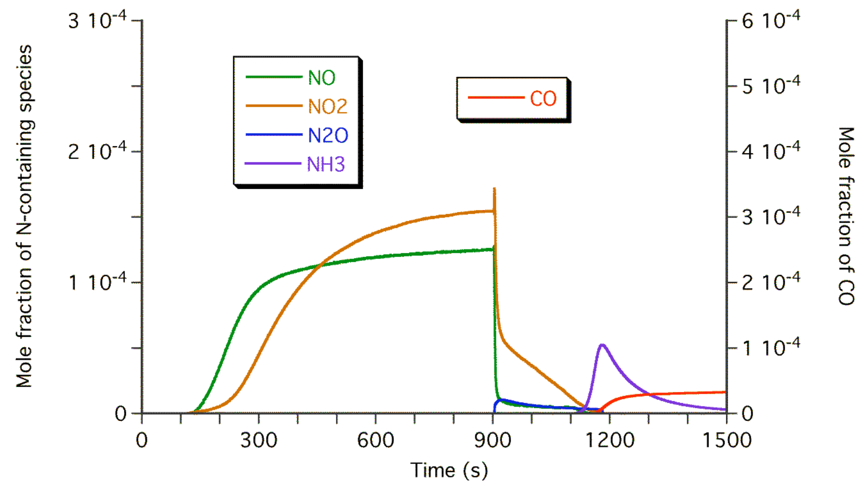
At 300 C, the spurious NO puff is now absent, but the timing of the NH3 peak is still inaccurate.

simulation



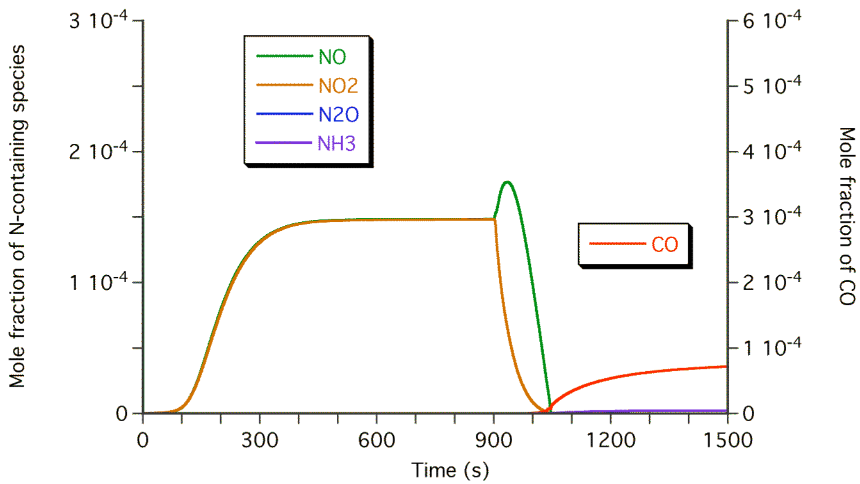
experiment



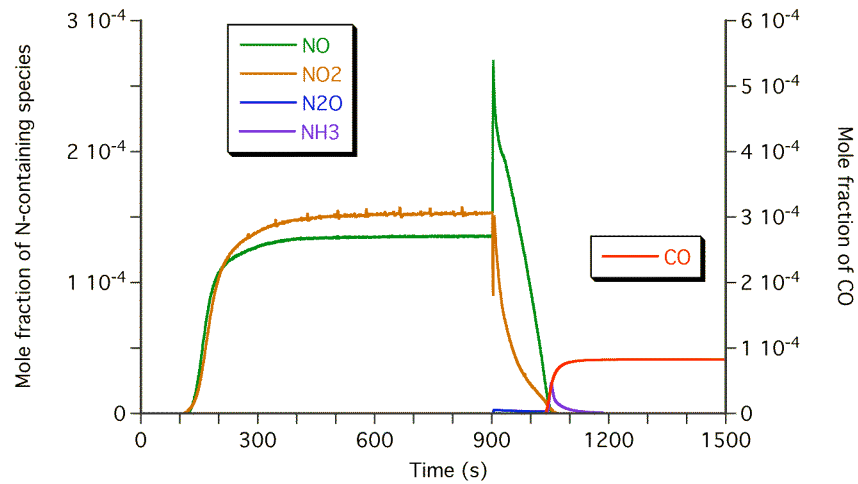
Outlet concentrations of gas-phase species during long storage/regeneration cycle at 300 C

At 400 C, the size of the NO puff is now somewhat underpredicted, and NH3 is completely absent.

simulation



experiment



Outlet concentrations of gas-phase species during long storage/regeneration cycle at 400 C

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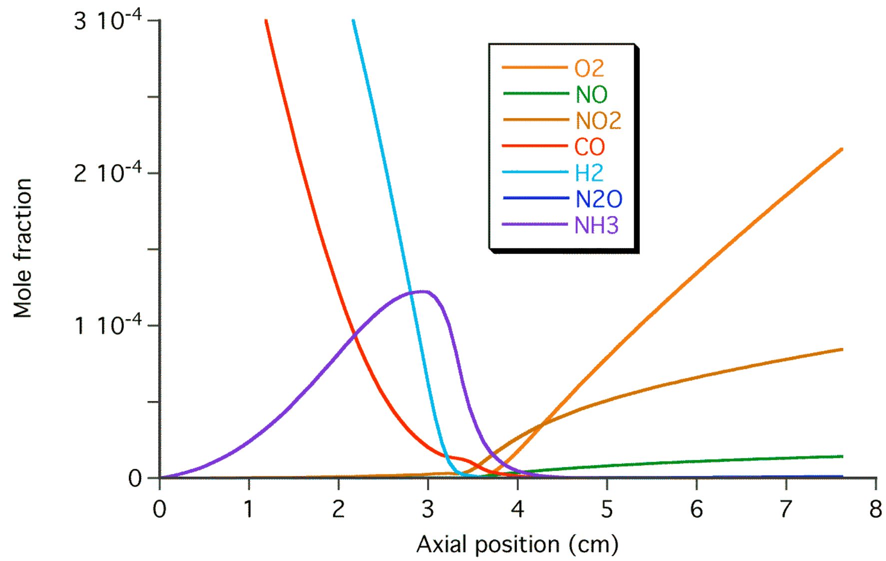
The simulations are consistent with hypotheses about the sequence of events during regeneration.

- **Near inlet, excess reductant converts desorbed NOx to NH3.**
- **As reductant is depleted, NH3 is oxidized by desorbed NOx and O2.**
- **After NH3 and reductant have been consumed, stored NOx and O2 desorb unhindered and exit the reactor.**

Axial profiles of gas-phase species concentrations at 944 s during long storage/regeneration cycle at 300 C



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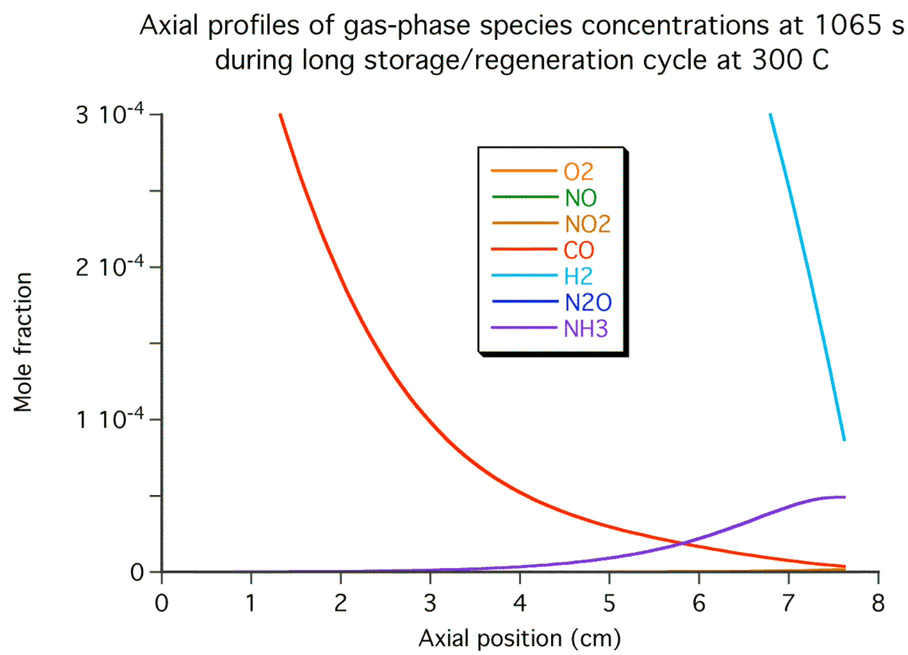
The simulations also explain the period of ammonia slip that follows the initial NOx escape.

- **The partially regenerated surface does not desorb sufficient NOx and O2 to deplete the reductants and fully oxidize the NH3 formed upstream.**
- **Ammonia slip ceases when all NOx has been desorbed (regeneration is complete).**



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Conclusions and future directions

- A thermodynamically consistent reaction mechanism that can simulate full LNT storage/regeneration cycles has been developed.
- To achieve completely satisfactory results, both the current reactor model and the previously obtained kinetic parameters for the precious metal phase may need to be modified.
- The simulations agree with previously proposed scenarios for the regeneration of the catalyst.
- A companion mechanism for sulfur poisoning and thermal desulfation is under development.

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