



Microkinetic Modeling of Lean NO_x Trap Storage/Regeneration and Sulfation/Desulfation

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Objectives

- Overall project goal: Obtain the fundamental surface chemistry knowledge needed for the design and optimal utilization of NO_x trap catalysts, thereby helping to speed the widespread adoption of this technology.
- Specific objective: Develop an elementary surface reaction mechanism, complete with values for the kinetic parameters, that accounts for the observed product distribution from a benchmark lean NO_x trap (LNT) during both normal cyclical operation and high-temperature desulfation, allowing for variations in both temperature and inlet gas composition.





Approach

- Assemble tentative reaction sets for precious metal (catalytic), baria (NO_x storage), and ceria (oxygen storage) sites.
- Infer kinetic parameters for precious metal sites by matching product distributions from steady flow experiments done at ORNL.
 - Use Chemkin plug flow code to simulate flow of reactant mixture through a catalyst monolith channel.
 - Use Sandia APPSPACK code to find kinetic parameters by optimizing overall fit to experimental data.
 - Apply thermodynamic constraints during fitting procedure in order to ensure complete consistency.
- Infer kinetic parameters for baria and ceria sites by matching product distributions from long cycle experiments.
 - Use transient plug flow code with allowance for radial mass transfer.
- Augment all three sub-mechanisms with reactions involving sulfur-containing species, and estimate parameters from sulfation and desulfation runs.





Storage mechanism

- The mechanism describing chemistry on the baria and ceria sites involves nine new chemical species.
 - On baria: $V(\text{BAO})$, $\text{NO}_2(\text{BAO})$, $\text{CO}_3(\text{BAO})$, $\text{NO}_3(\text{BAO})$, $\text{O}(\text{BAO})$, $(\text{OH})_2(\text{BAO})$, $\text{BA}(\text{NO}_3)_2$ (“bulk” nitrate)
 - On ceria: $V(\text{CERIA})$, $\text{O}(\text{CERIA})$
- Seven reversible reactions account for NO_x storage on baria sites:
 - $\text{O}_2 + 2V(\text{BAO}) = 2\text{O}(\text{BAO})$
 - $\text{NO}_2 + \text{O}(\text{BAO}) = \text{NO}_3(\text{BAO})$
 - $\text{NO}_2 + \text{NO}_2(\text{BAO}) = \text{NO} + \text{NO}_3(\text{BAO})$
 - $\text{NO}_2 + \text{CO}_3(\text{BAO}) = \text{NO}_3(\text{BAO}) + \text{CO}_2$
 - $(\text{OH})_2(\text{BAO}) + \text{NO}_2 = \text{NO}_3(\text{BAO}) + \text{H}_2\text{O}$
 - $(\text{OH})_2(\text{BAO}) + \text{CO}_2 = \text{CO}_3(\text{BAO}) + \text{H}_2\text{O}$
 - $\text{NO}_2(\text{BAO}) + \text{O}(\text{BAO}) = \text{NO}_3(\text{BAO}) + V(\text{BAO})$





Storage mechanism (continued)

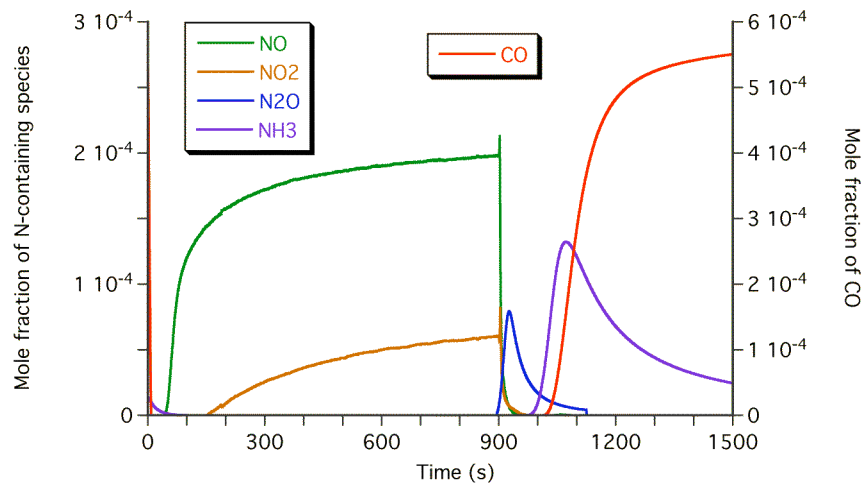
- Three reactions describe formation of “bulk” nitrate:
 - $2\text{NO}_3(\text{BAO}) = \text{BA}(\text{NO}_3)_2 + \text{O}(\text{BAO})$
 - $\text{NO}_3(\text{BAO}) + \text{NO}_2 = \text{BA}(\text{NO}_3)_2$
 - $\text{NO}_3(\text{BAO}) + \text{NO}_2(\text{BAO}) = \text{BA}(\text{NO}_3)_2 + \text{V}(\text{BAO})$
- There are five spillover reactions (involving species on both BAO and PT):
 - $\text{NO}_2(\text{PT}) + \text{V}(\text{BAO}) = \text{NO}_2(\text{BAO}) + \text{V}(\text{PT})$
 - $\text{NO}_3(\text{BAO}) + \text{H}(\text{PT}) = \text{NO}_2(\text{BAO}) + \text{OH}(\text{PT})$
 - $\text{NO}_3(\text{BAO}) + \text{CO}(\text{PT}) = \text{NO}_2(\text{BAO}) + \text{CO}_2 + \text{V}(\text{PT})$
 - $\text{BA}(\text{NO}_3)_2 + \text{H}(\text{PT}) = \text{NO}_3(\text{BAO}) + \text{OH}(\text{PT}) + \text{NO}$
 - $\text{BA}(\text{NO}_3)_2 + \text{CO}(\text{PT}) = \text{NO}_3(\text{BAO}) + \text{CO}_2 + \text{V}(\text{PT}) + \text{NO}$
- Oxygen storage on ceria is described by just one simple reaction:
 - $\text{O}_2 + 2\text{V}(\text{CERIA}) = 2\text{O}(\text{CERIA})$
- These reactions are combined with the precious metal mechanism and used with a transient plug flow code (including radial mass transfer resistance) to simulate complete storage/regeneration cycles.



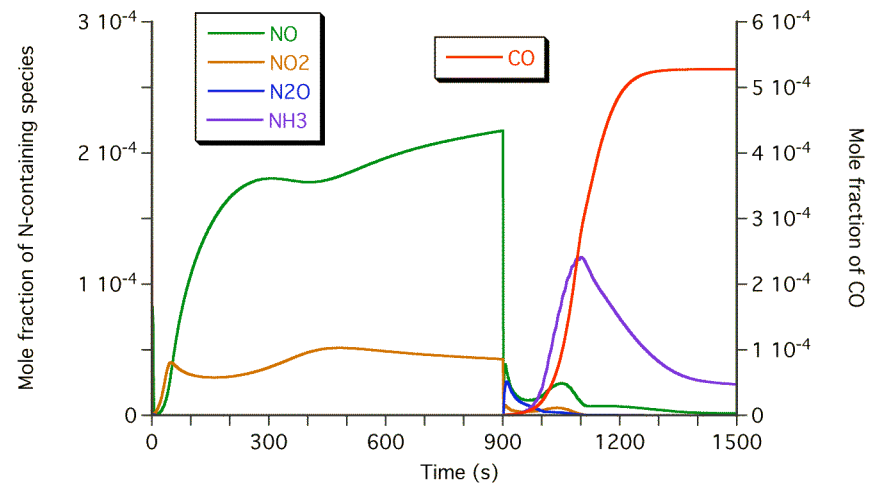


Simulation vs. experiment at 200 C

- Simulation of NO_x storage, release, and reduction (i.e., a complete storage/regeneration cycle) at 200 C is basically successful.
 - Artificially long cycle time is used to allow resolution of transients.
 - Feed gas contains 288 ppm NO and 10% O₂ during storage phase, 625 ppm CO and 375 ppm H₂ during regeneration phase.
 - Principal failures are underprediction of N₂O and overprediction of NO during early part of regeneration.



Experiment

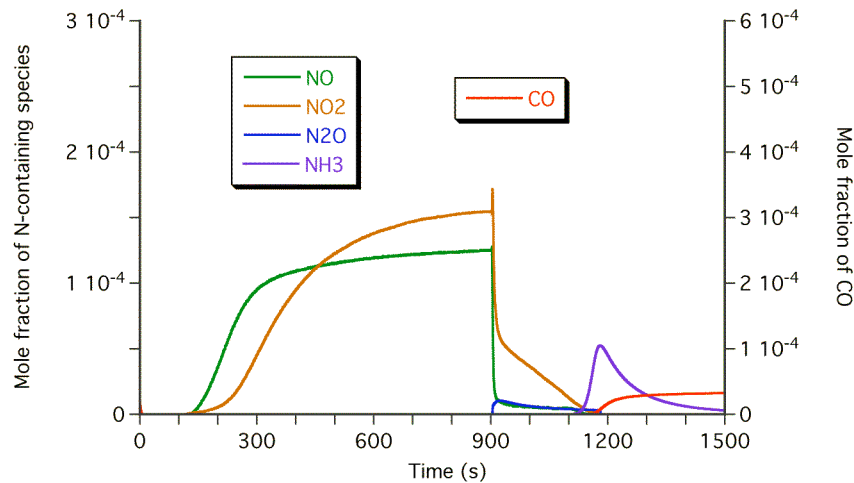


Simulation

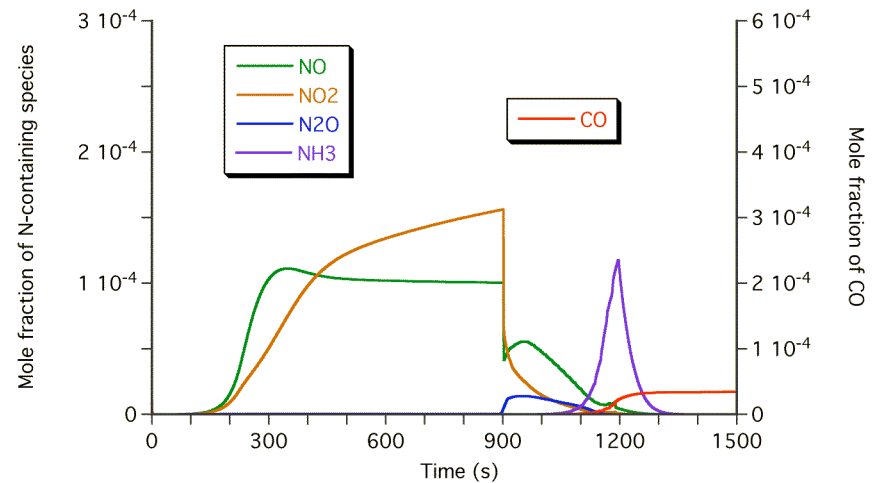


Simulation vs. experiment at 300 C

- The simulation at 300 C is likewise mostly successful but with some noticeable imperfections.
 - Predicted NO peak following the onset of regeneration is not observed experimentally, but predicted slip of total NO_x is not far off.
 - Timing of NH₃ spike is reproduced accurately, but peak is too high and narrow.
 - In this case, N₂O production is simulated fairly well.



Experiment

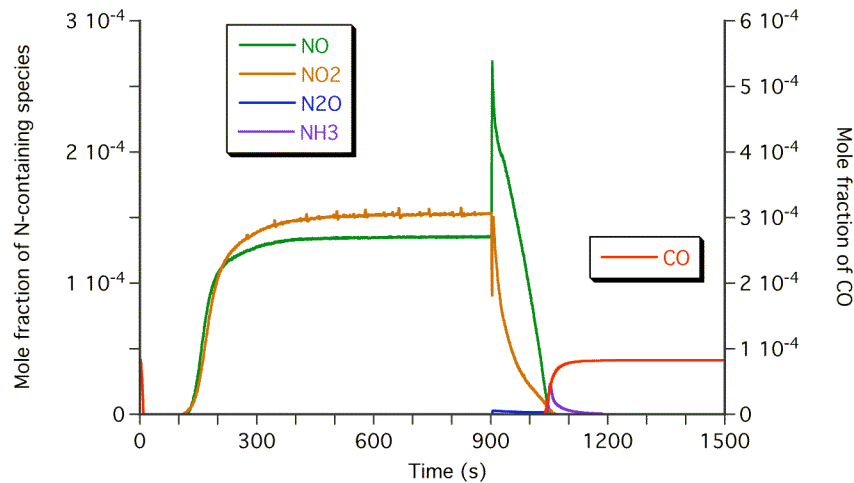


Simulation

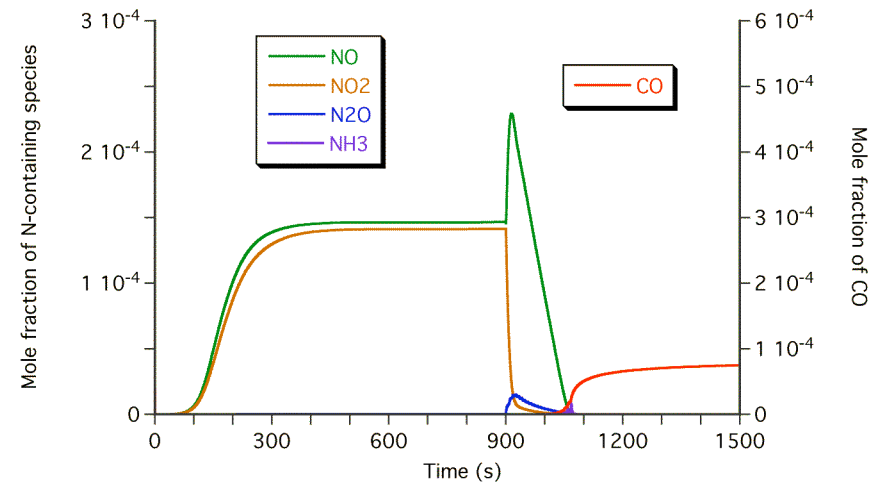


Simulation vs. experiment at 400 C

- Simulation of cycle at 400 C appears to be less demanding (presumably dominated by equilibrium) and is correct in most respects.
 - Falloff in NO₂ at onset of regeneration is somewhat too rapid.
 - Well-known NO puff is reproduced very well.
 - Once again, timing of NH₃ pulse (quite small here) is correctly reproduced.



Experiment

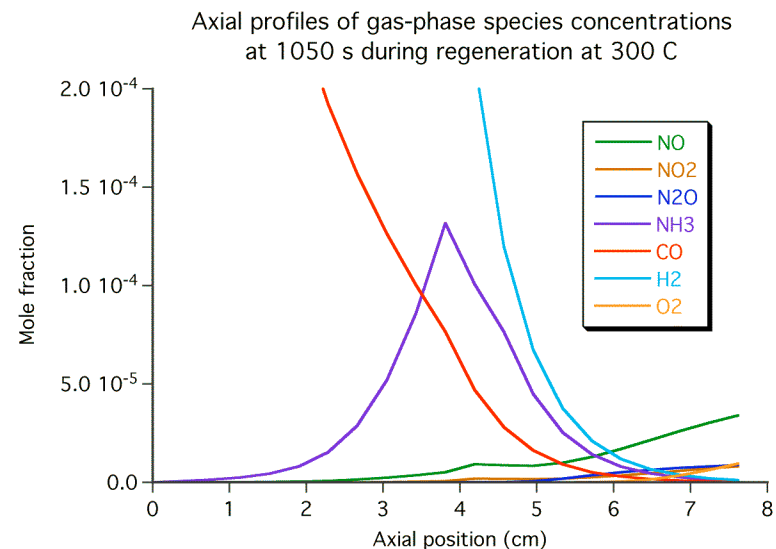
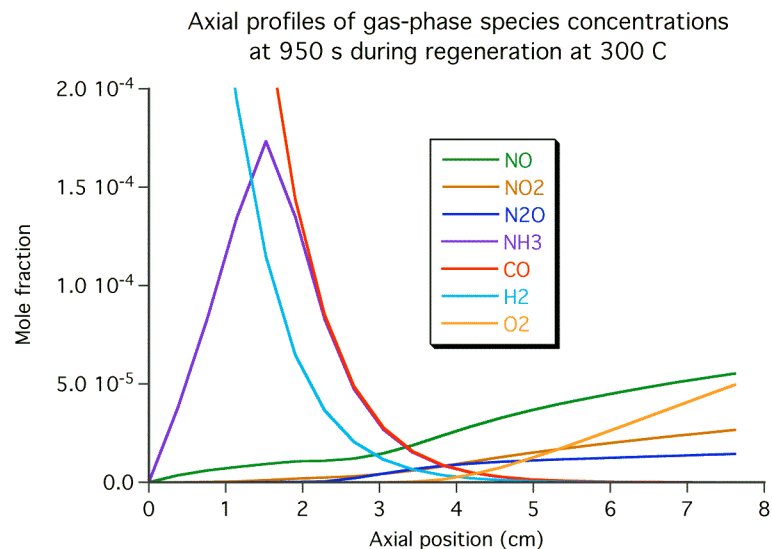


Simulation



Axial profiles — NH₃ as reduction intermediate

- The oft-proposed role of NH₃ as an intermediate in the reduction of released NO_x is consistent with the simulations.
 - Near the leading edge of the unregenerated zone, excess reductant converts desorbed NO_x to NH₃.
 - As reductant is depleted, NH₃ is oxidized by desorbed NO_x and O₂.
 - After NH₃ and original reductant have been consumed, stored NO_x and O₂ desorb unhindered and exit the reactor.

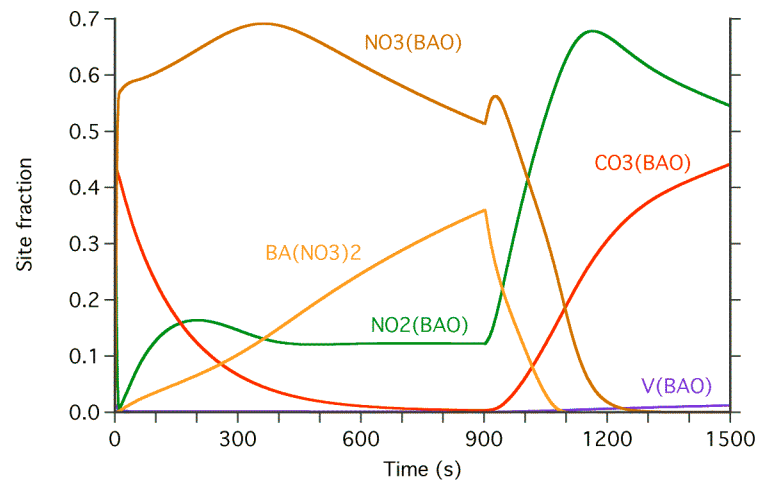




Evolution of storage phase compositions

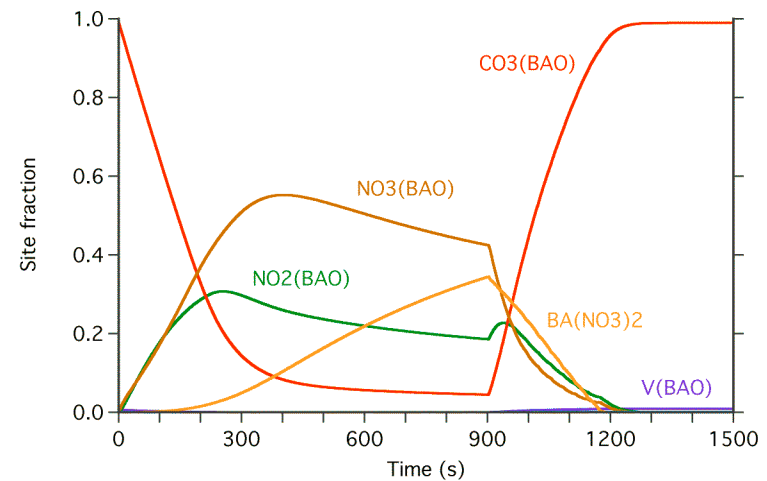
- The simulations predict the changes in the storage phase composition over the course of a cycle.
 - During NO_x storage, carbonates are (partially) replaced by nitrites and nitrates.
 - At both 300 C and 400 C, but not 200 C, the baria phase is completely cleansed of NO_x during regeneration.

Spatially-averaged concentrations of storage phase species during long storage/regeneration cycle at 200 C



200 C

Spatially-averaged concentrations of storage phase species during long storage/regeneration cycle at 300 C



300 C

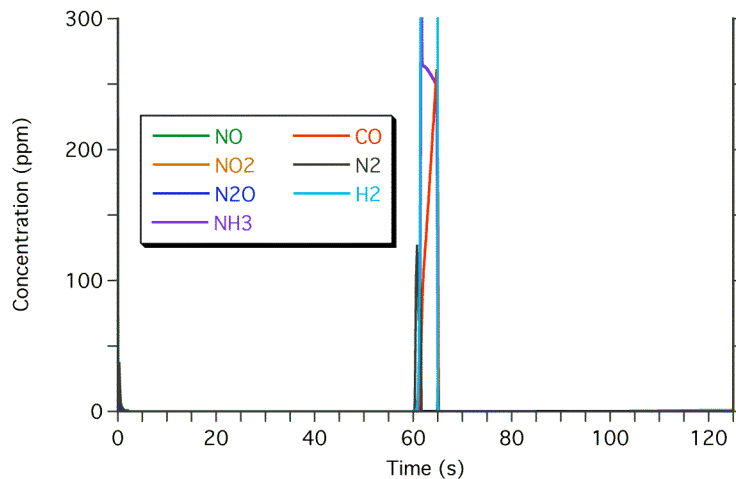




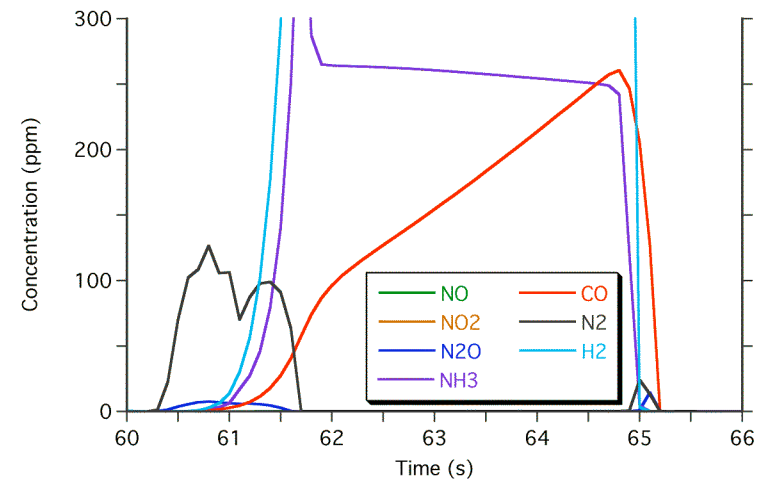
Predictions of short cycle behavior

- The mechanism inferred from long cycle experiments can be used to predict behavior during a short (60 s lean/5 s rich) cycle.
 - First cycle begins with a completely clean surface.
 - Simulation is isothermal (questionable) and now uses argon as the bath gas.
 - Essentially no NO_x escapes during first two lean periods.
 - NH₃ production during regeneration is attributable largely to CO.

Simulated outlet concentrations of gas-phase species during short storage/regeneration cycle at 325 C (lean: 300 ppm NO; rich: 2700 ppm H₂, 4500 ppm CO)



Simulated outlet concentrations of gas-phase species during first regeneration at 325 C (lean: 300 ppm NO; rich: 2700 ppm H₂, 4500 ppm CO)





Sulfation/desulfation mechanism

- A mechanism describing the effects of sulfur compounds on all aspects of the chemistry has been developed but not yet finalized.
 - 7 new species on PT: SO₂(PT), SO₃(PT), H₂S(P), SO(P), S(P), HS(P), COS(P)
 - 1 new species each on baria and ceria: SO₄(BAO), SO₄(CERIA)
 - 18 new reactions (tentatively) on PT, accounting for SO₂ oxidation during lean phase and reduction of SO₃ to H₂S during desulfation
 - 7 new reactions on baria and 1 on ceria, accounting for sulfate formation
- The overall mechanism has been used to simulate loss of NO_x storage capacity during normal cycling and evolution of products during high-temperature desulfation.
- The mechanism is currently too complex for all parameters to be extracted from experimental data; some reactions are inoperative.

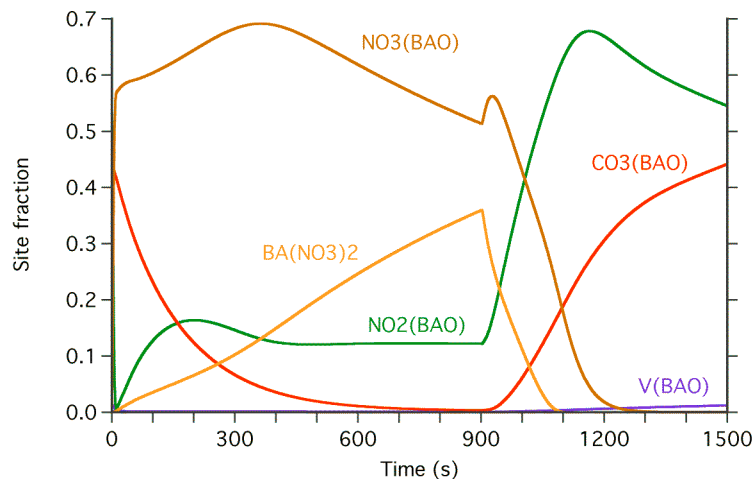




Simulation of long cycle with SO₂ in feed

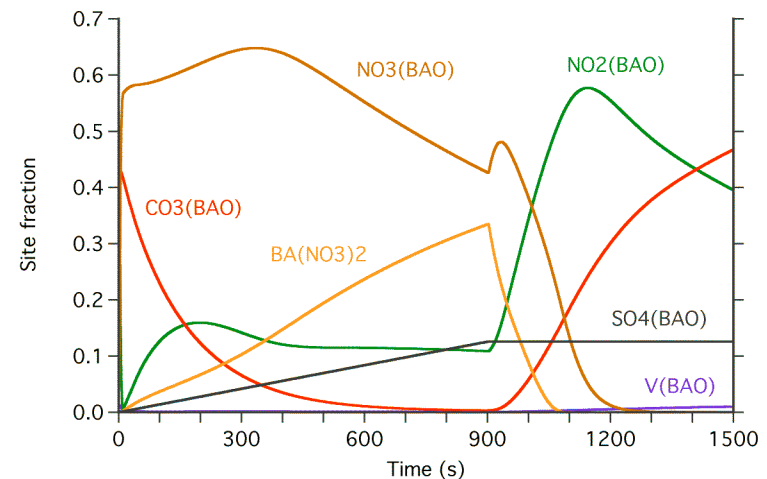
- Simulations of long cycles with SO₂ in the lean-phase feed can be carried out to check the mechanism for qualitatively correct behavior.
 - 10 ppm SO₂ is added to the 288 ppm NO and 10% O₂ already present.
 - Spatially-averaged sulfate level rises linearly during storage (no SO₂ slip) and remains constant during regeneration (no desulfation).

Spatially-averaged concentrations of storage phase species during long storage/regeneration cycle at 200 C



No SO₂ added

Spatially-averaged concentrations of storage phase species during long storage/regeneration cycle at 200 C



10 ppm SO₂ added

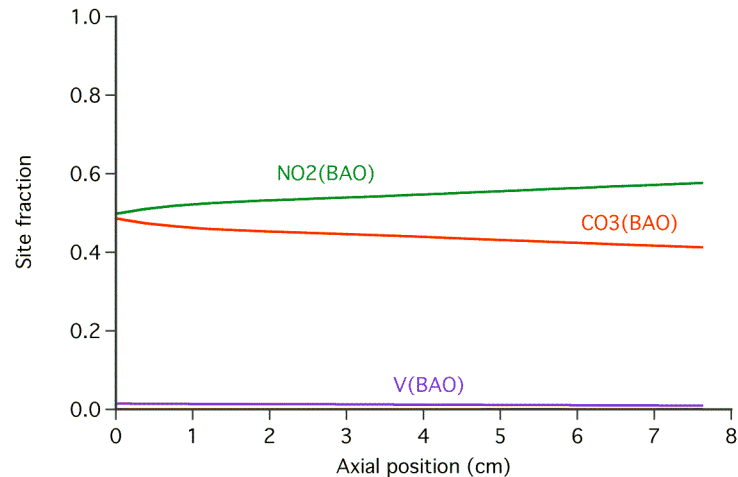




Spatial profile of sulfation

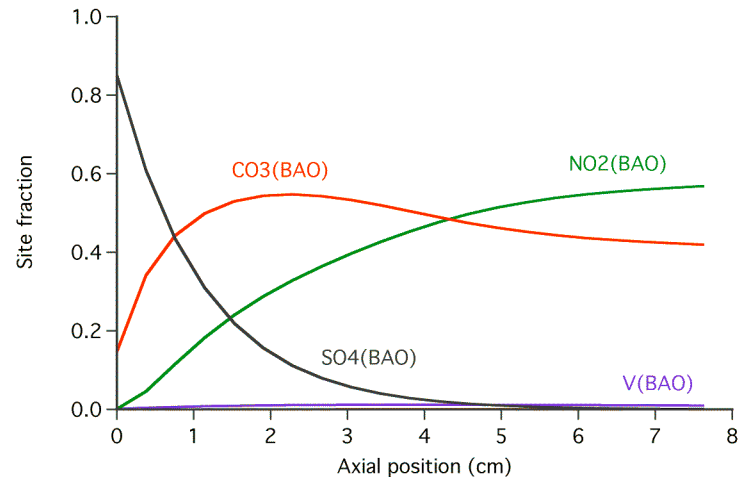
- The simulations are also consistent with the observation that sulfation of the NO_x storage sites tends to be concentrated at the front of the reactor.
 - At ordinary cycle temperatures, sulfate permanently displaces both nitrite and carbonate.

Simulated concentration profiles of baria-phase species at end of long storage/regeneration cycle at 200 C



No SO₂ added

Simulated concentration profiles of baria-phase species at end of long storage/regeneration cycle at 200 C



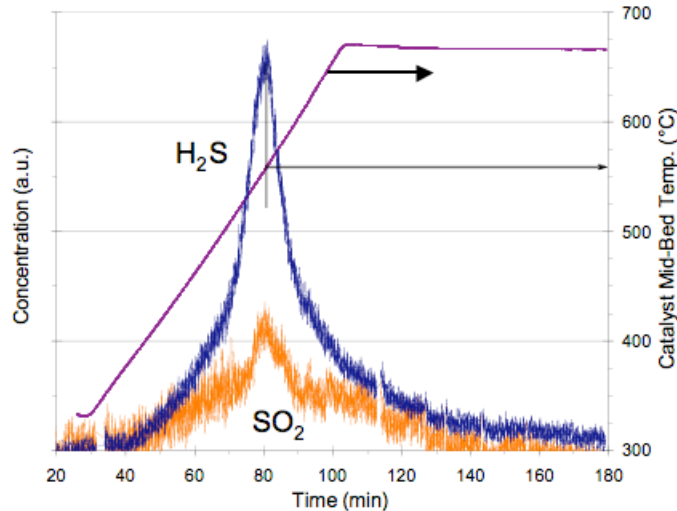
10 ppm SO₂ added



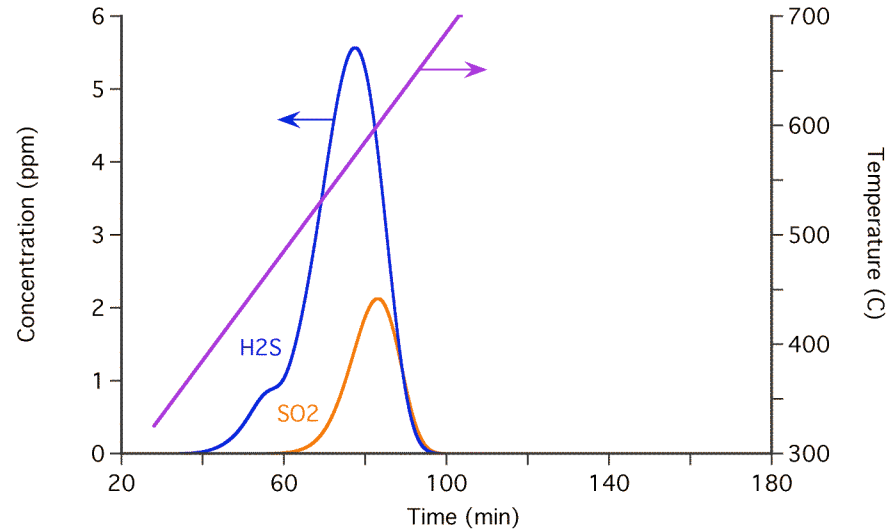


Preliminary simulation of desulfation

- Simulation of desulfation by temperature-programmed reduction is in reasonable qualitative agreement with experiment.
 - After sulfation at 300 C, temperature ramped at 5 C/min under 0.1% H₂.
 - Experimental concentrations are in arbitrary units (i.e., magnitude unspecified).
 - Simulated peaks should be shifted and reshaped by adjusting kinetic constants.



Experiment (ORNL)



Simulation



Future directions

- Complete evaluation of kinetic parameters describing sulfur chemistry on precious metal, baria, and ceria sites.
 - Reduce mechanism by discarding reactions if insufficient data exist to distinguish between parallel pathways.
- Augment mechanism with reactions accounting for reductants other than CO and H₂.
 - Unburned and/or partially burned hydrocarbons may play a role, depending on mode of operation.
 - Addition of reforming reactions should provide a bridge between hydrocarbon reductants and existing mechanism.
- Develop computational tools to handle fully nonisothermal simulations.
 - Current code uses imposed (e.g., experimentally determined) spatial and temporal variations in temperature.
 - The capability to compute temperatures internally is obviously desirable, especially for short cycle simulations.





Conclusions

- We have attempted to construct a complete mechanism for LNT operation (including sulfation/desulfation) which involves (a) elementary reactions obeying mass-action kinetics, (b) full and rigorous thermodynamic consistency, and (c) both H₂ and CO as reductants.
- We have used a three-tiered approach to developing the mechanism and benchmarking it against experimental data.
 - A mechanism for precious metal sites, based on steady flow experiments, has been completed and published.
 - A mechanism for NO_x and O₂ storage sites, based on long cycle experiments, has been tentatively completed, although future modifications are possible.
 - A supplemental mechanism for sulfur chemistry has been constructed, and preliminary parameter evaluation has been accomplished.
- A fourth tier, aimed at simulating the use of reductants other than H₂ and CO, is to be started shortly.
- Observed shortcomings in the simulations may be due to defects in the mechanism or overly simplified modeling of the reactor (monolith channel) itself.





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