Benchmark Reaction Mechanisms and Kinetics for Lean NOx Traps

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Overview

Timeline

- Project involves ongoing fundamental research that supports DOE/industry development efforts for advanced lean-burn engine aftertreatment systems.
- Project directions and continuation are evaluated annually.

Barriers

- Relevant barriers from 2006 ACEC Technical Roadmap:
  - Detailed understanding of catalyst fundamentals is lacking.
  - NOx adsorbers have a strong sensitivity to sulfur in the fuel.
  - NOx adsorbers are effective only within a relatively narrow temperature window.

Budget

- Project funded by DOE Vehicle Technologies Program:

  FY08 - $250K
  FY09 - $251K

Partners

- Principal collaborators: Oak Ridge National Laboratory (V. K. Chakravarthy, J. A. Pihl, C. S. Daw, and J.-S. Choi)

Objectives

- Overall project goal: Obtain the fundamental surface chemistry knowledge needed for the design and optimal utilization of NOx 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 NOx trap (LNT) during both normal cyclical operation and high-temperature desulfation, allowing for variations in both temperature and inlet gas composition.

Milestones

	FY07	FY08	FY09	FY10
Develop NOx reduction chemistry				
Develop NOx storage and release chemistry				
Develop sulfation and desulfation chemistry				
Develop chemistry for alternate reductants				
Study coupling of LNTs with other components				

Approach

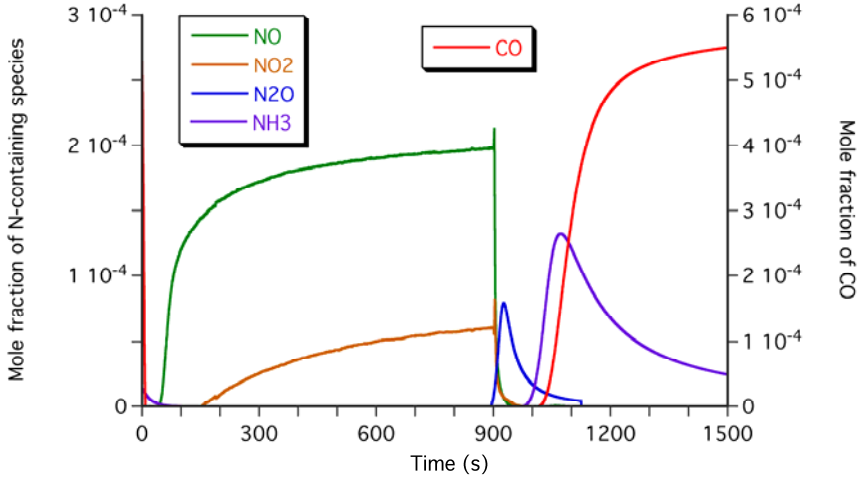
- Assemble tentative reaction sets for precious metal (catalytic), baria (NOx storage), and ceria (oxygen storage) sites.
- Infer kinetic parameters for precious metal sites by matching product distributions from steady flow experiments done at Oak Ridge National Lab (ORNL):
  - Use Chemkin plug flow 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 cycling (storage/regeneration) experiments.
- Augment all three sub-mechanisms with reactions involving sulfur-containing species, and extract parameters as before.

Technical Accomplishments

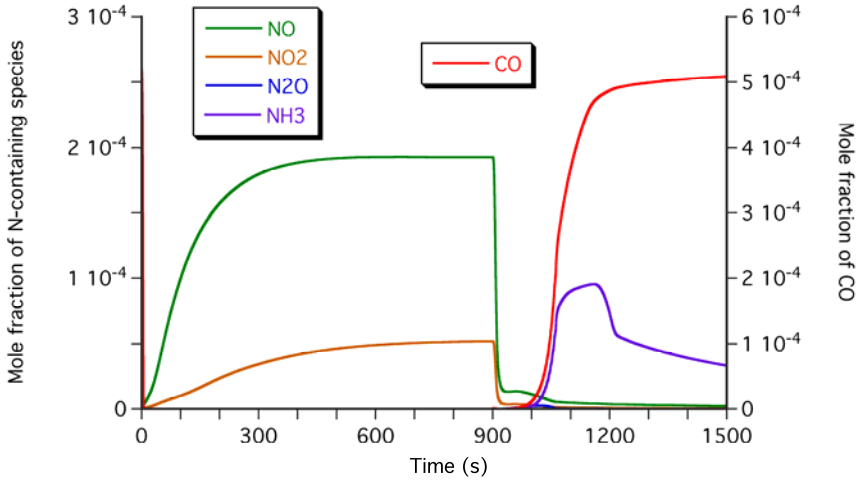
- The mechanism describing chemistry on the baria and ceria sites has been finalized (although future modifications are not ruled out):
  - 8 chemical species on baria, 2 on ceria
  - 11 reversible reactions involving baria sites, 1 (oxygen storage) involving ceria
- This is combined with the precious metal (nominally PT) mechanism and used with a transient plug flow code (including washcoat mass transfer resistance) to simulate complete storage/regeneration cycles.
- 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, 1 each (sulfate) on baria and ceria
  - 18 new reactions on PT (accounting for SO2 oxidation during lean phase and reduction of SO3 to H2S during desulfation)
  - 7 new reactions on baria, 1 on ceria (sulfation)
- The overall mechanism is used to simulate loss of NOx storage capacity during normal cycling and evolution of products during high-temperature desulfation.

Technical Accomplishments

- Simulation of NOx 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 NO and excess O2 during storage phase, reductants CO and H2 during regeneration phase.
  - Only obvious failure is severe underprediction of N2O production (cause unknown despite exhaustive attempts to overcome it).



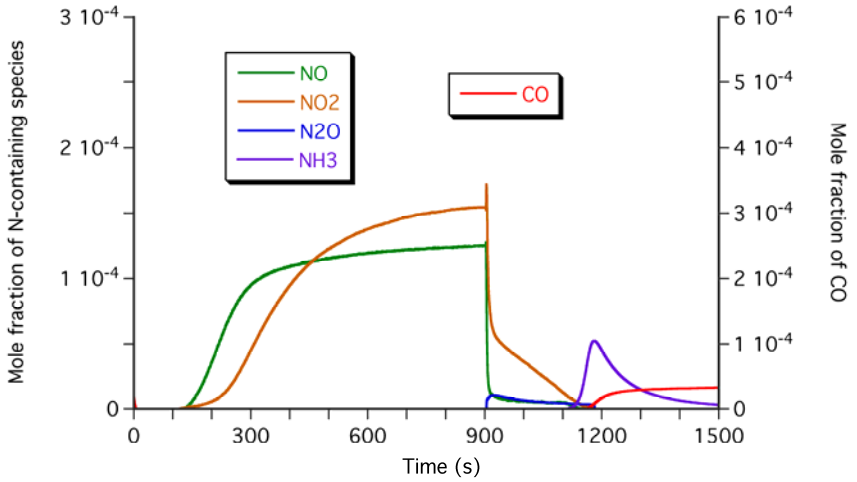
Experiment



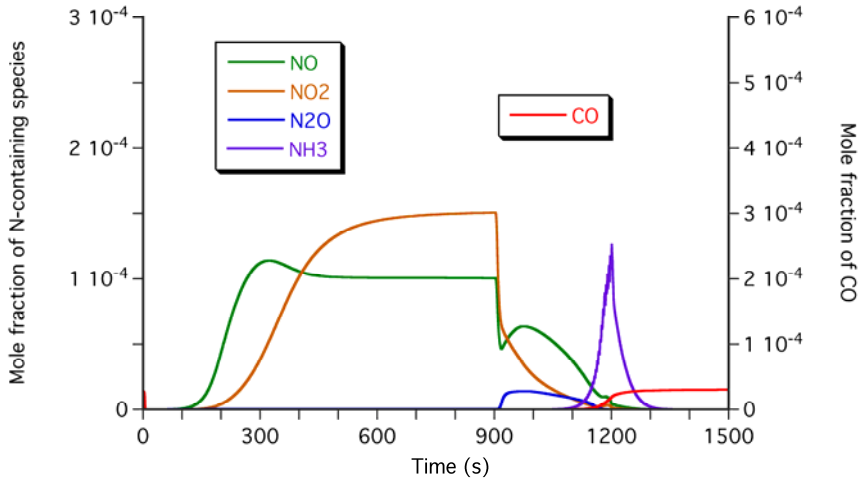
Simulation

Technical Accomplishments

- The simulation at 300 C is likewise mostly successful but with some noticeable imperfections.
  - Broad NO puff following the onset of regeneration is not observed experimentally.
  - Timing of NH3 spike is reproduced accurately, but peak is too high and narrow.
  - In this case, N2O production is simulated quite well.



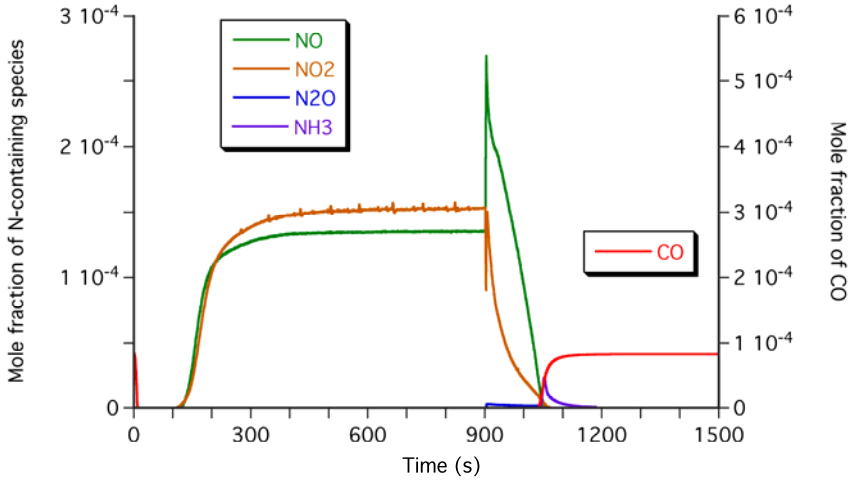
Experiment



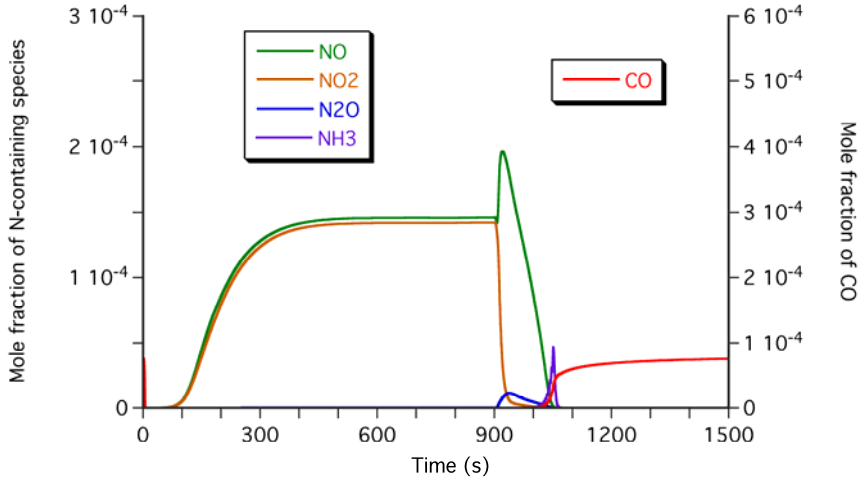
Simulation

Technical Accomplishments

- 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 reasonably well.
  - Once again, timing of NH3 pulse is correctly reproduced.



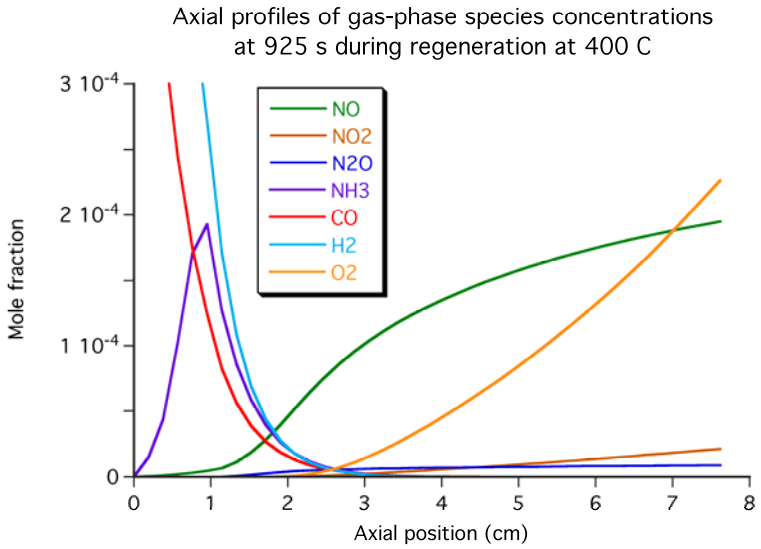
Experiment

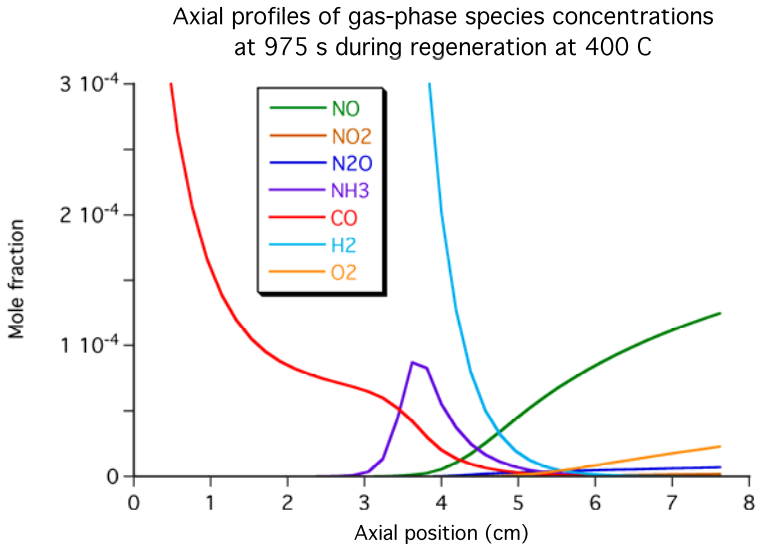


Simulation

Technical Accomplishments

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

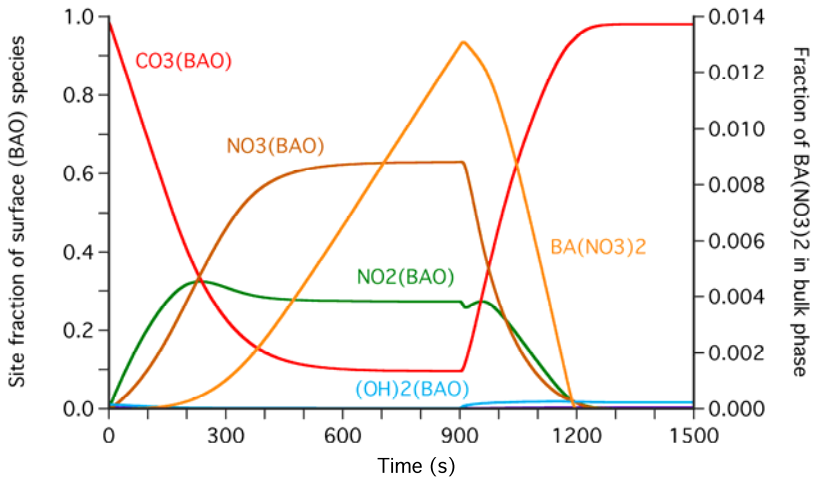




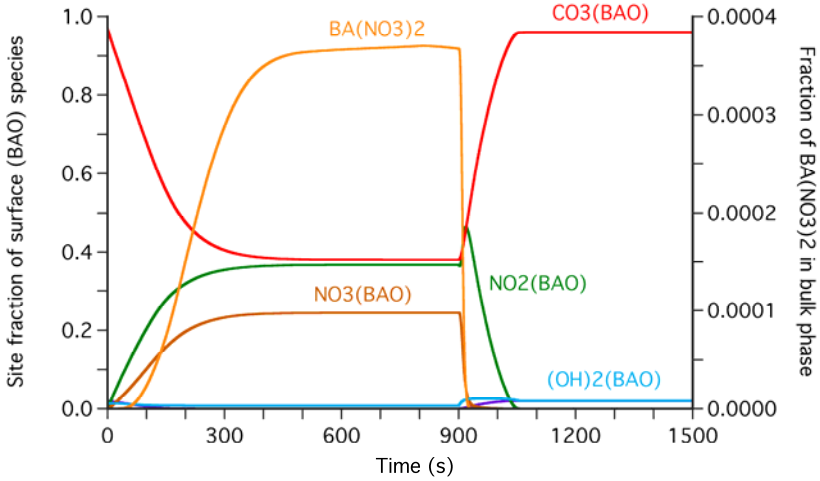
Technical Accomplishments

- The simulations predict the changes in the storage phase composition over the course of a cycle.
  - During NOx 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 NOx during regeneration.

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



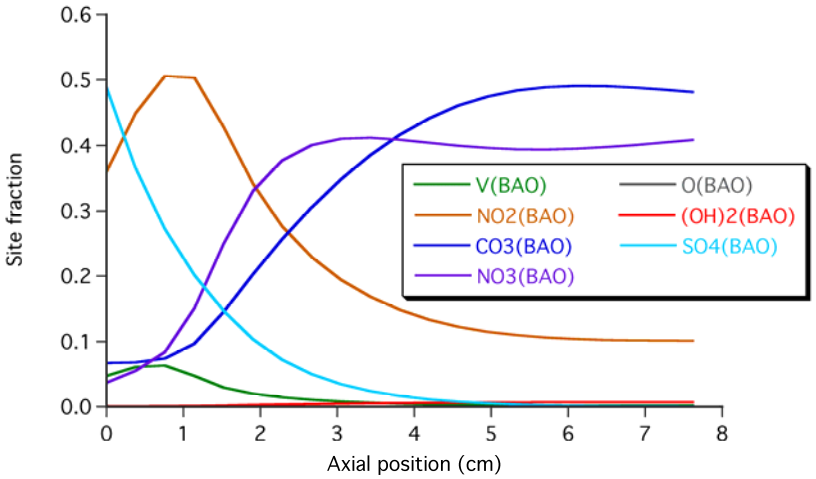
Spatially-averaged concentrations of storage phase species during long storage/regeneration cycle at 400 C



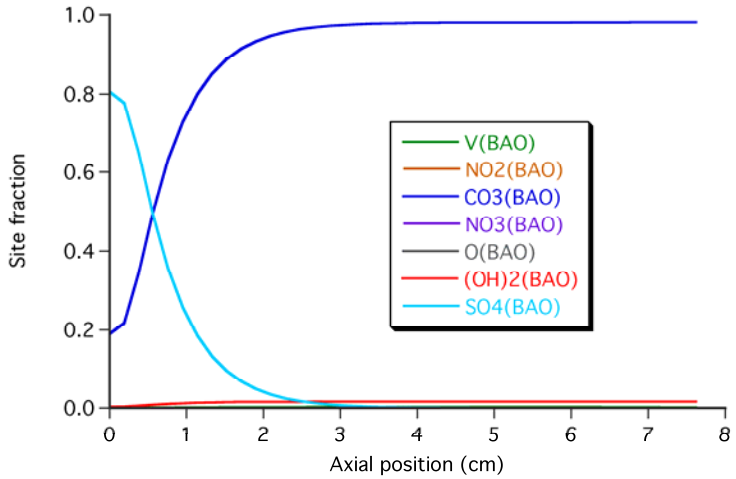
Technical Accomplishments

- Simulations of cycles with SO2 in the lean-phase feed are consistent with the observation that sulfation of the NOx storage sites is more plug-like at 300 C than at 200 C.

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

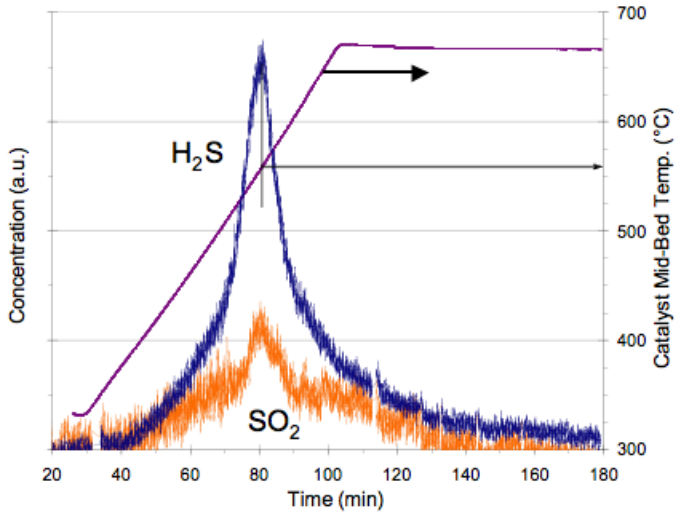


Simulated concentration profiles of baria-phase species at end of long storage/regeneration cycle at 300 C

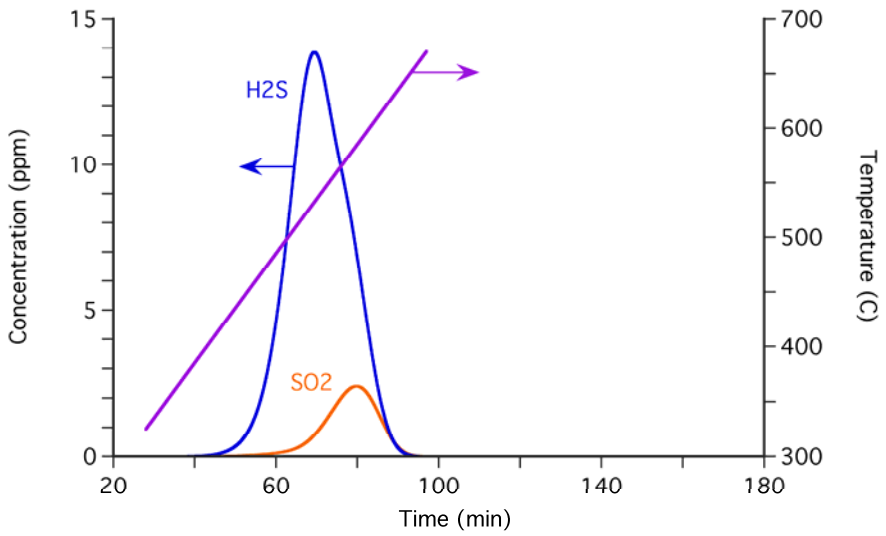


Technical Accomplishments

- Simulation of desulfation by temperature-programmed reduction is in reasonable qualitative agreement with experiment.
  - Temperature ramped at 5 C/min with a feed containing 0.1% H2.
  - Experimental concentrations are not quantitative.
  - Still, simulated peaks should be shifted and reshaped by adjusting kinetic constants.



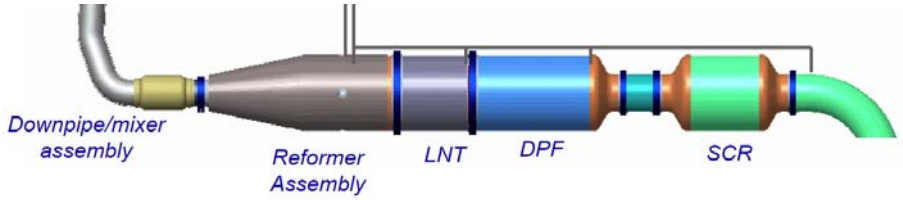
Experiment (ORNL)



Simulation

Future Work

- Complete evaluation of kinetic parameters describing sulfur chemistry on precious metal, baria, and ceria sites (FY09).
  - 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 (FY09+).
  - Unburned and/or partially burned hydrocarbons may play a role, depending on mode of operation.
- Use the completed mechanism to model integration of an LNT with other devices in the aftertreatment train (FY10).
  - While NH3 is often regarded as an undesirable byproduct, it can also be used as the feed to a selective catalytic reduction (SCR) component, as in the Eaton system.



Summary

- A fundamental understanding of LNT chemistry is needed to realize the full potential of this aftertreatment technology, which could lead to greater use of fuel-efficient lean-burn engines.
- We have used a three-tiered approach to developing an elementary chemical mechanism benchmarked against experimental data.
  - Mechanism for precious metal sites, based on steady flow experiments, has been completed and published.
  - Mechanism for NOx and O2 storage sites, based on long cycle experiments, has been tentatively completed, although future modifications are possible.
  - 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.
- Our ultimate goal is to facilitate improved designs for LNT-based aftertreatment systems and possibly to assist in the development of improved catalysts.