Development of Chemical Kinetic Models for Lean NOx Traps

Richard S. Larson
Sandia National Laboratories
Livermore, CA 94551-0969

DOE Vehicle Technologies Program Annual Merit Review
Arlington, VA
May 12, 2011

ACE035

Project 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.

Budget

- Project funded by DOE Vehicle Technologies Program:

  FY10 - $300K
  FY11 - $300K

Barriers

- Relevant barriers from 2010–2015 Multi-Year Program Plan:
  - NOx adsorbers have a strong sensitivity to sulfur in the fuel.
  - Modeling capability for lean-burn aftertreatment systems, especially in regard to performance degradation, is insufficient.
  - The cost of NOx removal technologies must be reduced to improve competitiveness.

Partners

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

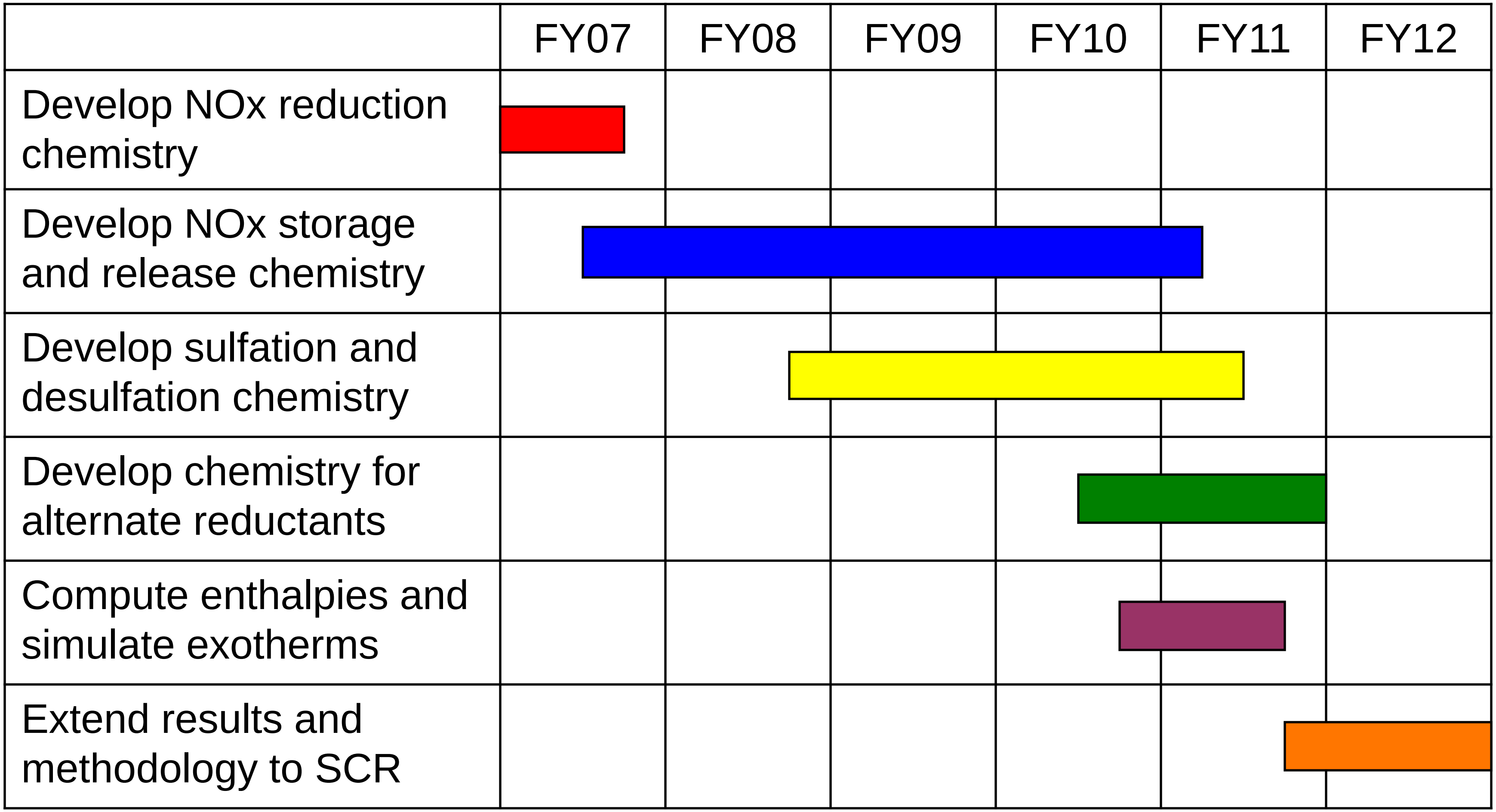
Objectives & Relevance

- 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.

- Relevance to VT Program goals: Effective, durable advanced aftertreatment systems for lean-burn engines must be available if the fuel economy advantages of these engines are to be realized.

- Specific current year objectives: Finalize development of a mechanism that accounts for all aspects of sulfation/desulfation behavior, which is central to durability. Develop the software tools and data necessary to simulate exotherms in the catalyst monolith.

Project Timeline and Milestones



	FY07	FY08	FY09	FY10	FY11	FY12
Develop NOx reduction chemistry	🟥					
Develop NOx storage and release chemistry	🟦	🟦	🟦	🟦	🟦	
Develop sulfation and desulfation chemistry		🟨	🟨	🟨	🟨	
Develop chemistry for alternate reductants				🟩	🟩	
Compute enthalpies and simulate exotherms				🟪	🟪	
Extend results and methodology to SCR					🟧	🟧

Overall Approach

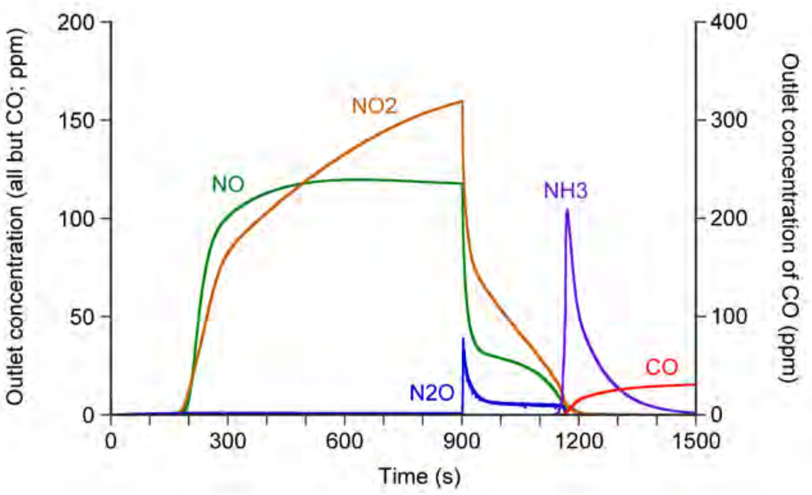
- Assemble tentative reaction sets for precious metal (catalytic), barium oxide (NOx storage), and cerium oxide (oxygen storage) sites.
- Infer kinetic parameters for four submechanisms in sequence by matching product distributions from experiments done at Oak Ridge National Laboratory (ORNL):
  - Precious metal chemistry (tentative) from steady flow experiments with storage minimized
  - NOx and oxygen storage/release chemistry from long cycle experiments
  - Sulfation/desulfation chemistry (all sites) from short cycle experiments using SO_2
  - Chemistry of hydrocarbon reductants from short cycle experiments using C_3H_6 and C_3H_8
- Use Chemkin-based plug flow codes to simulate flow of reactant mixture through a catalyst monolith channel.
- Use Sandia APPSPACK code to optimize fits to experimental data by adjusting kinetic parameters.
- Apply thermodynamic constraints during each fitting procedure in order to ensure complete consistency (often overlooked).

Current Year Accomplishments (overview)

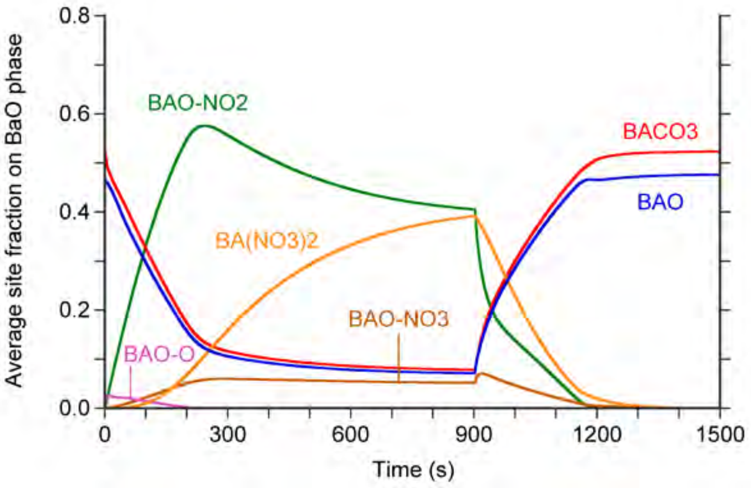
- Our NOx storage/release mechanism has been completely reconstructed in order to accord better with the consensus of the catalysis community.
    - Surface species involved are now the same as those used in conventional treatments.
    - Steady flow and long cycle experiments are simulated roughly as well as before, but with fewer and less contentious reactions.
- Our sulfation/desulfation mechanism has likewise been reformulated and finalized.
    - An experimental protocol involving sulfation under rapid cycling, periodic performance evaluation, and desulfation by temperature-programmed reduction is now simulated in detail.
    - All principal experimental observations (completeness of SO_2 trapping, plug-like sulfation of NOx storage sites, degradation of NOx storage capability, composition of desulfation product gas, completeness of desulfation, relative stability of barium and cerium sulfates) are reproduced at least semi-quantitatively.
- We have developed the tools necessary to simulate exotherms within the catalyst.
    - Reactor simulations to date have relied on measured rather than computed temperatures.
    - Our transient plug flow reactor code has been upgraded with a full energy equation, including axial conduction along the tube wall and heat loss from the annular tube end.
    - Self-consistent thermodynamic properties of all surface species in Chemkin format have been computed from previously inferred reaction equilibrium constants.

Technical Accomplishments

- Our new NOx storage and release mechanism provides a clearer and more conventional picture of the underlying chemistry.
  - Results shown here for an artificially long cycle (15 min lean with 300 ppm NO and 10% O_2, 10 min rich with 625 ppm CO and 375 ppm H_2) at 300ºC.
  - Regenerated surface is a mixture of carbonate and bare oxide.
  - During NOx storage, BaO–NO_2 forms first and is gradually replaced by $Ba(NO_3)_2$, while BaO–O and BaO–NO_3 function as reactive intermediates.



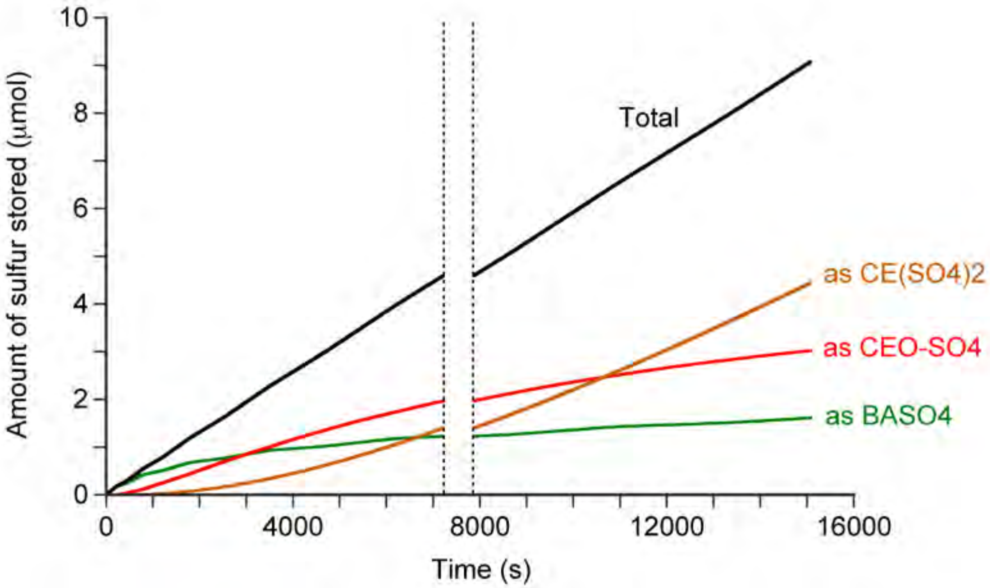
Exit gas concentrations



Spatially averaged surface concentrations

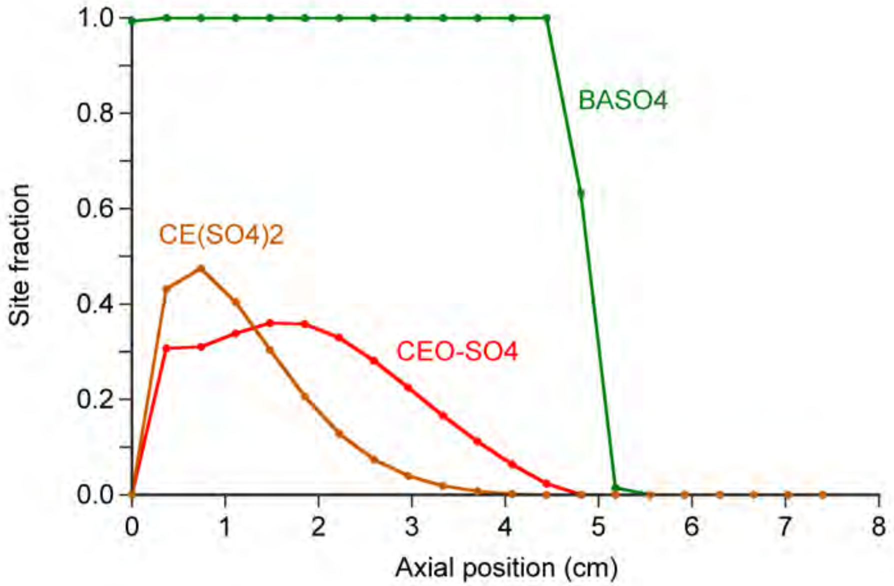
Technical Accomplishments

- Simulation of a complete experimental sulfation protocol (20 ppm SO_2 in feed) predicts changes in the surface composition.
  - Sulfation occurs during two sets of 111 short (60 s/5 s) cycles, interrupted by 10 sulfur-free cycles for performance evaluation.
  - Sulfur is trapped more readily on barium than on cerium, but barium sites near leading edge become saturated, and cerium becomes the primary sink.
  - Linearity of total sulfur curve indicates that essentially all incoming SO_2 is trapped.



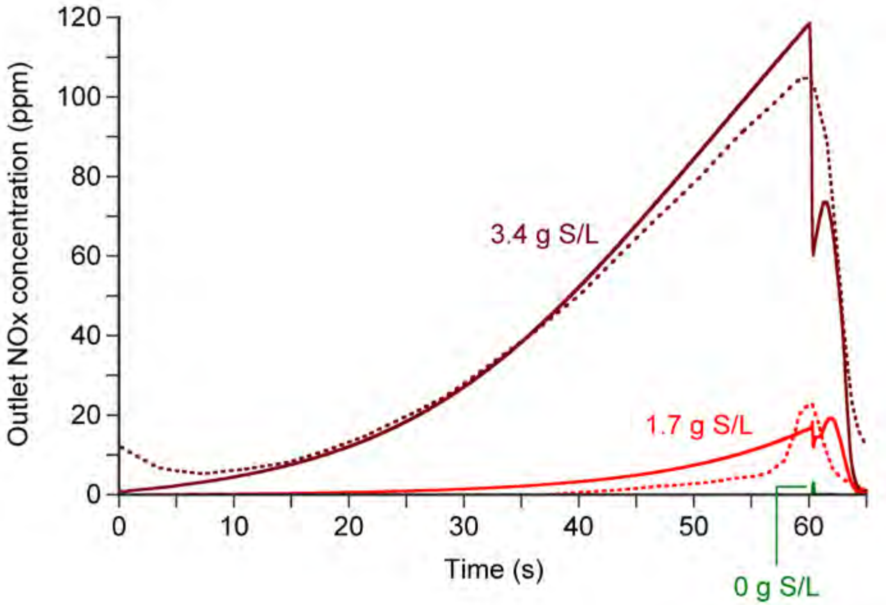
Technical Accomplishments

- Spatial profiles of sulfate species concentrations at the end of sulfation lend support to the proposed sequence of events.
  - Very strong trapping of sulfur by Ba leads to site saturation and a plug-like axial profile.
  - Due to weaker trapping by Ce, site saturation does not occur, so some oxygen storage capacity remains throughout the channel.
  - Ce is critical in preventing NOx storage capacity from being completely lost.



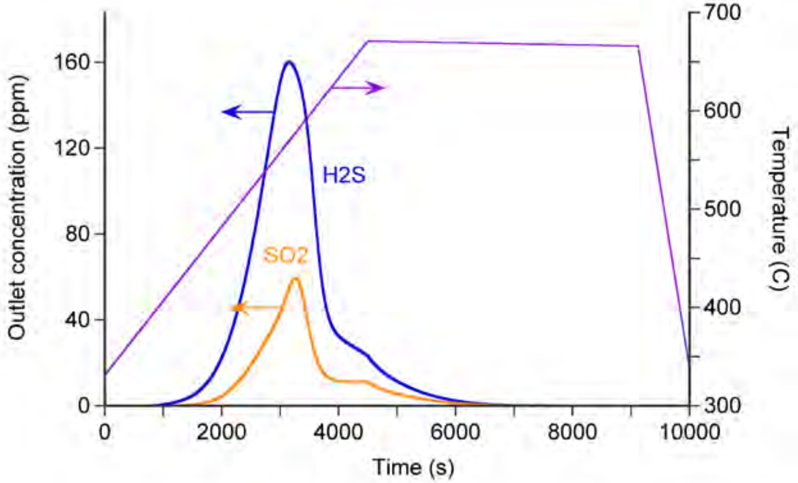
Technical Accomplishments

- The effect of sulfation on NOx trapping efficiency during normal cycling (60 s lean/5 s rich) is simulated very well.
  - Results shown here correspond to three distinct levels of sulfation.
  - Solid curves are simulation results, while dotted curves are published experimental data (J.-S. Choi et al., ORNL).
  - For an unsulfated catalyst, NOx slip is negligible, but increasing sulfation affects NOx trapping performance disproportionately.

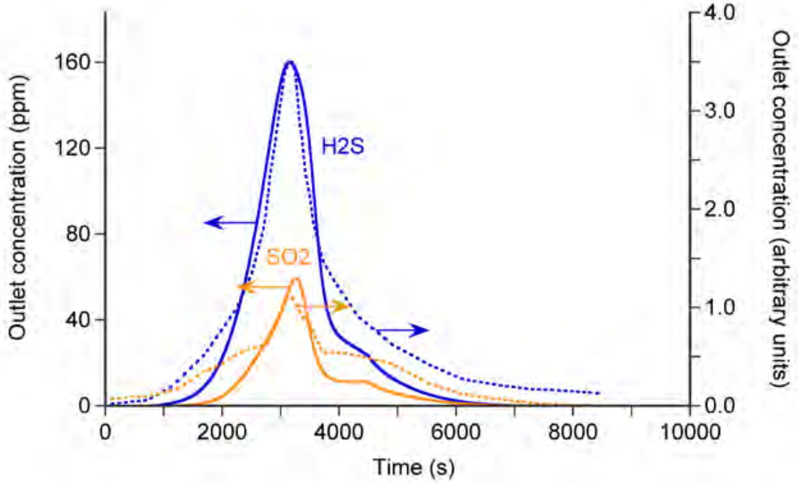


Technical Accomplishments

- Simulation of desulfation by temperature-programmed reduction is in good semi-quantitative agreement with experiment.
  - Temperature ramped at about 5ºC/min with a feed containing 0.1% H_2.
  - Experimental data (dotted curves) from published work of J.-S. Choi et al., ORNL.
  - Experimental concentrations are not quantitative (thus units are arbitrary).



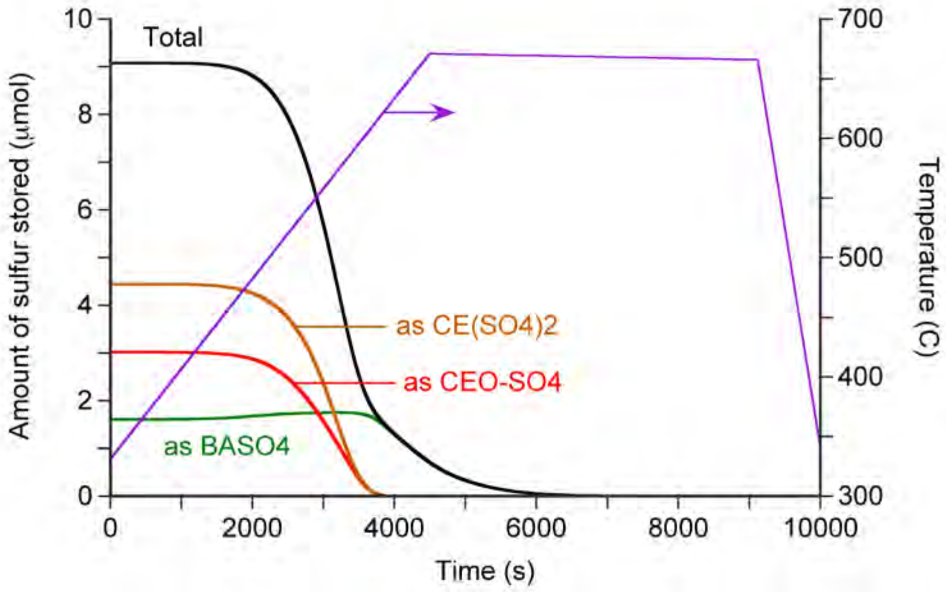
Simulation results vs. temperature



Simulation results vs. experiment

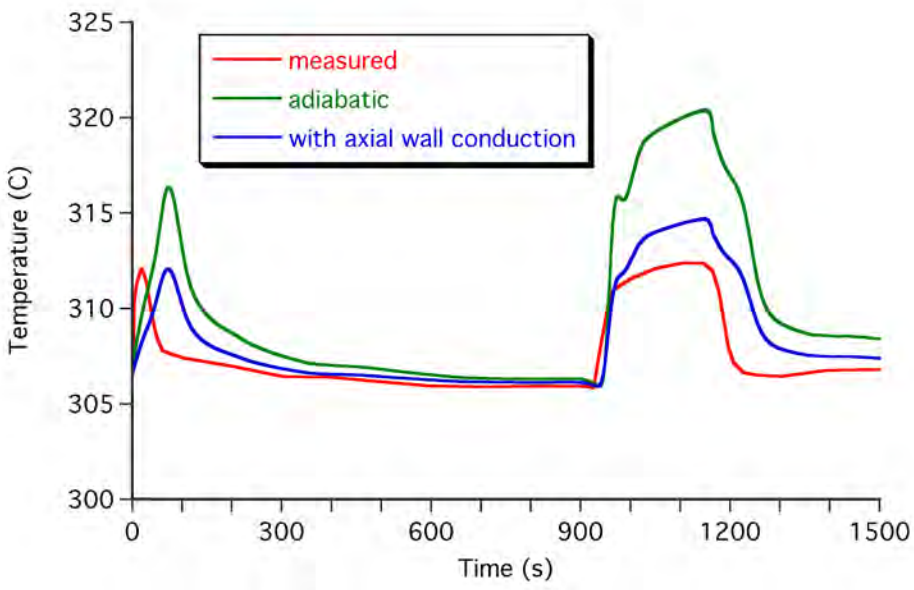
Technical Accomplishments

- The surface composition during desulfation again reflects the relative stabilities of the various sulfates.
  - No sulfate is removed below about 450ºC.
  - As observed experimentally, removal of sulfur from Ba requires higher temperatures than does removal from Ce.
  - Some sulfate released from Ce sites is actually redeposited on Ba, although this is temporary.



Technical Accomplishments

- We have developed the software tools and compiled the thermodynamic data needed to simulate exotherms in the channel.
  - Results are shown for the exit temperature during a long storage/regeneration cycle, nominally at 300ºC.
  - Matching of experimental temperature rises requires axial heat conduction in the tube wall and convective heat transfer from the annular wall end.



Collaborations

- Our principal collaboration is with the Fuels, Engines and Emissions Research Center at Oak Ridge National Laboratory.
  - V. K. Chakravarthy (mechanism development)
  - J. A. Pihl (experimental data – NOx storage and reduction)
  - J.-S. Choi (experimental data – sulfation/desulfation)
  - C. S. Daw (mechanism development, CLEERS program direction)
- We have a loose collaboration with the CLEERS consortium.
  - Tri-monthly technical teleconferences
  - Annual workshop
- We have also initiated a collaboration with General Motors with the aim of enhancing industrial relevance.

Future Work

- Complete investigation of the feasibility of simulating fully nonisothermal cycles (FY11).
  - Use of a one-dimensional reactor code is an inherent limitation, although separate gas and wall temperatures can be implemented.
  - Modeling capability must be highly refined for simulated temperatures to be more useful than measured values.
- Complete development of a submechanism accounting for reductants other than CO and H_2 (FY11).
  - Unburned and/or partially burned hydrocarbons may play a role.
  - A tentative list of candidate reactions has been assembled.
  - Short cycle data involving propylene and propane has recently been generated by ORNL and will allow for parameter estimation.
- Explore the extension of the methodology developed here to the microkinetic modeling of selective catalytic reduction (FY12).
  - This has been suggested on several occasions, including project reviews.
  - Neither NSR (NOx storage/reduction) nor SCR appears to be clearly preferable for all applications, so comparable analyses of both should be pursued.

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 multi-tiered approach to developing an elementary chemical mechanism benchmarked against experimental data.
  - Simulate a set of steady flow experiments, with storage effects minimized, to infer a tentative mechanism for chemistry on precious metal sites (completed).
  - Simulate a set of long cycle experiments to infer a mechanism for NOx and oxygen storage sites while simultaneously finalizing precious metal chemistry (completed).
  - Simulate a standard sulfation/desulfation protocol to obtain a supplementary set of reactions involving sulfur on all three kinds of sites (completed).
  - Investigate the role of reductants other than CO and H_2, in particular hydrocarbons and ammonia (underway).
- While simulation of isothermal experiments is the preferred way to extract kinetic parameters, simulation of realistic storage/regeneration cycles requires that exotherms be considered.
- Our ultimate goal is to facilitate improved designs for LNT (and potentially SCR)-based aftertreatment systems and to assist in the development of improved catalysts.