Development of Chemical Kinetics Models for Lean NOx Traps

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ACE035

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:

  FY09 - $265K
  FY10 - $300K

Partners

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

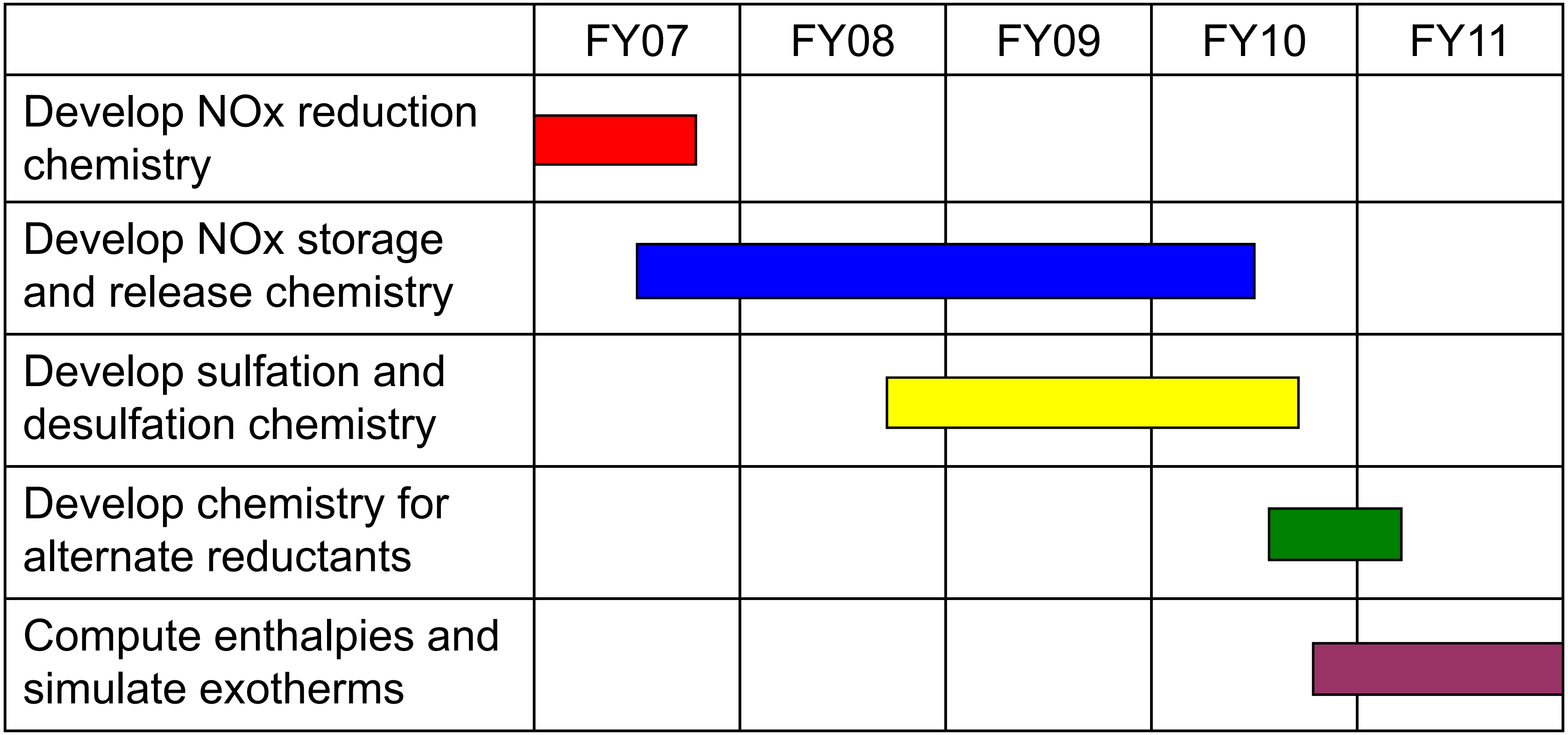
Objectives

- 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.

- 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 objective: Identify and correct any deficiencies in the previously developed reaction mechanism describing normal storage/regeneration cycles, and complete development of a supplementary mechanism accounting for the effects of sulfation.

Milestones



	FY07	FY08	FY09	FY10	FY11
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				🟪	🟪

Overall Approach

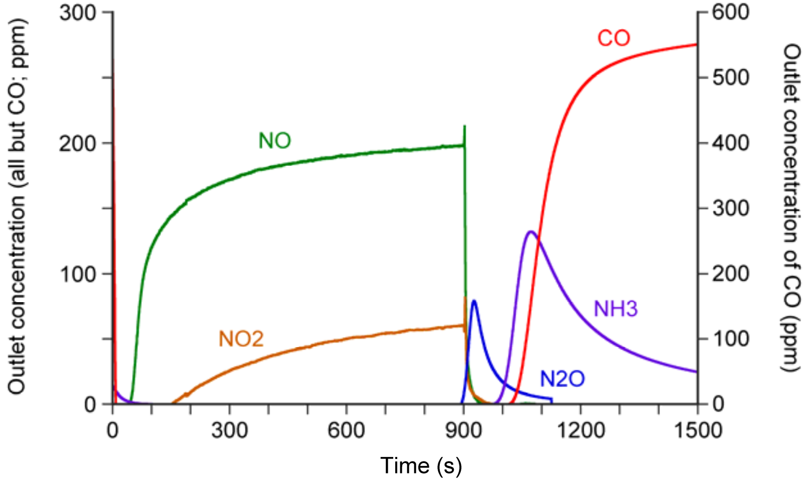
- Assemble tentative reaction sets for precious metal (catalytic), barium oxide (NOx storage), and cerium oxide (oxygen storage) sites.
- Infer kinetic parameters for three submechanisms in sequence by matching product distributions from experiments done at Oak Ridge National Laboratory (ORNL):
  - Precious 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
- 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).

Technical Accomplishments (overview)

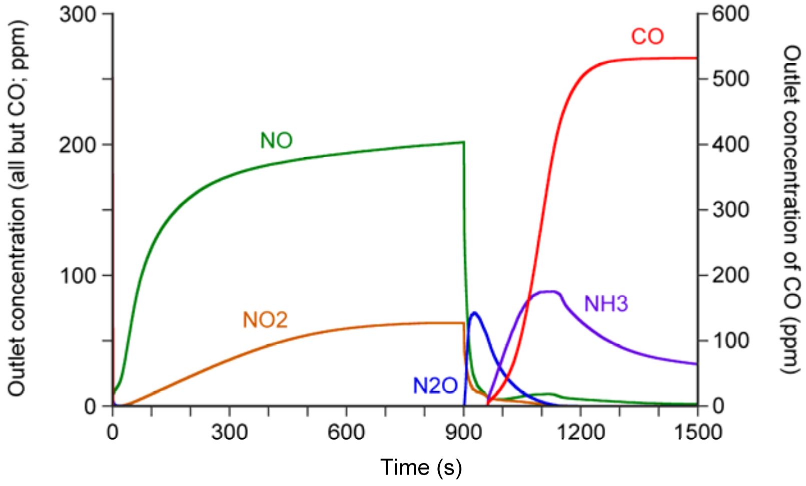
- Kinetic parameters for reactions on precious metal sites have been re-evaluated *simultaneously* with those on storage sites.
  - Storage effects were found not to be negligible in steady flow experiments after all.
  - Steady flow and long cycle experiments have now both been simulated with a transient code to extract all kinetic parameters involved in NOx storage and reduction at once.
- The NOx storage/release mechanism has been upgraded with new species and reactions, while mass-transfer resistances have been discarded.
  - NOx can now be stored as $Ba(NO_2)_2$ and $BANO_2NO_3$ (in addition to others).
  - New reactions involving spillover of N(Pt) account for N_2O formation at 200ºC.
  - Direction reduction of stored NOx by gas-phase H_2 and CO allows for successful simulation of short storage/regeneration cycles.
- The capabilities of our sulfation/desulfation mechanism have been greatly expanded, while the size has been reduced.
  - A modified CLEERS protocol involving sulfation, subsequent performance evaluation, and desulfation by temperature-programmed reduction is now simulated.
  - The principal experimental observations (completeness of SO_2 trapping, degradation of NOx storage capability, composition of desulfation product gas, completeness of desulfation) are reproduced at least semi-quantitatively.

Technical Accomplishments

- Simulation of NOx storage, release, and reduction at 200ºC is now more successful than before.
  - Feed gas contains NO and excess O_2 during storage phase (0–900 s), reductants CO and H_2 during regeneration phase (900–1500 s).
  - Artificially long cycle time is used to allow resolution of transients.
  - The mechanism now accounts well for N_2O production, although NH_3 is somewhat underpredicted.



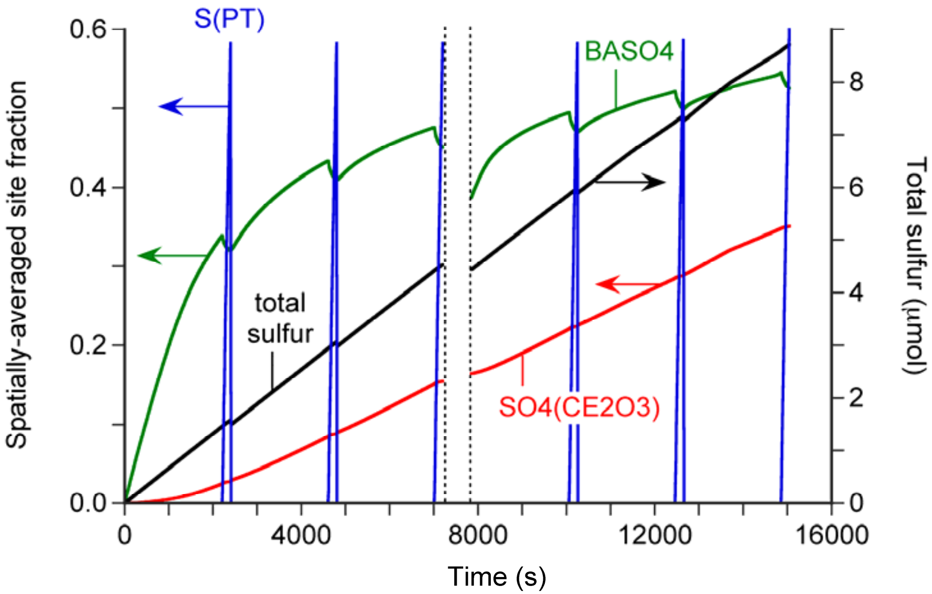
Experiment (J. A. Pihl, ORNL)



Simulation

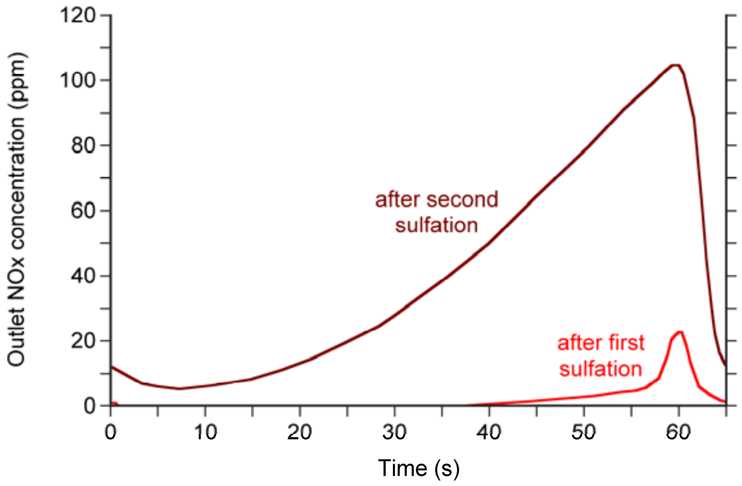
Technical Accomplishments

- Simulation of a modified CLEERS sulfation protocol (20 ppm SO_2 in feed) predicts changes in the surface composition.
  - Sulfation occurs during two sets of three long isothermal lean/rich cycles, separated by ten ordinary short cycles (not shown) for performance evaluation.
  - Sulfur is trapped more readily on barium than on cerium, but saturation occurs.
  - During rich phases, sulfur is trapped reversibly on Pt and some sulfate is lost from barium sites, but there is little if any loss of total sulfur.

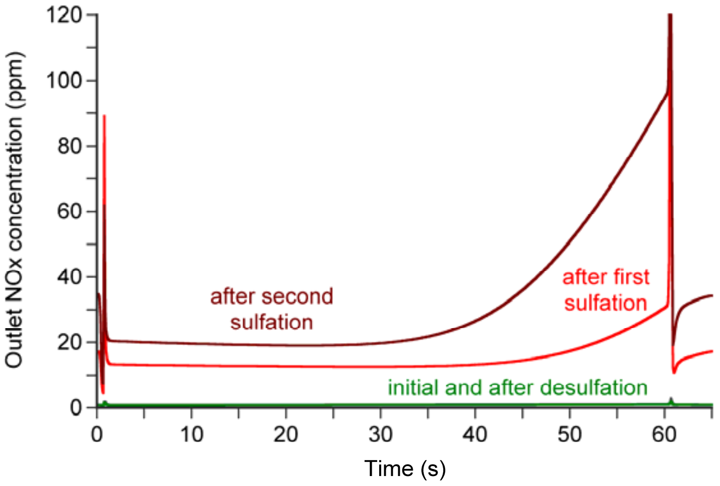


Technical Accomplishments

- The effect of sulfation on NOx trapping efficiency during normal cycling (60 s lean/5 s rich) is simulated reasonably well, although improvement is needed.
  - For an unsulfated catalyst, NOx slip is negligible (experimentally).
  - Simulation shows unwanted NOx spikes at feed transition points and excessive NOx slip early in lean phase.
  - Discrepancies may be due (at least partially) to neglect of exotherms.



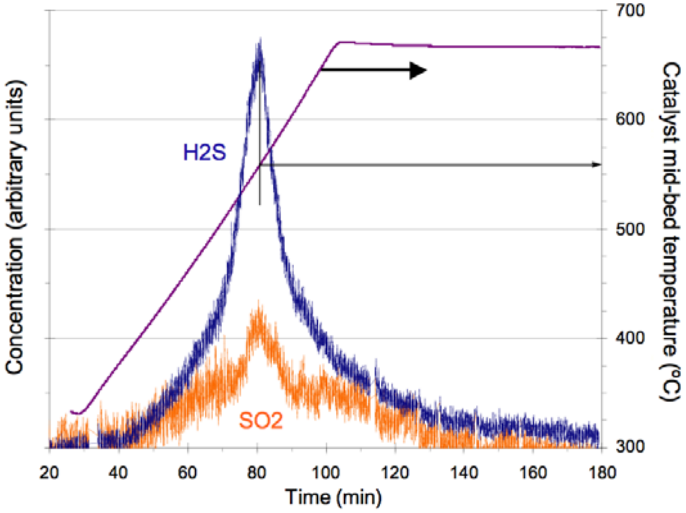
Experiment (J.-S. Choi, ORNL)



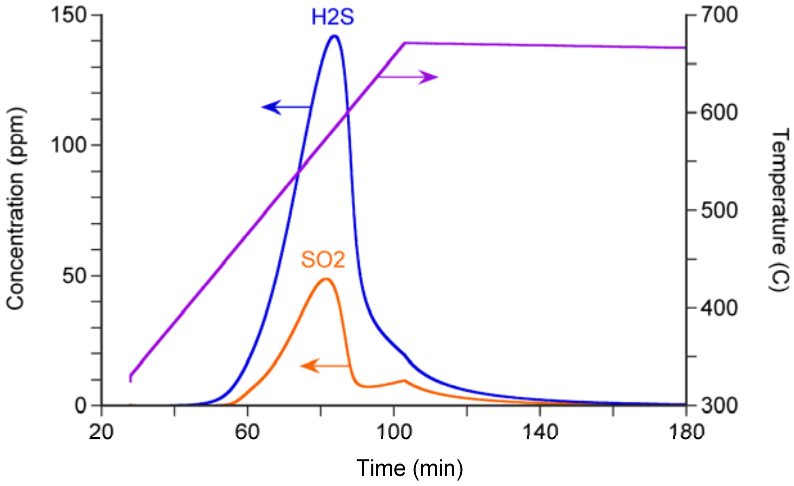
Simulation

Technical Accomplishments

- Simulation of desulfation by temperature-programmed reduction is in excellent semi-quantitative agreement with experiment.
  - Temperature ramped at about 5ºC/min with a feed containing 0.1% H_2.
  - Experimental concentrations are not quantitative (thus units are arbitrary).
  - For purposes of comparison, experimental and simulated concentrations are scaled by H_2S value at 80 min (near peak).



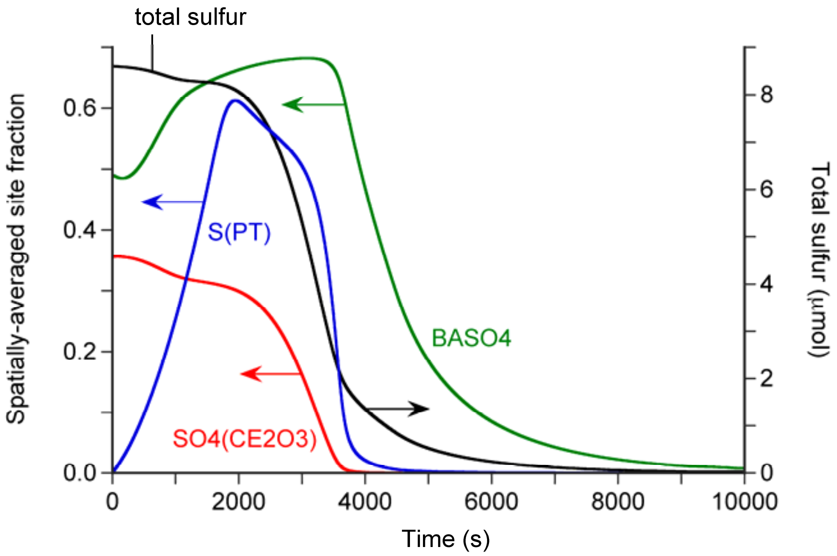
Experiment (J.-S. Choi, ORNL)



Simulation

Technical Accomplishments

- The surface composition is predicted to change in a complex manner during desulfation.
  - As sulfate is released and reduced, Pt sites become covered largely with sulfur.
  - Sulfate released from cerium sites is initially redeposited on barium, although total trapped sulfur decreases monotonically (as it must).
  - As observed experimentally, removal of sulfur from barium requires higher temperatures than does removal from cerium.



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 also have a loose collaboration with the CLEERS consortium.
  - Tri-monthly technical teleconferences
  - Annual workshop

Future Work

- Modify kinetic parameters and/or reaction set for sulfation/desulfation to account better for products observed during ordinary lean/rich cycling (FY10).
  - Try to match production rates of N_2O and NH_3 as well as NO/NO_2 ratio, although time resolution of experimental data may be problematic.
- Augment mechanism with reactions accounting for reductants other than CO and H2 (FY10+).
  - Unburned and/or partially burned hydrocarbons may play a role.
  - Deferred from last year due to need to address newly discovered issues.
- Develop computational tools and data needed to simulate fully nonisothermal cycles (FY11).
  - Implement general energy balance in Chemkin-based transient plug flow code.
  - Use previously inferred equilibrium constants to extract thermodynamic properties of surface species.

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 simplified sulfation/desulfation protocol to obtain a supplementary set of reactions involving sulfur on all three kinds of sites (nearly completed).
  - Investigate the potential role of reductants other than CO and H_2.
- 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-based aftertreatment systems and to assist in the development of improved catalysts.