Benchmark Reaction Mechanisms and Kinetics for Lean NOx Traps

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

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Purpose of Work

- 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.

- Current goal: 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 steady state and cyclical operation and under various conditions of temperature and inlet gas composition.

Barriers

- A cost-effective, durable exhaust aftertreatment system capable of meeting new EPA NOx regulations for lean-burn engines does not yet exist.
- “Development and optimization of catalyst-based aftertreatment systems are inhibited by the lack of understanding of catalyst fundamentals (e.g., surface chemistry …)” — 2006 ACEC Roadmap
- For greatest flexibility in engine operation, the temperature window for high NOx conversion efficiency in the LNT must be maximized.
- For greatest fuel efficiency, the reductant use during LNT regeneration (i.e., the fuel penalty) must be minimized.

Approach

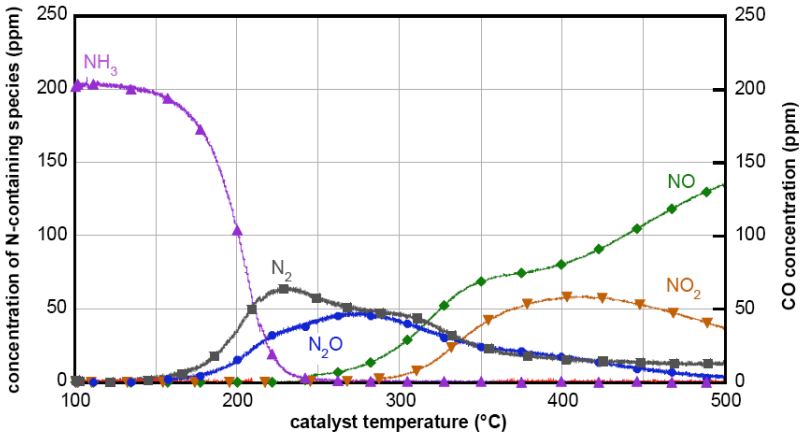
- Assemble tentative reaction sets for both precious metal (regeneration) and oxide (storage) sites.
- Infer kinetic parameters by matching product distributions from both steady flow and cycling (storage/regeneration) experiments done at Oak Ridge National Lab (ORNL).
  - Use Chemkin plug flow codes 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.

Technical Accomplishments

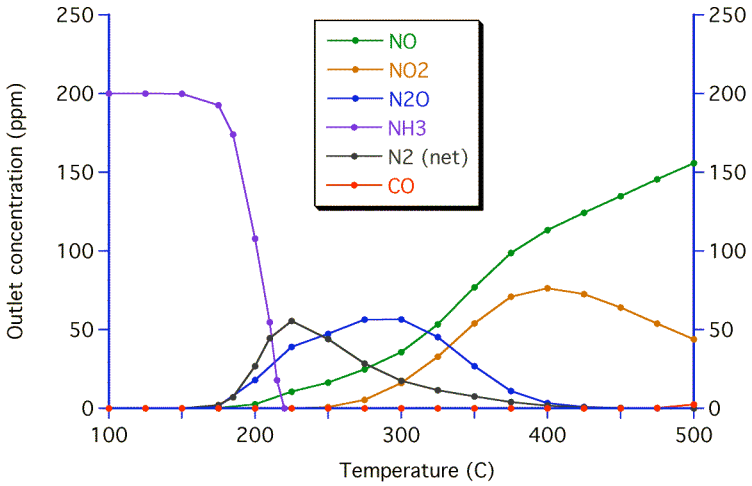
- Basic performance measure: Ability to reproduce (simulate) observed outlet gas compositions for both steady flow and cycling experiments over the entire range of temperatures and inlet gas compositions.
- Steady flow experiments have been simulated successfully with the precious metal mechanism alone (10 gas species, 13 surface species, 28 reversible surface reactions).
- A journal paper describing this mechanism is in press.
- Cycling experiments have been simulated reasonably well with the complete mechanism (10 gas species, 23 surface species, 46 reactions), but work is continuing.

Technical Accomplishments (continued)

- Oxidation of ammonia is one of the many steady flow processes simulated successfully with the precious metal mechanism
  - Temperature ramped slowly from 100°C to 500°C
  - Ammonia fed to reactor with a large excess of oxygen
  - Simulates secondary reaction of initial regeneration product
  - Full range of products observed, depending on temperature



Experiment



Simulation

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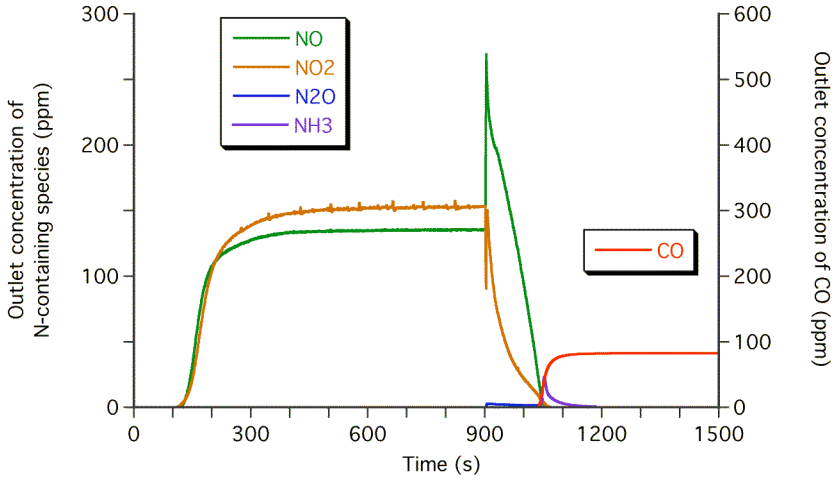
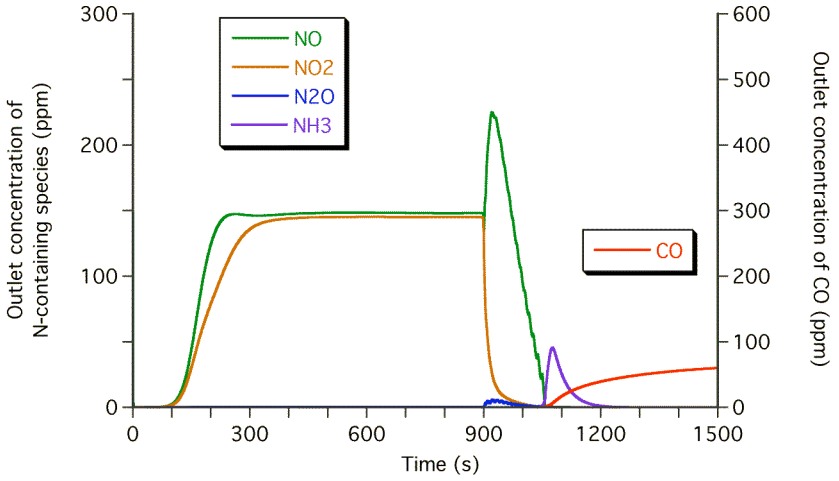
Technical Accomplishments (continued)

- Simulation of full storage/regeneration cycles is qualitatively accurate, but further refinement is needed
  - 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
  - Simulation of cycle at 400°C (shown) is largely correct



Experiment



Simulation

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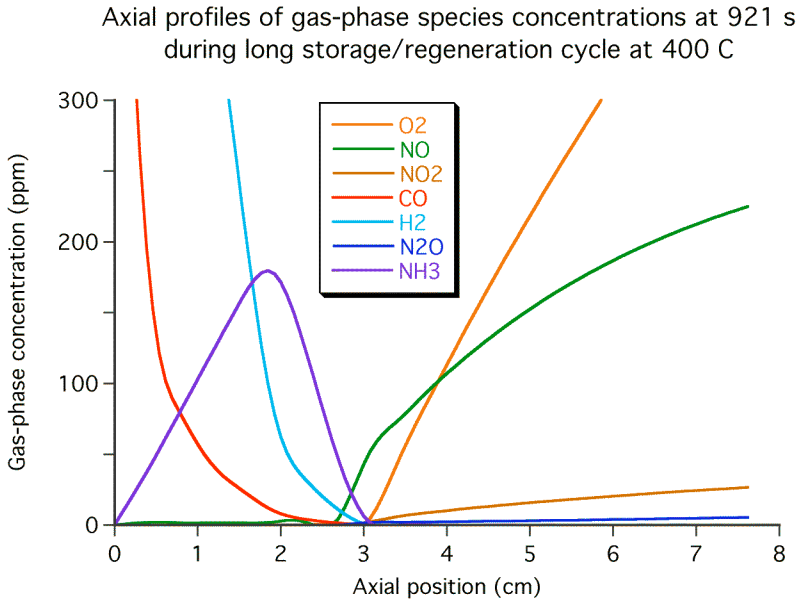
Technical accomplishments (continued)

- Simulations are consistent with hypotheses about the sequence of events occurring (spatially and temporally) during regeneration
  - Near the entrance, 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



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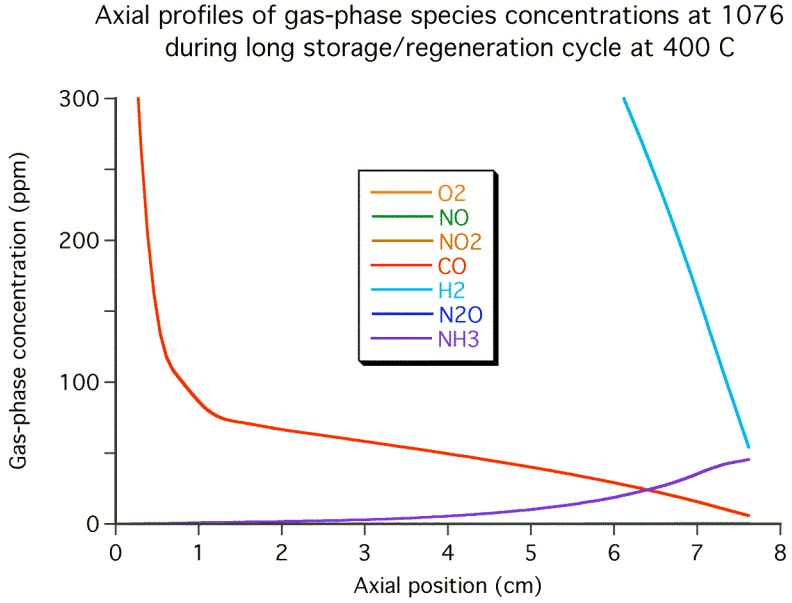
Technical accomplishments (continued)

- Simulations also explain the period of ammonia slip that follows the initial NOx escape
  - 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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Technology Transfer

- A preliminary version of the precious metal mechanism was made available to CLEERS industrial members who requested it.
- The final version is in the process of being published.
- The Umicore GDI catalyst is fully formulated and commercially available, so models of its behavior have direct industrial relevance.
- The combined storage/regeneration mechanism will allow simulations of LNT behavior under various conditions and thus should aid in aftertreatment system design and optimization.

Activities for Upcoming Year

- Complete development of combined storage/regeneration mechanism describing normal cyclical operation
  - Better description of solid-phase mass transfer needed
- Develop a companion mechanism for catalyst sulfation and desulfation
  - Needed to simulate degradation in LNT performance during normal operation and restoration of activity during desulfation
  - Account for poisoning of precious metal sites, conversion of sulfides to sulfates, and competitive sulfate/NOx storage
- 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

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.
- An elementary reaction mechanism has been developed by comparing the results of Chemkin-based reactor simulations to experimental data provided by ORNL.
- Agreement with a wide range of steady flow and full cycle experiments is generally good, although refinements continue.
- The completed regeneration mechanism for this commercial catalyst has been made available to the industrial community.
- The mechanism is to be augmented to account for sulfation and desulfation processes as well as alternative reductants.

Publications and Presentations

- R. S. Larson, V. K. Chakravarthy, J. A. Pihl, and C. S. Daw, "Mechanism Development for the Simulation of LNT Lean/Rich Cycling," Tenth CLEERS Workshop, Dearborn, MI, May 2, 2007.
- R. S. Larson, J. A. Pihl, V. K. Chakravarthy, and C. S. Daw, "Micro-kinetic modeling of Lean NOx Trap regeneration chemistry," 20th North American Meeting of the North American Catalysis Society, Houston, TX, June 21, 2007.
- R. S. Larson, J. A. Pihl, V. K. Chakravarthy, T. J. Toops, and C. S. Daw, "Microkinetic Modeling of Lean NOx Trap Chemistry under Reducing Conditions," *Catalysis Today*, in press (2008).

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