Comprehensive Microkinetic Modeling of LNT Chemistry

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Objectives

- Overall project goal: Obtain the fundamental surface chemistry knowledge needed for the design and optimal utilization of lean NOx trap (LNT) catalysts, thereby helping to speed the widespread adoption of this technology.

- Specific project objective: Develop an elementary (microkinetic), thermodynamically consistent surface reaction mechanism capable of describing LNT behavior under a wide range of operating conditions (such as temperature, feed composition, and cycle time).

- Current year objectives: (1) Reformulate the storage mechanism to be more in accord with conventional wisdom; (2) Finalize a corresponding sulfation/desulfation mechanism; and (3) Develop the software tools and data necessary to simulate exotherms in the catalyst monolith.

Overall Approach

- Assemble tentative reaction sets for precious metal (catalytic), barium oxide (NOx storage), and cerium oxide (oxygen storage) sites.
  - Site types intended to represent principal components of benchmark Umicore catalyst.
  - Use only (pseudo-)elementary reactions, allowing mass-action kinetics to be assumed.
- Infer kinetic parameters for four submechanisms in sequence by matching product distributions from experiments done at ORNL:
  - Precious metal chemistry (tentative) from steady flow experiments with storage minimized
  - NOx and oxygen storage/release chemistry from long cycle experiments (near-isothermal)
  - Sulfation/desulfation chemistry (all sites) from short cycle experiments using SO_2
  - Reforming and partial oxidation chemistry from experiments with hydrocarbon reductants
- 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 both internal and external consistency.

Summary of current year results

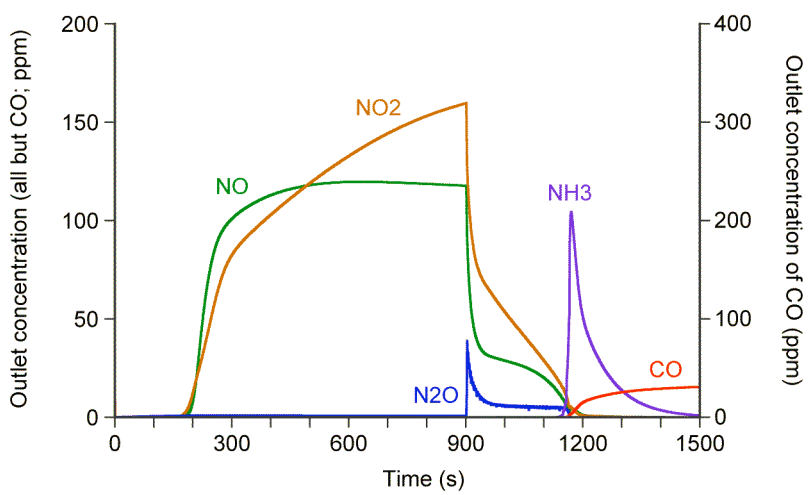
- The NOx storage/release mechanism has been completely reconstructed in order to accord better with the consensus of the catalysis community.
  - Surface species involved are now the same as those used in conventional treatments.
  - Steady flow and long cycle experiments are simulated roughly as well as before, but with fewer and less contentious reactions.
- The sulfation/desulfation mechanism has 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 monolith channel.
  - Reactor simulations to date have relied on measured rather than computed temperatures.
  - The 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.

New NOx storage/release mechanism

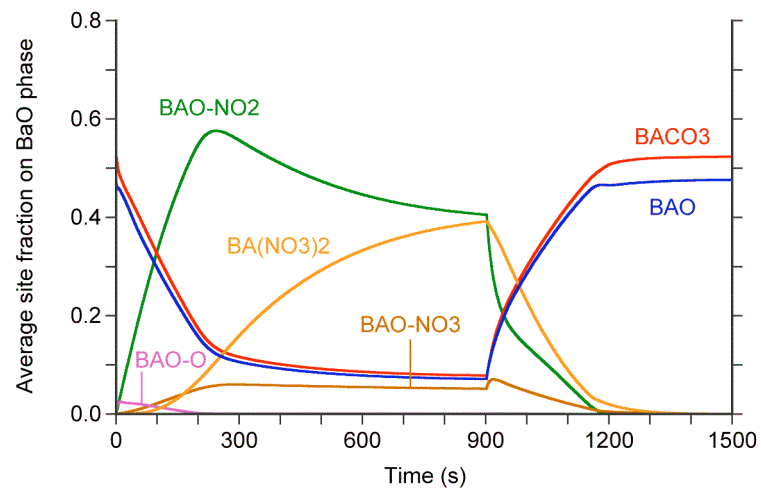
- Species on barium phase: BaO, $BaCO_3$, BaO–O, $BaO–NO_2$, $BaO–NO_3$, $Ba(NO_3)_2$
- Only five reactions occur entirely on this phase:
  - $CO_2 + BaO = BaCO_3$
  - $NO_2 + BaO = BaO–NO_2$
  - $NO_2 + BaO–NO_3 = Ba(NO_3)_2$
  - $NO_2 + BaO–NO_2 = NO + BaO–NO_3$
  - $BaO + NO_2 = BaO–O + NO$
- The last two are combinations of reactions appearing in the literature.
- There are also 11 spillover reactions involving species on both Ba and Pt sites.

Sample simulation results with new mechanism

- Kinetic parameters for the overall mechanism are inferred by fitting 21 steady flow temperature ramps and long cycles at 3 temperatures.
  - Results shown here are for a 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

Details of sulfation/desulfation submechanism

- Three new gas-phase species: SO_2, SO_3, H_2S
- Eight new surface species on three separate phases: SO_2(Pt), H_2S(Pt), SO(Pt), S(Pt), HS(Pt), $BaSO_4$, CeO–SO_4, $Ce(SO_4)_2$
- 11 new surface reactions (all reversible) involving all three phases:
  - $SO_2 + V(Pt) = SO_2(Pt)$
  - $H_2S + V(Pt) = H_2S(Pt)$
  - $SO_2(Pt) + V(Pt) = SO(Pt) + O(Pt)$
  - $SO(Pt) + V(Pt) = S(Pt) + O(Pt)$
  - $H_2S(Pt) + V(Pt) = HS(Pt) + H(Pt)$
  - $HS(Pt) + V(Pt) = S(Pt) + H(Pt)$
  - $SO_3 + BaO = BaSO_4$
  - $BaO–O + SO_2 = BaSO_4$
  - $CeO_2 + SO_3 = CeO–SO_4$
  - $CeO–SO_4 + SO_3 = Ce(SO_4)_2$
  - $SO_2 + 2CeO_2 = SO_3 + Ce_2O_3$

Test suite for sulfation/desulfation mechanism

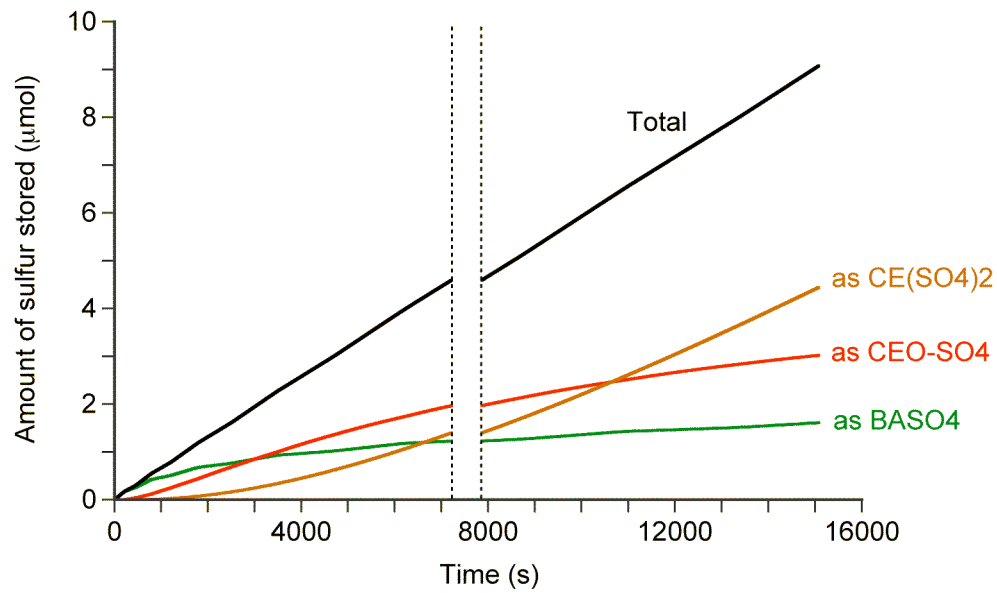
- Kinetic parameters are inferred by simulating a slightly modified version of the protocol in J.-S. Choi et al., *Appl. Catal. B Environ.* 77 (2007) 145:
  - One conventional short (60 s/5 s) NOx storage/reduction (NSR) cycle, predetermined to be repeatable, with an unsulfated catalyst to establish baseline behavior
  - 111 short cycles (totaling 2 hr), with 20 ppm SO_2 in the feed, to achieve the first level of sulfation (1.7 g S/L)
  - 10 short cycles (enough to ensure repeatability), with no SO_2 in the feed, to assess new NSR performance
  - 111 more short sulfation cycles to achieve the second level of sulfation (3.4 g S/L)
  - 10 more short NSR cycles for performance evaluation
  - Desulfation by temperature-programmed reduction, followed by an artificial cooldown to the starting NSR temperature
  - 10 more short NSR cycles for final performance evaluation
- All simulations are carried out using measured temperatures (dependent on time, axial position, and sulfation level for short cycles).
  - This is probably more accurate than attempting to simulate exotherms.
- Simulation of the entire sequence is extremely time-consuming (~13 hr).

Criteria for parameter set optimization

- The fitting process is semi-quantitative and involves an objective function that attempts to enforce five conditions:
  - Total sulfur slip through the catalyst during the sulfation episodes should be minimal.
  - The axial profile of $BaSO_4$ at the end of the second sulfation episode should be plug-like.
  - The evolution of product gases during desulfation should match that reported in the literature (J.-S. Choi et al., *ibid.*).
  - Following the temperature ramp and high-temperature soak, desulfation should be essentially complete.
  - The effects of sulfation and desulfation on subsequent NSR performance should be in line with experimental observations (J.-S. Choi et al., *ibid.*).

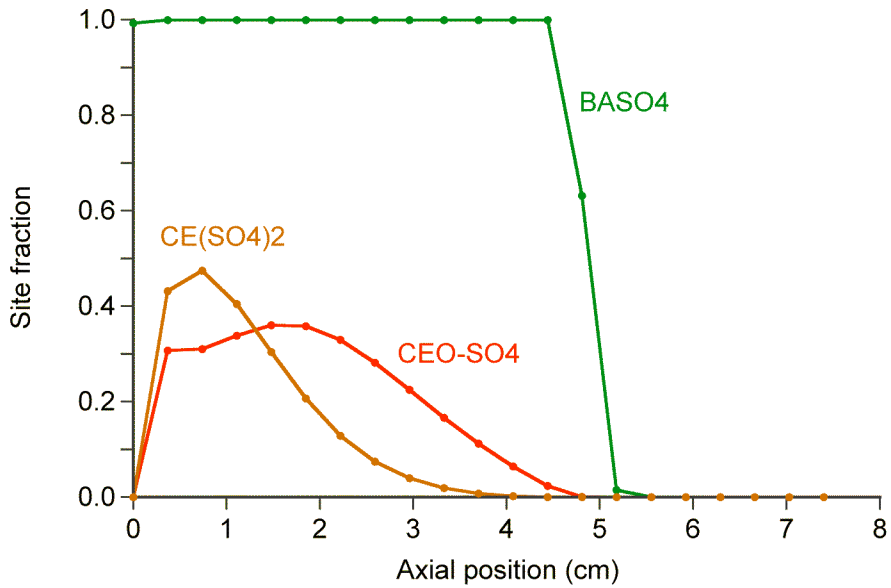
Predicted apportioning of stored sulfur

- Plot shows amount of sulfur stored in various forms during two long sulfation episodes (interrupted by 10 performance evaluation cycles).
  - Total includes sulfur trapped (reversibly) on Pt sites, but this is negligible.
  - 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, even during rich phases of sulfation cycles.



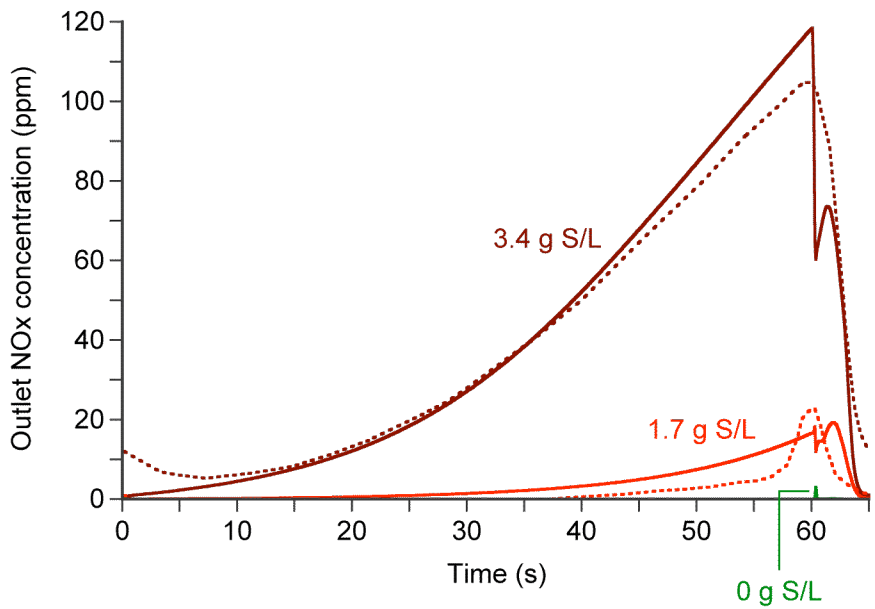
Predicted axial sulfation profiles

- Spatial profiles of sulfate species concentrations at the end of sulfation lend support to the proposed sequence of events.
  - 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 there, so some oxygen storage capacity remains throughout the channel.
  - As a result of its large capacity (and reasonable affinity) for sulfur, Ce is critical in preventing NOx storage capacity of Ba from being completely lost.



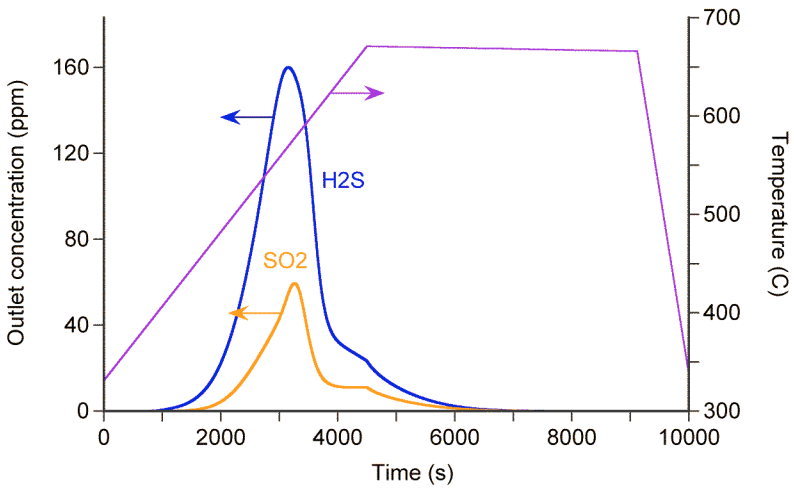
Effect of sulfation on NSR performance

- 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., *ibid.*).
  - For an unsulfated catalyst, NOx slip is negligible, but increasing sulfation affects NOx trapping performance disproportionately.

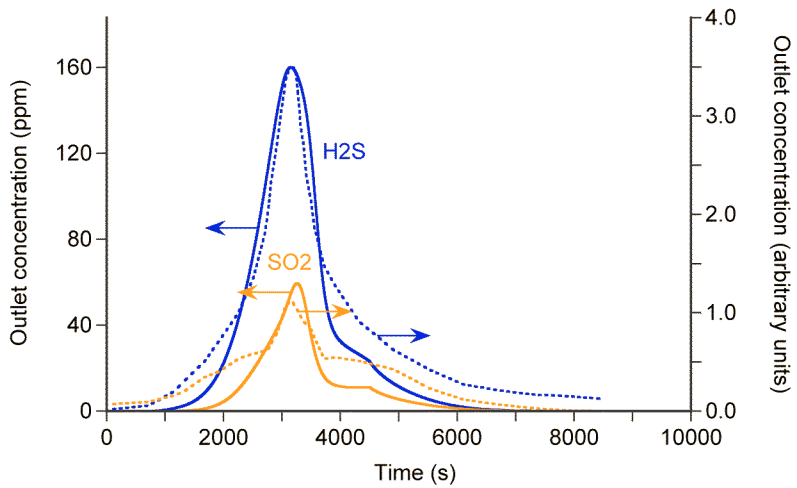


Composition of effluent gas during desulfation

- 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., *ibid.*
  - Note that experimental concentrations are in arbitrary units.
  - Broadness of experimental curves suggests greater diversity of sulfates.



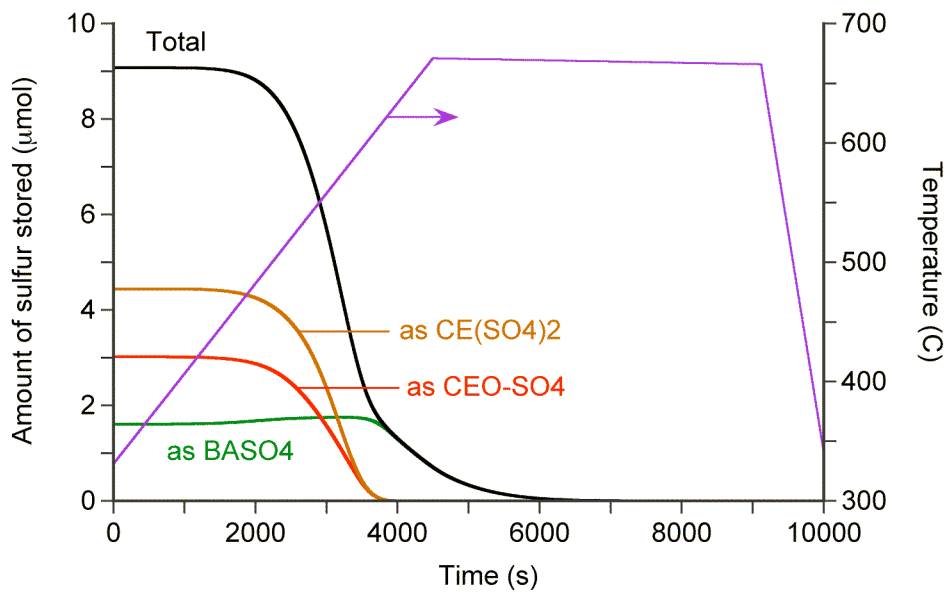
Simulation results vs. temperature



Simulation results vs. experiment

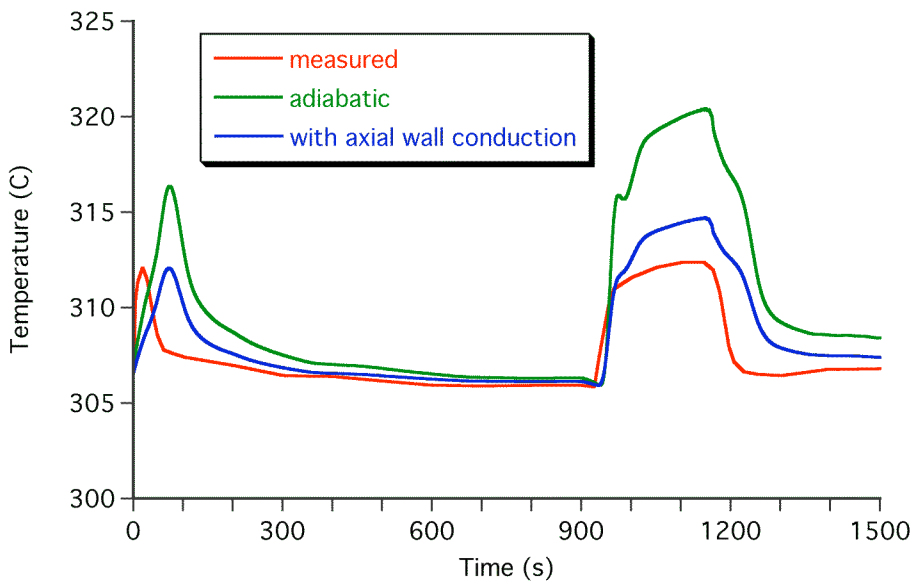
Predicted depletion history during desulfation

- 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.



Simulation of temperature variations

- We have developed the software tools and compiled the thermodynamic data needed to simulate exotherms in the channel.
  - Until now, only measured temperatures have been used in our simulations.
  - Predictions are shown here for the exit temperature during the long (15 min/10 min) storage/regeneration cycle, nominally at 300ºC, shown earlier.
  - Matching of experimental temperature rises requires axial heat conduction in the tube wall and convective heat transfer from the annular wall end.



Future Work

- Examine in more detail the effect of sulfation on product distribution during ordinary lean/rich cycling.
  - Work thus far has looked only at total NOx.
  - N_2O and NH_3 selectivities and NO/NO_2 ratio are also of interest.
- Complete development of a submechanism for hydrocarbon reductants.
  - Reforming and partial oxidation pathways are needed.
  - A tentative list of candidate reactions has been assembled.
  - Short cycle data involving propylene and propane have recently been generated by ORNL and should allow for parameter estimation.
- Explore the feasibility of a two-site model for NOx storage.
  - This has often been proposed and can obviously provide more flexibility, at the cost of additional unknown parameters.
- Use methods developed thus far to simulate the performance of the new catalyst being studied at ORNL.
  - Ultimate goal is to correlate differences in catalyst formulation with differences in chemical behavior.

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 a microkinetic 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 deduce a mechanism for NOx and oxygen storage sites while simultaneously finalizing precious metal chemistry (completed).
  - Simulate a detailed sulfation/desulfation protocol to obtain a supplementary set of reactions involving sulfur on all three kinds of sites (completed).
  - Investigate the reaction pathways of hydrocarbon reductants (underway).
- While simulation of isothermal experiments is the preferred way to extract kinetic parameters, simulation of realistic storage/regeneration cycles requires the ability to compute exotherms.
- Our ultimate goal is to facilitate improved designs for LNT-based aftertreatment systems and to assist in the development of improved catalysts.

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