



# Update on Microkinetic Modeling of Lean NO<sub>x</sub> Trap Chemistry

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# Objectives

- **Overall project goal:** Obtain the fundamental surface chemistry knowledge needed for the design and optimal utilization of lean NO<sub>x</sub> 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 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.





# Overall Approach

- Assemble tentative reaction sets for precious metal (catalytic), barium oxide (NO<sub>x</sub> storage), and cerium oxide (oxygen storage) sites.
  - Site types intended to represent principal components of benchmark Umicore catalyst.
  - Use only elementary reactions, allowing mass-action kinetics to be assumed.
- 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
  - NO<sub>x</sub> and oxygen storage/release chemistry from long cycle experiments (near-isothermal)
  - Sulfation/desulfation chemistry (all sites) from short cycle experiments using SO<sub>2</sub>
- 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

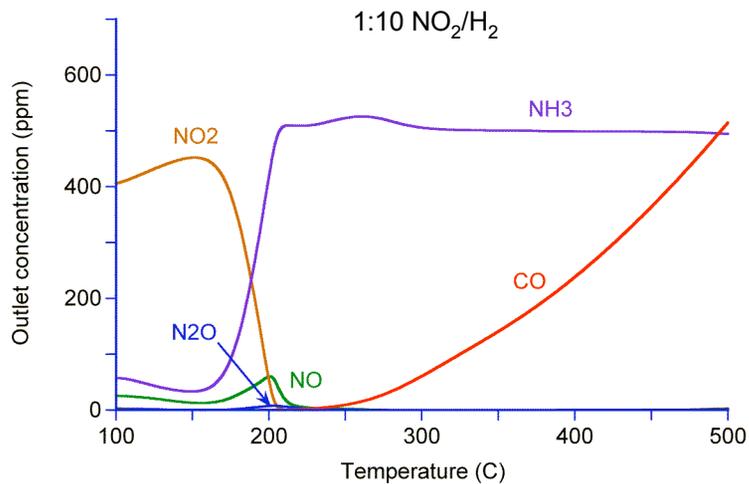
- Kinetic parameters for reactions on precious metal (nominally Pt) sites have been re-evaluated *simultaneously* with those on storage sites.
  - Storage effects were found not to be negligible in steady flow experiments after all.
  - Steady flow and long cycle experiments have now both been simulated 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  $\text{Ba}(\text{NO}_2)_2$  and  $\text{BaNO}_2\text{NO}_3$  (in addition to others).
  - New reactions involving spillover of N(Pt) account for  $\text{N}_2\text{O}$  formation at  $200^\circ\text{C}$ .
  - Direction reduction of stored NOx by gas-phase  $\text{H}_2$  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  $\text{SO}_2$  trapping, degradation of NOx storage capability, composition of desulfation product gas, completeness of desulfation) are reproduced at least semi-quantitatively.



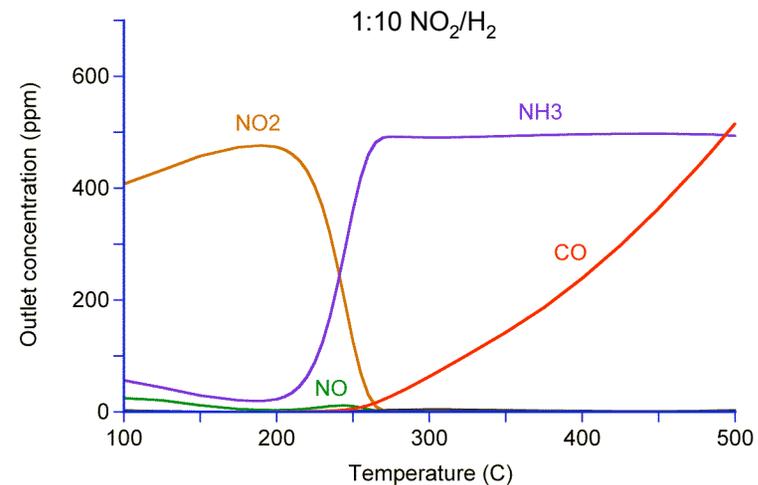


# Re-evaluation of kinetic constants for Pt sites

- Previous analysis involved only steady flow temperature ramp experiments and was based on two principal assumptions:
  - Storage effects were minimal, so only a Pt mechanism was needed.
  - The processes were pseudo-steady, so transient simulations were not needed.
- Consistency check following addition of storage/release mechanism showed that these assumptions were only roughly correct.
- Pt parameters have been re-evaluated as per preceding slide.



Full mechanism, transient

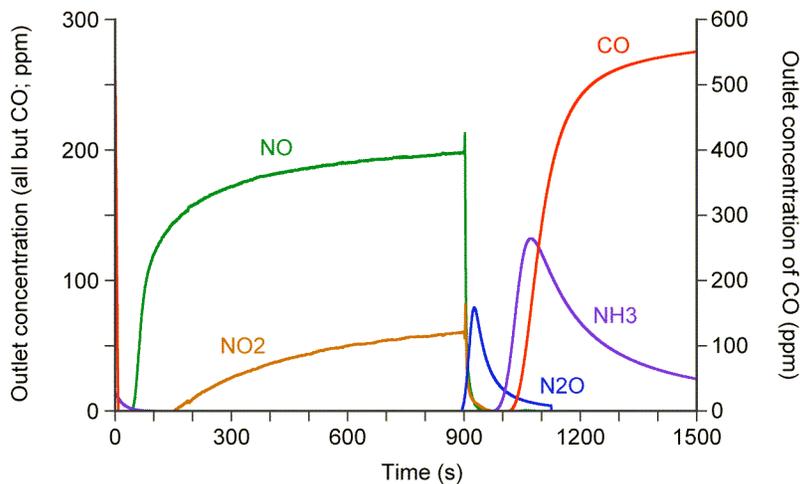


Pt reactions, pseudo-steady

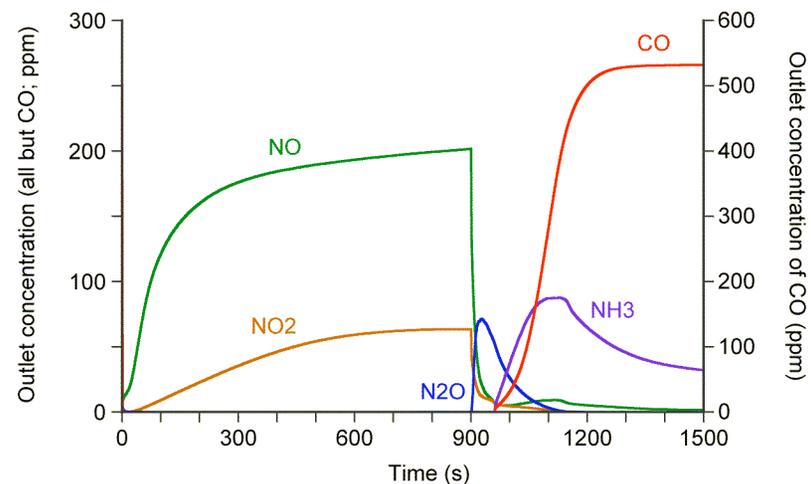


# Improvement of NO<sub>x</sub> storage/release mechanism

- Enhancements allow better simulation of long cycle experiments and better prediction of short cycle behavior.
  - Spillover reactions involving N(Pt) account for prompt N<sub>2</sub>O production during long cycle (15 min lean, 10 min rich) regeneration at 200°C, although NH<sub>3</sub> is somewhat underpredicted — see below.
  - Direct reduction of stored NO<sub>x</sub> by gas-phase rather than adsorbed H<sub>2</sub> and CO allows correct scaling of reaction rates with higher reductant concentrations used in short cycles.



Experiment (J. A. Pihl, ORNL)



Simulation



# Current state of sulfation/desulfation mechanism

- Three gas-phase species:  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{S}$
- Eight surface species on three separate phases:  $\text{SO}_2(\text{Pt})$ ,  $\text{SO}_3(\text{Pt})$ ,  $\text{H}_2\text{S}(\text{Pt})$ ,  $\text{SO}(\text{Pt})$ ,  $\text{S}(\text{Pt})$ ,  $\text{HS}(\text{Pt})$ ,  $\text{BaSO}_4$ ,  $\text{SO}_4(\text{Ce}_2\text{O}_3)$
- 14 surface reactions (all reversible) involving all three phases:
  - Adsorption of  $\text{SO}_2$ ,  $\text{SO}_3$ , and  $\text{H}_2\text{S}$  on Pt
  - Complete stepwise decompositions of  $\text{SO}_3(\text{Pt})$  and  $\text{H}_2\text{S}(\text{Pt})$
  - Reduction of  $\text{SO}_3(\text{Pt})$  by  $\text{CO}(\text{Pt})$
  - Sulfate formation via attack of  $\text{SO}_3$  on  $\text{BaCO}_3$ ,  $\text{BaNO}_2$ , and  $\text{O}(\text{Ce}_2\text{O}_3)$
  - Sulfate or  $\text{SO}_3$  formation via attack of  $\text{SO}_2$  on  $\text{BaNO}_3$
- Many other possible reactions, such as reduction of  $\text{SO}_3(\text{Pt})$  by  $\text{H}(\text{Pt})$ , have been discarded.



# Test suite for sulfation/desulfation mechanism

- Kinetic parameters are inferred by simulating a sequence of experiments similar to the CLEERS protocol, but modified for practicality:
  - One conventional short (65 s) NO<sub>x</sub> storage/reduction (NSR) cycle, predetermined to be repeatable, with an unsulfated catalyst to establish baseline behavior
  - Three long lean/rich cycles, totaling 2 hr, with 20 ppm SO<sub>2</sub> in the feed, to achieve the first level of sulfation; using short cycles would be preferable but is probably not practical for parameter optimization due to excessive computation time (more on this later)
  - Ten short NSR cycles (enough to ensure repeatability), with no SO<sub>2</sub> in the feed, to assess new NSR performance
  - Three more long sulfation cycles to achieve the second level of sulfation
  - Ten more short NSR cycles for performance evaluation
  - Desulfation by temperature-programmed reduction, followed by an artificial cooldown to the nominal temperature
  - Ten more short NSR cycles for final performance evaluation
- All simulations except desulfation/cooldown are isothermal at 325°C, even though significant exotherms are observed experimentally.
  - Simulations of exotherms await improved computational tools and data





## Criteria for parameter set optimization

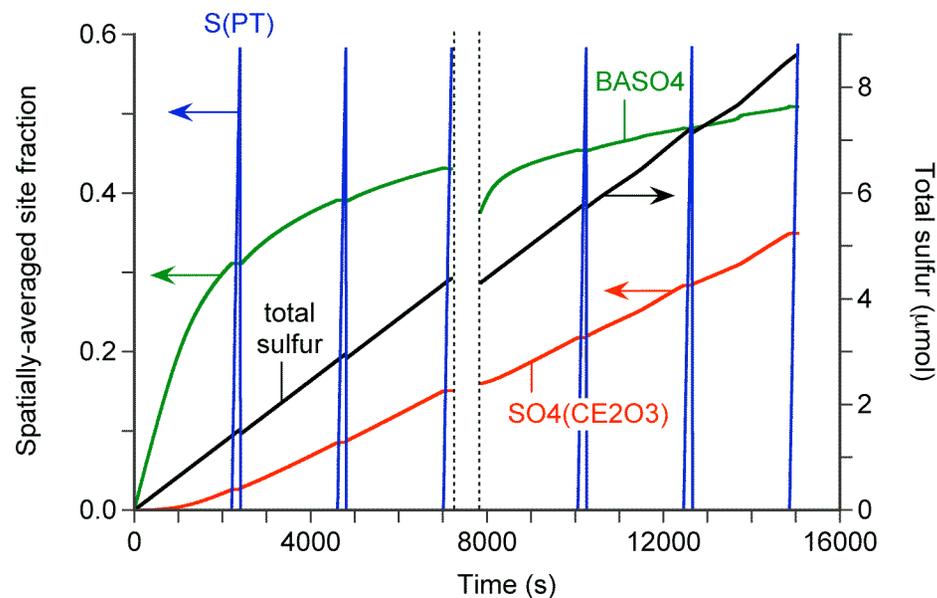
- The fitting process is semi-quantitative and involves an objective function that attempts to enforce five conditions:
  - SO<sub>2</sub> slip through the catalyst during the sulfation episodes should be minimal.
  - The axial profile of BaSO<sub>4</sub> at the end of the second sulfation episode should be plug-like.
  - The evolution of product gases during desulfation should match that reported in the literature (J.-S. Choi et al., *Appl. Catal. B Environ.* 77 (2007) 145).
  - 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.*), even though exotherms are not accounted for.





# Simulated surface compositions during sulfation

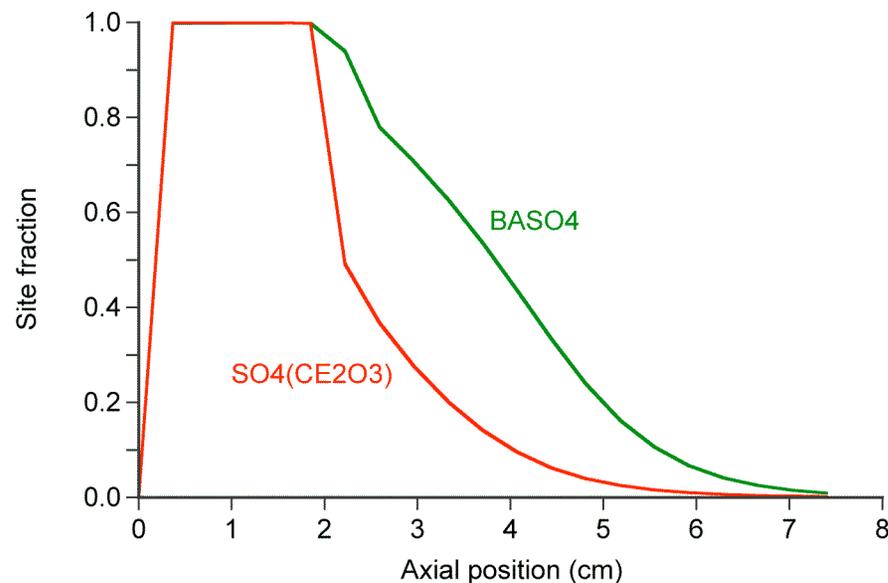
- Changes in the surface composition during sulfation are complex but generally in accordance with expectations.
  - Sulfur is trapped more readily on barium than on cerium, but saturation occurs.
  - During rich phases, sulfur is trapped reversibly on Pt and formation of sulfate stops, but there is very little loss of total sulfur.
  - During NSR cycling (details not shown), some  $\text{BaSO}_4$  is converted to  $\text{SO}_4(\text{Ce}_2\text{O}_3)$ , but again very little sulfur is actually lost.





# Sulfate concentration profiles after sulfation

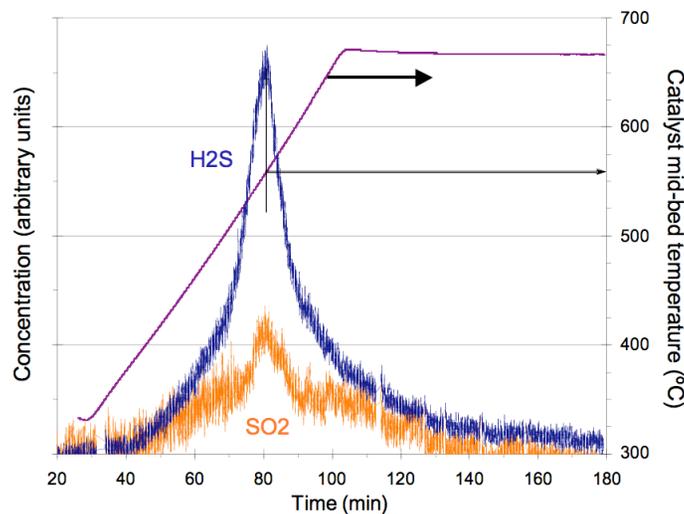
- Experimental observations suggest that sulfation is plug-like, especially with regard to the NO<sub>x</sub> storage component.
  - Simulation results agree with this only approximately.
  - Ironically, sulfation is more plug-like on cerium than on barium, even though only the latter is involved in the objective function.
  - There is no sulfation at the channel entrance because SO<sub>3</sub>, the primary sulfate precursor, is not present in the feed stream.



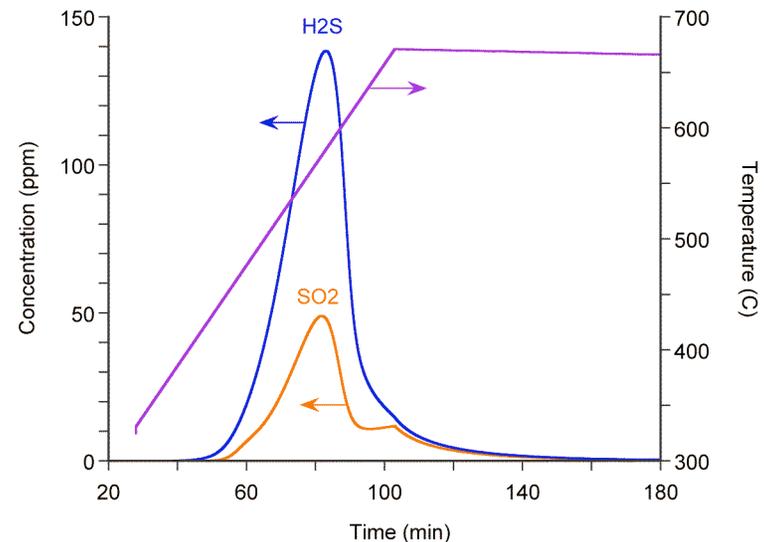


# Evolution of product gases during desulfation

- Simulation of desulfation by temperature-programmed reduction is in excellent semi-quantitative agreement with experiment.
  - Temperature is ramped at about 5°C/min with a feed containing 0.1% H<sub>2</sub>.
  - Experimental concentrations are not quantitative (thus units are arbitrary).
  - For purposes of comparison, experimental and simulated concentrations are scaled by H<sub>2</sub>S value at 80 min (near peak).



Experiment (J.-S. Choi, ORNL)

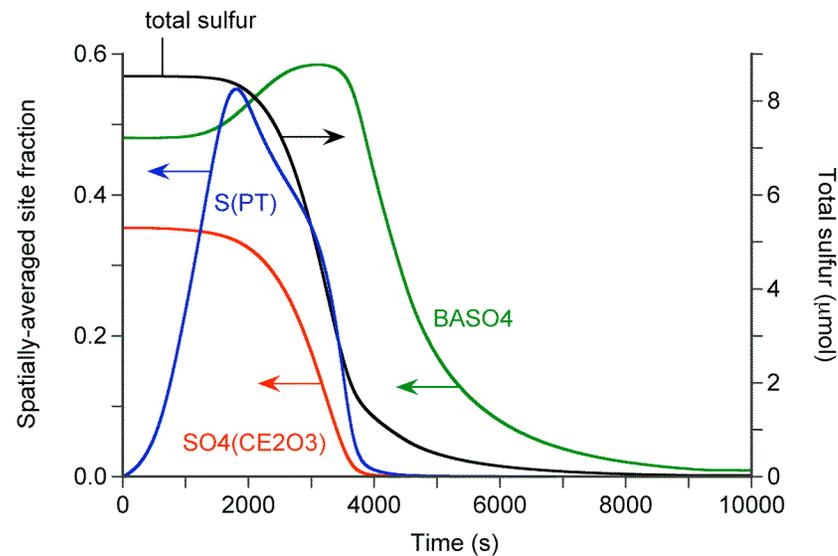


Simulation



# Simulated surface compositions during desulfation

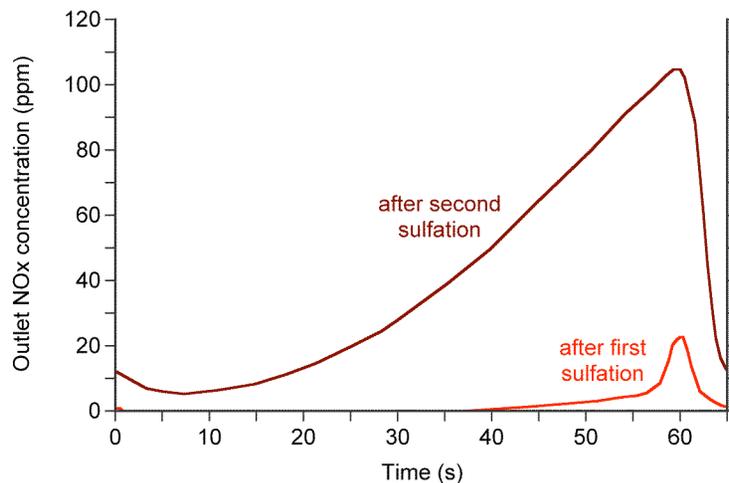
- The surface composition is predicted to change in a complex manner during desulfation.
  - As sulfate is released and reduced, Pt sites become covered largely with sulfur.
  - Some sulfate released from cerium sites is initially redeposited on barium, although total trapped sulfur decreases monotonically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



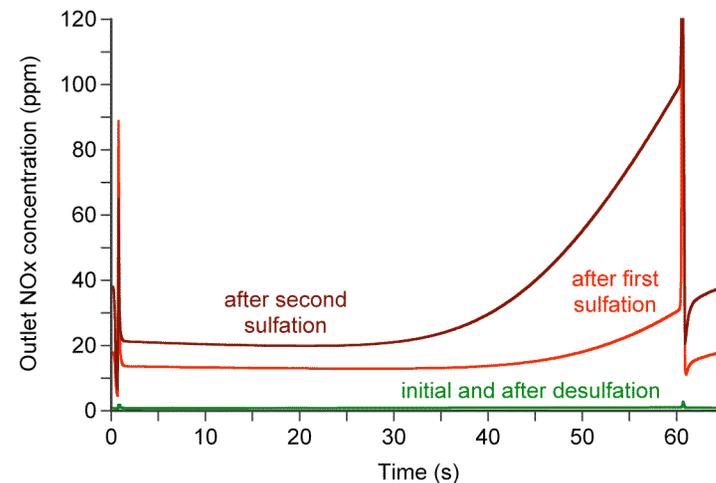


# Effects of sulfation on NSR performance

- The effect of sulfation on NO<sub>x</sub> trapping efficiency during normal cycling (60 s lean/5 s rich) is simulated reasonably well, although improvement is needed.
  - For an unsulfated catalyst, NO<sub>x</sub> slip is negligible (experimentally).
  - Simulations show unwanted NO<sub>x</sub> spikes at feed transition points and excessive NO<sub>x</sub> slip early in lean phase.
  - Discrepancies may be due (at least partially) to neglect of exotherms.



Experiment (J.-S. Choi, ORNL)



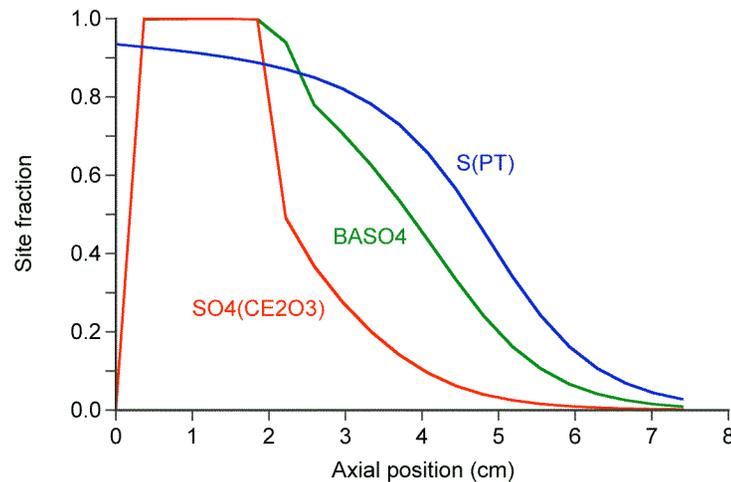
Simulation



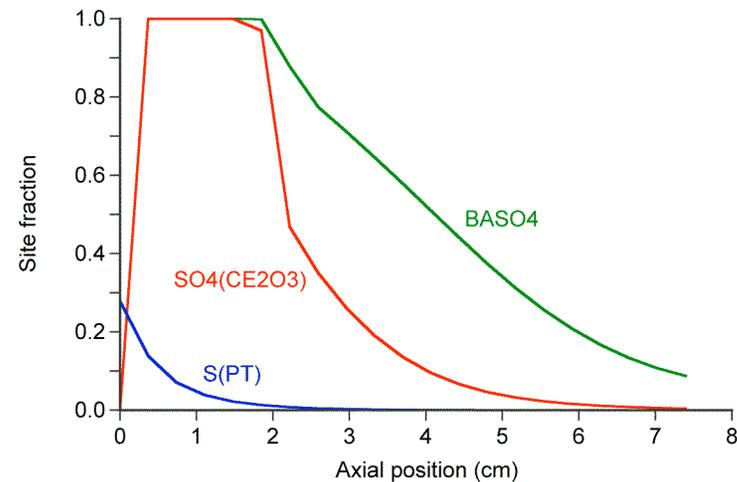


# Effect of sulfation cycle time on simulations

- An overly long cycle time (for fixed total loading) could affect the shapes of the sulfation profiles and thus also NSR performance.
- Increasing the number of sulfation cycles from 6 to 200 (72 s each) without altering the parameters has a modest effect on the  $\text{BaSO}_4$  profile and little effect on  $\text{SO}_4(\text{Ce}_2\text{O}_3)$  but strongly depresses S(Pt).
- Re-optimization is being attempted but CPU time is extreme.



using 6 sulfation cycles



using 200 sulfation cycles





## Future Work

- Modify kinetic parameters and/or reaction set for sulfation/desulfation to account better for products observed during ordinary lean/rich cycling.
  - Try to match production rates of  $N_2O$  and  $NH_3$  as well as  $NO/NO_2$  ratio, although exotherms and time resolution of experimental data may be problematic.
- Augment mechanism with reactions accounting for reductants other than CO and  $H_2$ .
  - 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.
  - 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 NO<sub>x</sub> 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<sub>2</sub>.
- 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.





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