Microkinetic Modeling of Lean NOx Trap Storage and Regeneration

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Overall objective

Develop an elementary surface reaction mechanism, to be used in conjunction with an appropriate reacting flow model, that accounts for the observed product distribution from a lean NOx trap during cyclical operation under various conditions of temperature and inlet gas composition.
Approach

• Assemble tentative mechanisms for precious metal (regeneration), baria (NOx storage), and ceria (oxygen storage) sites, using reactions from literature together with additional hypothesized steps.

• Infer tentative kinetic parameters for precious metal mechanism by matching product distributions from steady flow temperature ramp experiments done at ORNL.
  • Use Chemkin PLUG code to simulate (pseudo-) steady flow of reactant mixture through a catalyst monolith channel; temporarily discard storage mechanisms.
  • Use Sandia APPSPACK code to carry out optimization.
  • Apply thermodynamic constraints to kinetic parameters in order to ensure complete consistency.
Approach (continued)

• Infer kinetic parameters for storage mechanisms by matching product distributions from cycling experiments done at ORNL.
  • Use Chemkin-based transient plug flow code, modified to account for washcoat diffusion and accumulation, to simulate unsteady storage/regeneration processes.
  • Incorporate thermodynamic constraints on kinetic parameters in storage mechanisms as well.
  • Initially use precious metal kinetic parameters determined from temperature ramp experiments.
  • Assess the improvement achievable by allowing previously determined precious metal parameters to vary.
Accomplishments

• Completed construction of precious metal mechanism from temperature ramp experiments and published results in *Catalysis Today*.

• Assembled reaction sets for storage mechanisms and formulated corresponding thermodynamic constraints (all reactions treated as reversible with mass action kinetics).

• Modified transient plug flow code to account for washcoat diffusion and a finite capacity for “dissolved” gas while preserving one-dimensional nature.

• Inferred kinetic parameters for storage phases by fitting long cycle data, using both fixed and variable precious metal parameters.
Recap of precious metal mechanism

- 10 gas phase species: O2, NO, NO2, CO, H2, CO2, N2, H2O, N2O, NH3

- 13 surface species on precious metal (nominally platinum) sites: V(PT), O(PT), NO(PT), NO2(PT), CO(PT), H(PT), N(PT), OH(PT), H2O(PT), NH(PT), NH2(PT), NCO(PT), NH3(PT)

- 28 surface reactions, all of them reversible (in principle; 10 are found to be effectively irreversible):
  - 5 simple adsorptions
  - 6 dissociative adsorptions
  - 7 surface decompositions
  - 7 surface atom transfers
  - water-gas shift reaction
  - isocyanate formation and hydrolysis
The PT mechanism can simulate temperature ramp experiments even under oxidizing conditions.
Summary of storage mechanisms

- 6 surface species on baria sites: V(BAO), NO2(BAO), NO3(BAO), O(BAO), BACO3, BA(OH)2
- “bulk” nitrate species BA(NO3)2
- 2 surface species on ceria sites: V(CERIA), O(CERIA)
- 18 reactions, all of them reversible (in principle; effective irreversibility yet to be determined):
  - adsorption of NO2 on vacant baria sites to give nitrite
  - oxidation of vacant baria sites by O2
  - reaction of oxidized sites with CO2, H2O, NO, NO2 to give carbonate, hydroxide, nitrite, nitrate
Storage reactions (continued)

• reaction of carbonate with H2O, NO, NO2 to give hydroxide, nitrite, nitrate
• reaction of hydroxide with NO, NO2 to give nitrite, nitrate
• reaction of nitrite with NO2 to give nitrate (disproportionation)
• surface oxidation of nitrite to nitrate by oxidized sites, carbonate, hydroxide
• spillover of nitrite to precious metal sites
• conversion of surface nitrate to bulk nitrate
• oxidation of vacant ceria sites by O2
Key features of reactor model

• Transient plug flow model for gas in monolith channel

• Transient lumped parameter model for species diffusing through washcoat (to preserve one-dimensionality)

• All reaction rates evaluated at washcoat concentrations

• Effective diffusion layer thickness and effective capacity for dissolved gas are adjustable parameters

• Measured axial temperature profiles (not quite isothermal) are used as inputs
Summary of long cycle experiments (ORNL)

• Commercially available Umicore GDI LNT catalyst
• Space velocity 30,000/hr
• 15 min lean (300 ppm NO, 10% O2)
• 10 min rich (625 ppm CO, 375 ppm H2)
• 5% H2O, 5% CO2, N2 carrier gas in all flows
• Reactor nearly isothermal at 200, 300, or 400 C
• Chemiluminescent analyzers for NO and total NOx; FTIR for CO, NH3, and N2O
At 200 C, fitting results using fixed PT parameters are largely correct qualitatively but could be better.

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 200 C
At 300 C, the simulation incorrectly predicts substantial NO slip during regeneration.

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 300 C
At 400 C, the predicted NO puff is actually observed and results are generally satisfactory.

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 400 C
At least four explanations for the deficiencies in the fits using fixed PT parameters are possible.

- The precious metal mechanism alone, without storage reactions, may not be adequate to describe the chemistry in all of the temperature ramp experiments.

- The steady state plug flow reactor model, without washcoat diffusion, may not be adequate to describe the transport in the temperature ramp experiments.

- The description of transport, accumulation, and reaction within the washcoat in the transient plug flow model may be too simple to simulate the cycle experiments.

- The storage mechanisms used in simulating the cycle experiments may be incomplete or otherwise inadequate.

- At present the true explanation is not known.
At 200 C, allowing the kinetic parameters in the PT reactions to vary does give significant improvement.

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 200 C
At 300 C, the spurious NO puff is now absent, but the timing of the NH3 peak is still inaccurate.

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 300 C
At 400 C, the size of the NO puff is now somewhat underpredicted, and NH3 is completely absent.

Outlet concentrations of gas-phase species during long storage/regeneration cycle at 400 C
The simulations are consistent with hypotheses about the sequence of events during regeneration.

- Near inlet, 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.
The simulations also explain the period of ammonia slip that follows the initial NOx escape.

- The 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).
Conclusions and future directions

- A thermodynamically consistent reaction mechanism that can simulate full LNT storage/regeneration cycles has been developed.

- To achieve completely satisfactory results, both the current reactor model and the previously obtained kinetic parameters for the precious metal phase may need to be modified.

- The simulations agree with previously proposed scenarios for the regeneration of the catalyst.

- A companion mechanism for sulfur poisoning and thermal desulfation is under development.
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