Modeling the Regeneration Chemistry of Lean NOx Traps

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Principal objective

Develop an elementary surface reaction mechanism, complete with values for the kinetic parameters, that accounts for the observed product distribution from a lean NOx trap operating in the regeneration phase under various conditions of temperature and inlet gas composition.
Basic approach

- Assemble a tentative set of reaction steps and kinetic parameters for NOx reduction chemistry -- some from catalysis literature, others hypothesized.

- Use Chemkin PLUG code to simulate (pseudo-) steady state flow of reactant mixture through a monolith channel.

- Adjust kinetic parameters (pre-exponential factors and activation energies) to match product distributions from temperature ramp experiments done at Oak Ridge.

- Determine sensitivity of results to individual reactions and discard those found to be insignificant.
Basic approach (continued)

• Perform transient simulations for all cases in order to assess the validity of assuming pseudo-steady conditions.

• Apply thermodynamic constraints to reduced mechanism and re-optimize parameters to obtain a completely consistent set (in progress).
Features of current reaction mechanism

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

• 13 surface species on precious metal (nominally platinum) sites: *(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)

• No homogeneous gas phase reactions

• 17 reversible surface reactions

• 9 irreversible surface reactions
The reversible reactions consist mostly of adsorption/desorptions …

\[
\begin{align*}
\text{O}_2 + 2 \ast(\text{PT}) &= 2\text{O}(\text{PT}) \\
\text{NO} + \ast(\text{PT}) &= \text{NO(PT)} \\
\text{NO}_2 + \ast(\text{PT}) &= \text{NO}_2(\text{PT}) \\
\text{CO} + \ast(\text{PT}) &= \text{CO(PT)} \\
\text{H}_2 + 2 \ast(\text{PT}) &= 2\text{H}(\text{PT}) \\
\text{H}_2\text{O} + \ast(\text{PT}) &= \text{H}_2\text{O(PT)} \\
\text{NH}_3 + \ast(\text{PT}) &= \text{NH}_3(\text{PT}) \\
\text{N}_2 + 2 \ast(\text{PT}) &= 2\text{N(PT)}
\end{align*}
\]
... and decomposition/recombinations.

\[
\begin{align*}
\text{NO}_2(\text{PT}) + *(&\text{PT}) &= \text{NO}(\text{PT}) + \text{O}(\text{PT}) \\
\text{NO}(\text{PT}) + *(&\text{PT}) &= \text{N}(\text{PT}) + \text{O}(\text{PT}) \\
\text{OH}(\text{PT}) + *(&\text{PT}) &= \text{H}(\text{PT}) + \text{O}(\text{PT}) \\
\text{NH}(\text{PT}) + *(&\text{PT}) &= \text{N}(\text{PT}) + \text{H}(\text{PT}) \\
\text{NH}_2(\text{PT}) + *(&\text{PT}) &= \text{NH}(\text{PT}) + \text{H}(\text{PT}) \\
\text{NH}_3(\text{PT}) + *(&\text{PT}) &= \text{NH}_2(\text{PT}) + \text{H}(\text{PT})
\end{align*}
\]
Indirect reduction with CO can take place via two distinct pathways.

Hydrogen production via water-gas shift reaction:

$$H_2O(PT) + CO(PT) = 2H(PT) + CO_2$$

Reaction of water with isocyanate intermediate:

$$N(PT) + CO = NCO(PT)$$

$$NCO(PT) + H_2O(PT) \Rightarrow NH_2(PT) + CO_2 + *(PT)$$
Most remaining recombinations and atom transfers are treated as irreversible.

\[
\begin{align*}
2\text{NO(PT)} & \Rightarrow \text{N}_2 + 2\text{O(PT)} \\
\text{N}_2\text{O} + \text{H(PT)} & \Rightarrow \text{N}_2 + \text{OH(PT)} \\
\text{NO(PT)} + \text{N(PT)} & \Rightarrow \text{N}_2\text{O} + 2\text{*(PT)} \\
2\text{NO(PT)} & = \text{N}_2\text{O} + \text{O(PT)} + \text{*(PT)} \\
\text{NO}_2(\text{PT}) + \text{CO(PT)} & \Rightarrow \text{NO(PT)} + \text{CO}_2 + \text{*(PT)} \\
\text{NH(PT)} + \text{O(PT)} & \Rightarrow \text{NO(PT)} + \text{H(PT)} \\
\text{NH}_3(\text{PT}) + \text{O(PT)} & \Rightarrow \text{NH}_2(\text{PT}) + \text{OH(PT)} \\
\text{CO(PT)} + \text{O(PT)} & \Rightarrow \text{CO}_2 + 2\text{*(PT)} \\
\text{H(PT)} + \text{OH(PT)} & \Rightarrow \text{H}_2\text{O(PT)} + \text{*(PT)}
\end{align*}
\]
Summary of experimental program

- 21 separate runs with inlet compositions involving NO/H₂, NO/CO, NO₂/H₂, NO₂/CO, N₂O/H₂, N₂O/CO, NH₃/O₂, NH₃/NO, NH₃, H₂, or CO
- 5% H₂O, 5% CO₂, N₂ carrier gas in all runs
- Temperature ramped from below 100 C to 500 C at 5 C/min
- Space velocity 100,000/hr
- Commercially available Umicore GDI LNT catalyst
- Chemiluminescent analyzers for NO and total NOₓ; FTIR for CO, NH₃, and N₂O; net N₂ by difference
For a stoichiometric NO/H₂ feed, N₂ formation is favored at high temperatures.

Simulation of steady flow temperature sweep experiment for 1:1 NO/H₂
However, for NO with excess H$_2$, large amounts of NH$_3$ can be produced.
For 1:10 NO\textsubscript{2}/CO, a distinct two-step drop in CO is reasonably well reproduced by the model.
Even with a large excess of H2, reduction of N2O produces mostly N2 rather than NH3.
Direct oxidation of NH3 is accounted for quite accurately by the model.
Simple decomposition of NH₃ is also simulated successfully.
Summary

• Regeneration chemistry in a lean NOx trap can be simulated with a reasonably compact elementary mechanism.

• Water-gas shift and isocyanate pathways are both needed to explain observed patterns of CO consumption.

• The next step is to apply formal thermodynamic constraints to the proposed mechanism.

• Eventually the regeneration mechanism must be augmented with surface reactions taking place on storage (BaO) sites.

• The combined storage/regeneration mechanism will allow the simulation of fully transient LNT cycles.