Development of a global kinetic model for a commercial Lean NOx Trap based on laboratory measurements

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Outline

• Background
  • BMW LNT
  • CLEERS LNT Protocol
• Review Past Results
• NOx Storage Model
• NOx Reduction Model
• Conclusions
ORNL purchased a MY2008 BMW 1-series 120i lean gasoline engine vehicle with a N43B20 2.0-liter, 4-cylinder engine with direct injection.

The vehicle was characterized on a chassis dynamometer.

Engine measurement results are available on the CLEERS database.

A core from the LNT was made available for ORNL laboratory testing.

Preliminary modeling results were shown at the 2013 workshop.

Lean Gasoline Engine Reductant Chemistry During Lean NOx Trap Regeneration

James E. Parks, Vitaly Prikhodko, William Partridge, Jae-Soon Choi, Kevin Norman, Shean Huff and Paul Chambon

Oak Ridge National Laboratory

SAE, 2010-01-2267
CLEERS LNT Protocol

http://cleers.org/focus_groups/private/Lean-NOx/files/1113847174LNTmap_7_18_05.pdf

- Oxygen storage and reduction via CO, H₂
- Short-Cycle NOx storage and reduction via CO, H₂, HC
- Long-Cycle NOx storage and reduction via CO, H₂, HC
- Constant temperatures of 150, 209, 286, 393, 550°C
- Measured outlet data includes NO, NO₂, CO, N₂O, NH₃, O₂, H₂
Recap: NOx Storage Experiments

- Measurements available for 7 different cases

Variation with temperature of the NO and NO\textsubscript{2} storage indicates the complexity of the storage mechanism
NOx Storage Capacity

- NOx Stored [mol/m³]
- NOx Storage Capacity

- Initial 15 Minutes
- Extended Duration

Temperature [°C]
- NO 150
- NO 209
- NO 286
- NO 393
- NO 550
- NO2 150
- NO2 209
Recap: NOx Storage – $\text{NO}_2$ Feed Experiments

- Three-step disproportion needed to match peak NO outlet concentration at 150°C for largest density site

\[
\begin{align*}
\text{BaO} + 3\text{NO}_2 & \rightarrow \text{Ba(NO}_3)_2 + \text{NO} \\
\text{BaO} - \text{NO}_2 & \rightarrow \text{BaO}_2 + \text{NO} \\
\text{BaO}_2 + 2\text{NO}_2 & \rightarrow \text{Ba(NO}_3)_2
\end{align*}
\]

- Additional site needed to describe storage needed for delayed NO breakthrough

![Graphs showing concentration over time at 150°C and 209°C](image-url)
Recap: NOx Storage– NO Feed Experiments

- Typical mechanism
  - Two storage sites
  - Storage + release of both NO and NO₂
  - Retains satisfactory results with NO₂ experiments

- Additional work needed
  - Release at 150°C
  - Breakthroughs at 286°C and 393°C

- Data explicitly points to a required third storage site
Precedence for 3-Site Storage Mechanism

NOx Storage Mechanism

\[ \text{Ba}^I \text{O} + 2\text{NO} + 1.5\text{O}_2 \rightarrow \text{Ba}^I (\text{NO}_3)_2 \]
\[ \text{Ba}^I (\text{NO}_3)_2 \rightarrow \text{Ba}^I \text{O} + 2\text{NO}_2 + 0.5\text{O}_2 \]

\[ \text{Ba}^I \text{O} + 3\text{NO}_2 \rightarrow \text{Ba}^I (\text{NO}_3)_2 + \text{NO} \]

*3-step detailed disproportion

\[ \text{Ba}^{II} \text{O} + 3\text{NO}_2 \rightarrow \text{Ba}^{II} (\text{NO}_3)_2 + \text{NO} \]
\[ \text{Ba}^{II} (\text{NO}_3)_2 \rightarrow \text{Ba}^{II} \text{O} + 2\text{NO}_2 + 0.5\text{O}_2 \]
\[ \text{Ba}^{II} \text{O} + 2\text{NO} + 0.5\text{O}_2 \leftrightarrow \text{Ba}^{II} (\text{NO}_2)_2 \]
\[ \text{Ba}^{II} (\text{NO}_2)_2 + 0.5\text{O}_2 \rightarrow \text{Ba}^{II} (\text{NO}_3)_2 \]

60 mol/m³ Ba⁺

14 mol/m³ Ba⁺⁺

16 mol/m³ Ba⁺⁺⁺
NOx Storage Results

Graphs showing concentration [ppm] over time [min] at different temperatures and conditions.
NOx Reduction via CO, H₂, C₃H₆

- When feeding CO and C₃H₆ as reductants, H₂ is still a primary cleanser of stored NOx after being generated from WGS and SRR, respectively.
- NH₃ production occurs at lower temperatures and correlates to larger H₂ presence, as confirmed by others.
- Model captures effect of NH₃ breakthrough after disappearance of N₂O.
H₂ Reduction Mechanism Development

- **Left vertical axis:**
  - NO_sim
  - NO₂_sim
  - NH₃_sim
  - N₂O_sim
  - NO_exp
  - NO₂_exp
  - NH₃_exp
  - N₂O_exp

- **Right vertical axis:**
  - H₂_sim
  - CO_sim
  - H₂_exp
  - CO_exp

**Temperature Settings:**
- 150 °C
- 209 °C
- 286 °C
- 393 °C
- 550 °C
CO Reduction Mechanism Development
A three site model is needed to adequately simulate the NOx storage
- It is a physical approximation of the microkinetic conceptual model of Chaugule et al. (2010)

Storage experiments show that the LNT protocol needs to be modified to achieve storage saturation in some long cycle measurements

A full mechanism has been developed and implemented in GT-SUITE, including oxygen storage and NOx reduction steps

A manuscript is in preparation for submission and will contain all site densities and kinetics parameters