Development of an LNT reaction mechanism for the BMW 120i LNT catalyst, Phase 1

NOx Adsorption and Oxygen Storage
Acknowledgements

- This work was a joint collaboration among

Authors:

- Dominik Artukovic (GTI Stuttgart Gmbh)
- Dick Blint (N₂Kinetics Research, LLC)
- Stuart Daw (ORNL)
- Ryan Dudgeon (GTI)
- Enrico Pautasso (GTI Torino)
- Josh Pihl (ORNL)
- Syed Wahiduzzaman (GTI)
Background

• 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

 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
**Oxygen Storage**

Nominal fixed conditions: 30,000 1/hr SV.
Objective: Establish inherent oxygen storage (as reflected in reductant demand) exclusive of NOx.

<table>
<thead>
<tr>
<th>Run No.*</th>
<th>Temp (deg C)*</th>
<th>Gas Mix**</th>
<th>Lean period (s)</th>
<th>Injected Reductant</th>
<th>Regen peak (ppm)</th>
<th>Regen period (s)</th>
<th>No. of cycles</th>
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<tbody>
<tr>
<td>C1</td>
<td>T_{max}</td>
<td>M1</td>
<td>0</td>
<td>H2</td>
<td>10,000</td>
<td>900</td>
<td>1</td>
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<tr>
<td>C2</td>
<td>T_{max}</td>
<td>M2</td>
<td>60</td>
<td>CO</td>
<td>10,000</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>C3</td>
<td>0.75(T_{max}+T_{min})</td>
<td>M2</td>
<td>60</td>
<td>CO</td>
<td>10,000</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>C4</td>
<td>0.5(T_{max}+T_{min})</td>
<td>M2</td>
<td>60</td>
<td>CO</td>
<td>10,000</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>C5</td>
<td>0.5(T_{max}+T_{min})</td>
<td>M3</td>
<td>60</td>
<td>CO</td>
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<td>30</td>
</tr>
<tr>
<td>C6</td>
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<td>CO</td>
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</tr>
<tr>
<td>C8</td>
<td>T_{min}</td>
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<td>60</td>
<td>CO</td>
<td>10,000</td>
<td>30</td>
<td>50</td>
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</tbody>
</table>

Footnotes:
* T_{max} = 500°C and T_{min} = 175°C.
++ Gas inlet mix M1= 5% H2, 5% CO, balance N2
   Gas inlet mix M2= 5% H2O, 5% CO2, 1% O2, balance N2
   Gas inlet mix M3= 5% H2O, 5% CO2, 5% O2, balance N2
   Gas inlet mix M4= 5% H2O, 5% CO2, 1% O2, balance N2

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

• Original protocol evaluation, Epling, Currier and Yezerets

• Temperatures ranging from 150 – 550°C equally spaced in 1/T [K] to facilitate better reaction modeling
  – 150°C, 209°C, 286°C, 393°C, 550°C

• For this application 600 seconds lean was not sufficient to get complete NOx storage at all temperatures
  – Josh reran the long POx protocol and adjusted storage times to reach full NOx storage
New generation Lean GDI LNT
(benchmarking against CLEERS reference catalyst)

CLEERS reference
Lean GDI, 2004, provided by Umicore

New LNT
Lean GDI, 2009, from BMW 120i vehicle

New generation is more highly dispersed for most components
CLEERS LNT versus BMW LNT

<table>
<thead>
<tr>
<th>Property</th>
<th>CLEERS</th>
<th>BMW</th>
<th>Units</th>
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</thead>
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<tr>
<td>cell density</td>
<td>625 cells/in²</td>
<td>413</td>
<td></td>
</tr>
<tr>
<td>mass</td>
<td>465.83 g</td>
<td>853.24 g</td>
<td></td>
</tr>
<tr>
<td>area</td>
<td>109.36 cm²</td>
<td>117.24 cm²</td>
<td></td>
</tr>
<tr>
<td>length</td>
<td>7.5 cm</td>
<td>11 cm</td>
<td></td>
</tr>
<tr>
<td>volume</td>
<td>820 cm³</td>
<td>1290 cm³</td>
<td></td>
</tr>
<tr>
<td>density</td>
<td>567.9 g/L</td>
<td>661.6 g/L</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>CLEERS ref</th>
<th>BMW</th>
<th>Units</th>
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<tr>
<td>Ba</td>
<td>14.88</td>
<td>19.98</td>
<td>g/L</td>
</tr>
<tr>
<td>Ce</td>
<td>67.36</td>
<td>55.51</td>
<td>g/L</td>
</tr>
<tr>
<td>Zr</td>
<td>5.11</td>
<td>4.32</td>
<td>g/L</td>
</tr>
<tr>
<td>La</td>
<td>2.84</td>
<td>2.45</td>
<td>g/L</td>
</tr>
<tr>
<td>Pt</td>
<td>2.45</td>
<td>2.18</td>
<td>g/L</td>
</tr>
<tr>
<td>Pd</td>
<td>0.77</td>
<td>0.85</td>
<td>g/L</td>
</tr>
<tr>
<td>Rh</td>
<td>0.30</td>
<td>0.30</td>
<td>g/L</td>
</tr>
<tr>
<td>PGM</td>
<td>3.52</td>
<td>3.32</td>
<td>g/L</td>
</tr>
<tr>
<td>K</td>
<td>0.06</td>
<td>0.04</td>
<td>g/L</td>
</tr>
<tr>
<td>Sr</td>
<td>0.34</td>
<td>0.39</td>
<td>g/L</td>
</tr>
<tr>
<td>Na</td>
<td>0.03</td>
<td>0.07</td>
<td>g/L</td>
</tr>
<tr>
<td>Ca</td>
<td>N/A</td>
<td>0.09</td>
<td>g/L</td>
</tr>
</tbody>
</table>

Dispersion and cell density most significant differences

Ceria slightly less

Common NOx storage components

PGM similar
• Flow simulations were used to calculate measurement delays

• Measurement delays were calculated to vary from 0.1 second to 0.7 seconds

• For efficiency, the full flow architecture was not used for mechanism development
ORNL Laboratory Setup

JOSH
Modeling Approach

- GT-SUITE software
- 1D, quasi-steady flow solution
- GTI’s Advanced Adaptive chemistry solver

Ref: SAE 2007-01-4127
GT-SUITE  Advanced Adaptive Chemistry Solver

• Chemical kinetics creates stiff systems. To solve these systems robustly and accurately, the solver must be highly ADAPTIVE

• The solver uses adaptive:
  • Time steps
  • Axial steps
  • Non-linear iterations

• Highest stability standards are applied:
  • Fully coupled, no lagging
  • BDF (Backward Differentiation Formula) integration methods

• Numerically efficient:
  • 20 – 2000 times faster than real time depending on kinetics and inlet boundary conditions
Water-Gas-Shift Reaction Calibration

- WGS calibrated at 286°C and 393°C to match steady-state CO/H₂ ratio
  - Inactive at 150°C and 209°C; at chemical equilibrium at 550°C
- Ahrrenius plot of ln(rate) vs. 1/T gave kinetic rate constant fit

\[ y = -8090x + 24.18 \]
Oxygen Storage Protocol Measurements

- 60 second 10% $O_2$ storage, 30 second reduction by 1% CO
- Balance of OSC reaction and WGS shows a temperature-dependent oxygen storage capacity
- Water-gas-shift reaction calibrated to match steady-state CO/H$_2$ ratio

Thick lines: measured   Thin lines: model prediction
Oxygen Storage and Reduction Modeling

- Oxygen storage capacity increases with increasing temperature due to balance with WGS reactions.
- Maximum storage estimated from extrapolation $\approx 21.25 \text{ mol/m}^3$.
- Temperature-dependent equilibrium coverage controls storage capacity.

$$\theta_{Ce_2O_4}(T) = 1 - \frac{339}{\max(T,339)}$$

I am not sure that there is any substantiation in the literature for this.
NOx Storage Experimental Data

Measurements available for 7 different cases

- 300 ppm NO
- Inlet: 10% O₂, 5% CO₂, 5% H₂O, N₂ excess

Not equilibrated at 10 minutes

10 minutes not sufficient to stabilize NO₂ concentration

300 ppm NO
NO Oxidation from NO Inlet Experiments

- Protocol does not directly provide NO oxidation information
- \( \text{NO}_2/\text{NOx} \) reaches near steady-state in all cases
- NO oxidation kinetics were calibrated using \( \text{NO}_2/\text{NOx} \) ratio
NO Oxidation from NO Inlet

Experiments

$SV = 30,000 \text{ 1/hr}$
NOx Storage Modeling

- Equilibrium coverage method for NOx storage modeling has two major flaws

\[ R = k C_{NOx} C_{O_2} \text{sign}\left(\left(\theta_{eq}(T) - \theta_{NOx}\right)^2, \theta_{eq}(T) - \theta_{NOx}\right) \]

- When \( C_{O_2} = 0 \), \( R = 0 \), which is not supported by the data
  - NOx clearly releases from the surface when oxygen is absent

- When \( \theta_{eq}(T) < \theta_{NOx} \), \( R < 0 \), \( \rightarrow \) net rate is NOx release from surface
  - The net rate is still dependent on \( C_{NOx} \), which is not physical
NOx Storage Modeling

- NO₂ inlet experiments calibrated first
  - Reverse NO oxidation does not occur at 150°C; negligible at 209°C
- One-step disproportion reaction accounts for outlet NO at 209°C; 150°C approaches theoretical value at steady-state

\[ \text{BaO} + 3\text{NO}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 + \text{NO} \]

Where does the model get NO at time-0??

[Graphs showing concentration over time at 150°C and 209°C]
NOx Storage Modeling

- Three-step disproportion needed to match peak NO outlet concentration at 150°C
  \[ \text{BaO} + 3\text{NO}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 + \text{NO} \]
  Rate-limited at low temperature

- Two site storage needed for delayed breakthrough

- Quite possibly the low temperature adsorption is on ceria, see Chuan et. al, Applied Catalysis B: Environmental 119–20 (2012) 183–196

![Graphs showing concentration vs. time at 150°C and 209°C with thick and thin lines indicating measured and model prediction respectively.](image-url)
NOx Storage Modeling – NO Inlet Experiments

- Current mechanism
  - Two storage sites
  - Storage + release of both NO and NO$_2$
  - Retains satisfactory results with NO$_2$ experiments

- Additional work needed
  - Release at 150°C
  - Breakthroughs at 286°C and 393°C
Equilibrium NOx Storage Capacity

- Current model predicts storage capacity both quantitatively and qualitatively
Current Mechanism

\[ R1: NO + 0.5O_2 \leftrightarrow NO_2 \]
\[ R2: BaO + NO_2 \rightarrow BaO - NO_2 \]
\[ R3: BaO - NO_2 \rightarrow BaO_2 + NO \]
\[ R4: BaO_2 + 2NO_2 \rightarrow Ba(NO_3)_2 \]
\[ R5: BaO + 2NO + 1.5O_2 \rightarrow Ba(NO_3)_2 \]
\[ R6: Ba(NO_3)_2 \rightarrow BaO + 2NO + 1.5O_2 \]
\[ R7: Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + 0.5O_2 \]
\[ R8: Ba'O + 3NO_2 \rightarrow Ba'(NO_3)_2 + NO \]
\[ R9: Ba'O + 2NO + 1.5O_2 \rightarrow Ba'(NO_3)_2 \]
\[ R10: Ba'(NO_3)_2 \rightarrow Ba'O + 2NO + 1.5O_2 \]
\[ R11: Ba'(NO_3)_2 \rightarrow Ba'O + 2NO_2 + 0.5O_2 \]
\[ R12: H_2O + CO \leftrightarrow H_2 + CO_2 \]
\[ R13: Ce_2O_3 + 0.5O_2 \rightarrow Ce_2O_4 \]
\[ R14: Ce_2O_4 + CO \rightarrow Ce_2O_3 + CO_2 \]
\[ R15: Ce_2O_4 + H_2 \rightarrow Ce_2O_3 + H_2O \]

<table>
<thead>
<tr>
<th>Active Site Densities (moles/m^3 total catalyst volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Ba'</td>
</tr>
<tr>
<td>cerium</td>
</tr>
</tbody>
</table>
Current Mechanism

All rates are turnover number based
All concentrations in mol/m$^3$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>$T_3$ (K)</th>
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<tbody>
<tr>
<td>R1</td>
<td>6.56E7</td>
<td>5212</td>
</tr>
<tr>
<td>R2</td>
<td>0.23</td>
<td>0</td>
</tr>
<tr>
<td>R3</td>
<td>35.5</td>
<td>0</td>
</tr>
<tr>
<td>R4</td>
<td>1.1E10</td>
<td>10350</td>
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<tr>
<td>R5</td>
<td>0.001</td>
<td>0</td>
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<tr>
<td>R6</td>
<td>120900</td>
<td>12360</td>
</tr>
<tr>
<td>R7</td>
<td>2.2</td>
<td>5220</td>
</tr>
<tr>
<td>R8</td>
<td>3.55</td>
<td>0</td>
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<tr>
<td>R9</td>
<td>5.65</td>
<td>0</td>
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<tr>
<td>R10</td>
<td>231000</td>
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<tr>
<td>R11</td>
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<tr>
<td>R12</td>
<td>3.175E10</td>
<td>8090</td>
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<tr>
<td>R13</td>
<td>0.1</td>
<td>See Rate Form</td>
</tr>
<tr>
<td>R14</td>
<td>200000</td>
<td>See Rate Form</td>
</tr>
<tr>
<td>R15</td>
<td>53060</td>
<td>See Rate Form</td>
</tr>
</tbody>
</table>

\[ R1 = Ae^{\frac{-T_a}{T}} \left( C_{NO}C_{O_2}^{0.5} - \frac{C_{NO_2}}{K_{eq}} \right) / G \]

\[ R12 = Ae^{\frac{-T_a}{T}} \left( C_{H_2O}C_{CO} - \frac{C_{H_2}C_{CO_2}}{K_{eq}} \right) / G \]

\[ R13 = AC_{O_2} \max\left(0,1 - \frac{339.1}{\max(T,344.25)} - \theta_{Ce_2O_4} \right) \]

\[ R14 = AC_{CO}e^{\frac{-4500(1-1.775\theta_{Ce_2O_4}+2\theta_{Ce_2O_4}^2)}{T}} \]

\[ R15 = AC_{H_2}e^{\frac{-959(1-3.03\theta_{Ce_2O_4}+1.64\theta_{Ce_2O_4}^2)}{T}} \]

All other rate forms:

\[ R_j = Ae^{\frac{-T_a}{T}} \prod C_i \prod \theta_i \]

(order 1 concentrations and coverages)
Summary

• Experimental results at 150 °C provide significant additional information about the low temperature storage process

• The oxygen storage protocol is quite sufficient for developing kinetics; however, a two site storage model might be needed especially when the short cycle effects are modeled

• A three site model for NOx storage is needed perhaps due to NOx storage on ceria

• For this catalyst lean cycle times greater than 600 seconds are needed to reach steady state. In some cases times in excess of 2700 seconds seem to be needed

• At low temperature NO and NO\textsubscript{2} adsorption do not seem to be strongly connected through the NO oxidation step. NO and NO\textsubscript{2} have vastly different storage pathways

• Prediction of the temperature dependent NO and NO\textsubscript{2} storage appears to be good

• High temperature NOx adsorption appears to be a one site process

• This mechanism appears to describe both the NO and the NO\textsubscript{2} adsorption at low temperature; however, experiments for NO\textsubscript{2} storage in the absence of O\textsubscript{2} would be very informative
Future Work

• TPR experiment for NO oxidation for better transient modeling
• Refine the NOx storage kinetic parameters with additional modeling
• Calibrate NOx reduction by CO, H₂, and C₃H₆
• Model the short cycle lab experiments for transient kinetics development
• Simulation of the engine results may be considered
Current Mechanism

\[ G = T \left(1 + K_1 y_{CO} + K_2 y_{C_3H_6} \right)^2 \left(1 + K_3 y_{CO}^2 y_{C_3H_6}^2 \right) \left(1 + K_4 y_{NO} \right) \]

\[ K_1 = 65.5 \exp\left(\frac{961}{T}\right) \]
\[ K_2 = 2080 \exp\left(\frac{361}{T}\right) \]
\[ K_3 = 3.98 \exp\left(\frac{11611}{T}\right) \]
\[ K_4 = 479000 \exp\left(-\frac{3733}{T}\right) \]

\[ y_j \text{ : mole fraction} \]