A Global Kinetic Model for a Diesel Oxidation Catalyst Incorporating Mechanisms for Sulfur Poisoning and Surface Oxidation
Objectives

I. Develop a global kinetics model for a Pt/Pd + Zeolite Diesel Oxidation Catalyst (DOC)

II. Incorporate mechanisms for sulfur poisoning and surface oxidation to the global kinetics model

III. Assess the effects of sulfur poisoning and surface oxidation under multiple real driving emissions (RDE) cycles in series
Part I. DOC Global Kinetics Model
DOC Experimental Details

- SGB Tests to characterize oxidation and storage kinetics
  - Space velocity: 30,000 /h – 60,000/h
  - Linear temperature ramp from 80 C to 400 C
  - Feed gas contained multiple combinations of CO, C$_3$H$_6$, C$_{10}$H$_{22}$, NO and NO$_2$

- Reactor core extracted from standard square channel monolith
  - Core size: 1 x 3 in
  - Cell Density (cpsi): 400
  - Substrate thickness (mil): 4.5
  - Washcoat thickness (micron): 30
  - PGM site density (mole/m$^3$): 6.581
### DOC Reaction Mechanism

<table>
<thead>
<tr>
<th>#</th>
<th>Site</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zeolite</td>
<td>( Z + C_{10}H_{22} \rightarrow Z - C_{10}H_{22} )</td>
</tr>
<tr>
<td>2</td>
<td>Zeolite</td>
<td>( Z - C_{10}H_{22} \rightarrow Z + C_{10}H_{22} )</td>
</tr>
<tr>
<td>3</td>
<td>PGM</td>
<td>( CO + 0.5O_2 \rightarrow CO_2 )</td>
</tr>
<tr>
<td>4</td>
<td>PGM</td>
<td>( C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O )</td>
</tr>
<tr>
<td>5</td>
<td>PGM</td>
<td>( C_{10}H_{22} + 15.5O_2 \rightarrow 10CO_2 + 11H_2O )</td>
</tr>
<tr>
<td>6</td>
<td>PGM</td>
<td>( NO + 0.5O_2 \rightarrow NO_2 )</td>
</tr>
<tr>
<td>7</td>
<td>PGM</td>
<td>( C_3H_6 + 9NO_2 \rightarrow 9NO + 3CO_2 + 3H_2O )</td>
</tr>
<tr>
<td>8</td>
<td>PGM</td>
<td>( C_{10}H_{22} + 31NO_2 \rightarrow 31NO + 10CO_2 + 11H_2O )</td>
</tr>
<tr>
<td>9</td>
<td>PGM</td>
<td>( CO + NO_2 \rightarrow NO + CO_2 )</td>
</tr>
<tr>
<td>10</td>
<td>PGM</td>
<td>( C_3H_6 + 9(1 + y')NO \rightarrow 3CO_2 + 3H_2O + 4.5(1 - y')N_2 + 9y''N_2O )</td>
</tr>
<tr>
<td>11</td>
<td>PGM</td>
<td>( C_{10}H_{22} + 31(1 + y'')NO \rightarrow 10CO_2 + 11H_2O + 15.5(1 - y'')N_2 + 31y'''N_2O )</td>
</tr>
</tbody>
</table>

- Reaction mechanism form taken from Millo et al. [1] and Sampara et al. [2]
- \( y' \) and \( y'' \) are selectivity values for \( N_2O \) formation from \( C_3H_6 \) and \( C_{10}H_{22} \) [1]
DOC Model Development

- First order kinetics were assumed for all reactions
- Voltz-type inhibition functions were applied based on examination of experimental data:
  - $G_{-1} = (1 + K_1*[CO] + K_2*[C_3H_6] + K_3*[C_{10}H_{22}])^2$
  - $G_{-2} = 1 + K_4*[NO]$
  - $G_{-3} = 1 + K_5*[NO]$ (Applied only to Decane Oxidation)
  - $G_{-4} = 1 + K_6*[NO2]$ (Applied only to N$_2$O formation)
DOC Model Development

- GT-SUITE software used for simulations and post-processing
- In-built design optimizer used for identification of rate constants and inhibition function constants
DOC Model Validation

- A separate set of experiments were carried out to validate the model
Part II. Sulfur Poisoning and Surface Oxidation Mechanisms
4-site reaction mechanism taken from Hamzehlouyan et. al. [3].

Each site represents a different surface species:
- **S1**: Loosely bound SO₂
- **S2**: Surface sulfite
- **S3**: Surface sulfate
- **S4**: (Bulk) Sulfate on Alumina

SO₂ Temperature programmed desorption (TPD) experiments carried out to calibrate kinetics

Model validated with different set of TPD experiments
Sulfur Poisoning Model Development

• Interaction of different surface species with PGM reaction:
  – SO₂ adsorbed on S1 site is loosely bound
    • Desorbs at low temperature
  – SO₂ adsorbed on S4 site involves the bulk alumina
    • Should not effect PGM active sites
  – Surface sulfate and sulfite species are present between 200°C - 400°C
    • Temperature falls within typical DOC operating range
    • Both species should affect active sites on PGM

• Simplest method of affecting PGM reaction rates?
  – Multiply reaction rates by a function of empty site coverages
  – Reaction rates must be unaffected without SO₂ present
  – Formation of SO₂-S2 and SO₂-S3 → Lower reaction rates

• PGM Reaction Rate:

\[ r_{new} = r_{old} \times \left( \frac{\theta_{S2} + \theta_{S3}}{2} \right) \]
Surface Oxidation Model Development

• Inverse hysteresis: Catalytic activity during cooldown significantly lower than warmup

• Commonly observed during SGB tests for CO, NO Oxidation over Pt/Al₂O₃

• Micro-kinetic mechanism proposed by Votsmeier et. al. [4,5] to model surface oxidation of Pt by NO₂:
  1. O₂ + Pt ↔ Pt-O
  2. NO + Pt ↔ Pt-NO
  3. NO₂ + Pt ↔ Pt-NO₂
  4. Pt-NO + Pt-O ↔ Pt-NO₂ + Pt
  5. Pt-NO₂ ↔ PtOx + NO
Surface Oxidation Model Development

• Assumptions:
  – Rate-limiting reaction: Pt-O + Pt-NO ⇌ Pt-NO₂ + Pt
  – \( \theta_{Pt-O}, \theta_{Pt-NO} \ll \theta_{PtOx}, \theta_{Pt} \)

• Global kinetic model:
  – Surface oxidation: Pt + NO₂ → PtOx + NO
  – Surface reduction: PtOx + NO → Pt + NO₂

• Effect on NO Oxidation rate:
  – Second order coverage dependency
  – Rate of NO Oxidation:
    \[
    r = k \times \left( \frac{[NO][NO₂]}{K_{eq}} \right)^{0.5} \cdot \theta(Pt)^2
    \]
Surface Oxidation Model Validation

- NO Oxidation experiment:
  - Inlet temperature ramped up from 75°C to 350°C followed by cooldown
  - Significantly lower NO conversion efficiency during cooldown
- Proposed global kinetic model captures inverse hysteresis behavior accurately
Part III. Real World Driving Conditions
Real World Driving Emissions (RDE) Test

• The RDE measures pollutants emitted by cars driven on the road under several driving conditions:
  – Urban, rural and highway driving conditions
  – Low and high altitudes
  – High vehicle payloads

• To simulate the engine speed during an RDE cycle, a randomized RDE-compliant vehicle speed profile was applied to a vehicle model
Real World Driving Emissions (RDE) Test

- Engine speed predicted from RDE vehicle model
- Ran fast-running diesel engine model with detailed combustion and heat transfer submodels
- Extracted transient exhaust gas conditions:
  - Temperature
  - Mass Flow Rate
  - Composition
- Base DOC model
- DOC model with sulfur poisoning
- DOC model with surface oxidation
- Compared cumulative emissions over multiple RDE cycles for CO, NO, C\textsubscript{3}H\textsubscript{6} and C\textsubscript{10}H\textsubscript{22}
Cumulative Emissions – Sulfur Poisoning

- Sulfur poisoning has a significant effect on CO and NO emissions
  - 11% difference at steady state
Cumulative Emissions – Sulfur Poisoning

• Sulfur poisoning has a much lower effect of HC emissions
  – Less than 1% for C₃H₆
  – 4.25% for C₁₀H₂₂
Cumulative Emissions – Sulfur Poisoning

- Added 30-minute cooldown between RDE cycles
  - More realistic catalyst wall temperature
- Percentage difference changes for CO and $C_3H_6$:
  - 20% difference for CO
  - 1.5% difference for $C_3H_6$
Cumulative Emissions – Surface Oxidation

- NO Oxidation rate multiplier, $\theta(1 - PtOx)^2$ is $\sim 1$

- Surface oxidation had no effect on NO emissions

- NO$_2$ consumed by reactions with CO and HCs

- Rate constant for surface oxidation is much smaller

Chemical reactions:

- $C_3H_6 + 9NO_2 \rightarrow 9NO + 3CO_2 + 3H_2O$
- $C_{10}H_{22} + 31NO_2 \rightarrow 31NO + 10CO_2 + 11H_2O$
- $CO + NO_2 \rightarrow NO + CO_2$
Cumulative Emissions – Surface Oxidation

- Re-ran model without NO\(_2\) reduction reactions:
  - PtOx coverage reaches much higher value
  - 2.5% difference in NO emissions
Conclusions

Global kinetics model for a Pt/Pd + Zeolite was developed and successfully calibrated.

Sulfur poisoning has a significant (>10%) effect on CO and NO emissions under the following conditions:
- Timescale of 25+ RDE cycles (1500 miles distance)
- Diesel Fuel with 50+ ppm sulfur (Low Sulfur Diesel)

Surface oxidation by NO$_2$ is insignificant when CO and HCs are present at the inlet:
- Pt oxidation by NO$_2$ occurs at a much slower rate than NO$_2$ reduction by CO and HCs
- Pt oxidation from other species such as O$_2$, CO$_2$ needs to be modelled
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Thank you for your time!
References


Appendix

Please contact m.gayatri@gtisoft for additional information