Multiple Regression Analysis of OSC Characteristics Under Transient TWC Conditions

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Auto Exhaust Catalyst Business Group
Agenda

- Background and objective
- Theory: OSC function over TWC
- Experimental
  - Catalyst design
  - Measurement of OSC functions by TPD
  - Engine evaluation
  - DOE for modeFRONTIER analysis
- Results and discussions
  - Engine evaluation results
  - Multiple-analysis by modeFRONTIER
- Summary and path forward
Background and objective

- **Background**
  - TWC contain Oxygen Storage Component (OSC) materials to enhance HC, CO and NOx performance under A/F transient conditions. At the same time, it is necessary for the vehicle on board diagnostics (OBD) system to monitor that the catalyst OSC is functioning correctly. However, detailed understanding of how OSC characteristics can simultaneously match gas performance and OBD functionality are not well known.

- **Objective of this study**
  - To attempt to do the multiple-analysis on OSC functions (oxygen storage capacity & oxygen release rate) and engine control conditions (Temp., A/F amplitude and frequency).
  - To obtain some optimized OSC design and engine control conditions as a case study.
Theory
OSC function over TWC for OSC functions

Oxygen released from OSC can be used for HC and CO oxidation

L → R: \( \text{O}^{2-} \rightarrow \frac{1}{2} \text{O}_2 + 2e^- \)
(CeO\(_2\) → (a/2)O\(_2\) + CeO\(_{2-a}\))

【Ce4+ → Ce3+】

R → L: \( \frac{1}{2} \text{O}_2 + 2e^- \rightarrow \text{O}^{2-} \)
(CeO\(_{2-a}\) + (a/2)O\(_2\) → CeO\(_2\))

【Ce3+ → Ce4+】

Oxygen released from OSC can be used for HC and CO oxidation

Oxygen is supplied from the exhaust gas

OSC particle

ex. CeO\(_2\)
Experiment: Catalyst design

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>$E_a$ for O$_2$ release [kcal/mol]</th>
<th>Capacity [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSC-1</td>
<td>20%CeO$_2$/79%ZrO$_2$/1%A</td>
<td>45</td>
<td>2.8</td>
</tr>
<tr>
<td>OSC-2</td>
<td>20%CeO$_2$/79%ZrO$_2$/1%B</td>
<td>52</td>
<td>1.4</td>
</tr>
<tr>
<td>OSC-3</td>
<td>20%CeO$_2$/80%ZrO$_2$</td>
<td>50</td>
<td>1.0</td>
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</tbody>
</table>

Base catalyst design
Rh/[Al$_2$O$_3$(45)]+Al$_2$O$_3$(30)+OSC(40)

Oxygen release rate, $1/E_a$

OSC capacity

 OSC-1(40)  

OSC-2(70)  

OSC-3(40)  

Al$_2$O$_3$ only

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition</th>
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<tbody>
<tr>
<td>Cat-1</td>
<td>Rh/[Al$_2$O$_3$(45)], Al$_2$O$_3$(30), Al$_2$O$_3$(40)</td>
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<td>Cat-3</td>
<td>Rh/[Al$_2$O$_3$(45)], Al$_2$O$_3$(30), OSC-1(40)</td>
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<td>Cat-5</td>
<td>Rh/[Al$_2$O$_3$(45)], Al$_2$O$_3$(0), OSC-2(70)</td>
</tr>
</tbody>
</table>
Experimental Measurement of OSC functions by TPD

Analysis
- OSC capacity (integration of O_{desorped})
- O_{2_de_Ea} (by peak top analysis)

\[
\ln(Tp^2/ \beta) \propto \frac{E}{RTp}
\]

Tp = peak temp.
\(\beta\) = Ramping rate

Gas flow = 300 ml /min.
Sample amount = 50 mg
Results: Measurement of OSC functions by TPD

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
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<tr>
<td>OSC-1</td>
<td>20%CeO$_2$/79%ZrO$_2$/1%A</td>
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<td>20%CeO$_2$/79%ZrO$_2$/1%B</td>
</tr>
<tr>
<td>OSC-3</td>
<td>20%CeO$_2$/80%ZrO$_2$</td>
</tr>
</tbody>
</table>

\[ \ln\left(\frac{T_p^2}{\beta}\right) \propto \frac{E}{RT_p} \]

$T_p$ = peak temp.
$\beta$ = Ramping rate: 15°C/min
Experiment: Catalyst design

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>Ea for O2 release [kcal/mol]</th>
<th>Capacity [a.u.]</th>
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<tr>
<td>OSC-1</td>
<td>20%CeO$_2$/79%ZrO$_2$/1%A</td>
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</tbody>
</table>

Base catalyst design
Rh/[Al$_2$O$_3$(45)]+Al$_2$O$_3$(30)+OSC(40)

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition</th>
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<tbody>
<tr>
<td>Cat-1</td>
<td>Rh/[Al$_2$O$_3$(45)], Al$_2$O$_3$(30), Al$_2$O$_3$(40)</td>
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<tr>
<td>Cat-5</td>
<td>Rh/[Al$_2$O$_3$(45)], Al$_2$O$_3$(0), OSC-2(70)</td>
</tr>
</tbody>
</table>
Experiment
Engine Evaluation — Evaluation layout

Gasoline Engine (2.5L)

Engine
> perturbation ±0.5-4.0Hz
±1.0-1.0Hz
±2.0-0.5Hz
> rotation/boost 2400rpm/-300mmHg

<table>
<thead>
<tr>
<th>Perturbation frequency [Hz]</th>
<th>A/F±Amp.</th>
<th>0.5</th>
<th>1.0</th>
<th>4.0</th>
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<tbody>
<tr>
<td>A/F±Amp.</td>
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<td>1.0</td>
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<tr>
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<td>2.0</td>
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<td>Test-1</td>
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</tbody>
</table>
Experiment
Engine Evaluation—Sample converter

Catalyst
> size
φ86x75mm (0.4L)
> cell/mill
400/2.5
> Bed temp.
400 or 600C

> W/C
115g/L
> space velocity
261,474h⁻¹
> Aging
700°C for 10h in air
# Input parameters | Conditions | Div. |
--- | --- | --- |
1 | OSC type | OSC-0(Blank), OSC-1,2,3 | 4 |
2 | OSC load | 0, 40, 70 g/L | 3 |
3 | Temp | 400, 600°C | 2 |
4 | Amp (A/F amp.) | ±0.5, 1.0, 2.0 | 3 |
5 | f (A/F frequency) | 0.5, 1.0, 4.0 Hz | 3 |

# Output parameters | Remarks |
--- | --- |
1 | Time-lag_LR | Time lag from lean to rich |
2 | Time-lag_RL | Time lag from rich to lean |
3 | Cat_out_AF_lean | Cat. out A/F at lean |
4 | Cat_out_AF_rich | Cat. out A/F at rich |
5 | CO_conv_max | CO conversion of maximum, minimum and delta. |
6 | CO_conv_min | HC conversion of maximum, minimum and delta. |
7 | CO_conv_delta | NO conv_max | NOx conversion of maximum, minimum and delta. |
8 | HC_conv_max | NO conv_min |
9 | NO_conv_min | NO conv_delta |
10 | NO_conv_target | NO conv_delta |
Experiment
DOE made by Sobol sequence

<table>
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<tr>
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<td>2</td>
<td>0.5</td>
<td>40</td>
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</tbody>
</table>

4 types of OSC
1. OSC-0 (w/o OSC)
2. OSC-1
3. OSC-2
4. OSC-3

2 types of Temp.
1. 400°C
2. 600°C

3 types of A/F Amp.
1. ±0.5
2. ±1.0
3. ±2.0

3 types of A/F freq.
1. 4.0 Hz
2. 1.0 Hz
3. 0.5 Hz

3 types of OSC load
1. 0 g/L
2. 40 g/L
3. 70 g/L
Engine evaluation results

The cat.-3 used OSC-1 results

2.0/0.5Hz@400°C

0.5/4.0Hz@400°C

1.0/1.0Hz@400°C

2.0/0.5Hz@600°C

1.0/1.0Hz@600°C

0.5/4.0Hz@600°C

IN A/F

OUT A/F

▲ HC Conv.

▲ NO Conv.

▲ CO Conv.
Results: Engine evaluation/600C ±2.0/0.5Hz

The OSC capacity looks not enough for large amplitude and low perturbation frequency.
Results: Engine evaluation/600C ±1.0/1.0Hz

The OSC capacity looks working as a “buffer tank” of oxygen for medium amplitude and medium perturbation frequency.

![Graph showing HC, CO, NOx conversion over time/sec. with annotations for In A/F and Out A/F.]
Results: Engine evaluation/600C ±0.5/4.0Hz

The OSC capacity looks enough for small amplitude and high perturbation frequency.
Analysis by modeFRONTIER

- Relative coefficient analysis
- 2D diagram
- 3D RSM diagram
  - 3 figures for OSC type and loading
  - 2 figures for engine conditions
- Multiple optimization
- Analysis by SOM
Relative coefficient analysis results

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>Related parameters</th>
<th>Sensitivity</th>
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<tbody>
<tr>
<td>OSC type</td>
<td>OSC_Ea</td>
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<td>NOx_max</td>
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<tr>
<td>OSC load</td>
<td>OSC_cap</td>
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<td>OSC_Ea</td>
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<td>CO_delta</td>
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<td>NO_max</td>
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<td>Temp</td>
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<td>0.866</td>
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<tr>
<td></td>
<td>HC_delta</td>
<td>-0.653</td>
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</table>

| Amp (A/F amp.)   | Cat_out_AF_rich     | -0.927      |
|                 | Cat_out_AR_lean     | 0.895       |
|                 | CO_min              | -0.850      |
|                 | CO_max              | -0.601      |
|                 | CO_delta            | 0.750       |
|                 | HC_delta            | 0.556       |
|                 | NO_min              | -0.575      |
|                 | NO_delta            | 0.694       |

| f (A/F frequency)| Time_lag_LR         | -0.927      |
|                 | Time_lag_RL         | -0.755      |
|                 | NO_min              | 0.557       |
|                 | NO_max              | 0.714       |
2D diagram of Time_lag_LR and Time_lag_RL

May be due to the OSC characteristics difference, time_lag at R>L and L>R is different.

\[
\text{Time - lag - RL} < \frac{\text{Time - lag - RL}}{\text{Time - lag - LR}} < 1
\]
OSC loading amount was more sensitive than OSC types for time_lag_LR.
3D RSM diagram

- the relationship of the OSC type and OSC load to Cat Out AF lean

Any kind of OSC was effective to lower the Cat_out_AF_lean compared to w/o OSC. (showing oxygen storage in lean conditions)

A/F Amp.=±1.0
A/F frequency=1.0Hz
Temp.=400C

Blank sample
(w/o OSC)
OSC type 2 with some loading showed the lowest HC\_delta. This demonstrates the relationship between the OSC function and catalytic oxidation of HC.

A/F Amp. = ±1.0
A/F frequency = 1.0 Hz
Temp. = 400°C
Larger oxygen concentration change resulted in higher HC conversion delta.

3D RSM diagram
- the relationship of AF_f and Amp. to HC delta

OSC type=OSC-1
OSC load=40g/L
Temp.=400C
AF frequency was much more sensitive to Time\_lag\_LR than AF amplitude, meaning that the oxygen storage and release rate is dependant on how fast the atmosphere changes.

OSC type=OSC-1
OSC load=40g/L
Temp.=400C
Multiple optimization results (ex.)

Filtration conditions: Higher HC, CO and NOx perf. at T<420C

Cata. Design #12 exhibited the highest gas performance at high f. At lower f, designs #2574 were selected for better performance. These designs include small amount of OSC (5-10g/L) with OSC-1.

<table>
<thead>
<tr>
<th>Design #</th>
<th>OSC type</th>
<th>OSC load</th>
<th>A/F</th>
<th>A/F</th>
<th>Temp.</th>
<th>Time lag LR</th>
<th>HC Max.</th>
<th>HC min.</th>
<th>CO Max.</th>
<th>CO min.</th>
<th>NO Max.</th>
<th>NO min.</th>
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<td>OSC-2</td>
<td>40</td>
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<td>81.0</td>
<td>85.0</td>
<td>72.5</td>
<td>72.5</td>
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</table>
Analysis by SOM (Self Organized Map)

- Purpose (ex.)
  - To maximize CO_min, HC_min and NO_min.
  - To find out the best matching of catalyst design and engine control conditions.

- Features of SOM
  - Vertical and Horizontal direction don't mean special.
  - How similar values of the input variable are reported on neighbor units of the grid.
  - Each variable is displayed with its most correlated/anti-correlated counterparts.
  - SOM learns the structure of its input data, so it can be used to classify unseen data.
Results of SOM analysis
Some groups are observed in input/output parameters

Engine conditions

OSC parameters
Results of SOM analysis
Time_lag RL and LR showed quite similar trend.
Results of SOM analysis

CO_min, HC_min and NO_min showed slightly different trend. Maybe because of reaction mechanism.
Results of SOM analysis
#12 (one of the best solution at low temp.) relates to

- **Catalyst (OSC) design**
  - Mid-high OSC_cap
  - High OSC_Ea

- **Output parameters**
  - Low Time_lag
  - Low Cat_out_AF_lean
  - High Cat_out_AF_rich

- **Engine conditions**
  - High f
  - Low Amp.
  - CO_min

![Heatmap diagram showing results](image-url)
Catalyst (OSC) design

- Mid-high OSC_cap
- High OSC_Ea
Output parameters

- Low Time_lag
- Low Cat_out_AF_lean
- High Cat_out_AF_rich

![Heatmaps of Time_Lag_RL, Time_Lag_LR, Cat_out_AF_rich, Cat_out_AF_lean]
Engine conditions

- High $f$
- Low Amp.
Combination of SOM and multi-objective analysis
Summary

In this study, TWC catalysts were prepared with different OSC materials designed to have a wide range of oxygen storage capacity and activation energy for oxygen release. Five input parameter; OSC species, OSC loading in the catalyst, temperature, A/F amplitude and A/F frequency were studied. thirteen output parameter, such as gas performance, oxygen sensor response, etc, were monitored. Multiple regression analysis was performed using the multi-objective analysis software, modeFRONTIER.

From the modeFRONTIER analysis, correlation were shown between OSC (here OSC type and loading) and engine conditions (here A/F amplitude and frequency) with catalyst performance variables by means of relative coefficient charts and 3D diagrams.

Multiple regression optimizations were attempted to define the catalyst with higher gas performance in the case of lower or higher A/F frequency.
Path forward

- Investigation of vehicle test measuring the catalyst optimized by this model.

- Investigation of OBD function (Time lag LR, Time lag RL, Cata out AF etc.) by using this model.

- By incorporating the data of aged catalyst into the model, modeling of catalyst deterioration for better gas performance.

- Application of this model to more complicated system by measuring much kind of data (space velocity, cell/mill of substrate etc.).
Acknowledgment

I would like to thank Mr. Seiji Nishita of CD-adapco Japan Co., LTD for his support and contribution of this study.