

Multiple Regression Analysis of OSC Characteristics under Transient TWC Conditions

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ABSTRACT

Three Way Catalysts (TWC) contain oxygen storage components (OSC) to enhance HC, CO oxidation and NO_x reduction performance under standard operating conditions where there is rapid perturbation of the air-to-fuel ratio (A/F). The OSC function is required to store and to release oxygen, however the optimum storage capacity and release rate to maximize HC, CO and NO_x conversion varies as a function of engine operating conditions, such as A/F perturbation frequency, amplitude and temperature. At the same time it is necessary for the vehicle on board diagnostics (OBD) systems to monitor that the catalyst OSC is functioning correctly. Detailed understanding of how OSC characteristics can simultaneously match gas performance and OBD functionality are not well known.

In this study, several TWC catalysts were prepared with different types of OSC materials such that oxygen storage capacity and activation energy for oxygen release could be varied over a wide range. Five independent variables; OSC species, OSC loading in the catalyst, temperature, A/F amplitude and A/F frequency were controlled and fourteen dependent variables such as gas performance, oxygen sensor response, etc., were measured. Statistical analysis was performed using the multi-objective analysis software, modeFRONTIER.

INTRODUCTION

Three Way Catalysts (TWC) contain oxygen storage components (OSC) to enhance HC, CO oxidation and NO_x reduction performance under A/F perturbation conditions [1-4]. Here the OSC materials adsorb oxygen under lean conditions and release oxygen under rich conditions to oxidize HC and CO. Under lean conditions OSC materials enhance NO_x reduction performance by reducing local oxygen concentration around the active precious metal species in the catalyst (Pt, Pd and Rh). Thus the OSC function is required to store and release oxygen, however the optimum storage capacity and release rate to maximize gas performance is a function of engine conditions, such as A/F perturbation frequency, amplitude and temperature. At the same time, it is necessary for the

vehicle on board diagnostics (OBD) system to monitor the catalyst functionality. During the catalyst lifetime the OBD system monitors the status of the OSC materials [5-7]. The design of the OSC materials and their loading in the catalyst must be matched to the vehicle calibration. In this investigation, details of how OSC characteristics are matched to gas performance and OBD functionality will be explored.

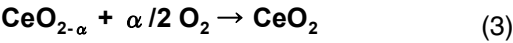
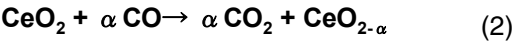
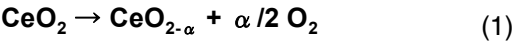
In this study, several TWC catalysts were prepared containing different types of OSC materials such that oxygen storage capacity and activation energy for oxygen release could be varied over a wide range. Here five input parameters; OSC species, OSC loading in the catalyst, temperature, A/F amplitude and A/F frequency were controlled and 14 output parameters, such as gas performance, oxygen sensor response, etc., were measured. Statistical analysis was performed using the multi-objective analysis software, modeFRONTIER [8]. In addition, the OSC species and its loading in the catalyst was optimized to obtain better gas performance.

THEORY

OSC REACTIONS

As mentioned above, OSC materials, such as CeO₂, adsorb oxygen under lean conditions and desorb oxygen under rich conditions. Reactions 1-3 below describe oxygen storage/release in an OSC using CeO₂ as an example. When the atmosphere is changed from lean to rich at sufficient temperature for CeO₂ to release a lattice oxygen (eq.1) there is an accompanying reduction in the valence of Ce changing its oxidation state from 4+ to 3+. Here the value of alpha depends on the rich period, temperature, space velocity, etc. The active oxygen released from the CeO₂ materials may be used for CO oxidation as shown in eq.2. Similar oxidation for HC is possible. The specific details of the reaction mechanism, however, are not the purpose of this study. Then when the atmosphere is changed back from rich to lean, the reduced CeO_{2-α} chemically adsorbs oxygen as shown in eq.3. The valence of Ce changes back from 3+ to 4+, and the value of alpha again will depend on the lean period, temperature, space velocity, etc.

The effective oxygen storage and release capacity and their reaction rates depend not only on the engine conditions but also on the physical and chemical properties of the OSC material species, such as the composition, oxygen ion and electron conductivities, particle size and proximity to precious metals..



EXPERIMENTAL

OSC FUNCTION MEASUREMENT

To measure the oxygen storage capacity and activation energy of oxygen release, temperature programmed desorption (TPD) measurement was performed. The test protocol is shown in Fig.1. TPD equipment used was a RIGAKU, TPD-type R with a 50mg sample size and a total gas flow of 300ml/min. The sample was pre-treated in 20%O₂/He at 600°C for 30min to adsorb oxygen. Then the temperature was cooled to 100°C and after purging with He the gas was changed to 1000ppm H₂/He. Finally the sample was heated up to 600°C in 1000ppm H₂/He. The released oxygen was detected as H₂O and the oxygen storage capacity was calculated by integrating the H₂O release profile during the temperature ramp from 200–600°C. As the ramping rate was varied (5, 10 and 15°C/min) the peak temperature of H₂O formation changed and the activation energy of oxygen release was calculated by peak top analysis [9].

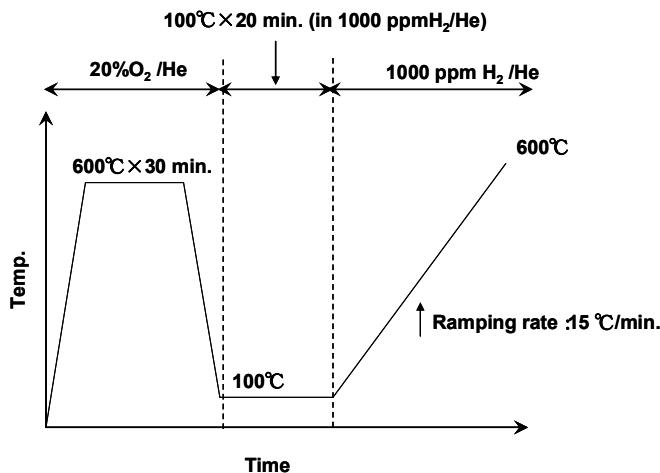


Fig.1 TPD measurement test protocol.

OSC MATERIAL PREPARATION AND CATALYST PREPARATION

100% CeO₂ and 20wt%CeO₂/80wt%ZrO₂ were used as standard OSC materials. 1wt% or 5wt% of ZrO₂

was replaced by several different dopant types. From the TPD measurement described above, three OSC materials were chosen as model OSC materials based upon differences in oxygen storage capacity and oxygen release rates. CZ (20wt%CeO₂/80wt%ZrO₂) is the standard and has middle activation energy (Ea) for oxygen release and low oxygen storage capacity. CZ-A (20wt%CeO₂/79wt%ZrO₂/1wt%dopnt-A) has lower activation energy for oxygen release and much higher oxygen storage capacity. CZ-B (20wt%CeO₂/79wt%ZrO₂/1wt%dopnt-B) has slightly higher activation energy for oxygen release and intermediate oxygen storage capacity between CZ and CZ-A.

Five model catalysts were prepared. Rh was used as the active precious metal catalyst with 1g/L concentration and the total wash-coat loading was maintained at 115g/L. The catalyst designs are shown in Table.2. Rh was impregnated just onto Al₂O₃ to obtain exactly the same Rh distribution for each catalyst. Cat-1 is a blank Rh/ Al₂O₃ catalyst with no OSC for comparison. Cat-2 to Cat-4 are the catalysts with CZ, CZ-A or CZ-B with 30g/L loading each. In Cat-5, the loading of OSC material CZ-B was increased from 40 to 70 g/L and balance Al₂O₃ was reduced to maintain the total wash-coat loading as 115g/L. The substrate used was 400cpai/2.5mil cordierite substrate (ϕ 86mm × 75mm). Each catalyst was de-greened at 700°C for 10hr in air atmosphere by electric furnace.

Table.1 OSC capacity and oxygen release Ea. Oxygen storage capacity was standardized by taking the value of OSC-3 as 1.

Code OSC-	Material	Ea [kcal/mol]	Capacity [a.u.]
1	20%CeO ₂ /79%ZrO ₂ /1%A	45	2.8
2	20%CeO ₂ /80%ZrO ₂ /1%B	52	1.4
3	20%CeO ₂ /80%ZrO ₂	50	1.0

Table.2 Model catalyst design.

Code	Composition
Cat-1	Rh/[Al ₂ O ₃ (45)], Al ₂ O ₃ (30), Al ₂ O ₃ (40)
Cat-2	Rh/[Al ₂ O ₃ (45)], Al ₂ O ₃ (30), OSC-3(40)
Cat-3	Rh/[Al ₂ O ₃ (45)], Al ₂ O ₃ (30), OSC-1(40)
Cat-4	Rh/[Al ₂ O ₃ (45)], Al ₂ O ₃ (30), OSC-2(40)
Cat-5	Rh/[Al ₂ O ₃ (45)], Al ₂ O ₃ (0), OSC-2(70)

EVALUATION CONDITIONS AND MULTIPLE ANALYSIS

The catalysts described above were evaluated using a gasoline engine bench at 400°C and 600°C. Here a 2.5L engine was used. Three different conditions of A/F amplitude and perturbation were selected as shown in Table.3. Test-1, with higher A/F amplitude and lower perturbation frequency favors a catalyst with higher OSC capacity. On the other test-3, with higher

perturbation frequency and lower A/F amplitude, favors a catalyst with higher oxygen storage and release rates. To stress catalyst differences a high space velocity of 260,000/hr was chosen for these tests.

Table.3 Engine evaluation conditions.

	Perturbation frequency [Hz]		
A/F $\pm$ Amp.	0.5	1.0	4.0
0.5			Test-3
1.0		Test-2	
2.0	Test-1		

Table 4 and Table 5 show the input and output parameters for multiple regression analysis by modeFRONTIER. A/F was measured in exhaust upstream and downstream of the catalyst by lambda sensors and each gas concentration was measured by MEXA-7500 (HORIBA). Each output parameter is defined in Fig.2 using an experimental example.

Table 4 Input parameters for multiple regression analysis.

#	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, 600C	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

Table 5 Output parameters for multiple regression analysis.

#	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 average.
6	CO_conv_min	
7	CO_conv_av	
8	HC_conv_max	HC conversion of maximum, minimum and average.
9	HC_conv_min	
10	HC_conv_av	
11	NOx_conv_max	NOx conversion of maximum, minimum and average.
12	NOx_conv_min	
13	NOxO_conv_av	

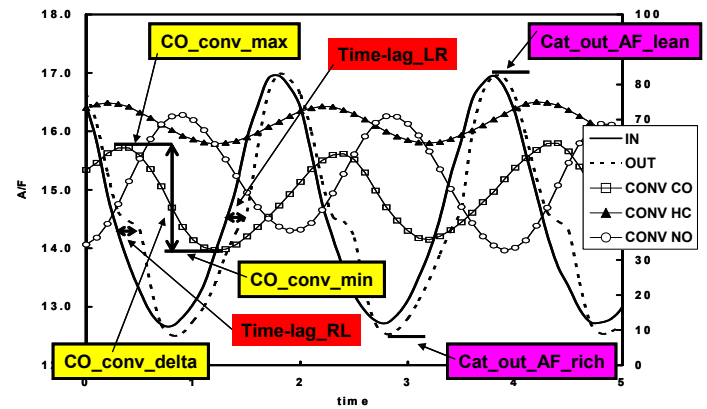


Fig.2 Definition of output parameter measurements. CO was shown as an example for gas species.

The DOE (design of experiment) matrix shown in Table.6 was designed by SOBOL sequence. An optimization tool, modeFRONTIER ver.4 was used to analyze the data package. Here the optimization calculation was performed using MOGA- II (multi-objective generic algorithm) [10] under the conditions of 100 of generation number and 0.1 of mutation probability.

Table.6 DOE matrix. OSC_type 0 is a blank sample (without OSC).

#	OSC_type	Temp	Amp	f	OSC_load
0	0	400	0.5	4	0
1	0	400	1	1	0
2	0	400	2	0.5	0
3	0	600	0.5	4	0
4	0	600	1	1	0
5	0	600	2	0.5	0
6	1	400	0.5	4	40
7	1	400	1	1	40
8	1	400	2	0.5	40
9	1	600	0.5	4	40
10	1	600	1	1	40
11	1	600	2	0.5	40
12	2	400	0.5	4	40
13	2	400	1	1	40
14	2	400	2	0.5	40
15	2	600	0.5	4	40
16	2	600	1	1	40
17	2	600	2	0.5	40
18	2	400	0.5	4	70
19	2	400	1	1	70
20	2	400	2	0.5	70
21	2	600	0.5	4	70
22	2	600	1	1	70
23	2	600	2	0.5	70
24	3	400	0.5	4	40
25	3	400	1	1	40
26	3	400	2	0.5	40
27	3	600	0.5	4	40
28	3	600	1	1	40
29	3	600	2	0.5	40