Research Report

New Direct Evaluation of Oxygen Storage/Release Capacity on Millisecond Time Scale

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Abstract

The amount of oxygen storage and release from catalysts on a millisecond scale (MS-OSC) is believed to play an essential role in automotive three-way catalysts. We have developed a new method to evaluate the MS-OSC based on the rapid detection of reaction products on catalyst surfaces immediately after CO and O_2 injections using pulsed valves by time-of-flight mass spectrometry.

CO and O_2 were passed over the surface of a slurry-coated catalyst on a planar cordierite substrate initially under high vacuum (10^{-7}Pa). This allowed the MS-OSC to be directly evaluated as the amount of CO_2 without gas diffusion effects. We applied this MS-OSC measurement technique to the following three catalysts: Pt/CeO_2-ZrO_2 (CeO_2:ZrO_2 = 1:1); Pt/CeO_2-ZrO_2 (CeO_2:ZrO_2 = 5:1); and Pt/CeO_2-ZrO_2-Y_2O_3 (CeO_2:ZrO_2:Y_2O_3 = 46.5:46.5:7.0). Pt/CeO_2-ZrO_2-Y_2O_3 was reported to improve the transient catalytic activity on a millisecond scale, which could not be explained by conventional thermo-gravimetric OSC measurements on the scale of seconds. Among these three catalysts, Pt/CeO_2-ZrO_2-Y_2O_3 was found to have the highest MS-OSC. This is supported by a previously reported set of engine test results.[1]

(MS-OSC)

MS-OSC

MS-OSC

CO O_2

(10^{-7}Pa)

CO O_2

CO_2

MS-OSC   3

Pt/CeO_2-ZrO_2(CeO_2:ZrO_2 = 1:1) Pt/CeO_2-ZrO_2(CeO_2:ZrO_2=5:1) Pt/CeO_2-ZrO_2-Y_2O_3 (CeO_2:ZrO_2:Y_2O_3 = 46.5:46.5:7.0)

Pt/CeO_2-ZrO_2-Y_2O_3 MS-OSC

Pt/CeO_2-ZrO_2-Y_2O_3

Pt/CeO_2-ZrO_2

OSC

MS-OSC

OSC   MS-OSC   -

-                -

1. Introduction

Enhancement of oxygen storage/release capacity (OSC) is one of the possible ways of developing high-efficiency automotive three-way catalysts (TWC). In fact, the performance of TWC is considered to be strongly linked to OSC, which used to be measured by O_2 sensors for on-board diagnostic (OBD) application.[2] OSC is usually defined as the amount of oxygen stored in and released from the catalysts on a time scale of seconds or minutes.[3-7] However, the exhaust gas composition in an engine tail pipe changes in tandem with the engine operating cycle on a millisecond time scale. Thus, the composition of gases that pass through a catalytic converter closely coupled to an engine varies greatly on a millisecond scale. Evaluation of the OSC on a millisecond scale (MS-OSC) is believed to be of great importance.

We have reported on the MS-OSC measurement method in a previous publication.[8] We will now compare it with the conventional OSC measurement method with regard to the three-way catalyst reaction (TWCR), Pt particle size, and support particle size. Finally, we will discuss the implications of MS-OSC from the standpoint of recent engine technology.

2. Experimental method

2. 1 MS-OSC measurement

A few studies have been presented on OSC, which was measured on a time scale shorter than a second.[9, 10] However, the time resolution of these methods seemed not to be sufficient for evaluating MS-OSC directly. The time resolution was determined by several factors: the response of the measurement system, and the rate of gas diffusion and adsorption. For example, when CO and O_2 react, the resultant CO_2 adsorbs strongly on zirconium oxide, causing slow diffusion. Thus, the results would not reflect the exact features of the MS-OSC. The surface science approach we employ in our newly developed apparatus[11, 12] allows us to consider MS-OSC directly as the amount of CO_2 detected.

Figure 1 schematizes the MS-OSC measurement apparatus, which consists of three pumped chambers. A planar catalyst holder and four pulse valves to inject the feed gas on the planar catalyst are arranged in the first chamber. The reaction products emitted from the catalyst are sampled through a skimmer aligned in a direction normal to the catalyst plane and are detected by the TOF mass spectrometer on a millisecond scale.

Figure 2(a) shows the procedure for MS-OSC measurement. The surface temperature of all the planar catalysts was kept at 270°C. The surface of the planar catalysts was pretreated with CO until no more CO_2 was observed. After the pretreatment, the catalyst was exposed to O_2 pulse. The pulse valve was opened for O_2 injection for 0.3 to 4.0 ms, which was proportional to the integrated amount of O_2. The amount of each O_2 pulse injection was about 0.1 cc with the pulse width set at 1 ms. After 5 s of O_2 pulsing, CO pulse, the valve for which was set to remain open for 2.0 ms, was supplied to the planar catalyst twice. CO adsorbed on the catalyst and reacted with the stored O_2 to form CO_2. This procedure was repeated 30 times to improve the signal to noise ratio. The integrated amount of CO_2 per two CO pulses intensity released from the planar catalyst is defined as MS-OSC.

2. 2 Catalyst preparation

The CeO_2-ZrO_2 support (CeO_2:ZrO_2 = 5:1 in molar ratio) was prepared by precipitation. The precipitate was filtered, dried at 110°C overnight,
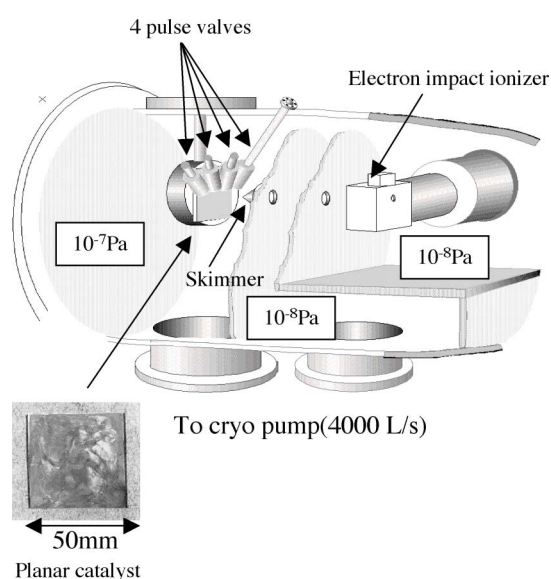
Fig. 1 Schematic of the apparatus and a planer catalyst for the MS-OSC experiment.

and then calcined in air for 1 h at 500°C. The calcined support is denoted as the $C_{0.83}Z_{0.17}$ support. For the compositions $CeO_2:ZrO_2 = 1:1$ and $CeO_2:ZrO_2:Y_2O_3 = 46.5:46.5:7.0$ in molar ratio, the supports were denoted as $C_{0.50}Z_{0.50}$ and $C_{0.465}Z_{0.465}Y_{0.070}$, respectively. The Pt loading amount was 0.1 wt% for each catalyst.

A slurry was prepared by adding the powdered catalyst to deionized water. The slurry was wash-coated onto a planar cordierite substrate (50 mm × 50 mm × 1mmt) to about 0.5 mm thickness, and then dried to obtain fresh planar catalysts for MS-OSC. The powdered catalysts were pressed, crushed, and then sieved to form 0.3-0.7 mm pellets for conventional measurement of OSC and TWCR using a laboratory reactor. Some pellets and planar catalysts were heated at 1000°C for 2 h in a gas flow whose composition was alternated between $1\%O_2/N_2$ and $1\%H_2/N_2$ every 5 min to obtain thermally aged catalysts.

Fresh planar catalysts with the compositions of 0.01, 0.1, and 1.0 wt% Pt/ $C_{0.465}Z_{0.465}Y_{0.070}$ were prepared using the same method as mentioned above to investigate the influence of the amount of Pt in the Pt/ $C_{0.465}Z_{0.465}Y_{0.070}$ catalyst on MS-OSC.

2. 3 Conventional OSC measurement

Figure 2(b) illustrates the conventional OSC measurement method that uses a thermo-gravimeter (TG). The pellet catalyst was first exposed to a feed stream of $50\%O_2/N_2$ at 500°C for 4 min, followed by $20\%H_2/N_2$ at 500°C. In this process, the oxygen stored in the catalyst reacts with H_2 to form H_2O, causing a weight loss of the catalyst. By measuring the weight loss, the amount of oxygen atoms from the catalyst was calculated to obtain the OSC.

2. 4 Three-way catalyst reactivity measurement

To investigate the TWCR for each light-off test, thermally aged catalysts were evaluated using the previously developed laboratory reactor.[13] The catalytic activity data were obtained using a conventional fixed-bed flow reactor at atmospheric pressure. The evaluation atmosphere was alternated every 2 s between A/F = 14.0 and 15.2, both of which lie close to the stoichiometric atmosphere.[14] Catalysts were exposed to a simulated exhaust gas at 3.3 l/min, while the temperature was decreased from 500°C to 100°C and the space velocity was about 200,000 h^{-1}. The reactivity of TWCR was expressed as the temperature at 50% conversion (T50) of NO, CO and HC.

2. 5 Measurement of Pt and support particle size and surface area of the catalyst

To determine the particle size of the Pt and support, XRD measurement was carried out using a RIGAKU RU-3L X-ray diffractometer with Co-Kα radiation. The particle sizes were calculated using Sherrer's equation.[15] The surface area of the catalysts was measured by the BET method with N_2 adsorption.

3. Results

Figures 3 (a), (b) and (c) show the time profile of the transient CO_2 production from the aged $0.1wt\%Pt/C_{0.87}Z_{0.17}$, $Pt/C_{0.50}Z_{0.50}$ and $Pt/C_{0.465}Z_{0.465}Y_{0.070}$ catalysts, respectively. The CO pulse was passed over the catalyst at 0 ms and 100 ms. O_2 stored in the catalysts was released as CO_2 when CO gas was passed over the catalysts. **Figure 4** shows the MS-OSC (the integrated amount of CO_2 per two CO pulses in Fig. 3) for the three kinds of catalysts as a function of the open-time of the O_2 pulse valve.
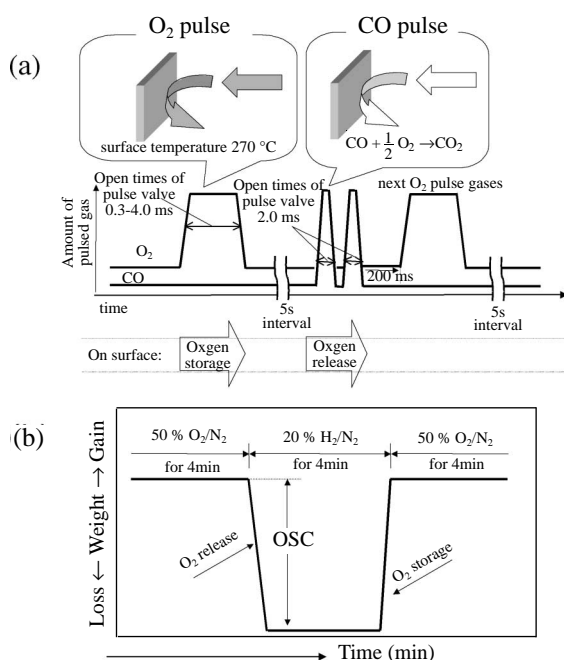
Fig. 2 Comparison of MS-OSC measurement with conventional OSC measurement, (a) procedures for MS-OSC measurement and (b) Conventional OSC measurement by TG apparatus.

Among these three catalysts, the greatest amount of CO_2 was released from the $Pt/C_{0.465}Z_{0.465}Y_{0.070}$ catalyst, indicating the highest MS-OSC. **Figure 5** shows that the MS-OSC of the catalysts increased with the amount of Pt. **Figure 6** shows that the results of conventional OSC measurement did not always agree with those of MS-OSC.

Figure 7 shows that the aged $Pt/C_{0.465}Z_{0.465}Y_{0.07}$ catalyst had a lower T50 indicating a higher catalytic activity as TWC than that of the $Pt/C_{0.50}Z_{0.50}$ catalyst. Characterization of the catalyts (**Fig. 8**) revealed that the superiority of $Pt/C_{0.465}Z_{0.465}Y_{0.07}$ over $Pt/C_{0.50}Z_{0.50}$ in catalytic activity is caused mainly by smaller Pt particle size and large surface area. Support particle size seems no strong relation to the catalytic activity.

4. Discussion

The enhancement of OSC has been considered as the necessary and sufficient condition for the development of TWC. The performance of a TWC correlates positively with its OSC. However, the present study indicates that MS-OSC is a more important factor than OSC for the performance of TWC. Recent advanced emission control maintains nearly stoichiometric exhaust gas mixtures, even during highly transient driving modes, for example, a sudden acceleration. The oscillation of the A/F ratio has become smaller than ever before. However the spike pulse of pollutant gases at this small oscillation have to be eliminated in order to meet the recent strict regulations of automobile exhaust gas. TWC needs to be capable of fast response. These requirements are even more serious in the case of a start converter closely coupled to an engine compared to an under-floor converter.

Oxygen storage was found to occur very fast not only on Pt-catalyzed CeO_{2-x} but also on pure ceria, whereas oxygen release was found to be slow.[16] In particular, the response of oxygen release must be connected to the limiting factor for the purification of exhaust gases from an automobile. The MS-OSC obtained in the present study agreed with other parameters such as T50 (Fig. 7) and Pt particle size
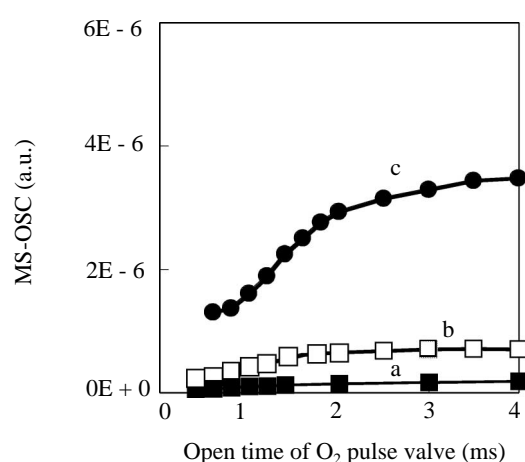
**Fig. 4** MS-OSC (integrated amount of CO_2 per two CO pulses in Fig. 3) of aged planar catalysts as a function of open time of O_2 pulse value: (a) $Pt/C_{0.83}Z_{0.17}$, (b) $Pt/C_{0.50}Z_{0.50}$, and (c) $Pt/C_{0.465}Z_{0.465}Y_{0.07}$.
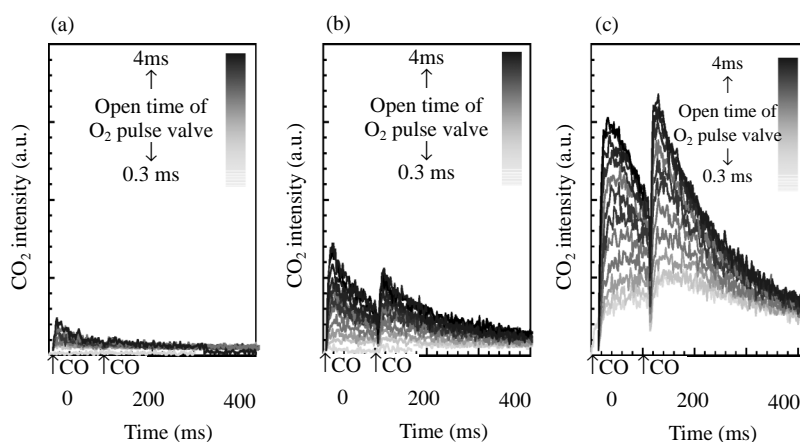
Fig. 3 Transient CO_2 production from aged 0.1wt%$Pt/C_{0.83}Z_{0.17}$, $Pt/C_{0.5}Z_{0.5}$, and $Pt/C_{0.465}Z_{0.465}Y_{0.07}$ planar catalysts by sequential injection of two CO pulses as indicated by the two arrows. (a)0.1wt%$Pt/C_{0.83}Z_{0.17}$, (b)$Pt/C_{0.50}Z_{0.50}$, and (c)0. 1wt% $Pt/C_{0.465}Z_{0.465}Y_{0.07}$ catalysts.

(Fig. 8(b)), as well as engine test results[1]. Therefore, MS-OSC is thought to be a suitable measure for comparing OSC in recent real engine emissions.
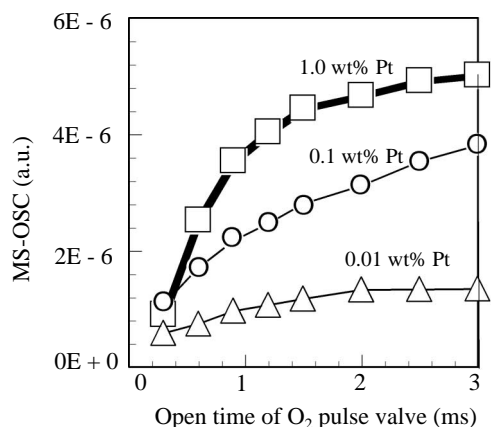
Fig. 5 Effect of Pt amount on MS-OSC of fresh Pt/$C_{0.465}Z_{0.465}Y_{0.07}$ catalysts: △:0.01wt%Pt; O 0.1wt%Pt; and □ 1.0wt%Pt.
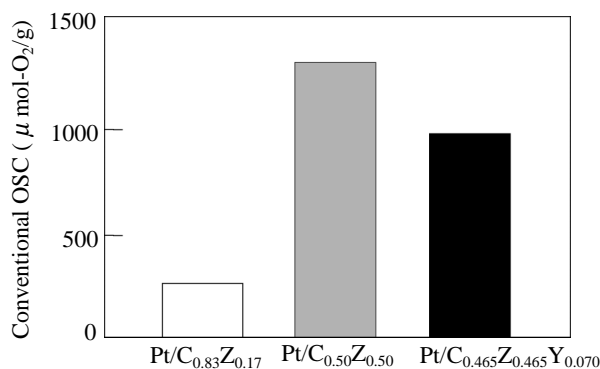

Fig. 6 Conventional OSC of aged pellet catalysts.

5. Conclusions

A new method for evaluating the fast response of OSC has been developed. The faster response of OSC is regarded to play a more important role than the slower response of the conventional OSC on the TWC in the purification of exhaust gases under transient atmosphere in a real engine. The new method is referred to as the MS-OSC method.

6. Acknowledgements
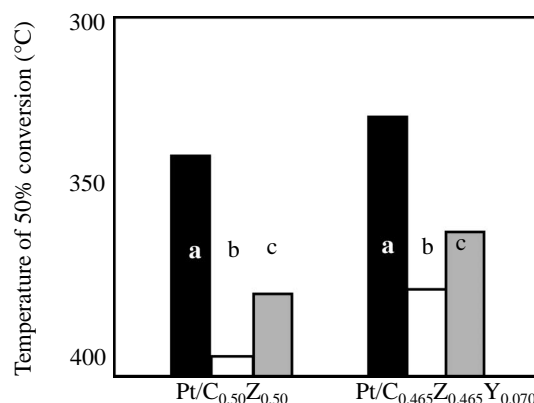
Fig. 7 Temperature at 50% conversion of NO, CO, and HC for aged pellet catalysts with 0.1wt%Pt heated at 1000°C : (a) NO, (b) CO, and (c) HC.
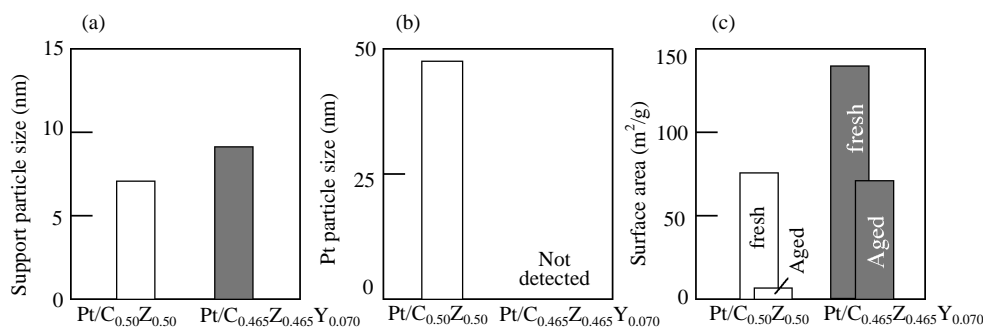
Fig. 8 Mean particle size for aged powdered catalysts and surface area for fresh and aged powders, (a) support particle size, (b) Pt particle size, (c) surface area.

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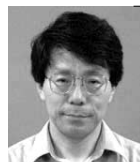
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