

CORRELATION BETWEEN ACTIVITY AND OXYGEN STORAGE CAPACITY OF CERIA ON Pd-ONLY THREE-WAY CATALYSTS

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Abstract – One way of enhancing the thermal stability and NO_x, THC and CO conversion of a catalyst is to improve the thermal stability and oxygen storage capacity (OSC) of the ceria. The appropriate mixing ratios of bulk and stabilized ceria are especially very important for designing Pd-only three-way catalysts. In this paper, we discuss the surface phenomena of stabilized and unstabilized (bulk) ceria, the OSC of catalysts, and the correlation between activity and OSC of Pd-only catalysts with mixing ratios of bulk ceria and stabilized ceria.

Key words: Thermal Stability, Oxygen Storage Capacity, Ceria, Stabilized Ceria, Pd-Only Catalyst, Three-Way Performance, Light-Off Performance

INTRODUCTION

Air pollution due to the emissions from automobiles has become a serious environmental problem in many countries. As a counter-measure, many industrially developed countries have strengthened the restrictions on automobile emissions. North America and Europe in particular have employed more stringent regulations [Brisley et al., 1995].

As a result, the number of catalytic converters mounted on vehicles is increasing, so that the consumption of Pt and Rh is greatly increased as a catalyst's activator. In this situation, the consumption of Pt and Rh is likely to continue to increase in the future. Of the three-way catalyst's components, rhodium has been thought to be an essential element for the reduction of nitrogen oxides. But since it is produced in very small quantities and most of it is used for automobile catalysts, a supply shortage is anticipated. Also, because of the rarity, maldistribution and high cost of Pt and Rh, its economical efficiency has deteriorated gradually. Therefore, a three-way catalyst without rhodium must be developed [Summers, 1988; Yoon et al., 1997].

Pd, which is cheap and stable in supply compared to Pt and Rh, is the most likely candidate as a substitute for rhodium. However, despite price and availability advantages, a number of problems have been connected with palladium's use. Pd deteriorates seriously when used at high temperature (800 °C) and exhibits low NO_x reduction performance under the reducing condition [Muraki, 1991].

Operation of three-way catalysts at these high temperatures (above 800 °C) results in significant activity losses due to the sintering of the alumina support, the noble metals and other catalyst components including the cerium oxide. Numerous

recent studies have characterized this thermal deactivation process in terms of support surface area loss, or noble metal and cerium oxide crystallite growth [Kubish et al., 1991].

It is reported that one way of enhancing the thermal stability and NO_x, THC and CO conversions of a catalyst is to improve the thermal stability and oxygen storage capacity of the ceria. Appropriate mixing ratios of bulk and stabilized ceria are very important for design principles of Pd-only three-way catalysts [Kubish et al., 1991; Diwell et al., 1991].

EXPERIMENTAL

1. Catalyst Preparation

In order to improve thermal stability and oxygen storage capacity (OSC) of ceria, stabilized ceria was prepared by coprecipitating aqueous solution of cerium nitrate and the corresponding nitrate of the stabilization agents. Stabilization agents investigated were Zr, La and Nd. Pd-only monolith catalysts were prepared by a washcoating procedure with different mixing ratios of bulk ceria and (Ce,Zr)O₂ as shown in Fig. 1.

2. Reaction Conditions

The catalysts were evaluated for three-way performance and light-off temperature. Three-way performance was estimated with average NO_x, THC and CO conversions at $\lambda=1.01$, 1.00 and 0.99. For the measurement, the λ values were varied continuously from 0.97 to 1.03 with a frequency of ± 0.5 Hz at 400 °C. The performance of light-off (T_{50}) was measured at the temperature of 50 % conversions of NO_x, THC and CO under stoichiometric ($\lambda=1$) conditions at a rate of 10 °C/min from room temperature to 400 °C. The space velocity was 40,000 hr⁻¹ during the measurement of both three-way performance and light-off performance. The activity measurement apparatus was as shown in Fig. 2.

In this paper, we discuss the surface phenomena of stabiliz-

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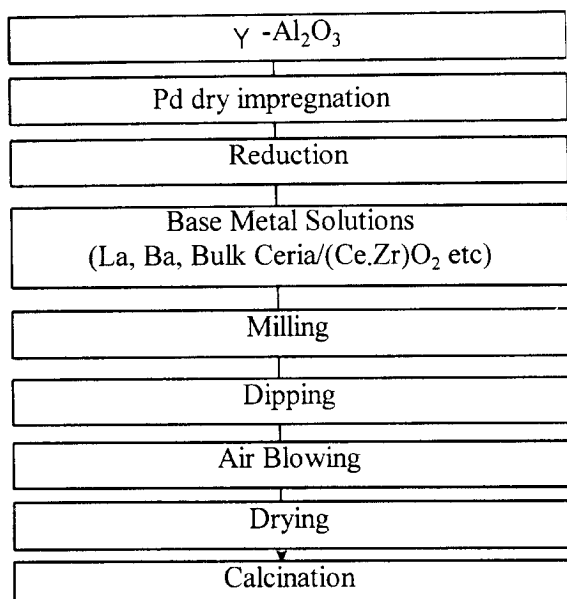


Fig. 1. Preparation of Pd-only monolithic catalysts.

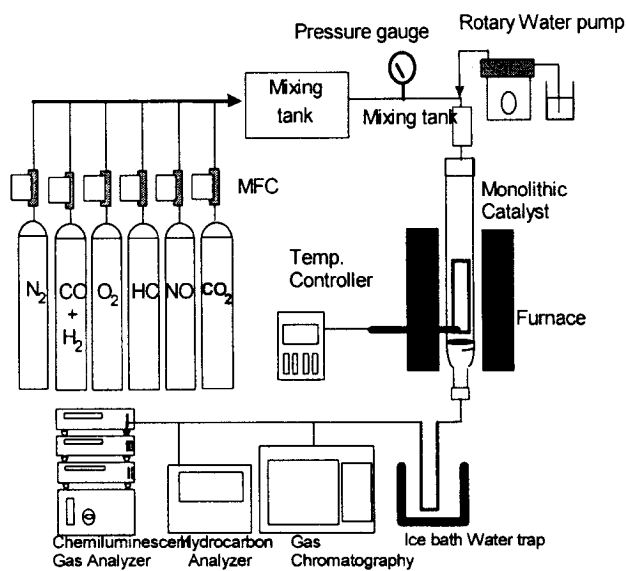


Fig. 2. Activity measurement apparatus.

ed and unstabilized (bulk) ceria, and the OSC of catalysts, and correlation between activity and OSC of Pd-only catalysts with mixing ratios of bulk and stabilized ceria.

3. Oxygen Storage Capacity Measurement

Ceria has been traditionally applied as an additive in automotive catalysts because of its ability to store oxygen and to improve dispersion of noble metals. Its role as an oxygen storage component is manifested in the ability of ceria-containing catalysts to store oxygen under lean operating conditions thus promoting conversion of NO_x and to release it under rich conditions by reaction with CO, H₂ and hydrocarbons [Diwell et al., 1991].

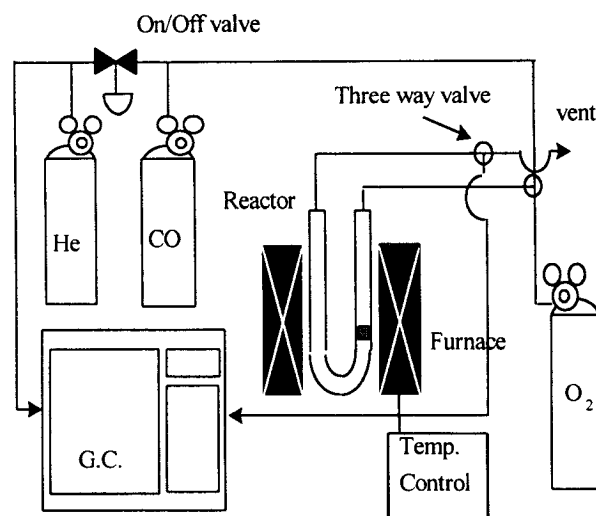
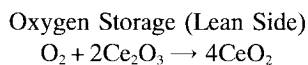
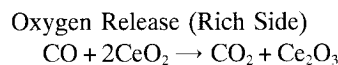


Fig. 3. Oxygen storage capacity measurement apparatus.

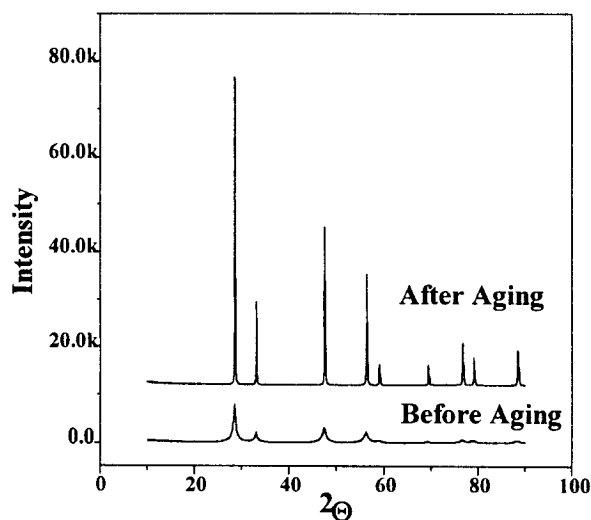


From this OSC mechanism of ceria, we measured OSC of the catalysts as follows: the catalyst was heated in He flow at 350 °C, then it was oxidized by oxygen, and then CO purged continuously. From this procedure, the OSC of catalysts was measured by CO₂ formation amounts. Fig. 3 shows the OSC measurement apparatus.

RESULTS & DISCUSSIONS

1. Comparisons of XRD and B.E.T. Surface Area Results Between Bulk and Stabilized Ceria

The XRD peak intensities of aged (950 °C, 12 hrs) bulk ceria were very much increased compared to fresh bulk ceria as shown in Fig. 4. It was considered that CeO₂ particles were crystallite growth under high temperature conditions as being reported [Kubish et al., 1991].

Fig. 4. XRD patterns of Bulk Ceria (CeO₂) (before and after aging).

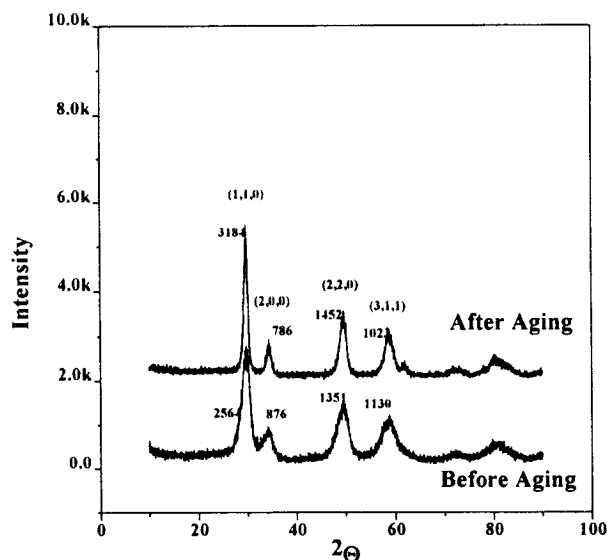


Fig. 5. XRD patterns of stabilized ceria [(Ce,Zr)O₂] (before and after aging).

This result showed that bulk ceria was very weak for thermal stability. In the case of (Ce,Zr)O₂, there was no significant change of peak intensities before and after aging, and rather decreased compared to peak intensities of fresh (Ce,Zr)O₂, at (2, 0, 0) and (3, 1, 1) phases, as shown in Fig. 5. It was considered that crystalline growth of CeO₂ was hindered by addition of Zr. That is, (Ce,Zr)O₂ has much better thermal resistance than that of bulk ceria. The peak intensities of (CeO₂.La₂O₃) and (CeO₂.Nd₂O₃) after aging (950 °C, 12 hrs) were very much increased compared to fresh peak intensities as shown in Fig. 6 and Fig. 7. These results mean that (CeO₂.La₂O₃) and (CeO₂.Nd₂O₃) have less thermal resistance than that of (Ce,Zr)O₂.

The above XRD analysis results coincide with the B.E.T. surface area results as shown in Table 1. In general, B.E.T. surface areas of bulk ceria and stabilized ceria were decreased

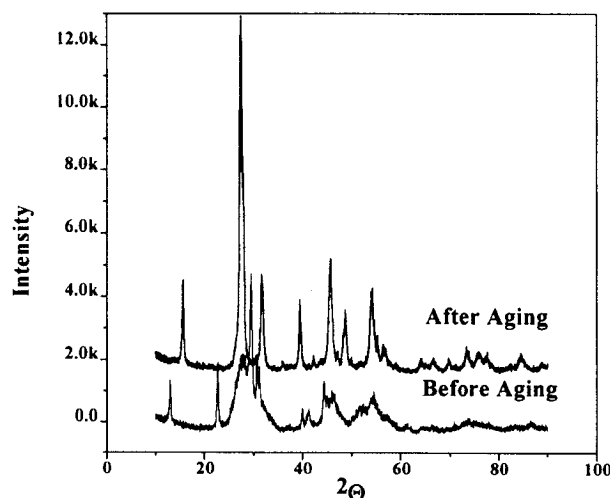


Fig. 6. XRD patterns of stabilized ceria (CeO₂.La₂O₃) (before and after aging).

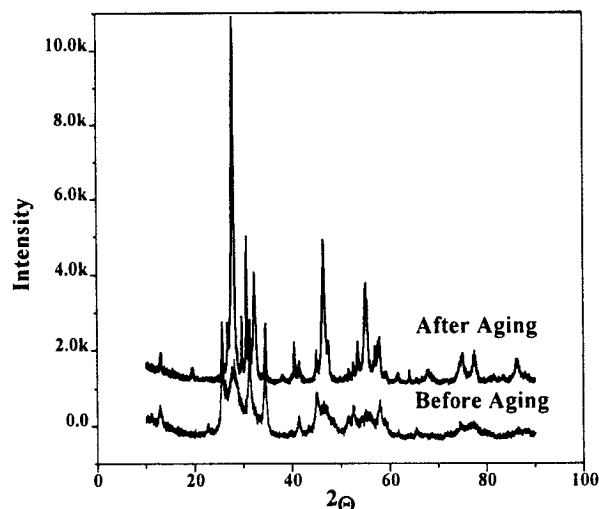


Fig. 7. XRD patterns of stabilized ceria (CeO₂.Nd₂O₃) (before and after aging).

Table 1. B.E.T. surface area of various ceria

Types of ceria	B.E.T. surface area (m ² /g)		Decrement ratios (%)
	Fresh	Aged	
Bulk ceria	212	1.8	99.2 %
(Ce,Zr)O ₂	142	17.4	87.7 %
(CeO ₂ .La ₂ O ₃)	14	5.2	62.9 %
(CeO ₂ .Nd ₂ O ₃)	19	10.6	44.2 %

ed after aging (950 °C, 12 hrs). Before and after aging, the decrement ratios of B.E.T. surface area on stabilized ceria were less than that of bulk ceria. Even though the decrement ratios of B.E.T. surface area on (CeO₂.La₂O₃) and (CeO₂.Nd₂O₃) were better than bulk ceria and (Ce,Zr)O₂, we couldn't expect satisfactory oxygen storage capacity because of its small B.E.T. surface area before and after aging.

From these results, we have chosen (Ce,Zr)O₂ in order to enhance thermal stability and OSC of CeO₂.

2. Results of OSC Measurement

Bulk ceria has less oxygen storage capacity than (Ce,Zr)O₂ before and after aging as shown in Fig. 8, 9.

From these results, we found that the addition of Zr promotes the oxygen storage capacity compared to bulk ceria. It was considered that CeO₂ particles convert into fine particles by addition of Zr, so that the dispersion of CeO₂ was improved. After aging (950 °C, 12 hrs), the oxygen storage capacity of bulk ceria was very much decreased compared to fresh bulk ceria, while (Ce,Zr)O₂ was enhanced after aging than before aging.

From the XRD results of (Ce,Zr)O₂ as shown in Fig. 5, it was considered that after aging, the peak intensities grow slightly except (2, 0, 0) and (3, 1, 1) phases, so that the (2, 0, 0) and (3, 1, 1) phases may be active phases for improving oxygen storage capacity.

The CO₂ formation amounts were very much decreased until 30 minutes, and then maintained so. It was considered that surface reaction proceeded until 30 minutes, and then CO reacted with the oxygen within (Ce,Zr)O₂ structure. Therefore, we suggest that Zr promotes the surface reaction and not the mi-

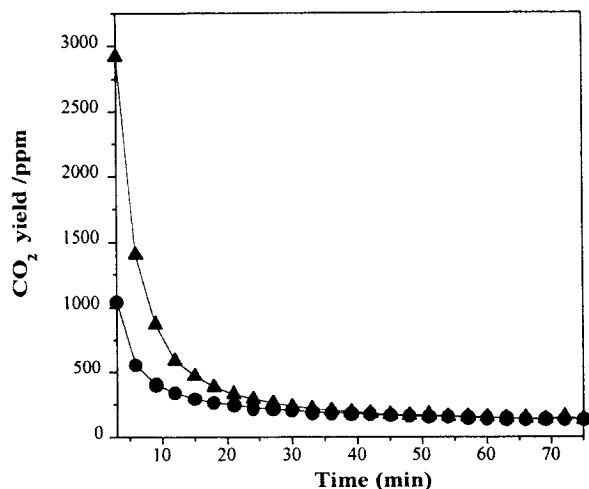


Fig. 8. OSC measurements of bulk ceria (CeO_2) and stabilized ceria $[(\text{Ce,Zr})\text{O}_2]$ before aging [●: bulk ceria, ▲: $(\text{Ce,Zr})\text{O}_2$].

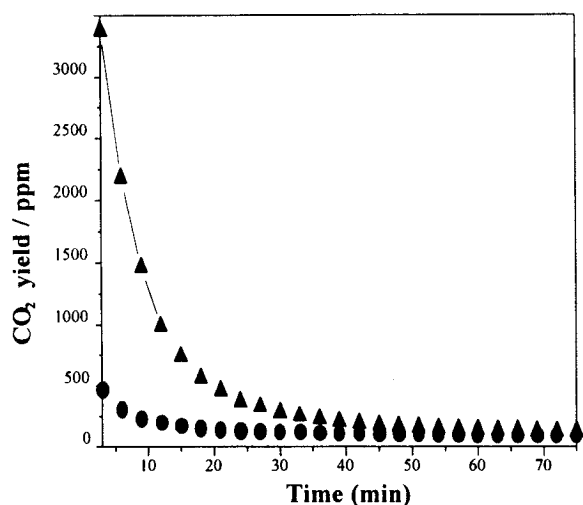


Fig. 9. OSC measurements of bulk ceria (CeO_2) and stabilized ceria $[(\text{Ce,Zr})\text{O}_2]$ after aging 950°C , 12 hrs [●: bulk ceria, ▲: $(\text{Ce,Zr})\text{O}_2$].

gration rate of bulk oxygen to the surface of the particles [Belton et al., 1997].

As shown in Fig. 10, 11, oxygen storage capacities of $(\text{CeO}_2, \text{La}_2\text{O}_3)$ and $(\text{CeO}_2, \text{Nd}_2\text{O}_3)$ have less than that of $(\text{Ce,Zr})\text{O}_2$ as expected from B.E.T. surface area results. The average oxygen storage capacities (=the area of below each curve divided by reaction time) were measured as shown in Fig. 12. As expected from results of XRD and B.E.T. surface area, $(\text{Ce,Zr})\text{O}_2$ has better average oxygen storage capacity than bulk ceria, $(\text{CeO}_2, \text{La}_2\text{O}_3)$ and $(\text{CeO}_2, \text{Nd}_2\text{O}_3)$. From these results, we have chosen $(\text{Ce,Zr})\text{O}_2$ in order to enhance thermal stability and OSC of CeO_2 .

In order to investigate the oxygen storage capacities which are dependent upon the different mixing ratios of bulk ceria and $(\text{Ce,Zr})\text{O}_2$, we prepared Pd-only monolithic catalysts as shown in Table 2.

As shown in Fig. 13, ES-3 catalyst, where the mixing ratio of bulk ceria and $(\text{Ce,Zr})\text{O}_2$ is 3 : 1, has better average OSC

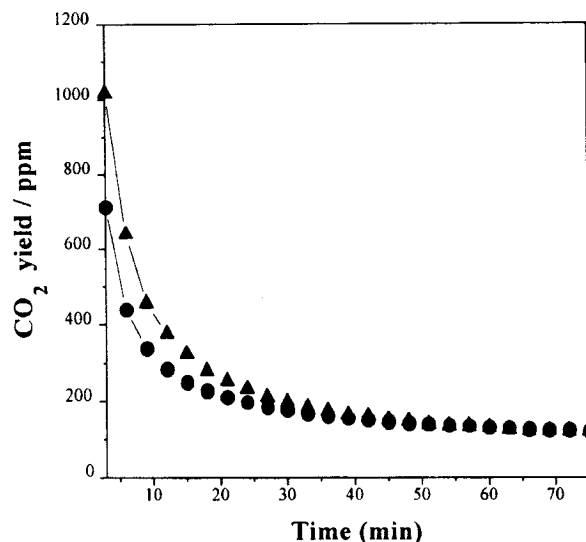


Fig. 10. OSC measurements of $(\text{CeO}_2, \text{La}_2\text{O}_3)$ and $(\text{CeO}_2, \text{Nd}_2\text{O}_3)$ after aging 950°C , 12 hrs [●: $(\text{CeO}_2, \text{Nd}_2\text{O}_3)$, ▲: $(\text{CeO}_2, \text{La}_2\text{O}_3)$].

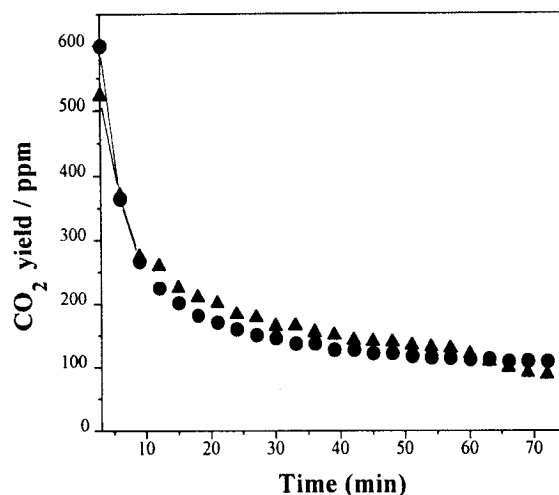


Fig. 11. OSC measurements of $(\text{Ce,La})\text{O}_2$ and $(\text{Ce,Nd})\text{O}_2$ after aging 950°C , 12 hrs [●: $(\text{CeO}_2, \text{Nd}_2\text{O}_3)$, ▲: $(\text{CeO}_2, \text{La}_2\text{O}_3)$].

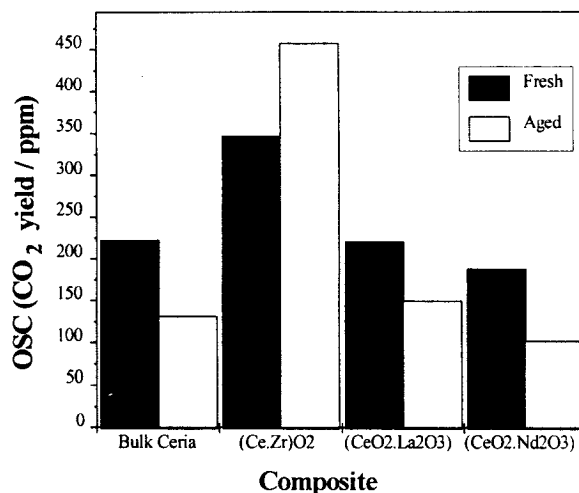
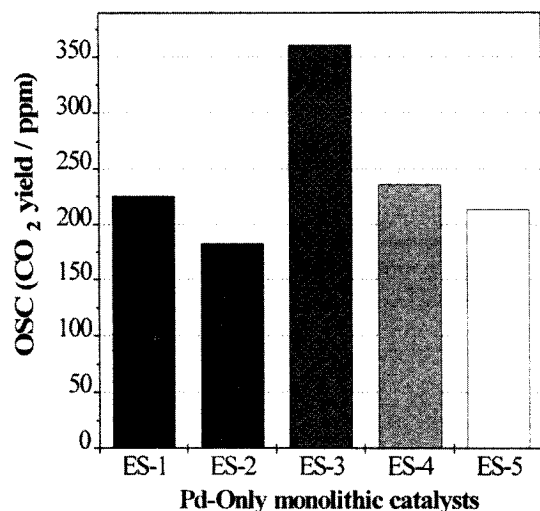


Fig. 12. Average OSC results on various stabilized ceria.

Table 2. Preparation of Pd-only catalysts with the different mixing ratios of bulk ceria and (Ce,Zr)O₂

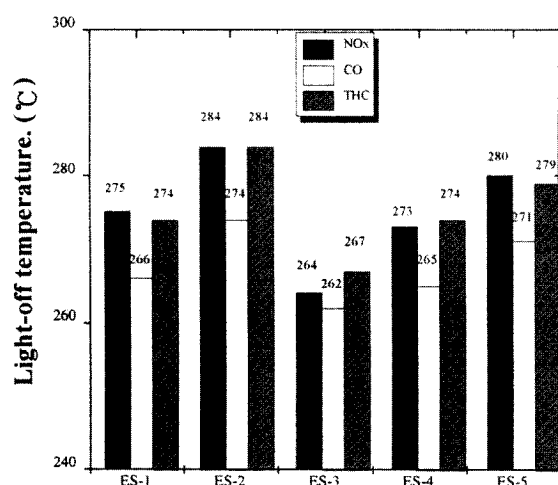
Catalyst	Loading amount	Ceria mixture bulk ceria : (Ce,Zr)O ₂
ES-1		5 : 1
ES-2	Pd : 2.8 wt%	4 : 1
ES-3	Ba : 4.0 wt%	3 : 1
ES-4	La : 0.9 wt%	1 : 1
ES-5		1 : 3

**Fig. 13. Average OSC of various Pd-only monolithic catalysts (950 °C, 48 hrs aged).**

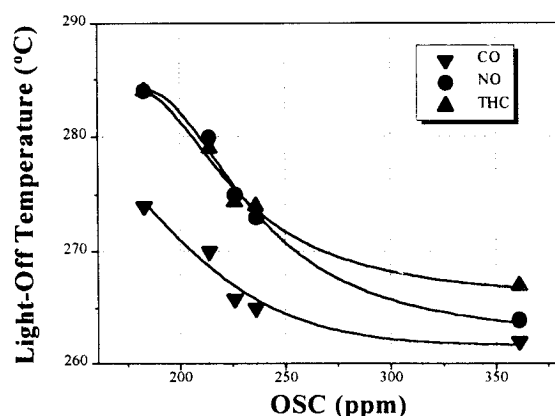
than any other catalyst. From these results, we found that the optimum ratio of bulk ceria and (Ce,Zr)O₂ was 3 : 1.

3. Correlation Between Activities and OSC of Pd-Only Monolithic Catalysts

In order to investigate the correlation between activities and OSC of Pd-only monolithic catalysts, we measured activities of Pd-only monolithic catalysts with the different mixing ratios of bulk ceria and (Ce,Zr)O₂ under 950 °C, 140 hrs

**Fig. 14. Light-off performance of various Pd-only monolithic catalysts (950 °C, 140 hrs aged).****Table 3. Oxygen storage amount of Pd-only monolithic catalysts with the different mixing ratios of bulk ceria and (Ce,Zr)O₂**

Catalyst	Ceria mixture bulk ceria : (Ce,Zr)O ₂	OSC amount (ppm)
ES-1	5 : 1	226
ES-2	4 : 1	183
ES-3	3 : 1	361
ES-4	1 : 1	236
ES-5	1 : 3	214

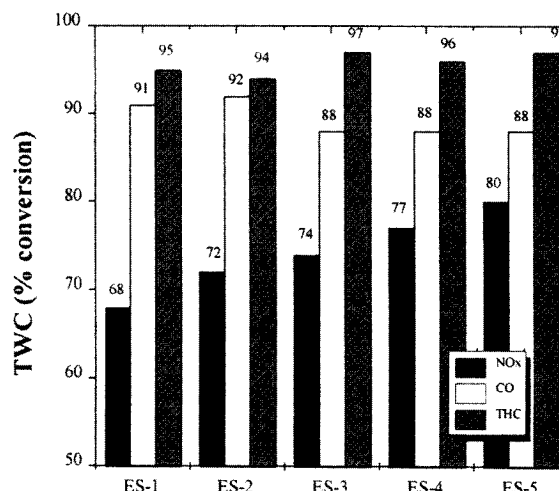
**Fig. 15. Correlation between LOT & OSC of various Pd-only monolithic catalysts.**

aging conditions.

Fig. 14 shows the light-off performance of Pd-only monolithic catalysts. With increasing (Ce,Zr)O₂ loading amounts, the light-off performance was enhanced. Especially, ES-3 catalyst where the mixing ratio of bulk ceria and (Ce,Zr)O₂ was 3 : 1 had the best light-off performance.

These results were closely connected with the OSC as shown in Table 3 and Fig. 15. We found that the light-off temperature of NO_x, THC and CO was inversely proportional to the OSC of catalysts.

As shown in Fig. 16, even though the three-way perfor-

**Fig. 16. Three-way performance of various Pd-only monolithic catalysts.**

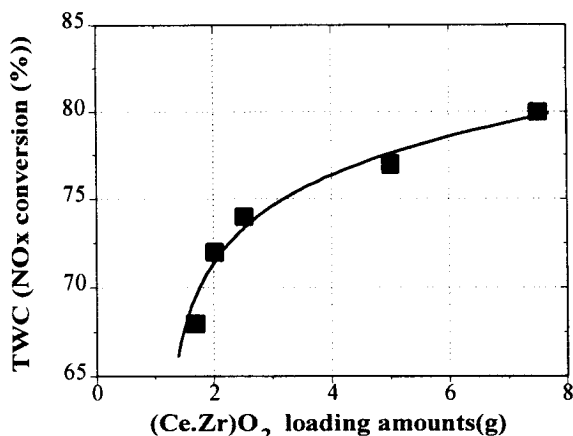


Fig. 17. Correlation between three-way performance and (Ce,Zr)-O₂ loading amounts.

manances of THC and CO were similar, the three-way performances of NO_x conversion were enhanced with increasing amounts of (Ce,Zr)O₂ loadings.

As a result, we found that NO_x conversions in three-way performance were proportional to the amounts of (Ce,Zr)O₂ loadings as shown in Fig. 17.

CONCLUSIONS

After aging (950 °C, 12 hrs), among the various types of stabilized ceria, (Ce,Zr)O₂ had the best thermal stability and OSC, compared to bulk ceria and other stabilized ceria. The performance of LOT (T₅₀) was closely connected with the OSC. On the other hand, three-way performance was not related

to the OSC. However, it was found that NO_x conversion of three-way performance was proportional to the (Ce,Zr)O₂ loading amounts.

In the design of Pd-only catalysts, characteristics of LOT (T₅₀) and three-way performances were dependent on the mixing ratios of bulk and stabilized ceria [(Ce,Zr)O₂].

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