Oxygen Store and Release of $\text{CeO}_2\text{-ZrO}_2\text{-MO}_{1.5}$ ($\text{M} = \text{La}, \text{Nd}$) Powders Prepared by Co-Precipitation Method

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共沈法により作製した $\text{CeO}_2\text{-ZrO}_2\text{-MO}_{1.5}$ ($\text{M} = \text{La}, \text{Nd}$) 粉末の酸素の吸収放出特性

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$\text{CeO}_2\text{-ZrO}_2\text{-MO}_{1.5}$ ($\text{M} = \text{La}, \text{Nd}$) powders to be used as three way catalysts for automotive exhaust gases were prepared from nitrate solutions by co-precipitation method. As a catalyst exposed to high temperature gas, a high thermal stability is required to keep high surface area. High oxygen storage capacity is also required. In this study, their oxygen storage capacity (OSC), surface area (SA) and temperature programmed reduction behavior (TPR) of $\text{CeO}_2\text{-ZrO}_2\text{-MO}_{1.5}$ powders were measured. The substitution of ZrO_2 by $\text{MO}_{1.5}$ increased the OSC value at calcination temperature 1000°C . SA values decreased as the calcination temperature increased, and SA was suppressed by the addition of $\text{MO}_{1.5}$. In both cases, the effect of $\text{LaO}_{1.5}$ addition was higher than that of $\text{NdO}_{1.5}$.

[Received April 23, 2004; Accepted June 24, 2004]

Key-words : Three way catalyst, OSC, Thermal stability, CeO_2 , $\text{LaO}_{1.5}$, $\text{NdO}_{1.5}$, Co-precipitation method

1. Introduction

Three way catalysts for automotive exhaust gases is applicable for a sudden change of concentration of gases, such as CO , HC , NO_x , in the range from ppm to %.¹⁾ The performance of three way catalysts depends on oxygen storage capacity (OSC) and surface area (SA) values of the subcatalyst powders. Up to date as subcatalyst powders, CeO_2 ,²⁾⁻⁴⁾ $\text{CeO}_2\text{-ZrO}_2$ ⁵⁾⁻⁸⁾ and $\text{CeO}_2\text{-LaO}_{1.5}$ ⁹⁾ have been studied. The $\text{CeO}_2\text{-ZrO}_2$ powders show a high OSC value and are used as the subcatalysts for purification of automotive exhaust gases.^{1),8)} When such catalysts are exposed to a high temperature gas, high thermal stability is required. A catalyst with low thermal stability will be sintered during a long time usage and will lose its performance with the decrease of SA. However, only a limited number of studies have been made on the OSC and SA values of the $\text{CeO}_2\text{-ZrO}_2$ subcatalysts.

Otsuka et al.¹⁰⁾ investigated the relationship between the crystal structure and desorption of oxygen in $\text{Ce}_2\text{Zr}_2\text{O}_8$ powder and showed that the oxygen storage reaction is based on the phase transition from pyrochlore-type, $\text{Ce}_2\text{Zr}_2\text{O}_{7+y}$ ($y=0-1$), to κ -type $\text{Ce}_2\text{Zr}_2\text{O}_8$, where oxygen is released by the reverse reaction. On the other hand, Suda et al.^{11),12)} reported a formation of the solid solution of fluorite structure, $\text{Ce}_{2+x}\text{Zr}_{2-x}\text{O}_8$ ($x=0-2$), on a heat treatment of $\text{CeO}_2\text{-ZrO}_2$ under a reduced atmosphere. They also showed the OSC value dependence in $\text{Ce}_{2+x}\text{Zr}_{2-x}\text{O}_8$ solid solution on the amount of the $\text{Ce}_2\text{Zr}_2\text{O}_8$ phase in the solid solution, and that order- $\text{Ce}_2\text{Zr}_2\text{O}_8$ solid solution gives almost theoretical OSC values according to the $2\text{Ce}^{3+}\text{O}_{1.5} + \text{O} \rightarrow 2\text{Ce}^{4+}\text{O}_2$ reaction. However when calcined at high temperature, order- $\text{Ce}_2\text{Zr}_2\text{O}_8$ exhibits a very low SA value.^{11),12)}

We have previously reported¹³⁾ that $\text{CeO}_2\text{-ZrO}_2$ powders by the co-precipitation method showed a maximum OSC value (per mole of CeO_2) at 20–30 mol% CeO_2 . Also we have reported¹⁴⁾ that $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{MO}_x$ powders, where M is rare earth element, by the co-precipitation method ex-

hibited an improved thermal stability and high SA values.

From the results reported above,^{13),14)} we can expect that La- or Nd-containing powders might exhibit high OSC values and high SA values associated with high thermal stability. In the present study, we prepared $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders ($\text{M} = \text{La}$ or Nd , $y=0-10$) by the co-precipitation method. We measured OSC values, temperature dependency of oxygen release (TPR: Temperature Programmed Reduction) and SA value and evaluated the influence of additive elements (La or Nd) and most appropriate calcination temperature for them.

2. Experimental

2.1 Preparation of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powder by the co-precipitation method

The flow chart of processing for the preparation of the powders is shown in Fig. 1. The $\text{Ce}(\text{NO}_3)_3$ and $\text{ZrO}(\text{NO}_3)_2$ aqueous solutions were prepared, which contained 20 mass% CeO_2 and 25 mass% ZrO_2 , respectively, by dissolving commercially available reagents $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99% purity) and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (99% purity) in ion-exchanged water. Aqueous solution containing 20 mass% La or Nd was prepared from its respective nitrate, $\text{La}(\text{NO}_3)_3$ or $\text{Nd}(\text{NO}_3)_3$. Each solution containing La or Nd was mixed with ion exchanged water so that 1 mass% of $[50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2] \cdot y\text{MO}_{1.5}$ (mol%), where $y=0-10$, is contained. The 5% ammonia aqueous solution was put into the mixed solution until pH=10.2 is attained. Hydroxides precipitated at this stage. After sucking filtration and washing of the resultant precipitates, the precipitate was calcined at 200°C to 1000°C for 3 h. The calcined solids were pulverized to less than 20 μm in diameter by use of a pulverizer (Ika Co., LTD., LABLRTCHNK) with rotor speed of 5500 rpm.

2.2 Measurement of oxygen storage capacity (OSC)

Before the measurement of OSC, the powder (0.5 g) was heat-treated at 600°C for 10 min in a 5% H_2/Ar stream to

Fig. 1. Flow chart of processing for the preparation of $\text{CeO}_2\text{-ZrO}_2\text{-MO}_{1.5}$ powders, $M=\text{La}$ and Nd .

reduce the Ce ion from Ce(IV) to Ce(III). OSC value of the powders was determined by measuring residual O_2 gas after a pulse injection of pure O_2 gas (0.5 ml, 0.1 sec). A gas chromatograph (Shimadzu Co., LTD., GC-8A) was employed for the measurement. The total amount of O_2 gas stored in the powders was read as the amounts of saturated OSC value corresponding to 600°C. OSC value is expressed in term of amount of oxygen per unit weight of powder ($\mu\text{mol-O}_2/\text{g}$).

2.3 Measurement of temperature programmed reduction (TPR)

Measurement of TPR curve of the powders was also made by use of MULTITASK T.P.R. (BEL JAPAN INC.). After oxidized in pure O_2 gas at 350°C for 60 min, the powder (0.10 g) was heated with a heating rate 10°C/min from 100 to 1000°C in a stream of 5% H_2/Ar gas. The rate of reduction of the powder was calculated from the amount of H_2O detected by the quadrupole mass spectrometer. TPR curve is expressed in terms of H_2O formed per unit weight of powder under a given heating rate.

2.4 Measurement of surface areas (SA)

SA value of powders, calcined at 300°C to 1000°C for 3 h, was measured by one point N_2 adsorption method by use of a surface area analyzer (Flowsorb-II2300 type, Shimadzu Co., Ltd.).

2.5 Measurement of X-ray diffraction (XRD)

The powder was analyzed by X-ray diffraction method (Rigaku Co., Ltd., RAD-2C) to identify the crystalline phase in the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders, in the range, $2\theta = 10\text{-}75^\circ$ with a scan speed of $1^\circ/\text{min}$ by $\text{Cu K}\alpha$ radiation and an electric current of 30 mA (50 kV) with a slit width of 1° .

3. Results and discussion

3.1 Store and release of oxygen in the powders

3.1.1 OSC

The relationship between OSC values and calcining temperature of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($y=0, 2, 4, 6, 10$) powders is shown in Table 1 and Fig. 2. Without La or Nd

Table 1. Effects of $\text{MO}_{1.5}$ Content and Calcining Temperatures on OSC Value of the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ Powders ($M=\text{La, Nd}$, $y=0\text{-}10\text{ mol}\%$) Calcined for 3 h

MO _{1.5} /mol%	OSC / μ mol-O ₂ /g			
	Calcining temp. / °C			
	600	750	900	1000
LaO _{1.5}				
0	233	263	261	229
2	242	252	269	246
4	240	245	260	262
6	240	269	269	273
10	227	225	247	243
NdO _{1.5}				
0	233	263	261	229
2	228	222	228	241
4	224	215	241	242
6	217	211	246	235
10	191	192	209	227

Fig. 2. Relationship between OSC values and calcining temperatures of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($M=\text{La}$ or Nd , $y=0\text{-}10\text{ mol}\%$) powders.

● 0 mol%, ▲ 2 mol%, ■ 4 mol%, ◆ 6 mol%, ▼ 10 mol%.

addition, OSC values increased with calcining temperature and reached a maximum at 750°C, and began to decrease at 1000°C. In the La-series, the powder with 6 mol% La showed higher OSC values than that of La free one at 750°C, but powders with 2, 4 or 6 mol% La showed higher OSC values at 900°C. OSC values of all La containing powders was higher than La free powder at 1000°C. In the Nd series, Nd addition did not increase OSC value at calcining temperatures 750°C–900°C, while OSC values of 2–6 mol% Nd containing powders was higher than that of Nd free powder at 1000°C. In conclusion, it may be said that 6 mol% La addition exhibits the highest OSC value of about $270 \mu\text{mol-O}_2/\text{g}$ at 750°C–900°C.

Figure 3 shows OSC values of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot$

Fig. 3. Comparison of OSC values between the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders (■ La, ▲ Nd) and $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders (□ La, △ Nd) ($y=0-10$ mol%) calcined at 1000°C for 3 h.

$y\text{MO}_{1.5}$ powders calcined at 1000°C as a function of M content. For comparison, OSC values of $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders¹⁴⁾ are also shown in broken lines. The base composition $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ exhibits an OSC value of $229 \mu\text{mol-O}_2/\text{g}$. La addition increased OSC values up to $273 \mu\text{mol-O}_2/\text{g}$ at 6 mol% La concentration, and then further addition decreased OSC value. In the Nd series (▲), OSC value was found to become maximum $242 \mu\text{mol-O}_2/\text{g}$ at 2 mol% Nd concentration. It is reported that the $\text{CeO}_2\text{-ZrO}_2$ solid solution (fluorite structure) increased with Nd addition.¹⁴⁾ The same result is expected in the case of La addition. If CeO_2 in fluorite structure plays an important role for oxygen storage reaction, the increase of the OSC values could be explained by the addition of $\text{M}=\text{La}$ or Nd.

As stated previously, $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powder, calcined at 1000°C , showed OSC value of $229 \mu\text{mol-O}_2/\text{g}$. This value is 27% of the theoretical OSC value ($847 \mu\text{mol-O}_2/\text{g}$), which is calculated by an assumption that the valence of Ce ion changes from three to four during the oxygen storage reaction.

Suda et al.¹²⁾ reported that Pt doped $\text{Ce}_2\text{Zr}_2\text{O}_8$ powder, heat-treated at 1200°C in CO gas atmosphere, showed a very high OSC value at 500°C ($753 \mu\text{mol-O}_2/\text{g}$) or 89% of the theoretical value. Omata et al.¹⁵⁾ showed that the reduction ratio, $\text{Ce}^{3+}/\text{Ce}^{3+} + \text{Ce}^{4+}$, of $\text{Ce}_2\text{Zr}_2\text{O}_8$ powder (tetragonal zirconia structure), heated at 1650°C for 5 h, was 0.406 and 0.96, respectively, when the powder was reduced at 600°C and 1300°C . They also reported that the amount of pyrochlore- $\text{Ce}_2\text{Zr}_2\text{O}_7$ increased with increasing reduction temperature.

The low OSC value of the present powders should be owing to a low reduction temperature. It is not certain whether or not La or Nd addition exerts an influence on the pyrochlore phase formation which is responsible for high OSC characteristics.

3.1.2 TPR

TPR curves for $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders are shown in Figs. 4(a) and (b). In every powder, a peak responsible to oxygen release is observed. The starting temperatures of oxygen release are shown in the figures. Also the starting temperatures and the peak temperatures of TPR curves are listed in Table 2.

The $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powder, calcined at 750°C , began to release oxygen at about 440°C and showed a peak release rate at about 600°C . The starting temperature and peak temperature increased as the calcining temperature increased. There was little effect of the La and Nd addition on the starting and peak temperatures for the powders calcined at 750°C and 900°C . However, the peak temperature of the powder, cal-

Fig. 4. TPR curves of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders ($\text{M}=\text{La}$ or Nd) calcined at 750, 900 and 1000°C for 3 h. Sample weight: 0.1 g

cined at 1000°C , was increased by the addition of La or Nd.

Table 2. Effects of $\text{MO}_{1.5}$ Content and Calcining Temperatures on TPR in the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders ($\text{M}=\text{La}$ or Nd , $y=0\text{--}10\text{ mol}\%$) Calcined for 3 h

$\text{LaO}_{1.5}$ /mol%	Calcining Temp. /°C	Oxygen release temp./°C		$\text{NdO}_{1.5}$ /mol%	Calcining Temp. /°C	Oxygen release temp./°C	
		Setting	Peak			Setting	Peak
0	750	440	593	0	750	440	593
2	750	439	601	2	750	437	601
4	750	439	598	4	750	437	593
6	750	441	598	6	750	443	602
10	750	441	604	10	750	443	594
0	900	480	622	0	900	480	622
2	900	480	615	2	900	480	626
4	900	478	620	4	900	482	610
6	900	479	611	6	900	483	613
10	900	481	618	10	900	483	609
0	1000	538	630	0	1000	538	630
2	1000	540	651	2	1000	542	634
4	1000	539	658	4	1000	542	641
6	1000	542	663	6	1000	542	649
10	1000	544	678	10	1000	545	653

Table 3. Effects of $\text{MO}_{1.5}$ Content and Calcining Temperature for SA of the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ Powders, ($\text{M}=\text{La}, \text{Nd}$, $y=0\text{--}10\text{ mol}\%$) Calcined for 3 h

$\text{MO}_{1.5}$ /mol%	SA / m^2/g						
	Calcining temp. / °C						
	300	400	500	600	750	900	1000
LaO_{1.5}							
0	176.4	106.6	77.1	61.9	47.3	20.8	10.1
2	174.2	99.6	76.1	63.0	43.6	27.8	12.9
4	179.0	100.9	76.4	66.3	51.0	27.2	13.4
6	199.2	126.4	90.3	75.3	57.5	32.9	15.2
10	175.7	125.6	86.6	74.0	49.4	29.8	13.8
NdO_{1.5}							
0	176.4	106.6	77.1	61.9	47.3	20.8	10.1
2	183.6	107.6	71.2	58.2	43.9	24.3	12.1
4	183.2	110.6	73.7	63.9	48.6	26.5	12.8
6	179.2	114.4	73.9	64.6	47.8	28.0	12.6
10	178.8	122.1	83.2	68.7	49.4	28.5	11.3

3.2 SA

The variation of SA values of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($\text{M}=\text{La}$ or Nd , $y=0\text{--}10\text{ mol}\%$) powders with calcination temperature is shown in Table 3 and Fig. 5.

Powders calcined at 300°C showed high SA values ($175\text{--}200\text{ m}^2/\text{g}$). SA values drastically decreased with the increase of calcination temperature and then reached low values ($10\text{--}15\text{ m}^2/\text{g}$) at 1000°C . The effect of $\text{M}=\text{La}$ or Nd addition on the calcination temperature was found to be small.

$\text{CeO}_2\text{-ZrO}_2\text{-MO}_{1.5}$ ($\text{M}=\text{La}, \text{Nd}$) powders are loaded on the surface of a honeycomb type monolithic support by doping the catalytic agents Pt or Pd to them. Since this type of

Fig. 5. Relationship between SA values and calcining temperatures of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders ($\text{M}=\text{La}$ or Nd , $y=0\text{--}10\text{ mol}\%$). ● 0 mol%, ▲ 2 mol%, ■ 4 mol%, ◆ 6 mol%, ▼ 10 mol%.

Fig. 6. SA values of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders ($y=0\text{--}10\text{ mol}\%$) calcined at 1000°C for 3 h, La (■), Nd (▲).

catalyst is used to purify automotive exhaust emission gas, the powders are required to have high thermal stability to maintain a high SA value during the usage at high temperatures. Figure 6 shows the variation of SA values with M content in $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders calcined at 1000°C . Without M addition, SA value is $10.1\text{ m}^2/\text{g}$. On the other hand, SA values increased with La content and reached a maximum ($15.2\text{ m}^2/\text{g}$) at 6 mol% La concentration and then gradually decreased. This maximum value is 50% higher than that of $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powder and obviously La addition improves its thermal stability. The SA value in the Nd series showed a maximum value ($12.8\text{ m}^2/\text{g}$) at 4 mol% Nd concentration. The effect of Nd addition on SA is smaller than that of La addition.

Sasaki et al.¹⁶⁾ reported that reduced $\text{Ce}_{0.55}\text{Zr}_{0.45}\text{O}_2$ solid solution which have SA value higher than $7\text{ m}^2/\text{g}$ oxidizes explosively at room temperature in air. This result means the solid solution which shows high a SA has a high oxygen storage power. Since the powders in this study showed

Fig. 7. XRD patterns of $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powders calcined at various temperatures for 3 h.

Fig. 8. XRD patterns of $50\text{CeO}_2 \cdot 40\text{ZrO}_2 \cdot 10\text{LaO}_{1.5}$ powders calcined at various temperatures for 3 h.

SA value higher than $7 \text{ m}^2/\text{g}$ by the introduction of La or Nd, they are expected to show an excellent OSC characteristics to work as the subcatalyst for automotive exhaust gases.

3.3 Crystals morphology of the powder

3.3.1 XRD pattern of the $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powders

Figure 7 shows XRD pattern of M free $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powders calcined at 200, 400, 600, 750, 900 and 1000°C . The sample showed broad diffraction peaks indexed by CeO_2 with fluorite structure¹⁷⁾ (c-type crystal). As the calcination temperature increased, each diffraction peak became stronger and shifted to higher angle. Shoulders were observed at higher angles. These shoulders were indexed as tetragonal zirconia structure¹⁷⁾ (t-type crystal). This result suggests that CeO_2 has precipitated first, and the amount of ZrO_2 precipitated increases as the calcination temperature rises. The shift of CeO_2 peak to higher angle indicates the amount of ZrO_2 soluted in CeO_2 increases with calcination temperature. Pyrochlore-type ($\text{Ce}_2\text{Zr}_2\text{O}_{7+y}$) and/or κ -type ($\text{Ce}_2\text{Zr}_2\text{O}_8$) crystal were not observed.

Yashima et al.¹⁷⁾ prepared $\text{CeO}_2\text{-ZrO}_2$ powders by the organic polymerized complex method. Their XRD patterns on these samples showed t-type crystal which resembled with those of present study. However, the formation of c-type crystal was not mentioned in the paper.¹⁷⁾ They reported that the precursor by the organic polymerized complex method was so homogeneous that only metastable tetragonal t'-form could be obtained instead of the mixture of c-type and t-type crystals. Therefore, the homogeneity of the present sample might be lower than that of Yashima's sample.

3.3.2 XRD pattern of the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ (M=La, Nd) powder

Figure 8 shows XRD patterns of $50\text{CeO}_2 \cdot 40\text{ZrO}_2 \cdot 10\text{LaO}_{1.5}$ powders calcined at 200, 400, 600, 750, 900 and 1000°C . It is obvious that c-type crystal was formed. In this figure, precipitation of t-type crystal was not confirmed. Figure 9 shows XRD patterns of $50\text{CeO}_2 \cdot 40\text{ZrO}_2 \cdot 10\text{NdO}_{1.5}$ powders. At low calcination temperatures, only c-type crystal was formed, but t-type crystals emerged as the calcination temperature increased. Though this tendency is same as the $50\text{CeO}_2 \cdot 50\text{ZrO}_2$

Fig. 9. XRD patterns of $50\text{CeO}_2 \cdot 40\text{ZrO}_2 \cdot 10\text{NdO}_{1.5}$ powders calcined at various temperatures for 3 h.

samples, the peak height of the t-type crystals is weaker.

Figures 10 and 11 show XRD patterns of the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($y=0, 2, 4, 6, 10 \text{ mol}\%$) powder calcined at 1000°C including various amounts of M. It is observed that the addition of M lowered the peak height of t-type crystal and peaks of t-type crystal were not detected for 10 mol% M containing powders in both figures. It is clear that the addition of M caused ZrO_2 to dissolve into c-type crystal. In $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{LaO}_{1.5}$ powder, t-type crystal disappeared at $y=6$ composition. The OSC value showed a maximum at the same composition ($y=6$). The OSC value should depend on the chemical state of Ce ion and the chemical state of Ce ion is strongly controlled by the dissolution of other oxides. Because the peak shift was little, M ion could enter the

Fig. 10. XRD patterns of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{LaO}_{1.5}$ powders ($y=0\text{--}10\text{ mol}\%$)

Fig. 11. XRD patterns of $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{NdO}_{1.5}$ powders ($y=0\text{--}10\text{ mol}\%$) calcined at 1000°C for 3 h.

Ce site but not the Zr site. Should M ion enter the Zr site, the peak shift should be larger because the difference of ion radii is larger between M and Zr than between M and Ce.¹⁸⁾

Since the peak width of c-type crystal for $50\text{CeO}_2 \cdot 40\text{ZrO}_2 \cdot 10\text{NdO}_{1.5}$ powder is broader than that for $50\text{CeO}_2 \cdot 40\text{ZrO}_2 \cdot 10\text{LaO}_{1.5}$, the powder might contain small amount of t-type crystal too small to be detected by XRD.

La containing powders had higher values of OSC and SA than Nd containing ones. This difference may be attributable to the amount of c-type crystal. The phase diagram in the $\text{CeO}_2\text{-ZrO}_2$ system¹⁴⁾ indicates at 1000°C about 20 mol% CeO_2 dissolves in the t-type crystal. CeO_2 dissolved in t-type crystal might show a lower OSC value than that in c-type crystal. If this assumption is correct, it is preferable to sup-

Table 4. Measurement Temperature Dependence of OSC Values in the $50\text{CeO}_2 \cdot 44\text{ZrO}_2 \cdot 6\text{LaO}_{1.5}$ Powder Calcined at 1000°C for 3 h

	Measurement temperature* / $^\circ\text{C}$							
	450	500	550	600	650	700	750	800
OSC/ $\mu\text{mol-O}_2/\text{g}$	0	12	81	273	274	284	304	322

* : Reduced at the same temperature for 10 min in a 5% H_2/Ar stream.

Fig. 12. Comparison of SA values between the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{LaO}_{1.5}$ powders and $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{LaO}_{1.5}$ powders, respectively, with $y=0, 2, 4, 6$ and $10\text{ mol}\%$ calcined for 3 h.

press the formation of t-type crystal to obtain high OSC value.

3.4. Relationship among OSC value, property of TPR curve and SA value.

Table 4 shows the OSC values measured at different temperatures $450\text{--}800^\circ\text{C}$ in $50\text{CeO}_2 \cdot 44\text{ZrO}_2 \cdot 6\text{LaO}_{1.5}$ (mol%) powders, calcined at 1000°C . OSC value was small at temperatures lower than the starting temperature in TPR curves (Fig. 4), and increased rapidly between 550 and 600°C . The OSC value at 600°C is close to the saturated value at 800°C . According to the TPR curve (Fig. 4), oxygen release reaction occurs at 600°C , and almost finishes at 800°C . OSC values at both temperatures were almost same. This means the amount of oxygen which the powder could release at 600°C is same as that at 800°C if it takes longer time at 600°C .

The OSC value at 450°C is null where oxygen is not released (TPR curve). OSC value is very small at 500°C that is lower than starting temperature. However OSC value is $273\ \mu\text{mol-O}_2/\text{g}$ at 600°C that is above the oxygen release temperature. This OSC value is equivalent to that at 650°C and at higher temperatures. It means at temperatures higher than oxygen release temperature, the $\text{CeO}_2\text{-ZrO}_2$ powder continues to release oxygen until saturated if it takes longer time. For example, the amount of oxygen to be released at 800°C as shown in Fig. 4(a) can be released at 600°C after longer time in a 5% H_2/Ar stream.

Figures 12 and 13 compare the SA values between the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($\text{M}=\text{La}$ or Nd) and $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($\text{M}=\text{La}$ or Nd) powders,¹⁴⁾ calcined at 1000°C . The SA values of 20 mol% CeO_2 series were larger than that of 50 mol% CeO_2 series. It can be inferred that the increase of ZrO_2 content is effective for the improvement of thermal stability. This result suggests that 50 mol% CeO_2 could stabilize the crystalline structure more than 20 mol% CeO_2 could.

Fig. 13. Comparison of SA values between the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{NdO}_{1.5}$ powders and $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{NdO}_{1.5}$ powders, respectively, with $y=0, 2, 4, 6$ and 10 mol% calcined for 3 h.

The starting temperature in TPR curve was lowered with the decrease of the calcination temperatures while SA values increased as shown in Table 2. As stated by Haneda et al.,⁴⁾ a diminution of particle size could lead to the increase of SA value and contribute to shift the oxygen release temperature towards lower temperature. The high SA powder is expected to have a higher rate of oxygen release, and also higher rate of oxygen storage.

The SA value is a parameter related to the reaction rate of oxygen release and storage and depends on the form of powder, while OSC value depends on the composition and crystal structure. Therefore, SA and OSC are independent parameters. Though the SA value of the powder calcined at 1000°C is one fifth of that calcined at 600°C , OSC variation with calcination temperature is small. This result indicates that even the powder of small SA value could be in equilibrium with the gas phase during OSC measurement.

It was confirmed that the $50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders have smaller SA values but larger OSC values than $20\text{CeO}_2 \cdot (80-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ powders. It is important to know the characteristics oxygen release and storage in Pt doped powders. Of course it is necessary to choose an appropriate support of catalyst by considering SA, TPR and OSC characteristics as a whole.

4. Conclusion

$50\text{CeO}_2 \cdot (50-y)\text{ZrO}_2 \cdot y\text{MO}_{1.5}$ ($M=\text{La}$ or Nd , $y=0-10$) powders were prepared from nitrate solutions by the co-precipitation method. The influence of La or Nd addition to the powders on the OSC, TPR and SA characteristic was evaluated.

The following results were obtained:

- (1) The substitution of ZrO_2 by $\text{MO}_{1.5}$ ($M=\text{La}$ or Nd) in

the range of $0-10$ mol% M concentration in the $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powder did not change much the OSC values. However, M addition increased OSC value of $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powder at the calcination temperature 1000°C . La addition showed a higher effect than Nd to improve OSC value.

(2) SA value of $50\text{CeO}_2 \cdot 50\text{ZrO}_2$ powders decreased drastically with the increase of calcination temperature, and M addition suppressed the decrease of SA. La addition has higher effect than Nd addition to improve the thermal stability of the powder.

(3) $50\text{CeO}_2 \cdot 44\text{ZrO}_2 \cdot 6\text{LaO}_{1.5}$ powders have the highest OSC value and highest thermal stability in this study.

(4) It is inferred that the suppression of the tetragonal ZrO_2 formation by M addition is the cause of the OSC increase.

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