Flaming Oxidation of Reduced $\text{CeO}_2\text{--ZrO}_2$ Solid Solution in the Near-Room-Temperature Range

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還元した $\text{CeO}_2\text{--ZrO}_2$ 固溶体の室温での発熱を伴う急激な酸化反応

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The oxidation behavior of reduced CeO_2 and $\text{CeO}_2\text{--ZrO}_2$ solid solution (CZS) was studied by measuring the weight and temperature change during oxidization, in the near-room-temperature range. A flaming oxidation at close to room temperature was observed in some of the reduced CZS. This oxidation takes place in the CZS reduced at much lower temperatures, 800°C and 1000°C, compared with CeO_2 , for which the temperature of 1400°C or so is required for the occurrence of the flaming oxidation. The oxidation was not observed in the CZS reduced at a temperature higher than 1200°C. The material, which exhibited the flaming oxidation, possessed a high oxygen storage capacity (OSC) and a large specific surface area. The dissolution of ZrO_2 into CeO_2 results in an increase of OSC and in the retardation of grain growth. These two effects lead reduced CZS to a flaming oxidation at close to room temperature.

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1. Introduction

Ceria-based materials have been widely used in automotive exhaust emission control systems because of their high oxygen storage capacity (OSC).¹⁾ In particular, the $\text{CeO}_2\text{--ZrO}_2$ solid solution (CZS) has a much higher OSC than CeO_2 itself. Moreover, the rate of the oxygen storage/release of CZS is much higher than that of CeO_2 . Due to these characteristics, CZS has been applied to clean exhaust gas at lower temperatures.^{2),3)} As described above, the most important properties of the auxiliary catalysts are a high OSC and high oxygen storage/release rate.

CeO_2 transforms into Ce_2O_3 under hydrogen atmosphere at 1400°C, and reoxidizes rapidly in air to CeO_2 near room temperature.⁴⁾ This reaction is exothermic and can proceed spontaneously.

This rapid and intense reoxidation at close to room temperature is favorable for realizing a fast and large oxygen absorption ability, or for obtaining excellent auxiliary catalysts. This is expected to be very useful for the development of auxiliary catalysts, because the ability of a catalyst can be judged easily at the early stage of the development.

On the other hand, this rapid reoxidation at close to room temperature has been little reported for $\text{CeO}_2\text{--ZrO}_2$ solid solutions. Meriani, and Ingo and Righni reported that the reduced $\text{CeO}_2\text{--ZrO}_2$ solid solution was oxidized with rapid oxygen absorption and heat release, using thermogravimetric and differential thermal analysis.^{5),6)} However, these reactions were observed only around 200°C. This reoxidation temperature seems to be too high from the view point of the OSC and oxygen storage/release rate, and some detailed research on the oxidation behavior at close to room temperature of reduced $\text{CeO}_2\text{--ZrO}_2$ solid solution will be required.

The purpose of this work is to investigate in detail the oxidation of the reduced $\text{CeO}_2\text{--ZrO}_2$ solid solutions at close to

room temperature.

2. Experimental procedure

CeO_2 and $\text{CeO}_2\text{--ZrO}_2$ solid solutions were synthesized by the co-precipitation method using an aqueous solution containing the corresponding nitrates.⁷⁾ In this study, two kinds of powders with Ce/Zr=100/0 and 55/45 (molar ratio) were prepared. The powder with Ce/Zr=55/45 is the solid solution of CeO_2 and ZrO_2 , according to X-ray powder diffraction (XRD) analysis. The reduced powders were prepared by heating the powders in a graphite furnace under static argon. The reduction was conducted at temperatures of 800°C, 1000°C, 1200°C and 1400°C, for 8 h.

The reduced powders were cooled and kept in the furnace at room temperature for at least 24 h, and then they were exposed to static air.

The changes in weight and temperature during oxidation were measured as follows: The weight change was measured in the static atmosphere using an electronic balance, and the temperature change was measured by a chromel–alumel thermocouple inserted in the central part of the specimen powder. After the oxidation at room temperature, these powders were oxidized completely at 800°C for 8 h in flowing oxygen. The amount of oxygen before oxidation was calculated from the weight change during oxidation, assuming the cerium ions are all of the valence of +4 after the oxidation.

The crystalline phase was identified by the XRD method using the RIGAKU, RINT-2200 diffractometer with $\text{Cu K}\alpha$ radiation. The specific surface area was measured by Brunauer–Emmett–Teller (BET) method after the exposure to air.

3. Results and discussion

The results of oxidation in air at room temperature are shown in Table 1. The reduction temperatures before oxidation and heat release are also shown in the table. CeO_2 reduced at 1400°C was oxidized rapidly and much heat was released. Little heat release during oxidation was observed for CeO_2 reduced at temperatures lower than 1400°C . This result implies that the reduction of CeO_2 below 1200°C was not sufficient to cause the rapid oxidation at close to room temperature.

The reduction and oxidation behavior of CZS differed completely from that of CeO_2 . For CZS reduced at 800°C and 1000°C , the rapid oxidation with much heat release started immediately after the start of the exposure to air at room temperature. On the other hand, the rapid oxidation with marked heat release was not observed for CZS reduced at 1200°C and 1400°C .

The color of the CZS reduced at 1000°C changes during the exposure to air at room temperature with time, as shown in Fig. 1. The color of surface changed from gray to yellow within 1 min. The weight change with time is shown in Fig. 2. The measurement was started with the delay of 1 min after exposure to air because of the experimental restrictions. Then, the weight change between 0 and 1 min was estimated by extrapolating the subsequent weight change to the beginning of the exposure. The weight increase of CZS reduced at 1000°C was 1.77%, and that of CZS reduced at

1200°C was about 0.04% in spite of the higher reduction temperature. This result agrees with the heat release behavior shown in Table 1. On the other hand, the weight increase of CeO_2 reduced at 1400°C was 2.6%.

The CZS exposed to air at room temperature was completely oxidized at 800°C , and the weight change was measured. The amount of oxygen released during the reduction was calculated from the weight difference between the reduced and the completely oxidized CZS. The amount of oxygen released during the reduction is plotted against the reduction temperature in Fig. 3, and the compositions calculated from the amount of released oxygen are shown in Table 2. As shown in Fig. 3, the amounts of oxygen released from each mole of CeO_2 in CZS reduced at even 800°C and 1000°C are quite large compared with that in the case of CeO_2 itself. This large difference can be explained as the result of the replacement of Ce by Zr. The introduction of ZrO_2 into CeO_2 leads to the increase of the oxygen mobility and makes the reduction of Ce easier.^{2),3),8)-10)} This difference in the amount of oxygen released from CeO_2 and CZS by reduction at 800 and 1000°C can be related to the difference of the oxidation behaviors by the exposure to air at room temperature. However, the reason why the flaming oxidation of CZS reduced at 1200°C and 1400°C was not ob-

Table 1. Heat Releases of CeO_2 and CZS, Reduced at Temperatures between 800°C and 1400°C , during Exposure to Static Air at Room Temperature

Reduction Temperature / $^\circ\text{C}$	Heat release	
	CeO_2	CZS
800	none	intense
1000	none	intense
1200	none	slight
1400	intense	none

Fig. 2. Oxidation curves for reduced CZS (reduction temperature = 1000°C , 1200°C) during exposure to air at room temperature.

Fig. 1. Photographs of reduced CZS powder (reduction temperature = 1000°C) at various stages of the oxidation during exposure to air at room temperature.

served cannot be explained completely from this finding, because the amounts of oxygen released from CZS reduced at 1200°C and 1400°C were much larger than those from CZS reduced at 800°C and 1000°C

In Fig. 4, the specific surface areas of CeO₂ and CZS are plotted as a function of the reduction temperature. The surface areas of CeO₂ and CZS before reduction are 42.3 m²/g and 70.8 m²/g, respectively. The surface area of CeO₂ decreased to 0.26 m²/g by the reduction at 800°C. On the other hand, those of CZS did not decrease so much, and were 24 m²/g and 7 m²/g after the reduction at 800°C and 1000°C, respectively. The surface area of CZS after the reduction was much larger than that of CeO₂. This differ-

ence is considered to be due to the retardation of grain growth caused by the replacement of Ce by Zr in CZS.^{11),12)} The surface areas of CZS reduced at 1200°C and 1400°C decreased to 1.7 m²/g and 0.5 m²/g, respectively. The change in the surface area during the reduction at various temperatures is related to the difference in the oxidation behavior of CZS. An anomalous increase of the surface area was observed in CeO₂ reduced at 1400°C. In most oxides, the surface area will usually decrease with increasing temperature, however the surface area of the reduced CeO₂ exhibits the opposite change. The reason for this is not understood fully.

X-ray diffraction (XRD) patterns of CeO₂ and CZS reduced at various temperatures and reoxidized at 800°C are shown in Figs. 5 and 6. All observed diffraction peaks were assigned to a cubic structure, and the crystal structures of all powders after oxidation are almost the same.

Some powders, Fig. 5(e) and Figs. 6(e) and (g), gave a much larger lattice constant than others. These powders were reduced at high temperatures, but they did not exhibit the flaming oxidation during exposure to air. Therefore, they would contain a large amount of Ce³⁺ ions with numerous oxygen defects. The lattice constant of cerium oxides and the related oxides increases with increase in the amount of released oxygen due to the large change in ionic radii of Ce³⁺ from Ce⁴⁺.^{13),14)}

Diffraction profiles of CZS became sharper with increas-

Fig. 3. Amount of oxygen released during the reduction plotted against the reduction temperature.

Table 2. Compositions of CeO₂ and CZS Reduced at Various Temperatures before Exposure to Air. Composition was Calculated from the Weight Change before and after Oxidation

Reduction Temperature / °C	Sample	
	CeO ₂	CZS
800	CeO _{2.00}	Ce _{0.55} Zr _{0.45} O _{1.91}
1000	CeO _{1.99}	Ce _{0.55} Zr _{0.45} O _{1.87}
1200	CeO _{1.80}	Ce _{0.55} Zr _{0.45} O _{1.78}
1400	CeO _{1.71}	Ce _{0.55} Zr _{0.45} O _{1.75}

Fig. 4. Specific surface area of CeO₂ and CZS reduced at various temperatures plotted as a function of the reduction temperature.

Fig. 5. Powder XRD patterns of CeO₂. (a), (c), (e), (g) : Reduced at 800°C, 1000°C, 1200°C, 1400°C and oxidized at room temperature. (b), (d), (f), (h) : Reduced at 800°C, 1000°C, 1200°C, 1400°C and oxidized at 800°C.

Fig. 6. Powder XRD patterns of CZS.

(a), (c), (e), (g) : Reduced at 800°C, 1000°C, 1200°C, 1400°C and oxidized at room temperature.
 (b), (d), (f), (h) : Reduced at 800°C, 1000°C, 1200°C, 1400°C and oxidized at 800°C.

▼ indicates the positions of the peaks assigned to the ordered arrangement of Ce and Zr.

ing reduction temperature, therefore, the crystallinity of CZS should be improved with reduction temperature. The diffraction peaks assigned to the ordered arrangement of Ce and Zr ions were observed for the CZS reduced at temperatures higher than 1000°C.^{15),16)} This ordered structure is known as $\kappa\text{-CeZrO}_4$, and the previous studies on the OSC of CZS showed that the increase of OSC of CZS was caused by this ordered structure.^{16),17)} As shown in Fig. 3, the amount of oxygen released from CZS at higher than 1000°C is significant. This is considered to be due to the appearance of the ordered structure, $\kappa\text{-CeZrO}_4$.

The amount of released oxygen during the reduction and the specific surface area of the CZS after reduction, which released much heat during the oxidation at room temperature, were very large. Therefore, the heat release during oxidation at room temperature can be concluded to be intense in the CZS with much released oxygen and a large surface area during and after the reduction.

In addition to the high OSC, a high rate of oxygen storage and release is required for an auxiliary catalyst. The rate of oxygen storage and release can be assumed to depend on the specific surface area of the powders when the composition and structure are the same. Moreover, the materials, which release a larger amount of oxygen, may give a higher OSC. Therefore, the requirements for the materials to be used as auxiliary catalyst would be to release a large amount of oxygen and to possess a large surface area.

Based on these considerations, the materials which release much heat during oxidation are thought to be useful for realizing auxiliary catalysts. The materials would be helpful for making catalysts to clean exhaust gas at lower temperatures, which is required today for automobiles. The suitability of the materials for auxiliary catalysts can be determined in a short time by observing the reoxidation behavior at close to room temperature. CZS proved again to be an excellent material for the auxiliary catalysts compared with CeO_2 , because CZS was oxidized, releasing much heat after the reduction at lower temperatures.

The temperature changes during oxidation are shown in Fig. 7. The temperature of the CZS powder reduced at 1000°C increased up to 266°C during oxidation. The amount of the released heat was estimated from the temperature change as follows: The exact value of the specific heat of the reduced CZS has never been reported so far, therefore, it should be estimated by a suitable method. The specific heat

Fig. 7. Temperature changes of CZS reduced at 1000°C and 1200°C during exposure to air at room temperature.

at high temperatures can be given by Dulong-Petit's law.¹⁸⁾ According to the law, the specific heat is given by the sum of each component in one molecular formula, and is estimated to be 286 J/mol·K as below from the composition $\text{Ce}_{2.2}\text{Zr}_{1.8}\text{O}_{7.48}$, which is equivalent to that of CZS reduced at 1000°C shown in Table 2.

$$C_V(\text{Ce}_{2.2}\text{Zr}_{1.8}\text{O}_{7.48}) = 3 \times A \times R \quad (1)$$

$$= 3 \times (2.2 + 1.8 + 7.48) \times 8.31$$

$$= 286 \text{ (J/mol} \cdot \text{K)}$$

C_V : Specific heat at constant volume

R : Gas constant

A : Number of atoms in one molecular formula

Furthermore, from another point of view of the composition, the composition is very similar to that of pyrochlore, $\text{Ce}_2\text{Zr}_2\text{O}_7$, and the specific heat of the reduced CZS can be given as that of pyrochlore. The value is about 234 J/mol·K at 298 K and 275 J/mol·K at 500 K.¹⁹⁾ Both values of the two approaches are similar to each other. The slight difference would come from the difference of the amount of oxygen, 7.48 and 7. Then, the amount of heat is calculated as 70.4 kJ/mol, using the value given by Dulong-Petit's law, 286 J/mol·K, and the temperature rise (266°C) shown in Fig. 7.

Another estimation can be obtained from the standard free energy change, ΔG^0 , of the following reactions involv-

ing κ -CeZrO₄ on the basis of reported literature as follows (3):²⁰⁾

$$\Delta G^0 = -229020 + 120.1 T \text{ J/mol} \quad (3)$$

$$\Delta G = -193 \text{ kJ/mol} \quad (T = 298 \text{ K}) \quad (4)$$

ΔG was calculated as -193 kJ/mol at 298 K by inserting the temperature, $T = 298 \text{ K}$, into the formula (3). The above calculation is based on a composition between Ce₂Zr₂O₇ and Ce₂Zr₂O₈. Then, the weight increase in the Reaction (2) is 2.78%, however the actual weight increase is different from this value, as shown in Fig. 2. This difference would be due to the difference of the amount of oxygen shown in Table 2. On the assumption that the heat release is proportional to the amount of the absorbed oxygen, it can be estimated by using the above equation and the value of weight increase (1.23%) at the maximum temperature (266°C, in Fig. 7) as

$$193 \times (1.23/2.78) = 85.4 \text{ kJ/mol.} \quad (5)$$

This calculated value is slightly larger than that estimated from the specific heat and the temperature rise, 70.4 kJ/mol. Although these two values are slightly different from each other, they are considered to be consistent with each other, taking the heat flow from the powders to the container and atmosphere into consideration. Therefore, the flaming oxidation is also thought to be caused by the replenishment of the oxygen defects. The flaming oxidation with replenishment of oxygen defects without crystal change observed in this study seems to be very unique. This phenomenon is considered to be closely related to the rate and the magnitude of oxygen storage/release of CZS.

4. Conclusions

The flaming oxidation of reduced CeO₂-ZrO₂ solid solution (CZS) was observed in the near-room-temperature range. The temperature of the CZS powder reduced at 1000°C increased up to 266°C during oxidation and the weight increase was 1.77%. This flaming oxidation was observed when CZS was reduced at lower temperatures ($\leq 1000^\circ\text{C}$).

The material, which exhibited the flaming oxidation, possessed a high oxygen storage capacity (OSC) and a large specific surface area. The dissolution of ZrO₂ into CeO₂ results in an increase of OSC and in retardation of grain growth. These two effects lead reduced CZS to a flaming oxidation at close to room temperature. This flaming oxidation of the CZS powder is estimated to be caused by the replenishment of the oxygen defects which were formed as

a result of reduction of the CZS powder.

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