Reduction Behavior of CeO_2−ZrO_2 Solid Solution Prepared from Cerium Zirconyl Oxalate

Toshiyuki Masui, Yumin Peng, Ken-ichi Machida, and Gin-ya Adachi*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

CeO_2−ZrO_2 solid solutions were prepared by means of thermal decomposition of cerium zirconyl oxalate in an argon flow at 1273 K followed by oxidation at 673−873 K in air. The reduction behavior of the obtained CeO_2−ZrO_2 powders was investigated and compared with the samples prepared by the other methods already reported to yield CeO_2−ZrO_2 powders with high redox activity. The CeO_2−ZrO_2 samples prepared from the oxalate showed excellent reduction behavior, despite their very low surface areas. The reason for the excellent oxygen evolution behavior of the powders was discussed, from the viewpoints of the structure and the preparation process, and was attributed to both the appearance of a cubic phase with a different oxygen arrangement and the reduction by carbon formed in the sample preparation process.

1. Introduction

Recently, an environmental problem has been highlighted on a world scale. Among several causes of the destruction of the environment is automobile exhaust gas, and effective cleaning has been hoped for a long time. It is therefore notable that the simultaneous, effective conversion of the three main pollutants in the automobile exhaust gas, i.e., CO, NO_x, and hydrocarbons, to CO_2, N_2, O_2, and H_2O, can be achieved with a single heterogeneous catalyst system. Such a catalyst is called a three-way catalyst and it usually consists of precious metals (Pt, Rh, etc.), promoters (CeO_2, etc.), and supports (γ-alumina, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, etc.).[1,4] It is known that CeO_2 addition as a promoter provides an improvement in the performance of the three-way catalyst.[1,2] To establish high conversion efficiency in the three-way catalyst, the air to fuel (*A/F*) ratio has to be controlled near the theoretical value ($\approx$14.6) within a so-called "window",[1] and the operational width of the window is decided by the oxygen storage capacity (OSC) of CeO_2.[2] Since CeO_2 can easily absorb and desorb oxygen owing to its nonstoichiometric behavior,[3] it can provide oxygen under rich fuel conditions and absorb it under lean fuel conditions. As a result, the width of the window enlarges. Moreover, the addition of CeO_2 to the three-way catalyst provides other advantages such as thermal stabilization of the alumina support,[4] better noble metal dispersion,[5] and promotion of the water−gas shift reaction.[6] Therefore, CeO_2 is an indispensable component as a promoter in the three-way catalyst.

However, after an automobile catalyst has undergone thermally severe conditions, it deactivates by CeO_2 sintering. Many studies on the improvement of the performance of the promoter (CeO_2) in the three-way catalyst at high temperatures have been carried out, and it has been found that the reducibility and the thermal stability of CeO_2 are greatly enhanced by mixing with zirconium oxide to form CeO_2−ZrO_2 solid solutions.[7−14]

Recently, Fornasiero and co-workers[9] investigated the redox properties of a number of Rh-loaded $Ce_xZr_{1−x}O_2$ (*x* = 0.1−0.9) solid solutions prepared by a high-temperature solid-state reaction, and they observed a strong promotion of the reduction of the mixed oxide support due to the incorporation of ZrO_2 into the CeO_2 framework. Reduction of the support occurred in the bulk at temperatures between 600 and 700 K, which allows one to obtain high OSC notwithstanding the very low surface areas (about 1 m^2 g^{-1}) of the samples investigated. It was also clearly shown that the redox behavior of the $Ce_xZr_{1−x}O_2$ (*x* = 0.1−0.9) strongly depends on both the composition and the structure of

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the solid solution: the cubic $Ce_{0.5}Zr_{0.5}O_2$ sample was the easiest one to be reduced.

Moreover, they also disclosed that the $Ce_{0.5}Zr_{0.5}O_2$ mixed oxide also showed an unusual improvement of the redox behavior upon sintering induced by a repetitive reduction/oxidation of the solid solution.[10,11] They attributed this enhancement of the reducibility to an increased oxygen mobility in the bulk induced by the addition of the Zr into the CeO_2 lattice, which gives unusual redox properties to these systems.

Similar results were also reported by Yao and co-workers.[15] They employed a CeO_2-ZrO_2, which was reduced at 1323 K in Ar + H_2 + H_2O gas mixtures and reoxidized at 873 K in O_2 gas, and noted that the obtained CeO_2-ZrO_2 showed an unusual improvement of the reduction behavior over the samples only calcined in air. The evolution behavior of oxygen from the CeO_2-ZrO_2 powders at low temperatures was explained on the basis of the appearance of a new cubic κ phase.

In this paper, CeO_2-ZrO_2 solid solutions were prepared by thermal decomposition of the oxalate in an argon flow, followed by oxidation in air. The reduction behavior of the obtained CeO_2-ZrO_2 powders was investigated and compared with the samples prepared by the other methods already reported to obtain CeO_2-ZrO_2 powders with high redox activity. The aims are to prepare cubic $Ce_{0.5}Zr_{0.5}O_2$ by taking advantage of the thermal decomposition of the oxalate in an inert gas atmosphere and to verify the influence of the preparation process of the solid solution on the reduction process.

2. Experimental Details

2.1. Chemicals and Synthesis. Aqueous solutions of cerium nitrate (Shin-Nippon Kinzoku Kagaku Co., Ltd.) and zirconyl nitrate (Shin-Nippon Kinzoku Kagaku Co., Ltd.) were of purity >99.9%. Ammonium hydroxide (Nacalai Tesque, Inc.), acetone (Wako Chemical Co., Inc.), and oxalic acid (Wako Pure Chemical Industries Ltd.) of the best quality commercially available were used without further purification.

Cerium zirconyl oxalate powders were prepared by the coprecipitation method. Forty milliliters of the mixed solution of cerium nitrate and zirconyl nitrate was added to 55 mL of oxalic acid solution. The concentration of the cerium nitrate, zirconyl nitrate, and oxalic acid aqueous solution was fixed to 0.5 mol L^{-1}, and the mixing ratio of Ce:Zr was adjusted to 1:1. To facilitate the precipitation, 3 mol L^{-1} of ammonium hydroxide was added until the pH value of the solution became about 2. After settling overnight, the white precipitate was filtered, washed with water and acetone in succession, and dried with a heating mantle at 393 K. The cerium zirconyl oxalate powders were decomposed at 1273 K in an argon flow for 5 h, and the obtained CeO_2-ZrO_2 powders were calcined at 673–873 K in air for 2 h. Hereafter, the sample prepared from the oxalate is denoted "oxa-CeO_2-ZrO_2".

Cerium–zirconium hydroxide was also prepared by adding an ammonium hydroxide solution to a solution mixture of cerium nitrate and zirconyl nitrate. The mixing ratio of Ce:Zr was also adjusted to 1:1, and a CeO_2-ZrO_2 solid solution was obtained by calcining these hydroxides at 1173 K in air for 5 h. This sample is denoted "calcined CeO_2-ZrO_2" hereafter. In addition, a CeO_2-ZrO_2 sample reoxidized by oxygen after hydrogen reduction was prepared by a slight variation of the procedure described elsewhere.[15] The calcined CeO_2-ZrO_2 powders were heated in a flow of H_2 (1%) in Ar (25 mL

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Table 1. Composition and BET Surface Area Data for the CeO_2-ZrO_2

CeO_2-ZrO_2 sample	CeO_2 content/mol %	phase	BET surface area/m^2 g^{-1}
oxa	45	cubic	4
reduced/reoxidized	45	cubic	20
calcined	45	tetragonal	23

Table 2. Classification of the Phases in the CeO_2-ZrO_2 Binary System[11]

phase	composition range/% mol Ce	tetragnality[a]	space group
monoclinic (m)	0–20		$P2_1/c$
tetragonal (t)	20–40	>1	$P4_2/nmc$
tetragonal (t')	40–65	>1	$P4_2/nmc$
tetragonal (t'')	65–80	1	$P4_2/nmc$
cubic (c)	80–100	1	$Fm3m$

[a] Defined as axcial ratio c/a.

min^{-1}) at 1273 K for 5 h, and the obtained powders were reoxidized in an oxygen flow (25 mL min^{-1}) at 873 K for 5 h. This sample is denoted "reduced/reoxidized CeO_2-ZrO_2" hereafter. The reduction behavior of the oxa-CeO_2-ZrO_2 samples was compared with those of the calcined and the reduced/reoxidized CeO_2-ZrO_2.

2.2. Instruments and Characterization. The composition of the obtained CeO_2-ZrO_2 was identified by an X-ray fluorescence spectrometer (Rigaku System 3270A). The CeO_2-ZrO_2 particles were characterized by XRD using CuKα radiation (MAC Science M18XHF-SHA) and BET specific surface area (Micromeritics FlowSorb II 2300). FT-Raman spectra were obtained on the Ultimate Raman System (Jobin Yvon T64000). The spectra were exited with an Ar ion laser operating at 514.5 nm wavelength, and the laser power was 150 mW.

Temperature-programmed reduction (TPR) experiments of the CeO_2-ZrO_2 powders were carried out in a conventional gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector. Before the TPR experiment, the sample (15 mg) was preheated in He (25 mL min^{-1}) at 873 K for 5 h to eliminate the contribution of surface carbonates. Neither CO nor CO_2 evolution could be detected after the heat treatment. The reduction was carried out up to 1173 K in a flow of H_2 (60 mL min^{-1}) using a heating rate of 10 K min^{-1}. The amount of H_2 uptake in the TPR was estimated according to the methods described in refs 10 and 11, that is, it was calculated from the integrated peak areas by comparison with those obtained by using CuO as a standard.

3. Results

The sample composition of the CeO_2-ZrO_2 samples determined by an X-ray fluorescence spectrometer is summarized in Table 1 along with the BET specific surface area. Although the tendency for zirconium enrichment was detected in all samples, the Ce content in each sample was equal. The BET surface area of the sample prepared from the oxalate was smaller than those of the samples prepared from the hydroxide. The color of the sample obtained from the thermal decomposition of the oxalate in an argon atmosphere was black, but it changed to light yellow after the calcination.

The characteristics of all the phases of the CeO_2-ZrO_2 system were summarized by Fornasiero and co-workers,[11] as cited in Table 2. Below 1273 K, the phase diagram shows a single-phase region of monoclinic structure for the CeO_2 molar contents of less than 20%, while for the CeO_2 contents higher than 80% a cubic
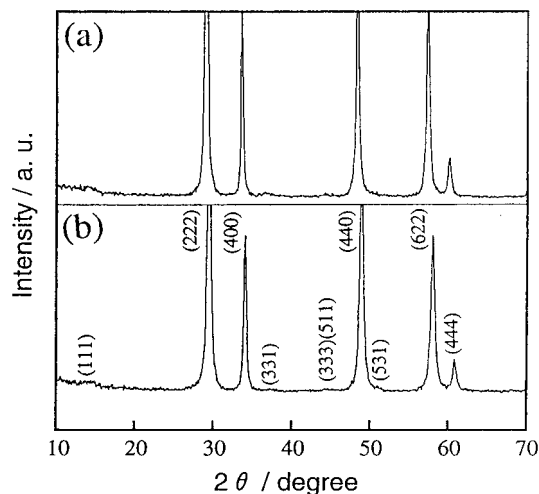
Figure 1. XRD patterns for the CeO₂−ZrO₂ powders prepared by the heating of the oxalate at 1273 K for 5 h in an Ar flow: (a) as-prepared, (b) after calcination at 673 K for 2 h.

phase was reported.[16,17] In the intermediate region, the true nature of the CeO₂−ZrO₂ phase diagram is still unidentified, due to the presence of many stable and metastable tetragonal phases.[16−19] According to the recent literature,[18,20−23] three different phase, t, t′, and t″, can be distinguished on the basis of XRD and Raman characterization. The t phase is stable and is formed through a diffusional phase decomposition. The t′ phase is obtained through a diffusionless transition and it is metastable. The t″ phase is generally referred to as a cubic phase because its XRD pattern is indexed in the cubic *Fm*3*m* space group. This is due to the fact that the XRD pattern is generated essentially by the cation sublattice.

Figure 1 shows the XRD patterns of the CeO₂−ZrO₂ powders prepared by the thermal decomposition of the coprecipitated oxalate in an argon flow. The traces a and b in Figure 1 showed the patterns of the powders before and after the calcination, respectively. The XRD pattern in Figure 1a is attributed to a cubic phase. The small peaks at about 36° and 44° in the XRD patterns are characteristic of a cubic pyrochlore-type structure.[24] Oxidation induced a contraction of the lattice because all the peaks in Figure 1b are shifted to higher angle compared to those in Figure 1a. Therefore, the pattern in trace b in Figure 1 is also attributed to a cubic phase. This is an interesting point, since it was reported that the oxygen mobility and desorption were strongly favored in the cubic structure compared to the tetragonal one.[9,15] The redox processes in the solid solution are associated with the Ce³⁺/Ce⁴⁺ couple, and the
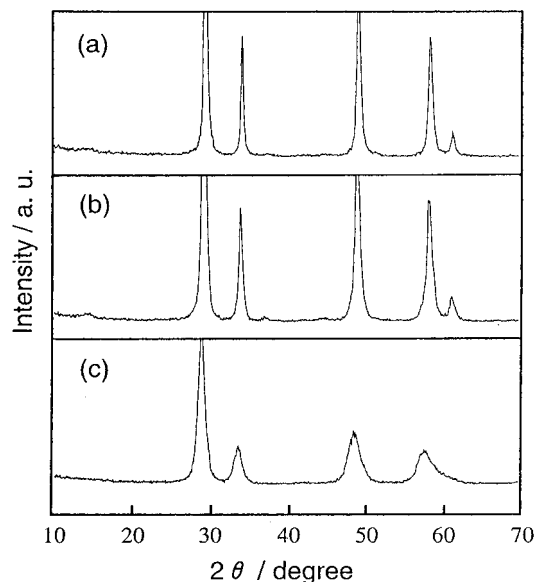
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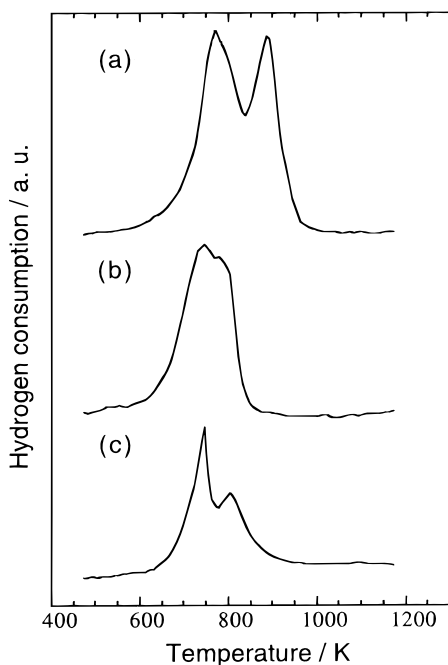(24) X-ray Powder Diffraction Standards, ASTM, Philadelphia, PA, Card 80-221 (Ce₂Zr₂O₇).

Figure 2. XRD patterns for the CeO₂−ZrO₂ powders: (a) oxa-CeO₂−ZrO₂, (b) reduced/reoxidized CeO₂−ZrO₂, and (c) calcined CeO₂−ZrO₂.

contraction of the lattice is therefore due to the oxidation from Ce³⁺ (0.11 nm) to Ce⁴⁺ (0.097 nm). From these results, it is suggested that the sample just prepared from the decomposition of the oxalate in an argon flow was highly reduced oxides, and they oxidized upon heating at 673 K in air, to maintain a cubic phase.

Figure 2 shows the XRD patterns of the oxa, reduced/reoxidized, and calcined CeO₂−ZrO₂. The pattern for the oxa-CeO₂−ZrO₂ shown in Figure 2a is the same one in Figure 1b, and it also completely corresponded to the pattern of the reduced/reoxidized CeO₂−ZrO₂ shown in Figure 2b. The XRD pattern is attributed to a cubic phase, and the small peaks at about 37° and 45° are also observed in both patterns. Therefore, the CeO₂−ZrO₂ solid solution prepared by the decomposition of the oxalate in an Ar atmosphere had the same cation arrangement as the one prepared by means of the hydrogen reduction of the oxide. Although Figure 2c also shows the cubic phase, it is attributed to the fluorite structure.

The effects of the preparation process on the reduction behavior of the CeO₂−ZrO₂ samples were examined by measuring the TPR profiles. The TPR spectra are shown in Figure 3, and the peak temperatures and total H₂ consumption are summarized in Table 3. The TPR profiles of the oxa-CeO₂−ZrO₂ samples showed two peaks centered at 773 and 888 K, respectively. The amount of H₂ consumption in a TPR spectrum which corresponds to oxygen evolution was estimated from the integrated peak area. Although the peak temperature of the second peak was higher than that of the reduced/reoxidized CeO₂−ZrO₂, the total amounts of H₂ consumption in the oxa-CeO₂−ZrO₂ samples were larger than those from the calcined and the reduced/reoxidized CeO₂−ZrO₂ in the temperature region between 573 and 973 K. The total amount of desorbed oxygen from the oxa-CeO₂−ZrO₂ sample was 1.5 times that of the reduced/reoxidized CeO₂−ZrO₂ sample, which showed more oxygen desorption than the calcined one. This clearly shows that the sample prepared by our method can be reduced more easily than those prepared by the

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Figure 3. TPR profiles of the CeO_2-ZrO_2 powders: (a) oxa-CeO_2-ZrO_2, (b) reduced/reoxidized CeO_2-ZrO_2, and (c) calcined CeO_2-ZrO_2.

Table 3. Composition and BET Surface Area Data for the CeO_2-ZrO_2

CeO_2-ZrO_2 sample	peak temperatures/K		H_2 consumption/mL g^{-1}
oxa	773	888	35.6
reduced/reoxidized	746	778	24.4
calcined	747	803	19.9

other methods, that is, the oxa-CeO_2-ZrO_2 evolves more oxygen than the others. After the TPR measurement, the oxa-CeO_2-ZrO_2 sample was calcined in air at 673 K and the TPR spectrum was measured again. The spectrum was reproducible.

It is generally accepted that the low-temperature reduction process is a reduction of the surface. Because the calcined and the reduced/reoxidized CeO_2-ZrO_2 have larger surface areas than the oxa-CeO_2-ZrO_2, the first reduction peak is lower by about 25 K. It has been also reported that a progressive decrease of surface area caused the low-temperature peak to decrease for the redox cycled $Ce_{0.5}Zr_{0.5}O_2$.[10,11] Since the BET surface area of the sample prepared from the oxalate was small, we attribute the peaks at 773 and 888 K to reduction processes in the bulk of the solid solution.

The Raman spectra of the CeO_2-ZrO_2 solid solutions are shown in Figure 4. The calcined CeO_2-ZrO_2 features a strong band centered at 473 cm^{-1} with weak bands at 137, 307, and 608 cm^{-1}. The peak at 473 cm^{-1} has been attributed[11] to the presence of a cubic phase, and the peaks observed at 137 and 307 cm^{-1} have been attributed to the t′ or the t phase. The spectrum for the reduced/reoxidized CeO_2-ZrO_2 (trace b in Figure 4) is almost same that reported in ref 11, and the spectrum for the oxa-CeO_2-ZrO_2 (trace a) was completely different from the others. The attribution of the peaks is difficult since oxygen displacement from the ideal positions in the fluorite structure affects the Raman spectrum. However, the Raman spectra in Figure 4 suggest that there is clear a difference in the arrangement of
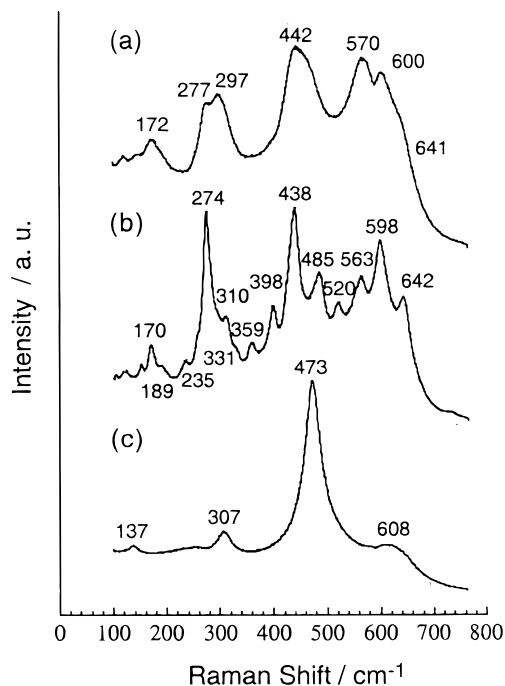

Figure 4. Raman spectra of the CeO_2-ZrO_2 powders: (a) oxa-CeO_2-ZrO_2, (b) reduced/reoxidized CeO_2-ZrO_2, and (c) calcined CeO_2-ZrO_2.

oxygen anions among the oxa, reduced/reoxidized, and calcined CeO_2-ZrO_2.

4. Discussion

Our data suggests that differences in the preparation process and oxygen arrangement of CeO_2-ZrO_2 are responsible for the unusual promotion of the reduction in the bulk of the oxa-CeO_2-ZrO_2. The change in reduction behavior in the CeO_2-ZrO_2 can be explained from a structural point of view.
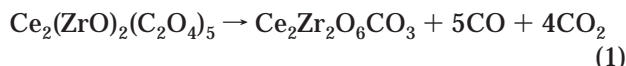
In view of the XRD results, the structure of the oxa and the reduced/reoxidized CeO_2-ZrO_2 seems to be the pyrochlore; however, pyrochlore is the precursor for both of them. The oxa-CeO_2-ZrO_2 was made by calcination of a precursor which gave the XRD pattern of the pyrochlore, as shown in Figure 1a. The reduced/reoxidized CeO_2-ZrO_2 was made by calcination of a precursor prepared by annealing at 1323 K in a reducing gas. It has been found that the CeO_2-ZrO_2 that has been reduced to the pyrochlore by hydrogen and then oxidized at 873 K mainly consists of a cubic phase in the composition range of 45−55 mol % of Ce.[15,25] This new cubic phase has been named the κ phase. Recently, it has been found that the precursor of the κ phase prepared at 1373 K has some additional peaks which are forbidden for the pyrochlore structure with the space group $Fd3m$.[25] This implies that the κ phase may not be belong to the $Fd3m$ space group due to the displacement of the oxygen atoms, although the cations take an ordered arrangement similar to the pyrochlore.

The different oxygen displacement may change the reduction of the CeO_2-ZrO_2 solid solutions. The appearance of the κ phase explains why the oxygen evolution behavior of the reduced/reoxidized CeO_2-ZrO_2

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is much better than that of the calcined CeO_2−ZrO_2.[15] This κ phase is formed by way of a pyrochlore $Ce_2Zr_2O_7$ solid solution which has a cubic structure with regular oxygen vacancies in the lattice. The cubic structure remains after the reoxidation, and as a result, the oxygen inserted in the lattice is unstable, enhancing oxygen mobility and desorption over a stable tetragonal structure.[9,13] The oxygen evolution behavior was the best in the 45−65 mol % composition range of ZrO_2 in which the κ phase appeared.

In the case of this study, the preparation process also contributed to the unusual promotion of the reduction. Taking into account the thermal decomposition of neodymium zirconyl oxalate,[26] the following scheme is proposed for the thermal decomposition of cerium zirconyl oxalate.

$$Ce_2(ZrO)_2(C_2O_4)_5 \rightarrow Ce_2Zr_2O_6CO_3 + 5CO + 4CO_2 \tag{1}$$

$$Ce_2Zr_2O_6CO_3 \rightarrow Ce_2Zr_2O_7 + CO_2 \tag{2}$$

In addition, the end products of the decomposition in an argon flow were black, suggesting the deposition of finely divided carbon particles. The same color was observed after the thermal decomposition of neodymium oxalate in a He atmosphere.[27] For neodymium oxalate, it was proposed[27] that the carbon particles are formed by the disproportion of CO gas that evolves during the thermal decomposition of $Ce_2(ZrO)_2O_3(CO_3)_2$ to $Ce_2Zr_2O_6CO_3$.

The black color shown by the sample after the oxalate decomposition could also be due to the reduction by the organic compounds and the carbon particles, since it is possible to detect the same effect on a ceria sample reduced by hydrogen at 1073 K and lower temperatures. The reduction by the organic compounds and the carbon takes place effectively on the whole of the sample because they are produced uniformly in the sample. Moreover, since the Gibbs free energy at 1273 K for the reduction of CeO_2 to Ce_2O_3 by carbon was lower than for the reduction by hydrogen or carbon monoxide,[28] thermal decomposition of the oxalate in an argon atmosphere would more effectively produce the pyro-

chlore $Ce_2Zr_2O_7$ solid solution than would the hydrogen reduction process.

After reoxidation, the sample prepared via oxalate decomposition has more unstable oxygen anions than that prepared via hydrogen reduction, and the excessive fine carbon particles are eliminated by the calcination process. This leads to a different oxygen displacement in the oxa-CeO_2−ZrO_2 than that in the reduced/reoxidized CeO_2−ZrO_2. Therefore, the CeO_2−ZrO_2 samples prepared from the oxalate have more OSC than do those prepared by the hydrogen reduction process. The use of the oxygen displacement to explain the difference in the reduction behavior is also supported by the Raman spectra.

5. Conclusions

CeO_2−ZrO_2 powders having a cubic phase were prepared by means of the thermal decomposition of cerium zirconyl oxalate in an Ar flow and followed by oxidation in air. The CeO_2−ZrO_2 showed an excellent reduction behavior at low temperature, and the total amount of desorbed oxygen was larger than for samples prepared by previously reported methods. We suggest that a structural modification of the oxygen anions in CeO_2−ZrO_2 increases the oxygen mobility in the lattice, which in turn enhances the redox properties of this catalytically interesting material. Therefore, the CeO_2−ZrO_2 prepared from the oxalate shows promise as a promoter for automotive exhaust catalysts.

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