NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Atmospheric pressure solvothermal synthesis of ceria–zirconia solid solutions and their large oxygen storage capacity

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Abstract Ceria–zirconia solid solution has a function as an oxygen storage material, which keeps air to fuel ratio (A/F) on a stoichiometric composition at the surface of three-way catalyst (TWC) for automotive exhaust. When A/F could be kept stoichiometric, TWC shows good catalytic activity. At first, ceria which dissolves 20 mol% of zirconia was developed by Ozawa et al. in 1987. After that, the ceria–zirconia solid solution was improved to achieve a complete solubility in the solid state at nano-level by surfactant modified homogeneous coprecipitation (J catal 169:490, 1997). Nano-level solid solution of ceria and zirconia could have been made by various methods. Those materials have similar amount of oxygen storage capacity (OSC). The improvement of OSC comes from the larger amount of bulk oxygen that can contributes OSC by the larger amount of zirconia dissolving into ceria (Catal Lett 33(1–2):193–200 1995). Solvothermal synthesis is usually done in a higher temperature than that can be reached under atmospheric pressure. The higher temperature accelerates generation of precipitation; however, a pressure vessel is necessary, and such a hermetically closed system is unsuitable to the material synthesis of the low-value-added product. Atmospheric pressure solvothermal (APS) synthesis was applied to ceria-zirconia solid solutions in this study. The APS ceria-zirconia showed larger amount of OSC. The excellent OSC performance was presumed to come from further uniformity of zirconium ions in the ceria lattice.

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Introduction

Three-way catalysts are overwhelmingly multiuse for exhaust purification in the world now. The three-way catalyst is used as a three-way catalyst system. The system is composed of the regulating system to always keep a stoichiometric composition of fuel and oxygen in the combustion gas by using the air flow meter, the electronic controlled fuel injector, and O_2 sensors, etc and the three-way catalyst. The three-way catalyst is used as a coating of its thickness from several 10 μm to hundreds on the surface of the honeycomb substrate made of cordierite or stainless steel. The composition of the three-way catalyst consists of precious metals such as platinum, rhodium, and palladium, catalyst supports such as gamma-alumina and the oxygen storage materials. The oxidation of CO and hydrocarbons, and the reduction of NO_x, are done at the same time in the three-way catalyst in which atmosphere is being kept at near chemically stoichiometric composition. However, the purification performance tends to deteriorate because the system by an electronic, mechanical control cannot follow to the rapid change of transient atmosphere when acceleration or deceleration, and the exhaust atmosphere come off from the stoichiometric value. Therefore, exhaust catalysts must have an oxygen storage capacity to keep chemical stoichiometry on the surface of the catalyst; the oxygen storage material is added to the three-way catalyst almost without exception. In the ceria-zirconia solid solution, a valence of the Ce ion can reversibly change; when Ce ion is reduced to Ce^{3+}, oxygen in the material can be released, and when Ce ion is oxidized to Ce^{4+}, oxygen can be absorbed. The reaction can continue reversibly and the oxygen storage and release capacity presents. In the first research in the latter half of 1980s, the effect of zirconia addition to ceria was discovered for increasing heat

resistance of ceria by keeping a high specific surface area during high temperature use [1, 2]. At the same time, Yashima et al. reported highly detailed information about crystal structures of ceria–zirconia solid solution phases [3–5]. Then, complete solubility in the solid state in ceria–zirconia binary system within nano-level crystallite was found [6–8]. It was clarified that complete solid solution including a higher content of zirconia than solubility limit showed an excellent oxygen storage capacity (OSC) [8–12]. Especially, ceria–zirconia solid solution having high specific surface area showed high OSC. Afterwards, it was reported that ceria–zirconia solid solution which has a high specific surface area could be synthesized by a variety of synthesis methods [13–16]. OSC of those materials were almost similar at 500 °C, and were very high compared with the material before. However, only a half of the theoretical limit value of OSC had been achieved. Theoretical limit value of OSC is defined as the value obtained when all of the contained Ce ions change their valence and contribute OSC. Exceptionally, it was reported that nearly theoretical limit value of OSC could be obtained in the reversible reaction between kappa-phase ($Ce_2Zr_2O_8$), beta-phase ($Ce_2Zr_2O_{7.5}$) and phi-phase (pyrochlore; $Ce_2Zr_2O_7$) [17, 18]. It is understood that the ordered arrangement of the Ce ions and the Zr ions in these crystal phases is unstable in the oxidation atmosphere. The ordered arrangement easily transforms into disordered normal fluorite structure in oxidation atmosphere [19–21]. On the other hand, an OSC near the theoretical limit value might be obtained in ceria-zirconia of a usual fluorite structure, when Ce ion would put in a state of infinite dilution in ZrO_2 [12]. So that if ultimate uniform dispersion of Ce ions would be achieved, a similar circumstance would be made around each Ce ion, and the theoretical OSC could be expected. The purpose of this research is to increase dispersivity of Ce ions and Zr ions each other in the fluorite structure of the ceria–zirconia solid solution, and to attempt to verify a hypothesis. The hypothesis is that uniform dispersion of Zr ions in the ceria–zirconia solid solution make the theoretical limit value possible in OSC.

Experimental procedure

Material preparation

The synthesis method used aqueous solution of cerium nitrate ($Ce(NO_3)_3$-$6H_2O$) and aqueous solution of zirconium oxide nitrate ($ZrO(NO_3)_2$-$2H_2O$). Concentration of each solution was 20 wt.% of CeO_2 and 20 wt.% of ZrO_2, respectively as an oxide. Both solutions were put into 100 mL of ethylene glycol at desired concentrations which are shown in Table 1. Then, the each ethylene glycol

Table 1 Desired concentration of starting solutions

CeO_2 (mol)	ZrO_2 (mol)	Ethylene glycol (mL)
0.179	0.0	100
0.161	0.018	100
0.148	0.037	100
0.133	0.057	100
0.118	0.079	100
0.102	0.102	100
0.084	0.126	100
0.065	0.152	100
0.045	0.180	100
0.023	0.211	100
0.0	0.234	100

solution was stirred by magnetic hot stirrer. The surface temperature of the plate of the stirrer was kept at 150 °C. A NO_x-like brown colored gas came out from the solution during the heating. The solution gelled at around 90 °C as a certain amount of water and ethylene glycol evaporated. The each gel was put in a calcination furnace and heated up 50 °C per hour up to 500 °C, and then the temperature was kept for 5 h. Finally, burned mass was pulverized into powder. Similar techniques are reported in a category of glycothermal process [22, 23]. The process in this study is classified in one of the solvothermal process with using glycol as a solvent. A significant difference of the process in this article from already existing glycothermal process is easy elimination of by-product of a reaction. It promotes the reaction efficiently. And also pressure vessel is not necessary.

Method of platinum loading

About 1 wt.% of Pt was loaded on each of the powder, pure CeO_2, pure ZrO_2, and CeO_2–ZrO_2 solid solutions, by impregnation process using acidic aqueous solution of $Pt(NO)_2(NH_3)_2$ and diluted nitric acid. Then they were heated at 500 °C for 5 h in air.

OSC measurement

Oxygen storage capacity was measured by thermo gravimetric analysis. A 15 mg of Pt-loaded catalyst powder was set up on a thermo gravimetric analyzer, SHIMADZU TGA-50. First of all the catalyst was reduced in 17% H_2 (N_2-balanced) with increasing temperature from room temperature to 500 °C, and was kept for 5 min. Next, the gas flow was switched from hydrogen to oxygen (29% O_2
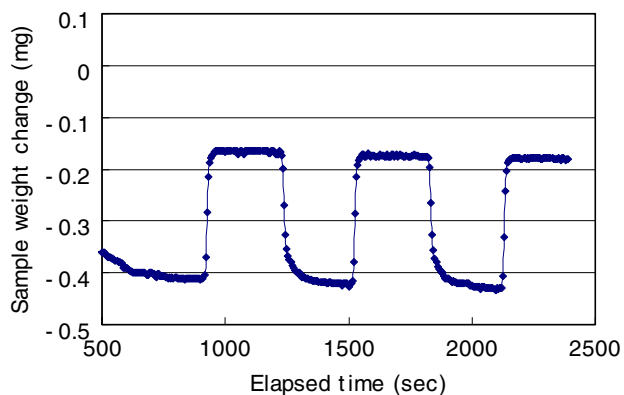
Fig. 1 An example of a TGA curve for the estimation of OSC of a CeO$_2$–ZrO$_2$ sample. This data corresponds to a composition of 50 mol% of CeO$_2$ and 50 mol% of ZrO$_2$

(N$_2$-balanced)), in which the temperature of the catalyst kept at 500 °C for 5 min. Then, the gas flow was switched again from oxygen to the former concentration of hydrogen and was kept for 5 min at 500 °C. The alternative gas flow switching was repeated at least 5 times. OSC was derived from the reversible weight loss and gain of a sample. The soaking time of 5 min is almost enough to attain saturation according to a previous work [24]. Figure 1 shows an example of a TGA curve for the estimation of OSC of a CeO$_2$–ZrO$_2$ sample. This data corresponds to a composition of 50 mol% of CeO$_2$ and 50 mol% of ZrO$_2$. The data shows both of the oxygen storage and release rate are largest just after a moment when their atmosphere is changed.

Identification of crystal phase

Identification of crystal phase was done by X-ray diffraction of Cu-Kα radiation with using RINT2200 (Rigaku Co. Ltd.).
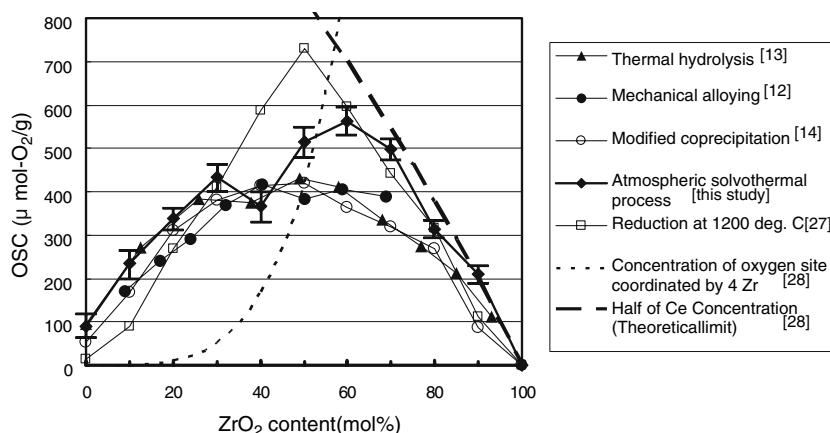
## Results and discussion

Relations of OSC and CeO$_2$/ZrO$_2$ molar ratio of five kinds of CeO$_2$–ZrO$_2$ complex oxide and two kinds of theoretical calculation are shown in Fig. 2. A calculation, half of Ce concentration corresponds to a theoretical value in which all of Ce ions contribute reduction and oxidation. Another theoretical value is concentration of oxygen sites coordinated by four Zr ions. The latter calculation is based on a hypothesis that the oxygen sites coordinated by four Zr ions are only effective at 500 °C. Other oxygen sites, coordinated by 3, 2, 1, or 0 Zr ions exist in the fluorite structure. They have higher oxygen stability and more difficult to be vacant than those coordinated by four Zr ions. This hypothesis was thought up via the report that oxygen sites coordinated by four Zr ions only active in pyrochlore structure [25]. As a coordination number of Zr increase, oxygen in the oxygen site is thought to become unstable. The reason is understood as follows; the ionic radius of Zr is too small to make a stable fluorite structure, so that the coordination number of Zr ion increase, free volume in the lattice also increase to make the oxygen stability lower. The OSC values of three kinds of the materials made by thermal hydrolysis [13], mechanical alloying [12], and surfactant-modified homogeneous coprecipitation [14] have some difference, though they are almost the same in a large sense. The OSC values of the material made in this study, atmospheric solvothermal synthesis, are obviously high in the composition range from 50 to 90 mol% of ZrO$_2$. Especially, in 70, 80, and 90 mol% of ZrO$_2$ composition, the OSC values are very close to the calculated value, half of Ce concentration. The OSC amplification effect of ZrO$_2$ in the CeO$_2$–ZrO$_2$ complex oxides bring out at a maximum in the materials made by atmospheric solvothermal synthesis. The OSC amplification effect of ZrO$_2$ in the CeO$_2$–ZrO$_2$ complex oxides is thought that smaller ionic radius of Zr ion moderates the strain caused by a reduction expansion of Ce ion

Fig. 2 Relations of OSC and CeO$_2$/ZrO$_2$ molar ratio of five kinds of CeO$_2$–ZrO$_2$ complex oxide and two kinds of theoretical calculation

Fig. 3 X-ray diffraction patterns of CeO$_2$–ZrO$_2$ complex oxide made by atmospheric pressure solvothermal synthesis
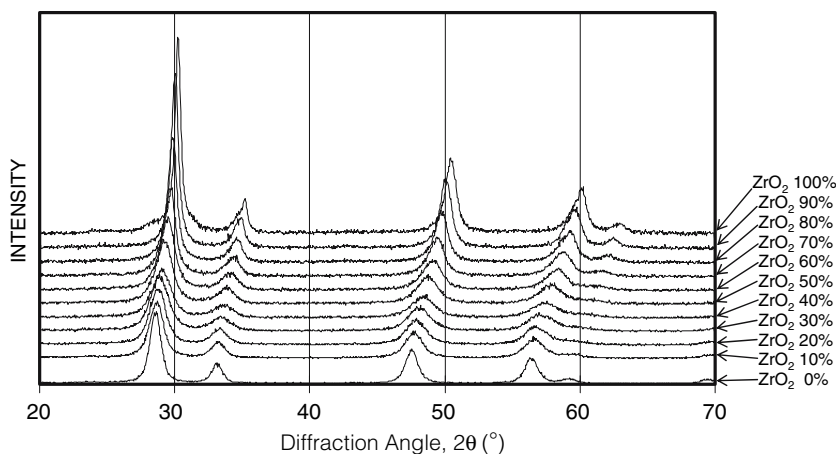
from Ce^{4+} to Ce^{3+} [12]. The moderation effect of Zr ion might be brought out at a maximum by uniform ZrO$_2$ dispersion in CeO$_2$ lattice. Therefore, the high OSC of this result represents that complete ZrO$_2$ dispersion might be achieved in the CeO$_2$–ZrO$_2$ solid solution made by atmospheric pressure solvothermal synthesis, especially in the composition range from 70 to 90 mol% ZrO$_2$. The OSC value of 60 mol% ZrO$_2$ of atmospheric pressure solvothermal synthesis shows highest OSC other than that of the material made by reduction at 1,200 °C. This trend coincides with the cross-point of the two kinds of calculated OSC value. This coincidence suggests the correctness of the understanding that coordination number of Zr ions of an oxygen site controls the stability of an oxygen ion in the site. However, the disjunction between the OSC value of 60 mol% ZrO$_2$ of atmospheric solvothermal synthesis and calculated OSC implies that this material has some faultiness left in it. A little nonuniformity of the Zr ion dispersion seems to remain in it. The extremely high OSC was achieved by reduction process at 1,200 °C. Such a high OSC of the material synthesized by reduction process at 1,200 °C comes from the uniform dispersion of Zr ions in cation-ordered structure in pyrochlore phase [26]. The cation-ordered structure of pyrochlore and cation-disordered structure of fluorite are totally different. The highest OSC can be earned at 50 mol% of ZrO$_2$ in pyrochlore structure [27], because in cation-ordered structure the two kinds of calculated values cross at 50 mol% of ZrO$_2$; the half of Ce concentration and the concentration of the oxygen site coordinated by four Zr ions are equivalent in pyrochlore structure, Ce$_2$Zr$_2$O$_7$. On the other hand, the highest OSC could be earned at 57 mol% of ZrO$_2$ in cation-disordered structure of the normal CeO$_2$–ZrO$_2$ solid solution [28].

Figure 3 shows XRD patterns of CeO$_2$–ZrO$_2$ mixed oxides made by atmospheric solvothermal synthesis. Data of Fig. 3 show peak shifts of each lattice plane which occur linearly with composition change. These samples consist of small size of crystallites under 10 nm and lattice constant of each composition follows Vegard' law. These points are almost the same as those of the materials made by above mentioned other synthesis methods. However, there is an extremely noteworthy point in the pattern of pure ZrO$_2$. In other synthesis methods, pure ZrO$_2$ have mixed state of tetragonal and monoclinic phase. But, data of Fig. 3 shows almost tetragonal phase only. This result implies that atomic level dispersed state was well quenched in a precursor of ethylene glycol complex of atmospheric solvothermal synthesis. XRD patterns of the materials including cation-ordered phases must have a totally different trend from those of Fig. 3 [27]. It is clear that the causes of higher OSC of CeO$_2$–ZrO$_2$ mixed oxides of Fig. 3 are obviously different from the existence of cation-ordered phases. It is natural to understand that the high OSC of the materials in Fig. 3 comes from the excellent uniformity of CeO$_2$ and ZrO$_2$ dispersion in atomic level. Further information is necessary to clarify the reason of high OSC performance of the material made by atmospheric pressure solvothermal synthesis.

Conclusions

A new synthesis method, atmospheric pressure solvothermal synthesis, was designed. Novel CeO$_2$–ZrO$_2$ solid solutions, which have nearly theoretical limit value of OSC, were synthesized by using the new synthesis method in the composition range from 70 to 90 mol% ZrO$_2$. The mechanism of the large OSC is speculated as uniform dispersion of CeO$_2$ and ZrO$_2$ in the material, however, it is different from the uniformity in ordered cation structures of pyrochlore (Ce$_2$Zr$_2$O$_7$) and kappa-phase (Ce$_2$Zr$_2$O$_8$). Further study will be necessary to prove the understanding about the high OSC correct or not. At least, this novel process is clearly beneficial to the synthesis of high performance OSC material.

References

1. Ozawa M, Kimura M, Isogai A (1993) J Alloys Compd 193:73
2. Miyoshi N, Matsumoto S, Ozawa M, Kimura M (1989) SAE Paper 891970
3. Yashima M, Morimoto K, Ishizawa N, Yoshimura M (1993) J Am Ceram Soc 76(7):1745–1750
4. Yashima M, Ohtake K, Kakihana M, Yoshimura M (1994) J Am Ceram Soc 77(10):2773–2776
5. Kakihana M, Kato S, Yashima M, Yoshimura M (1998) J Alloys Compd 280(1–2):125–130
6. Suda A, Kandori T, Terao N, Ukyo Y, Sobukawa H, Sugiura M (1998) Mater Sci Lett 17:89–90
7. Suda A, Kandori T, Ukyo Y, Sobukawa H, Sugiura M (2000) J Ceram Soc Jpn 108:473–477
8. Suda A, Sobukawa H, Suzuki T, Kandori T, Ukyou Y, Sugiura M, Kimura M (1995) Japanese patent 3341973 filed on 1995
9. Balducci G, Fornasiero P, DiMonte R, Kaspar J, Meriani S, Graziani M (1995) Catal Lett 33(1–2):193–200
10. de Leitenburg C, Trovarelli A, Zamar F, Maschio S, Dolcetti G, Llorca J (1995) J Chem Soc Chem Commun 2181
11. Trovarelli A, Zamar F, Llorca J, de Leitenburg C, Dolcetti G, Kiss JT (1997) J Catal 169:490
12. Suda A, Sobukawa H, Suzuki T, Kandori T, Ukyo Y, Sugiura M (2001) J Ceram Soc Jpn 109:177–180
13. Hirano M, Suda A (2003) J Am Ceram Soc 86:2209–2211
14. Sugiura M, Ozawa M, Suda A, Suzuki T, Kanazawa T (2005) Bull Chem Soc Jpn 78:752–767
15. Colon G, Pijolat M, Valdivieso F, Vidal H, Kaspar J, Finocchio E, Daturi M, Binet C, Lavalley JC, Baker RT, Bernal S (1998) J Chem Soc Faraday Trans 94(24):3717–3726
16. Terribile D, Trovarelli A, Llorca J, de Leitenburg C, Dolcetti G (1998) Catal Today 43(1–2):79–88
17. Otsuka-Yao-Matsuo S, Omata T, Izu N, Kishimoto H (1998) J Solid State Chem 138(1):47–54
18. Sasaki T, Ukyo Y, Kuroda K, Arai S, Muto S, Saka H (2004) J Ceram Soc Jpn 112(1308):440–444
19. Nagai Y, Yamamoto T, Tanaka T, Nonaka K, Suda A (2003) Proc 92th Annual Meeting Catal Soc Jpn
20. Nagai Y, Yamamoto T, Tanaka T, Yoshida S, Nonaka T, Okamoto T, Suda A, Sugiura M (2001) J Synchrotron Radiat 8(2):616–618
21. Suda A, Ukyo Y, Yamamura K, Sobukawa H, Sasaki T, Nagai Y, Tanabe T, Sugiura M (2004) J Ceram Soc Jpn 112(11):586–589
22. Feldmann C, Jungk HO (2001) Angew Chem Int Ed 40(2):359–362
23. Fievet F, Lagier JP, Figlarz M (1989) MRS Bulletin Dec p 29
24. Suda A, Yamamura K, Sobukawa H, Ukyo Y, Tanabe T, Nagai Y, Dong F, Sugiura M (2004) J Ceram Soc Jpn 112(12):623–627
25. Thomson JB, Armstrong AR, Bruce PG (1996) J Am Chem Soc 118:11129–11133
26. Nagai Y, Yamamoto T, Tanaka T, Yoshida S, Nonaka T, Okamoto T, Suda A, Sugiura M (2002) Catal Today 74(3–4): 225–234
27. Suda A, Ukyo Y, Sobukawa H, Sugiura M (2002) J Ceram Soc Jpn 110(2):126–130
28. Suda A, Yamamura K, Ukyo Y, Sasaki T, Sobukawa H, Tanabe T, Nagai Y, Sugiura M (2004) J Ceram Soc Jpn 112(1311): 581–585