A Cu-added Zr-Ce-Sn-Pr-O mixed oxide phase with a high oxygen storage capacity

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Abstract. Phases, oxygen release and absorption behaviour was investigated for Zr-Ce-Sn-Pr-O mixed oxides \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Sn}_{y/8}\text{Pr}_{(6-x-y)/8})\text{O}_{2-z} \) \((x=1.5, 4.5, y=0.5)\) together with the effect of Cu addition. Major phases of Sn-added samples were similar to those of Sn-free \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Pr}_{(6-x)/8})\text{O}_{2-z} \) phases, that is, CaF2-like \( \lambda \) and C phases for Pr-rich and Ce-rich compounds, respectively. All samples contained a SnO2 or a Sn phase. When Cu was added, repetitive oxidation and reduction appeared to promote the fine dissolution of Sn and Cu through bulk phases. OSC values of both \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Pr}_{(6-x)/8})\text{O}_{2-z} \) and \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Sn}_{y/8}\text{Pr}_{(6-x-y)/8})\text{O}_{2-z} \) were larger than those of the corresponding Sn-free samples. For the Ce-rich sample, Cu addition improved both the OSC value and its on-set temperature.

1. Introduction

Oxide materials that have high oxygen storage capacity (OSC) at low temperatures and that possess high thermal stability at high temperatures are indispensable for use as advanced automotive exhaust catalysts. Zr-Ce-O mixed oxide is currently used as an OSC material [1-2]. Candidates for high efficiency OSC materials should have compositions of \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Pr}_{(6-x)/8})\text{O}_{2-y} \) \((x=0-6)\) because small amounts of Ce stabilize single phases of \( \lambda-(\text{Zr}_{0.25}\text{Pr}_{0.75})\text{O}_{2-y} \) that have a broad oxygen nonstoichiometry. One may expect that the addition of cations of three valence states: 0, +2 and +4 rather than Ce ions with +3 and +4 under a conventional atmosphere may be effective. We thus investigated different phases and their oxygen release behaviour for Zr-Ce-Sn-Pr-O mixed oxides \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Sn}_{y/8}\text{Pr}_{(6-x-y)/8})\text{O}_{2-z} \) \((x=1.5, 4.5, y=0.5)\). Another approach to improve the OSC property may be the addition of noble catalytic metals such as Cu but not rare-elements such as Pt. We have recently discovered that Cu addition greatly improved OSC behaviour at temperatures lower than 573 K for Zr-Ce-Pr-O mixed oxides [3]. An interesting feature was that Cu addition induced a striking change in the phase structure of the bulk oxide. In this study, the phases of Cu-added Zr-Ce-Sn-Pr-O mixed oxides \( (\text{Zr}_{2/8}\text{Ce}_{x/8}\text{Sn}_{y/8}\text{Pr}_{(6-x-y)/8})\text{Cu}_{0.5/8}\text{O}_{2-z} \) \((x=1.5, 4.5, y=0.5)\) as well as their oxygen release and absorption behaviour were investigated. Samples were subjected to XRD and the release and absorption properties were determined by OSC analysis and TPD oxygen gas analysis by means of TG/DTA in Ar+5% H2 gas.
2. Experimental

2.1. Preparation of sample powders and OSC measurements

Zr(NO₃)₂, Ce(NO₃)₃, Pr(NO₃)₃, and SnCl₄ were dissolved in water so that the solution concentration of the composition corresponding to \[(\text{Zr}_{2/8}\text{Ce}_{x}\text{Sn}_{y}\text{Pr}_{(6-x-y)/8})\text{O}_{2-z}\] was 100 g/L. To obtain hydroxides of Zr⁴⁺, Ce⁴⁺ and Pr⁴⁺ the same molar quantity of H₂O₂ as the molar quantity of the metal elements was added to the aqueous solution. The aqueous mixture was added dropwise to ammonia-water to enable uniform precipitation. The hydroxide mixture was calcined at 673 K after filtration and washing. Cu was then added as a Cu(NO₃) solution by an impregnation technique and calcined at 673 K. Powder samples were annealed at 1473 K in air for 1 h. These powders were then reduced at 1373 K in H₂ gas. The powders were oxidized again at 973 K in air. Sample phases obtained through these reduction and oxidation processes were examined using the powder XRD analysis technique. As described below for TPD analysis it has been previously found that oxygen release was greatly improved by repetitive reduction and oxidation [3]. Oxide powders that were re-oxidized at 973 K in air were thus used as samples for OSC measurements. OSC was measured using a gas adsorption device (Ohkura Riken Inc.:BP-1). Powder samples of 0.5 g were loaded into a special measurement cell and heated to preset temperatures (373 K to 973 K). Samples were reduced by passing H₂ gas for 0.9 ks. The gas was then substituted by passing He gas for 0.3 ks. Finally, 1 cm³ of O₂ gas was introduced into the cell several times using a pulse and the total amount of oxygen absorbed by the samples was measured by TCD (Thermal Conductivity Detector).

2.2. TPD oxygen gas analysis

Oxygen release behaviour was examined using TG/DTA equipment (Seiko Instruments Inc.: TG/DTA 6300). The hydroxide was calcined at 673 K and then annealed in O₂ gas at 1373 K. Powders of 100 mg were loaded into a platinum crucible and heated from 303 K to 773 K at a rate of 5 K(60 s)⁻¹ in an O₂ gas atmosphere. The sample powders were then cooled to 303 K at a rate of 5 K(60 s)⁻¹ in O₂ gas. The O₂ gas was then replaced by Ar for 0.9 ks. An Ar+5%H₂ atmosphere mixture was then used. After 7.2 ks, samples were heated from 303 K to 1373 K at a rate of 5 K(60 s)⁻¹ (1st TPD oxygen analysis). The samples were then maintained at 1373 K for 10.8 ks and cooled to 303 K over 13.2 ks. The samples were then heated to 773 K in O₂ gas at a rate of 5 K(60 s)⁻¹ and then cooled to 303 K followed by the 2nd TPD oxygen analysis in a flowing Ar+5%H₂ gas mixture. This operation was repeated three times. The oxygen discharge rate and reproducibility were improved greatly by repeating this operation. In this research, the result of the 3rd oxygen release experiment was adopted as the discharge characteristic of oxygen.

3. Results and Discussion

Figure 1 and Figure 2 show XRD patterns for Pr-rich and Ce-rich samples subjected to repetitive oxidation and reduction, respectively. As seen in those figures, when Cu was not added, major phases for the samples containing Sn resembled those for the Sn-free sample [3]. The main diffraction peaks for \[(\text{Zr}_{2/8}\text{Ce}_{1.5/8}\text{Sn}_{0.5/8}\text{Pr}_{4/8})\text{O}_{2-z}\] and \[(\text{Zr}_{2/8}\text{Ce}_{4.5/8}\text{Sn}_{0.5/8}\text{Pr}_{1/8})\text{O}_{2-z}\] could be identified based on CaF₂ structures and were therefore attributed to the λ and C phases for Pr-rich and Ce-rich compounds, respectively. In the case of the Pr-rich composition, the A-Pr₂O₃ phase appeared after reduction. The appearance of a λ phase for the Pr-rich composition, λₚr, after re-oxidation at 973 K resulted from the uneven dissolution of A-Pr₂O₃ into the λ phase [3]. The reduction process in H₂ gas promoted the precipitation and growth of the Sn metal phase. Thus, the XRD peaks of SnO₂ that were observed in the oxidation atmosphere increased during repetitive reduction and oxidation.

For all samples prepared in this work, when Cu was added, the pyrochlore-like phase appeared together with λ and C phases for Pr-rich and Ce-rich compositions, respectively. We have recently investigated the effect of Cu addition on the phase states for \[(\text{Zr}_{2/8}\text{Ce}_{x}\text{Pr}_{(6-x)/8})\text{Cu}_{0.5/8}\text{O}_{2-y}\] with various Pr and Ce composition ratios and we found that the pyrochlore-like phase appears together with a CaF₂-type phase in the composition range of 0<x<5 [3]. The lattice constant of the latter phase was
almost unaffected by the appearance of the pyrochlore-like phase. Our current results are consistent with this previous report. A small change in the lattice constant of the \( \lambda \) phase by Cu addition may be attributed to the effect of Sn. For both Pr-rich and Ce-rich samples, the diffraction peaks due to SnO\(_2\) showed an obvious decrease with Cu-addition. The appearance of Cu-Sn compounds for the Ce-rich sample may be an important feature. We found that the Cu\(_6\)Sn\(_5\) phase decreased faster than the Cu\(_3\)Sn phase by repeating the successive reduction and oxidation several times. This result confirms that Cu and Sn ions gradually disperse into the bulk oxide by repetitive oxidation and reduction.

**Figure 1** XRD patterns of Pr-rich Zr-Ce-Sn-Pr-O mixed oxide powders obtained by repetitive oxidation and reduction and compared with those of Cu-added Zr-Ce-Sn-Pr-O mixed oxide powders. (a): (Zr\(_{2/8}\)Ce\(_{1/8}\)Sn\(_{0.5/8}\)Pr\(_{1/8}\))O\(_{2/3}\), (b): (Zr\(_{2/8}\)Ce\(_{1/8}\)Sn\(_{0.5/8}\)Pr\(_{1/8}\))Cu\(_{0.5/8}\)O\(_{2/3}\); (i): annealed at 1473 K in air; (ii): reduced at 1373 K in H\(_2\) gas after annealing at 1473 K in air; (iii): re-oxidated at 973 K in air. ○: \( \lambda \)-phase, #:\( \lambda \)pr, †:pyrochlore-like, ■:SnO\(_2\), □:Sn, ▼:A-Pr\(_2\)O\(_3\), ▲:CuO, ×:Cu.

**Figure 2** XRD patterns of Ce-rich Zr-Ce-Sn-Pr-O mixed oxide powders obtained by repetitive oxidation and reduction and compared to those of Cu-added Zr-Ce-Sn-Pr-O mixed oxide powders. (a): (Zr\(_{2/8}\)Ce\(_{4.5/8}\)Sn\(_{0.5/8}\)Pr\(_{1/8}\))O\(_{2/3}\), (b): (Zr\(_{2/8}\)Ce\(_{4.5/8}\)Sn\(_{0.5/8}\)Pr\(_{1/8}\))Cu\(_{0.5/8}\)O\(_{2/3}\); (i): annealed at 1473 K in air; (ii): reduced at 1373 K in H\(_2\) gas after annealing at 1473 K in air; (iii): re-oxidation at 973 K in air. ●: C-phase, ‡:pyrochlore-like, ■:SnO\(_2\), □:Sn, ▲:CuO, ▼:Cu\(_6\)Sn\(_5\), ×:Cu\(_3\)Sn.

Figure 3 shows OSC data for Pr-rich and Ce-rich samples. OSC values for samples containing Sn were larger than those for the corresponding Sn-free samples. The on-set temperature shifted to a lower temperature. For the Ce-rich sample, Cu-addition further improved the OSC value and its on-set temperature and this result is in line with the fact that SnO\(_2\) and CuO particles are distributed throughout the bulk phase after repetitive reduction and oxidation. Figure 4 shows TPD results used to obtain oxygen release properties as measured by TG/DTA. The weight loss of samples and the slopes of their graphs with time correspond to the total amount of oxygen released and the release rate.

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respectively. As seen in the figure for the Ce-rich composition both the total amount and rate of oxygen release increased according to the following order: Sn-free < Sn-addition < (Sn+Cu)-addition. This result is consistent with the OSC data shown in Figure 3(b). However, the on-set temperature for the TPD data did not increase in this order. Further investigation of the chemical properties of oxide samples with fine precipitation is needed.

Figure 3 OSC data plotted against temperature. (a): Pr-rich composition, (b): Ce-rich composition.

4. Conclusion
For Cu-added samples, Cu$_6$Sn$_5$ and Cu$_3$Sn phases were formed during reduction at 1373 K in H$_2$ and successive oxidation appeared to promote a fine distribution of Sn and Cu ions throughout the bulk phases. Improvement of OSC values and on-set temperatures may be attributed to a change in the phase-state. We expect that a fine distribution of oxide phases would lead to highly durable automobile catalysts and a reduction in the amount of noble metals used in them.

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