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Microstructure and oxygen release properties of catalytic alumina-supported CeO_2–ZrO_2 powders

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Abstract

This paper describes the phase analysis and oxygen release characteristics of catalytic mixed oxides in the system of CeO_2–ZrO_2/Al_2O_3 heated at 800°C. The potential oxygen storage capacity is improved by the addition of ZrO_2 to CeO_2 in the case of alumina-supported oxides that are easy to prepare by wet impregnation process.

Keywords: Catalysis; CeO_2; ZrO_2; Oxygen storage capacity; Three-way catalyst

1. Introduction

A three-way catalyst (TWC) for automobile exhaust treatment generally operates in a narrow range of air–fuel ratio (A/F). A common catalyst consists of precious metals (Pt, Rh, etc.), promoters and supports such as transition aluminas. One of the most important promoters, CeO_2, plays the role of oxygen storage capacity (OSC) that provides oxygen for oxidizing CO and HC, and reduces NO_x under fluctuating A/F [1–4]. The system of CeO_2–ZrO_2 is more effective to improve oxygen release and storage properties, resulting in high performance for TWC [5–15]. A practical catalyst is generally a composite powder with multi-components as solid-state materials. The materials aspects of such catalytic composite powders are important for the advancement of performance and optimization of practical catalysts. This paper describes the phase analysis and oxygen release characteristics of catalytic promoters in a CeO_2–ZrO_2/Al_2O_3 system in the temperature range up to 800°C.

2. Experimental

Starting powdered γ-Al_2O_3 support had a surface area of 135 m^2/g and a purity of 99.9%. The dried Al_2O_3 powder was immersed into the aqueous mixed solutions of cerium (Ce) nitrate and zirconium (Zr) oxynitrate with various Ce/Zr ratios, followed by agitation of the suspension. The suspensions were dried at 110°C for 8 h, and heated at 500°C for 3 h in air. The Ce–Zr-impregnated γ-Al_2O_3 powder was ground again and further heated at 800°C for 3 h in air. The mixtures were prepared of $(Ce_{1-x}Zr_xO_2)_{0.3}(Al_2O_3)_{1.0}$ where x is 0–1. A powder X-ray diffraction (XRD) apparatus (Rigaku, Rint2000, Japan) with a Cu Kα source (20 kV–30 mA) was used for the characterization of phases formed in samples. The morphology of powders was examined by transmission electron microscopy (TEM, JEOL-2000cx). Potential automotive catalytic performance was tested by oxygen release characteristics of powders under dry air ($P_{O_2} = 0.2$ atm) at temperatures of 30–800°C. The change of weight for a ca. 0.5-g sample was monitored by thermogravimetry (TG) measurement under cyclic heat treatment in flowing air. The heat cycle consisted of a first heating treatment to 800°C, cooling to 150°C, and a second heating treatment to 800°C. All heating and cooling rates were 5°C/min. The weight loss of samples in the second heating TG data was used as a measure of oxygen release properties of the composite powders between 300 and 800°C.

3. Results and discussion

Table 1 summarizes the phase and surface area of powder fabricated from impregnation process for x in a series of $Ce_{1-x}Zr_xO_2/Al_2O_3$ which was heated at 800°C for 3 h in air. The heat treatment temperature (800°C) corresponds to the moderate thermal conditions of practical automotive exhaust gases. The XRD data (Fig. 1) indicated

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Table 1
The phase and surface area of $Ce_{1-x}Zr_xO_2/Al_2O_3$ powders heated at 800°C in air for 3 h[a]

x in $Ce_{1-x}Zr_xO_2/Al_2O_3$	Phases	Surface area (m^2/g)
0	c-CeO_2 + γ-Al_2O_3	63
0.2	c-CeO_2 s.s. + γ-Al_2O_3	65
0.5	c-CeO_2 s.s. + t-ZrO_2 s.s. + γ-Al_2O_3	73
0.7	c-CeO_2s.s. + t-ZrO_2 s.s. + γ-Al_2O_3	75
1.0	t-ZrO_2 + γ-Al_2O_3	86

[a] t, tetragonal; m, monoclinic; c, cubic; s.s., solid solution.

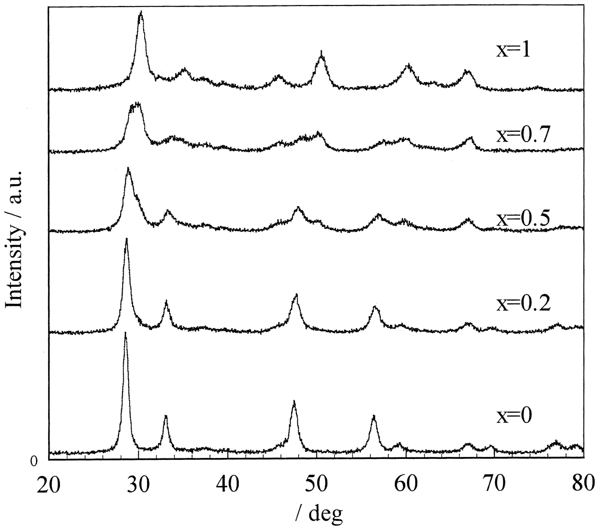

Fig. 1. The XRD profiles of $Ce_{1-x}Zr_xO_2/Al_2O_3$ powders with $x = 0$–1, heated at 800°C.

the formation of cubic CeO_2–ZrO_2 solid solution (s.s.) in $x < 0.3$, the mixed phases of CeO_2-rich cubic and ZrO_2-rich tetragonal solid solutions in the central region of composition, and a single phase of tetragonal ZrO_2 s.s. at $x = 1.0$. The phase separation, depending on x, is explained by previous phase diagrams [16–20]. TEM revealed the various morphologies of composite powders; two separated agglomerates in Ce-rich composition, while well-dispersed Ce–Zr oxides on supports were observed for Zr-rich powders. The surface area was higher as the ratio of Zr to Ce increased (Table 2).

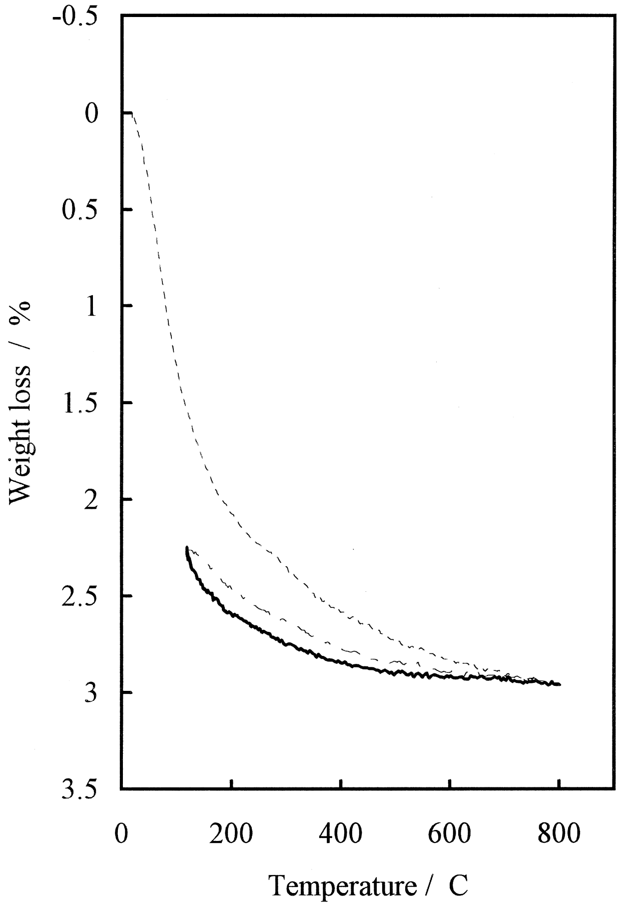

Fig. 2. A plot of the decrease of weight versus temperature at 300–800°C, measured in flowing air for $Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ powder: (· · ·) the first heating, (– · – · –) cooling, and (—) the second heating stages.

Fig. 2 shows a typical curve of TG measurement for $Ce_{0.5}Zr_{0.5}O_2/Al_2O_3$ heated at 800°C. The first heating treatment induced a large decrease of weight, corresponding to the release of both water molecules (from surface) and oxygen (from CeO_2–ZrO_2). The recovery of weight was seen in a cooling back stage. A small decrease of weight was observed in the second heating step. The weight loss in the second heating stage at the temperature range of 300–800°C corresponds to the potential oxygen release capacity of powders in ordinary air atmosphere. Depending on temperature at $P_{O_2} = 0.2$ atm, a part of cerium ion (Ce^{4+}) in CeO_2 changes to Ce^{3+}. This idea for the evaluation is essentially the same as described in previous research of oxygen storage capacity (OSC) on ceria-based oxide [21–24].

Table 2
The weight loss of $Ce_{1-x}Zr_xO_2/Al_2O_3$, and the corresponding increase of oxygen vacancy concentration, δ, in $Ce_{1-x}Zr_xO_{2-\delta}$ during heat treatment in the temperature range of 300–800°C in flowing air

x in $Ce_{1-x}Zr_xO_2/Al_2O_3$	Weight loss (%)	δ
0	0.13	0.04
0.2	0.26	0.08
0.5	0.45	0.14
0.7	0.2	0.06
1.0	0.06	0.02

The reaction of oxygen release from CeO_2 is described as,

$$CeO_2 \rightarrow Ce_2O_3 + 1/2O_2 \tag{1}$$

Table 2 lists the measured value of weight loss for $Ce_{1-x}Zr_xO_2/Al_2O_3$, and the oxygen vacancy content of CeO_2–ZrO_2 (on alumina) which are induced through heat treatment (at 300–800°C). Since the value of vacancy content is very small, the reaction must be written for oxides with oxygen vacancy content δ and little structural change as the following,

$$Ce^{4+}_{1-x}Zr_xO_2 \text{ s.s.} \rightarrow (Ce^{4+}_{1-2\delta}Ce^{3+}_{2\delta})_{1-x}Zr_xO_{2-\delta} \text{ s.s.} + \delta/2\,O_2 \quad (2)$$

The results (Table 2) indicate the increase of oxygen vacancy when the content of ZrO_2 increases in the range of $x=0$–0.5. The potential OSC is improved by the addition of ZrO_2 to CeO_2 in the case of alumina-supported oxide powder. In addition, the ratio of δ to Ce content largely increases as x increases in $Ce_{1-x}Zr_xO_2/Al_2O_3$. For example when $x=0.5$, the ratio becomes as 7 times large as that in CeO_2/Al_2O_3 ($x=0$). This means that the balance of Ce^{4+} versus Ce^{3+} at 800°C is shifted to the Ce^{3+}-rich side in solid solution containing ZrO_2. The redox potential (to practical reducing state versus temperature) of Ce becomes lower with increasing x in $Ce_{1-x}Zr_xO_2$ in the range of $x=0$–0.5.

This anomaly is practically useful for the development of the OSC component, CeO_2–ZrO_2/Al_2O_3. The ZrO_2 addition is able to increase the amount of active oxygen or induce the lower redox potential of Ce ion for OSC at 300–800°C. Several workers have already claimed the importance of the solid solution in the CeO_2–ZrO_2 system [5–15]. Also, the effect of support of ZrO_2 for CeO_2 or some structural interaction of them has been discussed. The more practical system of CeO_2–ZrO_2–Al_2O_3, including this work, has a very complex microstructure and/or interaction between compositions. Also, we should finally point out that the control of microstructures is also an important factor for the improvement of OSC in this system. Fig. 3 shows a TEM photograph of CeO_2–ZrO_2/Al_2O_3 the microstructure of which depends on the content of ZrO_2 in CeO_2. The CeO_2/Al_2O_3 powder contained CeO_2 particles mixed with Al_2O_3 support. On the other hand, the small aggregate of CeO_2–ZrO_2 as supported on alumina was observed in CeO_2–ZrO_2/Al_2O_3. The trend of agglomeration in CeO_2–ZrO_2 depends on the ratio of Ce and Zr in the starting aqueous solutions. The relationship between microstructure and activity for catalysis awaits more detailed investigation. Here, we have provided positive results for the use of alumina-supported OSC mixed oxides (the CeO_2–ZrO_2–Al_2O_3 system) that are very easy to fabricate in practical TWC products.

4. Conclusion

This work described the phase analysis and oxygen release properties of catalytic promoters from a wet impregnation process in CeO_2–ZrO_2/Al_2O_3 heated at 800°C. The heat-induced release of oxygen during the heating process of composite oxides at 300–800°C was improved by ZrO_2 addition when x is lower than 0.5. The potential OSC was improved by the addition of ZrO_2 to CeO_2 in alumina-supported oxide promoters which are easy to prepare in practical TWC.

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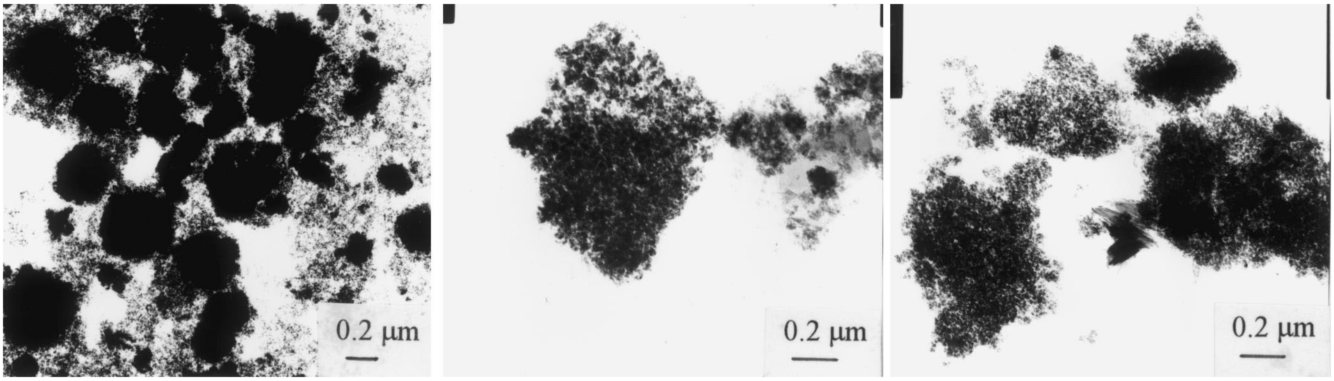

Fig. 3. Transmission electron micrograph of $Ce_{1-x}Zr_xO_2/Al_2O_3$ powders: (a) $x=0$, (b) $x=0.5$, (c) $x=1.0$.

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