Effect of additive component on activity of ceria-based catalysts for soot combustion

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Abstract: Ceria-based oxides have been investigated as promising materials for diesel particulate combustion. In this study, we focused on cobalt and/or lanthanum-added ceria catalysts. The cobalt-added and cobalt–lanthanum-added ceria catalysts exhibited higher activity than ceria. The role of the additive components in the combustion reaction was examined by oxygen exchange reaction tests using oxygen isotope. The cobalt additive promoted the oxygen exchange, especially at low temperatures. The lanthanum-added ceria catalyst showed the larger exchange amount of oxygen than ceria.

Keywords: Soot combustion, Ceria, Oxygen isotope.

1. Introduction

Diesel engines have been widely used as energy conversion technologies due to their superior fuel efficiency, low emission of CO_2, and high durability. However, nitrogen oxides (NO_x) and particulate matter (PM) in the exhaust gas can cause environmental and health problems. Diesel particulate matter is mainly composed of soot (carbon), organic compounds, and sulfate. The elimination of PM is accomplished using diesel particulate filters (DPFs). In the DPF system, catalysts coated on the filter oxidize the trapped PM for the regeneration of filter.

The development of catalysts for the PM combustion has attracted the interest of many researchers. Ceria-based materials are one of the promising catalysts for the soot combustion due to the prominent property to store and release oxygen. Many studies have reported that the addition of transition metal and rare earth elements to ceria improved the catalytic activity for the soot oxidation because of the enhancements of oxygen storage/release capacity and surface area[1–4]. In this study, we focused on the additive effect of cobalt and lanthanum elements on the catalytic activity of ceria for the soot combustion. The role of the additives in the combustion reaction was examined by oxygen exchange reaction tests using oxygen isotope of $^{18}O_2$.

2. Experimental

The catalysts of ceria and cobalt and/or lanthanum-added ceria were synthesized by the citric acid complex method. Commercial nitrates of $Co(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and $Ce(NO_3)_3 \cdot 6H_2O$ were used as starting materials. Citric acid was added to an aqueous solution of the nitrates in a molar ratio of 1.1:1.0 to the metal cation. After evaporation at 90 ºC, the obtained precipitate was heated at 350 ºC for 1 h and then calcined at 650 ºC for 5 h. The resulting samples are hereafter represented as CeO_2, Co–Ce oxide, La–Ce oxide, and Co–La–Ce oxide. The atomic ratios of Co and La to metal elements were 5% and 10%, respectively, for the mixed oxides. The crystal structure of samples was studied by x-ray diffraction (XRD).

A carbon black (Cabot Inc., V–XC72R, surface area: 224.0 $m^2\ g^{-1}$) was applied as a model diesel soot for the evaluation of combustion reaction. The sample under tight contact condition was fabricated by mixing the catalyst and carbon black with a weight ratio of 4:1. The oxidation behavior of carbon black over the ceria-based catalyst at 200–500 ºC in air by thermogravimetric (TG) analysis. Prior to the measurement, nitrogen was supplied with a flow rate of 100 ml min^{-1} during heating the sample at 300 ºC for 1 h to remove the absorbed water.

The oxygen exchange reaction for the prepared catalysts was conducted at constant temperatures using closed-circulation reactor with the following procedure. The sample was heated at 500 ºC for 3 h in 100 kPa

He, followed by the treatment at desired temperature for several hours in 100 kPa $^{16}O_2$. After cooling to room temperature, the sample was kept for 1 h and then heated again up to the desired temperature in vacuum. Finally, the sample was exposed to 1.4 kPa $^{18}O_2$ at the temperature. The oxygen species in the reactor were analyzed by a mass spectrometer.

3. Results and discussion

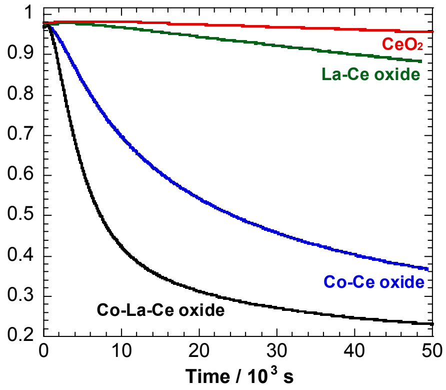
The resulting materials were examined by XRD. The results revealed that the cobalt additive was highly dispersed on the ceria-based oxides and the lanthanum additive was incorporated into the ceria lattice to form a solid solution. The carbon oxidation over the prepared catalysts was studied in air by TG analysis. The order of activity was as follows: Co–La–Ce oxide > Co–Ce oxide > CeO_2 oxide > La–Ce oxide.

The oxygen exchange behavior of the catalysts was evaluated with the closed-circulation reactor. Figure 1 shows time courses of ^{18}O–isotope fraction in the gas phase inside the reactor during isothermal oxygen isotope exchange reaction at 300 ºC and 400 ºC. The fraction of ^{18}O–isotope in the gas phase (α) was defined as the following equation.

$$\alpha = \frac{n_{18}}{n_{16}+n_{18}} = \frac{1}{2}C_{34} + C_{36} \qquad (1)$$

where n_{16} and n_{18} are the number of ^{16}O and ^{18}O, respectively, and C_{34} and C_{36} are the molar fraction of $^{16}O^{18}O$ and $^{18}O_2$, respectively, in the gas phase inside the reactor. The samples containing cobalt additive exhibited much higher oxygen exchange capacity than the other oxides at 300 ºC, indicating that the cobalt additive promoted the oxygen exchange reaction. On the other hand, a large number of oxygen in the La–Ce oxide was exchangeable at 400 ºC. This implied that the doping of lanthanum element to ceria increased the amount of oxygen species, which were readily incorporated and released between the sample surface and the gas phase, and were easily mobile in the lattice of sample. Combined with the previous report[4], the oxygen species would react with carbon at the interface between cobalt compontent and ceria-based material, and the lanthanum-doped ceria should incorporate oxygen species from the gas phase into the lattice and supply the active oxygen species to the interface in the Co–La–Ce oxide catalyst.

(a) 300 °C



(b) 400 °C

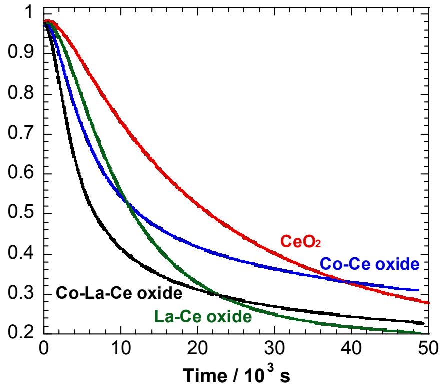


Figure 1. Fraction of ^{18}O–isotope in the gas phase *vs.* time in isothermal oxygen isotope exchange reaction at (a) 300 ºC and (b) 400 ºC. Reaction atmosphere: pO_2 = 1.4 kPa.

4. Conclusions

The cobalt and/or lanthanum-added ceria catalysts were investigated in terms of the carbon oxidation and the oxygen exchange reactions. The obtained results indicated that the carbon oxidation was promoted at the interface between the cobalt compontent and ceria-based material. The doping of lanthanum species into ceria should facilitate the incorporation of oxygen species into the lattice and the supply of the active species to the interface in the cobalt–lanthanum-added ceria catalyst.

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