Cobalt doped ceria-zirconia supported paradium-alumina catalyst with high oxygen storage capacity for CO oxidation

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Abstract. The Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_2$/Pd-Al$_2$O$_3$ composite prepared by a mechanochemical route with high BET surface area of 33 m$^2$ g$^{-1}$, exhibited the high oxygen storage capacity (OSC), and high CO oxidation activity at the low temperatures even after calcination at 1000˚C for 20 h.

1. Introduction

Ceria (CeO$_2$)-based materials have attracted considerable interests for more than half a century for its far-ranging applications in catalysts, fuel cell, cosmetics, gas sensors, solid-state electrolytes, and especially the crucial application as promoters of three-way catalysts (TWCs), which are commonly used to reduce the emissions of CO, NO$_x$, and hydrocarbons from automobile exhausts$^{[1-9]}$ because of their excellent oxygen storage capacity (OSC). In the last two decades it has been established that the partial incorporation of Zr$^{4+}$ into CeO$_2$ lattice results to form Ce$_x$Zr$_{1-x}$O$_2$ mixed oxides, which show enhanced structural/textural features and redox properties with improved thermal stability at elevated temperatures$^{[10-12]}$. For example, Fornasiero et al. have reported that an optimum composition, like Ce$_{0.5}$Zr$_{0.5}$O$_2$ can exist as a cubic phase, which can have excellent redox property$^{[13]}$. The most important role of Ce$_x$Zr$_{1-x}$O$_2$ is to store and release oxygen in minimizing the fluctuation of the air-to-fuel (A/F) ratio under transient conditions, and this is accomplished by the transformation of cerium chemical states between Ce$^{4+}$ and Ce$^{3+}$.

At present, Al$_2$O$_3$ supported CeO$_2$-based materials have been extensively used and proven to be the most advanced materials for TWCs$^{[14-18]}$. Due to the lower cost and superior oxidation properties to Pt and Rh, Pd has been widely used in TWC formulations$^{[19]}$. When supporting Pd on a binary Ce$_x$Zr$_{1-x}$O$_2$/Al$_2$O$_3$ support several factors, such as thermal stability of support, surface CeO$_2$ sites, and interaction with CeO$_2$-Al$_2$O$_3$, can affect the catalytic performance$^{[20]}$. Pd supported on binary Ce$_x$Zr$_{1-x}$O$_2$/Al$_2$O$_3$ support is a common approach to study this interaction. Using Pd /Ce$_x$Zr$_{1-x}$O$_2$/Al$_2$O$_3$ model catalyst, Ranga Rao et al. showed that CeO$_2$ promoted NO and CO conversion through Pd-Ce interaction$^{[21,22]}$. On the other hand, by comparing with Pd-Ce interaction, Martínez-Arias et al. reported that Pd-Al$_2$O$_3$ interaction promoted NO reduction with a minor impact on CO oxidation$^{[23,24]}$. However, there are few reports on the relationship between OSC and catalytic activities (simultaneous oxidation of CO, hydrocarbon, and reduction of NO$_x$). Moreover, after the high-temperature treatment for the long time, the retention of reduction behavior for the TWCs remains elusive because of a loss...
Consequently, in terms of the practical application as an automotive exhaust catalyst, the new OSC material with enhanced OSC is a requisite for developing advanced TWCs.

In the present work, on the basis of previous work, we describe the preparation of a new oxygen storage capacity material of Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$/Pd-Al$_2$O$_3$ (designated as CeZrCo/P-A) catalysts via a mechanochemical route. CeO$_2$/Pd-Al$_2$O$_3$ (designated as Ce/P-A) and Ce$_{0.5}$Zr$_{0.5}$O$_2$/Pd-Al$_2$O$_3$ (designated as CeZr/P-A) catalysts were also prepared via the same method as the reference materials. All samples were finally calcined at 1000 °C for 20 h in air.

2. Experimental section
The stoichiometric amounts of (NH$_4$)$_2$Ce(NO$_3$)$_6$, ZrO(NO$_3$)$_2$ and Co(NO$_3$)$_2$ were dissolved in 60 ml distilled water. NH$_4$OH solution was slowly dropped into the above mixed solution, and the pH value was maintained at 9. The yellow mixed solution was introduced in a 100 ml Teflon®-lined autoclave, which was maintained at 200°C for 24 h, then cooled to room temperature naturally. The obtained products were washed with distilled water and dried in air at 100°C for 12 h to form the Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$. Then, Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$/Pd-Al$_2$O$_3$ catalysts were prepared by mechanically mixing Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$ and 2 wt % Pd-Al$_2$O$_3$ powder, (Weight ratio of Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$Pd-Al$_2$O$_3$=50:50). Finally, all samples were finally calcined at 1000 °C for 20 h in air. The same synthesis route was employed for the preparation of the CeO$_2$/Pd-Al$_2$O$_3$ and Ce$_{0.5}$Zr$_{0.5}$O$_2$/Pd-Al$_2$O$_3$.

The morphology and size of the samples were determined by a transmission electron microscopy (TEM, JEOL JEM-2010). High resolution transmission electron microscopy (HRTEM) images were obtained on a ZEISS LEO 922 with an accelerating voltage of 200 kV. The specific surface area and pore size were measured using BET analysis (NOVA 4200e).

The OSC of catalysts was determined using a thermogravimetric differential thermal analysis (TG-DTA, Rigaku TAS-200). Before the measurements, the samples were held in flowing air at 600°C for 30 min to remove residual water and other volatile gases. The mixed gas of CO-N$_2$ (100 cm$^3$ min$^{-1}$) and air (100 cm$^3$ min$^{-1}$) was flowed alternatively at 150-600°C.

The CO oxidation activity of the synthesized sample was evaluated in a fixed-bed flow reactor by passing gas mixtures of 2 vol.% CO in N$_2$ and 2 vol.% O$_2$ in N$_2$ at a rate of 500 cm$^3$ min$^{-1}$ over 0.15 g sample. The sample was pressed, crashed and sieved to obtain granules of 212 to 355 µm in diameter and mounted into a quartz tube reactor of 6 mm in diameter. The samples were heated at a heating rate of 10°C min$^{-1}$ from room temperature to 600 °C. A gas FTIR spectrometer (MIDAC Co., IGA-4000) was employed for in situ analysis of gas composition. The conversion of CO was obtained by using the formula XCO = (1-[CO] / [CO]$_0$) × 100 %, where [CO]$_0$ and [CO] are initial and transient concentration of CO, respectively.

3. Results and discussion
The morphology and crystalline growth of samples were confirmed by TEM images (Figure 1). The crystalline sizes of CeZr and CeZrCo on Pd-Al$_2$O$_3$ were about 60 and 45 nm, respectively. However, the Ce/P-A exhibited large particle size of 100-150 nm as shown in Table 1.

![Figure 1. TEM images of (a) Ce/P-A, (b) CeZr/P-A and (c) CeZrCo/P-A samples.](image-url)
Table 1. Particle sizes, BET specific surface areas, and OSC values (600 °C) of Ce/P-A, CeZr/P-A and CeZrCo/P-A samples.

| Chemical composition | Particle size (nm) | Surface area (m² g⁻¹) | OSC (µmol-O g⁻¹) |
|----------------------|-------------------|------------------------|------------------|
| Ce/P-A               | 100-150           | 9                      | 142              |
| CeZr/P-A             | 60                | 22                     | 456              |
| CeZrCo/P-A           | 45                | 33                     | 614              |

The BET nitrogen adsorption-desorption analysis was undertaken to measure the specific surface area of as-prepared samples. As a result, the CeZrCo/P-A displayed much higher specific surface area (33 m² g⁻¹) than Ce/P-A (22 m² g⁻¹) and CeZr/P-A (9 m² g⁻¹) as shown in Table 1.

Figure 3. Oxygen release/storage properties (TG profiles) of (a) Ce/P-A, (b) CeZr/P-A and (c) CeZrCo/P-A samples at 600 °C.

The OSC values of the samples were determined at 600 °C with a continuous flow of CO-N₂ gas and air alternatively. Figure 3 shows the typical oxygen release/storage profiles of the Ce/P-A, CeZr/P-A and CeZrCo/P-A samples at 600 °C with time. CeZrCo/P-A exhibited the highest OSC of 614 µmol-O g⁻¹, when compared with those of Ce/P-A (142 µmol-O g⁻¹) and CeZr/P-A (456 µmol-O g⁻¹) samples (Table 1). Moreover, the temperature-dependent OSC was evaluated by increasing the temperature in a stepwise manner from 150 to 500 °C, as shown in Figure 4, it is indicated that the OSC increased with temperature for all samples, and CeZrCo/P-A showed higher OSC than those of CeZr/P-A and Ce/P-A at the same temperature, for example, OSC values of Ce/P-A, CeZr/P-A and CeZrCo/P-A were 26, 128 and 216 µmol-O g⁻¹ at 300 °C, respectively.

Figure 4. OSC values of (a) Ce/P-A, (b) CeZr/P-A and (c) CeZrCo/P-A samples at different temperatures.
In the present work, higher surface area is exhibited by CeZrCo/P-A whenever compared with CeZr/P-A and Ce/P-A. The CeZrCo/P-A show considerably higher oxygen storage capacity than CeZr/P-A and Ce/P-A. The enhanced OSC is not only due to the high surface area but also due to chemical state of the Ce and Co species in the materials, which is the involvement of Ce$^{4+}$/Ce$^{3+}$ and Co$^{3+}$/Co$^{2+}$ redox couples utilized for CO oxidation.

Figure 5. CO oxidation activity curves of (a) Ce/P-A, (b) CeZr/P-A and (c) CeZrCo/P-A samples.

The activity curves of CO oxidation for all samples are plotted in Figure 5. Comparing with the light-off temperatures of Ce/P-A (295°C) and CeZr/P-A (283°C) CeZrCo/P-A showed the lowest light-off temperature of 274°C, indicating that CeZrCo/P-A was the most active catalyst. It is recognized that the OSC at low temperature can store and release oxygen in minimizing the fluctuation of the air-to-fuel, which can contribute to the oxidation of CO, that is one of the reactions of interest in the catalysis process of the automotive exhaust cleaning process. Based on these results, it can be suggested that the high OSC activities at low temperatures (200-300 °C) play an important role in the oxidation of CO at low temperatures, in other words, the order of activity is directly related to the OSC of the catalysts, which demonstrates that catalyst with higher OSC at low temperature possesses superior activity for CO oxidation.

4. Conclusion
In summary, a new OSC material of Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$/Pd-Al$_2$O$_3$ is prepared via a mechanochemical method. Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$/Pd-Al$_2$O$_3$ showed the high OSC even after calcination at 1000°C for 20 h. Studies using CO oxidation as a model reaction, showed that the high oxidation activity of the sample at low temperatures correlates with their enhanced OSC. The prepared Ce$_{0.5}$Zr$_{0.4}$Co$_{0.1}$O$_{1.95}$/Pd-Al$_2$O$_3$ has the potential to be a key material in advanced catalytic converters in the design of excellent three-way catalysts (TWCs).

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