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# Role of Surface Adsorption in Fast Oxygen Storage/Release of $CeO_2$ -$ZrO_2$ Mixed Oxides

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**Abstract**: Four kinds of $CeO_2$-$ZrO_2$ mixed oxides, i.e., a physical mixture of ceria and zirconia (CZP), zirconia-coated ceria (ZCC), ceria-coated zirconia (CCZ) and a chemical mixture of ceria and zirconia (CZC), were prepared. The oxygen storage capacity (OSC) measurements at 500 ℃ were performed under transient and stationary reaction conditions. All the curves of $CO_2$ evolution during CO-$O_2$ cycles presented a bimodal shape. The first peak was primarily the result of the reaction of CO with the oxygen from the oxides, which was mainly determined by the nature of the material. The second peak was mostly related to the $CO_2$ adsorption behavior and was highly influenced by the surface area and the number of surface active sites. As a result, OSC activity of the samples followed in the order of CZC > CCZ > ZCC ≈ CZP.

**Key words**: $CeO_2$-$ZrO_2$; microstructure; surface properties; oxygen storage capacity; rare earths
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$CeO_2$ has been widely employed in automotive three-way catalysts (TWCs) as an oxygen storage component via the $Ce^{3+}/Ce^{4+}$ redox couple. The introduction of Zr cations into the ceria lattice, resulting in the formation of structural defects and hereby high mobility of bulk oxygen ions, shows higher oxygen storage capacity (OSC) and better resistance to thermal and redox aging[1]. Local structure around Ce and Zr is believed to be a determining factor of the OSC of $CeO_2$-$ZrO_2$ mixed oxides. Mamontov et al. [2] reported that aged $Ce_{0.5}Zr_{0.5}O_2$ revealed an intracrystalline nanodomain structure consisting of nanoscale compositional heterogeneity. The OSC was correlated with the domain size, i.e., the interfacial area between $CeO_2$ and $ZrO_2$ enriched regions rather than with the surface area of the samples. It was also concluded from the quantitative curve-fitting analysis of external X-ray absorption fine structure (EXAFS) that homogeneous $Ce_{0.5}Zr_{0.5}O_2$ solid solutions at atomic level exhibited higher OSC than the mixture of pure $CeO_2$ and $ZrO_2$ and $CeO_2$-$ZrO_2$ solid solutions with the Ce- and Zr-rich domain[3,4].

On the other hand, specific surface area plays an important role in oxygen storage/release process for pure ceria as the OSC is attributed mainly to the release of surface oxygen[5]. However, no consensus opinions have been achieved on the role of surface area in $CeO_2$-$ZrO_2$ mixed oxides. In some studies, the surface area is not suggested to be a determining factor for total OSC[6,7]. Whereas, Hori et al.[8] suggested that surface processes, rather than migration of oxygen in bulk, were limiting the reduction process rate

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In this study, four kinds of $CeO_2$-$ZrO_2$ mixed oxides with the same composition (Ce/Zr = 1) were prepared. The microstructure was characterized by XRD, BET, TEM and XPS, and the oxygen release performance was investigated using CO-$O_2$ cycle and CO step measurements.

## 1 Experimental

### 1.1 Catalyst preparation

In order to prepare the so-called zirconia-coated ceria (ZCC) sample, coarse $CeO_2$ powders were added into aqueous ammonia as precursors. $ZrO(NO_3)_2$ solution was added and vigorously stirred. The precipitate was filtered and washed with deionized water, followed by drying at 110 ℃ overnight and calcination at 500 ℃ for 3 h in static air. Similarly, the ceria-coated zirconia (CCZ) sample was precipitated by using coarse $ZrO_2$ powders and $Ce(NH_4)_2(NO_3)_6$ as precursors. $CeO_2$-$ZrO_2$ solid solutions were precipitated by using $Ce(NH_4)_2(NO_3)_6$ and $ZrO(NO_3)_2$ as precursors. The obtained chemical mixture was referred as to CZC. On the contrary, coarse $CeO_2$ and $ZrO_2$ powders were mixed carefully with a spatula for 0.5 h. The obtained physical mixture was also calcined at 500 ℃ for 3 h and was referred to as CZP.

### 1.2 Catalyst characterization

The powder X-ray diffraction (XRD) experiments were performed on a Japan Science D/max-RB diffractometer employing Cu Kα radiation ($\lambda$ = 0.15418 nm. The X-ray tube was operated at 40 kV and 120 mA. The X-ray powder diffractogram was recorded at 0.02° intervals in the range of $20° \leqslant 2\theta \leqslant 80°$ with scanning velocity of 6 (°) · $min^{-1}$.

The specific surface areas of the samples were estimated using the $N_2$ adsorption isotherm at 196 ℃ by the one-point Brunauer-Emmett-Teller (BET) method using an automatic surface analyzer (Quantachrome NOVA instrument). The samples were degassed in flowing $N_2$ at 200 ℃ for 2 h.

The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI-5300 ESCA system with Al Kα radiation under UHV ($1.33 \times 10^{-8}$ Pa), calibrated internally by the carbon deposit C1s binding energy (BE) at 285 eV.

The temperature-programmed reduction (TPR) was carried out on an HPR20 HIDEN catalytic surface analyzer. Typically, 100 mg of the sample was employed. The flow of 5% $H_2$/He passed through the powders for 40 min at room temperature (RT) as a pretreatment process. The samples were analyzed under flowing $H_2$(5% in Ar, 30 ml · $min^{-1}$) from RT to 900 ℃ (10 ℃ · $min^{-1}$).

### 1.3 Oxygen storage capacity measurement

At least two forms of OSC have been developed[9~12]: fast or dynamic OSC, which is related to the most readily available oxygen atoms, and total OSC which is the total oxygen available from the catalyst under specific conditions. Here, two forms of OSC measurements, CO-$O_2$ cycle and CO step, were carried out at 500 ℃. The measurements were carried out in a flow reactor system equipped with solenoid valves for rapid introduction of 4% CO/He or 2% $O_2$/He pulses. Typically, 25 mg powders were loaded into a 1.0 cm i.d. quartz tube reactor and a total gas flow rate of 300 $cm^3$ · $min^{-1}$ was employed. One percent Ar was injected along with He as an internal standard for quantification of gas concentrations. The signals of the outlet gas were detected by an on-line quadrupole mass spectrometer (Omnistar 200).

For CO-$O_2$ cycle measurements, alternate 4% CO/He (2, 5 or 10 s) and 2% $O_2$/He (2, 5 or 10 s) pulses were injected. The dynamic OSC was quantified in terms of micromoles of $CO_2$ produced per gram of catalyst (μmol $CO_2$/g cat.) by calculating integrated amounts of $CO_2$ produced during every single CO-$O_2$ cycle.

Prior to CO step measurements, the sample was first heated in 2% $O_2$/He at 500 ℃ for at least 20 min. The sample was further purged in pure He for 30 min to remove oxygen from the system and then exposed to 4% CO/He. The accumulated amount of $CO_2$ per gram of catalyst was monitored as a function of time.

## 2 Results and Discussion

### 2.1 Structural and textural properties

Preparation methods obviously affect the structural features of the samples. The mean lattice constant $d$ of the samples was calculated according to Bragg equation and the result is listed in Table 1. Since the ionic radius of $Zr^{4+}$ (0.084 nm) is smaller than those of $Ce^{4+}$ (0.097 nm) and $Ce^{3+}$ (0.114 nm), the contraction of the crystal cell of CZC implies the formation of homogeneous solid solutions. For the coated samples, CCZ and ZCC, the mean ceria lattice constants are slightly smaller than that of CZP. In the XRD patterns of the samples (not shown), the diffraction peaks of monoclinic $ZrO_2$ are apparently observed in CZP, which weakens in ZCC, intensifies in