The Origin and Dynamics of Tremendous Oxygen Storage/ Release Function of a Pt/ordered CeO$_2$-ZrO$_2$ Catalyst Studied by Time-Resolved XAFS Technique

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**Supporting Information 1:** X-ray crystallographic structures of Ce$_2$Zr$_2$O$_x$ (x=7 or 8).

**Supporting information 2:** Serial time-resolved Zr K-edge XANES spectra of Pt/CZ at 773 K during the oxygen release and storage processes at 773 K

**Supporting information 3:** Effect of the sample amount on the oxygen storage rate on Pt/CZ measured in the in situ XAFS cell

**Supporting information 4:** Thermogravimetric analysis of Pt/CZ under oxygen and hydrogen atmospheres at 773 K

**Supporting information 5:** Arrhenius plots for the oxygen storage and release processes of Pt/CZ

**Supporting information 6:** Tetrahedral ($T_d$) and octahedral ($O_h$) sites in a fluorite Ce$_2$Zr$_2$O$_8$ structure based on the oxygen sub-lattice ($O_h$ sites are not occupied). Oxygen atoms begin to migrate by moving from $T_d$ site to $O_h$ site.

**Supporting information 7:** Measurement and analysis of energy dispersive XAFS
Supporting Information 1: X-ray crystallographic structures of Ce$_2$Zr$_2$O$_x$ (x=7 or 8). Both Zr and Ce ions in κ-Ce$_2$Zr$_2$O$_8$ are +4 and 8-fold coordinated. In pyrochlore Ce$_2$Zr$_2$O$_7$ Ce ions are +3 and 8-fold coordinated, while Zr ions are +4 and 6-fold coordinated. In the transformation between κ-Ce$_2$Zr$_2$O$_8$ and Ce$_2$Zr$_2$O$_7$, Zr sites change the number of coordinated oxygen without any change in the valence, whereas Ce sites change its valence without changing the coordination number due to its ion bonding property. The number of coordinated oxygen to Ce cation during the transformation is not sure, but there may be some rearrangement of the coordination sphere. The space groups of the present samples have been determined by analysis of powder X-ray diffraction patterns $^{[1]}$.


![Ce$_2$Zr$_2$O$_7$ (Fd3m)](image1)

Pyrochlore structure
(lattice parameter: 1.074 nm)

![Ce$_2$Zr$_2$O$_8$ (P43m or P23)](image2)

Fluorite structure (κ-phase)
(lattice parameter: 1.052 nm)
**Supporting information 2:** Serial time-resolved Zr K-edge XANES spectra of Pt/CZ at 773 K during the oxygen release and storage processes at 773 K. The absorption edge energy does not shift during the OSC processes.

**Supporting information 3:** Effect of the sample amount on the oxygen storage rate on Pt/CZ determined by volumetric analysis in the in situ XAFS cell. P(O₂) = 26.7 kPa, T = 773 K.
Supporting information 4: Thermogravimetric analysis of Pt/CZ under oxygen and hydrogen atmospheres at 773 K in a different apparatus from the XAFS cell. It takes 20 s to reach the equilibrium. The OSC rate is much lower than the redox rate of the Ce site determined by energy dispersive XANES.

Supporting information 5: Arrhenius plots for the oxygen storage and release processes of Pt/CZ at the (a) initial and (b) middle range (fraction range: 0.4 – 0.1). To evaluate activation energy for the OSC function, the average values are adopted and listed in Table 1.
Supporting information 6: Tetrahedral ($T_d$) and octahedral ($O_h$) sites in a fluorite $\text{Ce}_2\text{Zr}_2\text{O}_8$ structure based on the oxygen sub-lattice ($O_h$ sites are not occupied). Oxygen atoms begin to migrate by moving from $T_d$ site to $O_h$ site.

Supporting information 7: Energy dispersive XAFS measurement and analysis

Energy dispersive XAFS is an in-situ characterization technique to monitor X-ray intensities in whole energy range simultaneously with a sub-second order time-resolution. Time-resolved energy dispersive XAFS spectra at Ce L$_3$-edge and Zr K-edge in the energy ranges 5.67-5.87 and 17.8-18.8 keV, respectively, were measured at NW2 in PF. Si(111) (Ce L$_3$-edge) and Si(311) (Zr K-edge) bent-crystal polychromators (Bragg-type) were utilized to obtain elliptical optics for focusing incident X-rays at the sample. Higher harmonics were suppressed with a pair of Rh-coated mirrors with incidence angle of 2.8 mrad for Zr K-edge and 6 mrad for Ce L$_3$-edge. A self-scanning photodiode array (PDA: 1024 sensing element: 25 $\mu$m width and 2.5 mm height for each element) manufactured by HAMAMATSU Photonics (S3904-1024FX) was used as a position-sensitive linear detector. The energy calibration at each sensing element of the PDA was performed by comparison with usual XAFS spectra of Zr foil or crystalline CeO$_2$ powder taken at usual XAFS stations in a transmission mode. The obtained Pt/Ce$_2$Zr$_2$O$_8$ sample (10 mg for Ce L$_3$-edge and 30 mg for Zr K-edge XAFS measurements) was pressed to a disk (10 mm$\phi$) and placed at a holder in an in situ cell (465 ml), followed by evacuation at 773 K for 1 h. The time-resolved energy dispersive XAFS spectra for oxygen storage/release processes
were recorded every 2 ms for Zr K-edge and 300 ms for Ce L3-edge under 12.4 kPa of O2 or H2 in the temperature range 573-773 K. The X-ray absorption spectra were calculated by ln(I0(E)/I(E)), where I(E) and I0(E) are X-ray intensity with and without sample as a function of X-ray energy (E). The obtained Zr XAFS spectra were analyzed by using the UWXAFS package. After the background subtraction by the AUTOBK program, Fourier transformation for the k^3-weighted EXAFS oscillation was performed in k-ranges of 30 - 115 nm⁻¹. The structural parameters were determined by a curve fitting procedure in the R space by using the FEFFIT program involving multiple scattering effects. The backscattering amplitude, phase shift functions, and the mean free paths were generated by the FEFF8 code that account for energy resolution of the energy dispersive XAFS spectrometer (4.0 eV). The Debye-Waller factors of all the contributions were fixed at the values estimated by usual XAFS measurements at the same temperature as energy dispersive XAFS measurements to reduce the number of free parameters in the fitting procedure.