Local Structure and Redox Properties of Amorphous CeO$_2$-TiO$_2$ Prepared Using the H$_2$O$_2$-Modified Sol-Gel Method

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Abstract: Amorphous CeO$_2$-TiO$_2$ nanoparticles synthesized by the H$_2$O$_2$-modified sol-gel method were investigated in terms of the Ce-O-Ce and Ti-O-Ti linkage, local structure, and redox properties. The decrease in the crystallinity of CeO$_2$-TiO$_2$ by H$_2$O$_2$ addition was confirmed. The metal–oxygen linkage analysis showed the difference in size of the metal–oxygen network between crystalline CeO$_2$-TiO$_2$ and amorphous CeO$_2$-TiO$_2$ due to the O$_2^{2-}$ formed by H$_2$O$_2$. The local structure of CeO$_2$-TiO$_2$ was analyzed with an extended X-ray absorption fine structure (EXAFS), and the oscillation changes in the k space revealed the disordering of CeO$_2$-TiO$_2$. The decrease in Ce-O bond length and the Ce-O peak broadening was attributed to O$_2^{2-}$ interfering with the formation of the extended metal–oxygen network. The temperature-programmed reduction of the H$_2$ profile of amorphous CeO$_2$-TiO$_2$ exhibited the disappearance of the bulk oxygen reduction peak and a low-temperature shift of the surface oxygen reduction peak. The H$_2$ consumption increased compared to crystalline CeO$_2$-TiO$_2$, which indicated the improvement of redox properties by amorphization.

Keywords: CeO$_2$-TiO$_2$ nanoparticle; metal–oxygen linkage; peroxy ions; disordered oxygen; redox property

1. Introduction

Metal oxides have been widely studied in from a number of research angles, including their uses in catalysts, in electrochemistry, and as gas sensors [1]. Cerium oxide, CeO$_2$, is an important rare-earth oxide with a redox pair of Ce$^{3+}$/Ce$^{4+}$, which enables the storage/release of oxygen located at the tetrahedral site under an oxidation/reduction atmosphere [2]. However, CeO$_2$ is mainly used with other metal oxides because of its low redox property, specific surface area, and the thermal stability of pure CeO$_2$. TiO$_2$ has been extensively investigated as a CeO$_2$-TiO$_2$ mixed oxide due to its advantages, such as a highly specific surface area, outstanding thermal and chemical stability, and non-toxicity. CeO$_2$-TiO$_2$ nanoparticles have attracted much interest for use in various areas where oxidation/reduction reactions of cerium ions are important, such as de-NOx catalysts, photocatalysts, and water gas shift catalysts [3–5]. CeO$_2$-TiO$_2$ nanoparticles have various properties depending on their crystallinity, and many studies have reported the improvement of the catalytic performance of CeO$_2$ and TiO$_2$ through amorphization [6,7].

Amorphous oxides have great potential, and their method of synthesis has been highlighted, as amorphous oxides have excellent physicochemical properties compared to crystalline oxides [5]. CeO$_2$-TiO$_2$ nanoparticles are synthesized by the sol-gel method, hydrothermal routes, and coprecipitation [9–11]. The sol-gel method is widely used and has the advantages of obtaining uniform particles and a highly specific area [12]. The structure of the oxide synthesized through this method is modified according to the degree of hydrolysis, which is affected by additives or the amount of H$_2$O [13,14]. Modifying the hydrolysis and condensation reaction causes changes in structure—for
example, in the crystallinity and microstructure [15–17]. Therefore, it is important to understand the mechanism of hydrolysis and condensation reactions in terms of local structure in the sol-gel reaction and to reveal the relationship between structural properties and physicochemical properties.

In this study, the metal–oxygen linkage, local structure, and redox properties of CeO$_2$–TiO$_2$ nanoparticles were synthesized by the H$_2$O$_2$-modified sol-gel method. The effect of H$_2$O$_2$ on the linkage in the sol-gel was verified by Fourier transform infrared spectroscopy. The local structure was analyzed using an extended X-ray absorption fine structure (EXAFS). The relationship between the local structure and the redox properties was examined by H$_2$-temperature-programmed reduction.

2. Experimental Procedure

2.1. Sample Preparation

The samples were synthesized by the sol-gel method with a molar ratio of Ce:Ti = 3:7; cerium nitrate and titanium isopropoxide (TTIP, Ti[OCH(CH$_3$)$_2$]$_4$, Sigma-Aldrich, St. Louis, MO, USA, 97%) were used as precursors of CeO$_2$ and TiO$_2$, respectively. TTIP was added to ethanol while stirring. Here, we added H$_2$O$_2$ at a volume ratio of TTIP:35% H$_2$O$_2$ = 1:5 after the addition of TTIP. Distilled water was poured into the mixed solution to start the hydrolysis of TTIP. Cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, Sigma-Aldrich, St. Louis, MO, USA, 99%) was added to the mixed solution, then ammonia hydroxide solution (NH$_4$OH 25% in H$_2$O, Junsei, Tokyo, Japan) was slowly added until the pH of the mixed solution reached approximately 10. The filtered precipitate was dried at 80 °C and calcined at 550 °C to obtain a CeO$_2$–TiO$_2$ powder. The prepared oxides were named CT and CT$_{H_2O_2}$ according to the H$_2$O$_2$ addition.

2.2. Characterization

Powder X-ray diffraction (XRD) was measured by an X-ray diffractometer (X’pert pro MPD, Almelo, The Netherlands) with Cu Kα (40 kV, 40 mA) radiation. High-resolution transmission electron microscopy (HR-TEM) images and selected-area electron diffraction (SAED) patterns were obtained using field emission (JEOL JEM-2100, Tokyo, Japan) at the KBSI Busan Center. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Vertex 80 v FTIR spectrometer (Bruker, Billericay, MA, USA) over the range of 400–4000 cm$^{-1}$ with KBr pellets.

X-ray absorption spectroscopy experiments were conducted at the Ce $L_3$-edge using the extended X-ray absorption fine structure (EXAFS) facility of the 10C-wide XAFS beam line at the Pohang Accelerator Laboratory (Pohang, Korea). The storage ring was operated at 2.5 GeV with an injection current of 251 mA using a Si (111) double-crystal monochromator. The X-ray absorption spectroscopy (XAFS) data at the Ce $L_3$ edge were collected at room temperature in transmission mode. The background intensity was removed and normalized using Fourier transform under k-weight 3 to measure the interatomic distance. The XAFS data were analyzed using the Athena and Artemis software packages.

The Brunauer–Emmett–Teller (BET) surface area was measured by N$_2$ adsorption/desorption with a Micromeritics 2020 M instrument (Micromeritics, Norcross, GA, USA). H$_2$ temperature-programmed reduction (H$_2$-TPR) was performed using a Quantachrome with a Chem BET chemisorption analyzer (Micromeritics, Norcross, GA, USA) with 100 mg of the sample in a quartz tube reactor with a thermal conductivity detector (TCD). The sample was preheated from room temperature to 200 °C for 1 h and then cooled down to room temperature. TPR was performed at 10 °C/min up to 800 °C using 10 vol% H$_2$ in He gas. CuO was used as a reference for calibration to quantify the total amount of H$_2$ consumed.

3. Results and Discussion

The crystallinity and phase of the synthesized CeO$_2$–TiO$_2$ were investigated by XRD analysis, as shown in Figure 1, and each pattern corresponded to CT and CT$_{H_2O_2}$. Anatase
TiO₂ and CeO₂ peaks were confirmed in the CT pattern, revealing that CT consisted of CeO₂ and TiO₂ and that there were no secondary peaks. On the other hand, the broadening of those peaks was observed in the pattern of CT_H₂O₂ compared to CT, indicating that CT_H₂O₂ had a low crystallinity of CeO₂ and TiO₂ or consisted of very small nanoparticles. This finding is similar to that of previous studies, indicating that CT_H₂O₂ had very low crystallinity through a broad peak and a low intensity [18,19]. Further analysis was performed to examine the structure of the CeO₂-TiO₂ changed by H₂O₂.

![XRD patterns of CT and CT_H₂O₂.](image)

The microstructure and crystallinity of CT and CT_H₂O₂ were verified through TEM images and SAED patterns, as displayed in Figure 2. Particles of approximately 10 nm with lattice fringes were observed in the TEM image of CT, indicating that they had a crystalline structure (Figure 2a). These crystalline structures were composed of a CeO₂ (111) plane with an interplanar spacing of 0.31 nm and a TiO₂ (101) plane with a 0.35 nm interplanar spacing. The SAED pattern of CT showed ring patterns, meaning that CT existed in crystalline form (Figure 2b). In contrast, an amorphous structure was found in the TEM image of CT_H₂O₂ (Figure 2c), and a diffuse ring pattern was confirmed (Figure 2d). Based on these results, H₂O₂ addition was the cause of the amorphization of CeO₂-TiO₂.
FTIR analysis was carried out to investigate the effect of H$_2$O$_2$ on CeO$_2$-TiO$_2$ linkage formation in sol-gel chemistry. The calcination process is generally necessary in the sol-gel synthesis of oxides, and impurities—including OH groups and organic matter—are removed when calcination is performed for precipitation [20]. The FTIR spectra of CT and CT$_H$$_2$O$_2$ before and after calcination are shown in Figure 3, and all peaks were classified through the literature [21–25]. The characteristic absorption peak of TTIP was in the range of 1085–1050 cm$^{-1}$. Since characteristic peaks were not detected for all samples, all TTIPs participated in the sol-gel reaction. A reduced CH$_3$ peak at 1338 cm$^{-1}$ revealed that the organic matter was removed by calcination. Peaks assigned to the -OH group appeared at 3542 cm$^{-1}$ and 1630 cm$^{-1}$, and the peak intensities of the samples before calcination were greater than those after calcination. It should be noted that CT$_H$$_2$O$_2$ had stronger OH peaks than CT and had an O–O peak representing a peroxy group at 900 cm$^{-1}$. In addition, the Ce-O$_2$$^{2-}$ peak at 842 cm$^{-1}$ demonstrated that H$_2$O$_2$ formed O$_2$$^{2-}$ [26]. The difference between the OH peaks of CT and CT$_H$$_2$O$_2$ is explained by O$_2$$^{2-}$ (peroxy ions).

Figure 2. TEM images and SAED patterns of (a,b) CT and (c,d) CT$_H$$_2$O$_2$. 
The Ce-O-Ce and Ti-O-Ti peaks in the fingerprint region of 800 to 400 cm\(^{-1}\) indicate the metal–oxygen linkage and bonding network. The one large peak in this region is due to the Ce-O-Ti linkage, confirming that the cerium species react via a cross-link and covalently bond on the Ti-O-Ti [25,27]. A wide peak in this region in the CT spectrum indicated a large network [28]. The intensity of this peak decreased after adding H\(_2\)O\(_2\), and the intensity of this peak indicates the size of the Ce-O-Ce or Ti-O-Ti network. This decrease occurred because O\(_2^{2-}\) interfered with the hydrolysis and condensation reactions and thus affected the formation of the Ti-O-Ti network.

EXAFS is a powerful technique for analyzing the local structure of amorphous materials [26]. The EXAFS \(k^3\) data and Fourier transform (F.T.) of Ce L\(_3\) edge are shown in Figure 4. It was confirmed that CT had a long-range order but that CT\(_{H_2O_2}\) had a short-range order resulting from the broken order. As corresponding results, the oscillation differences between CT and CT\(_{H_2O_2}\) were clearly seen in the red dotted circle of the \(k\) space at the Ce L\(_3\)-edge (Figure 4a), and severe noise due to the disordered structure of the amorphous phase was observed. EXAFS F.T. data at the Ce L\(_3\) edge (Figure 4b) provide information on the bond length and the disordering around the Ce atoms. The first and third peaks are assigned to the 1st shell and 2nd shell, respectively, indicating the distances between the Ce-O and Ce-Ce atoms. The second peak is the Ce-Ti bond assigned to an interaction between Ce-Ti forming amorphous Ce [29]. In CT, the bonding length of Ce-O was 1.84 Å and that of Ce-Ce was 3.53 Å. For CT\(_{H_2O_2}\), the bond length of Ce-O decreased to 1.68 Å, and no Ce-Ce peak was observed. Additionally, the broadening of the 1st shell peak was confirmed with the addition of H\(_2\)O\(_2\), which is related to amorphization due to disordering, revealing the disordering of the oxygen around Ce [30]. The peak intensity ratio of the 1st shell and the 2nd shell (I\(_{2\text{nd}}\)/I\(_{1\text{st}}\)) indicates the degree of amorphousness, and this ratio decreased from 0.56 to 0.15, indicating amorphization by H\(_2\)O\(_2\).

Figure 3. FTIR spectra of CT and CT\(_{H_2O_2}\) before calcination.
Figure 4. (a) Extended X-ray absorption fine structure (EXAFS) $k^3 \chi(k)$ data and (b) Fourier transform of the EXAFS $k^3 \chi(k)$ data at the Ce $L_3$-edge EXAFS of CT and CT$_2$H$_2$O$_2$.

This disordering occurs because the strong nucleophilicity of O$_2^{2-}$ causes strong bonding with Ti ions, which interferes with the binding of OH (Figure 5). In more detail, this could be described as the hydrolysis reaction (Equations (1) and (2)) and condensation reaction (Equations (3) and (4)) in sol-gel chemistry [15,17].

Hydrolysis: Ti(OiPr)$_4$ + 2H$_2$O → Ti(OH)$_4$ + 4iPrOH,

Ti(OiPr)$_4$ + H$_2$O$_2$ + 2H$_2$O → Ti(OO)$_2^{2-}$ + 4iPrOH + 6H$^+$,

Condensation: -Ti-OH + HO-Ti → -Ti-O-Ti$^-$ + H$_2$O,

-Ti-OH + iPrO-Ti$^-$ → -Ti-O-Ti$^-$ + iPrOH.
TTIP (Ti(OiPr)$_4$) reacts with H$_2$O and a hydrolysis reaction occurs to form -Ti-OH (Equation (1)). The condensation reaction also simultaneously occurs to release one H$_2$O or iPrOH molecule, forming an extended network of Ti-O-Ti (Equations (3) and (4)). In the H$_2$O$_2$ addition, O$_2^{2-}$ is strongly bound to Ti ions, eventually inhibiting the binding to OH (Equation (2)). As a result, the hydrolysis and condensation reactions of TTIP would have partially occurred. It is concluded that the extended network of Ti-O-Ti was not formed due to partial hydrolysis by O$_2^{2-}$, leading to amorphization.

The redox properties of CeO$_2$-TiO$_2$ according to amorphization were analyzed by H$_2$-TPR, and the results are illustrated in Figure 6. The H$_2$ consumption and specific surface area were 1110 mmol/g and 103.0 m$^2$/g for CT, and 1354 mmol/g and 113.1 m$^2$/g for CT$_{H2O2}$, respectively as shown in Table 1. This is due to the smaller particle size of CT$_{H2O2}$ or the formation of dangling bonds due to the disordering of Ce-O [31–33]. These two facts suggest that the active surface area of CT$_{H2O2}$ is larger. CT had two peaks observed at 490 °C and 767 °C, which corresponded to the reduction from Ce$^{4+}$ to Ce$^{3+}$ by the surface oxygen of CeO$_2$ and the lattice oxygen of CeO$_2$, respectively [34]. CT$_{H2O2}$ showed a peak due to the surface oxygen at only 468 °C and 558 °C, and there was no reduction peak assigned to the lattice CeO$_2$, which implies that CT$_{H2O2}$ is amorphous [35,36]. The surface CeO$_2$ peak shifted to low temperature by amorphization, and the H$_2$ consumption increased, confirming the improvement of the redox property. The atoms of the crystalline oxide are tightly bonded by strong intermolecular forces, while the atoms of the amorphous oxide are loosely bonded. Consequently, the improvement of the redox property was because the Ce-O-Ce bond was weak and easily reduced by the disordered structure of CT$_{H2O2}$.

Table 1. H$_2$-TPR results and BET surface area of CT and CT$_{H2O2}$.

| Sample   | Surface Oxygen Reduction Temp. (°C) | Bulk Oxygen Reduction Temp. (°C) | H$_2$ Consumption (mmol/g) | BET Surface Area (m$^2$/g) |
|----------|------------------------------------|---------------------------------|---------------------------|----------------------------|
| CT       | 490                                | 797                             | 1110                      | 103.0                      |
| CT$_{H2O2}$ | 468                           | Not observed                  | 1354                      | 113.1                      |
4. Conclusions

We studied the effect of H2O2 on the Ce-O-Ti linkage in the sol-gel reaction in terms of local structure for the first time. The decrease in the crystallinity of CeO2-TiO2 with the addition of H2O2 was verified through XRD peak broadening, and it was confirmed that the SAED pattern of CeO2-TiO2 became a diffuse pattern. CeO2 and crystalline TiO2 were observed for CT, whereas an amorphous structure was observed for CT_H2O2. In the FTIR spectrum of CT_H2O2, the O22− peak attributed to H2O2 was observed, and the broadening of the metal–oxygen peak showed that the size of the metal–oxygen network decreased due to O22−. The local structure of the synthesized samples was analyzed using EXAFS. Severe noise and oscillation differences in the k space were observed by the disordered structure in CT_H2O2; furthermore, the decrease in the Ce-O bond length and the broadening of the Ce-O peak in R space were identified. It was found that O22− interfered with the formation of the metal–oxygen extended network. In the H2-TPR analysis to investigate the redox property according to the amorphization, a low-temperature shift in the surface CeO2 reduction peak and an increase in H2 consumption indicated an improvement in the redox property due to amorphization. The improved redox property of amorphous CeO2-TiO2 resulted from the metal–oxygen bond being weakened by disordered oxygen.

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