1. Introduction

Glycerol is a by-product of biodiesel production, which is achieved by the transesterification of triglycerides (e.g. vegetable oils and waste fats) and methanol. Recent increase in the demand for biodiesel has caused the oversupply of glycerol [1–3]. Recently, the selective catalytic oxidation of glycerol has received significant attention because of its ability to transform glycerol into value-added compounds, such as glyceric acid (GA), glyceraldehyde (GLA), and dihydroxyacetone [4–9]. In the medical field, research interest has focused on GA [10], because GA and its derivatives have been reported to show biological activities, such as the anti-trypsin activity [11], acceleration of ethanol and acetaldheyde metabolism [12], enhancement of the viability of ethanol-exposed cells [13], and activation of the proliferation of dermal cells [14]. GA is also used in the production of amino acids, such as serine [15]. Thus, GA is a promising chemical in life science; however, GA is expensive for investigational use [14].

To produce GA, noble metal-based catalysts, such as Pt, Pd, and Au, have been explicitly studied [16–24]. García et al. reported that the combination of a Pd/C catalyst and the addition of a base (NaOH) resulted in a high GA yield of 70% (glycerol conversion: 90%, GA selectivity: 77%) under the conditions comprising a pH = 11 (controlled by the addition of 30% NaOH aq.) at a temperature of 60°C in atmospheric pressure (airflow at 0.75 mL min⁻¹) for 3 h [21]. In addition, Au/graphite in the presence of NaOH under the pressure of 0.6 MPa O₂ is reported to show a further high GA yield of 84% (estimated from the glycerol conversion (91%) and the GA selectivity (92%)) after the reaction for 3 h at 60°C [22]. However, because they require a continuous supply of a base and an additional process is needed to obtain GA from sodium glycerate salt, the base-free synthesis route has recently received considerable attention. According to Hou et al., Pt/S-grafted carbon nanofibers can convert glycerol into GA with a high yield of 74.8% (estimated from the glycerol conversion (89.9%) and the GA selectivity (83.2%)) under the base-free condition [23], while high pressure (0.4 MPa O₂ and 1.6 MPa N₂) and heating at 60°C are necessary. It was recently reported that under base-free and atmospheric pressure conditions, Pt–CeO₂/graphene nanotubes can produce GA from glycerol with a yield of 75.8% (estimated from the glycerol conversion (97.2%) and GA selectivity (78%)) [24]. However, heating at 60°C and a pure oxygen gas flow (150 mL min⁻¹) is needed to supply the oxygen species to the catalyst. In the case of the air condition as well as atmospheric pressure, only a few studies have been reported, e.g. Pt/C showed a high GA yield of 55% (glycerol conversion: 90%) under the conditions consisting of a pH = 7 at a temperature of 60°C in atmospheric pressure (airflow at 0.75 mL min⁻¹) [21].
The ideal condition for the catalytic reaction is an atmospheric open-air system at room temperature without any additives or gas flow. Such mild conditions led to a considerable decrease in the catalytic oxidation ability. Therefore, it is important to introduce a promoter that can supply an active oxygen species from inside the crystal lattice. In our previous study, the CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ solid solution showed high oxygen release and storage abilities, where Fe$_2$O$_3$ was introduced into the CeO$_2$–ZrO$_2$ lattice to enhance the redox properties, owing to the redox cycle between Ce$^{3+/4+}$ and Fe$^{2+/3+}$, and to facilitate the oxide ion migration through the replacement of the Ce$^{4+}$ and Zr$^{4+}$ sites for the lower-valent Fe$^{2+/3+}$ ions [25]. Furthermore, to produce GLA, which is the intermediate compound in the oxidation process from glycerol to GA, a CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ promoter and Pt activator were dispersed onto a high surface area mesoporous silica Santa Barbara Amorphous No. 16 (SBA-16), resulting in Pt/CeO$_2$–ZrO$_2$–Fe$_2$O$_3$/SBA-16 catalysts. The introduction of Fe$_2$O$_3$ effectively improved the catalytic activity, and the GLA yield of 22.1% were achieved without any additives or oxygen gas flow under mild conditions comprising the temperature of 30°C in the atmospheric open-air with a reaction time of 4 h [26], where the formation of GA was also observed (GA yield: 28.0%). The high GLA yield is attributed to the fact that the effective oxygen supply from CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ toward Pt accelerated the oxidation of glycerol, while milder conditions could suppress the further oxidation of GLA. In addition, the acidity of catalyst supports facilitates the desorption of GLA, resulting in the suppression of the further oxidation of GLA to GA [27]. The product yield might also be affected by the acidic sites on the CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ promoter caused by the oxygen vacancies. These considerations suggest that the important factors that cause the high yields of GA are the increase in the oxygen release and storage abilities, even under mild conditions, and the lowering of the number of acidic sites. Since our previous study aimed to produce GLA, the GA yield was relatively low 28.0% [26]; therefore, the strict catalyst design would improve the GA yield. A simple and effective method to achieve these factors is to increase the loading amount of CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ compared to the case in the previous study (16 wt%) [26], which was optimized for the effective GLA production. The increase in the amount of CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ promoter is considered to enhance the oxygen release and storage abilities of CeO$_2$–ZrO$_2$–Fe$_2$O$_3$/SBA-16. Furthermore, the acidic sites on the promoter surface are expected to be lowered by crystallite growth and/or particle aggregation due to the high loading amount of CeO$_2$–ZrO$_2$–Fe$_2$O$_3$.

Herein, we increased the CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ loading amount in Pt/CeO$_2$–ZrO$_2$–Fe$_2$O$_3$/SBA-16 to produce GA effectively, and their catalytic activities for selective glycerol oxidation were investigated under mild conditions of an atmospheric open-air system at room temperature of 30°C.

2. Experimental

Mesoporous silica SBA-16 was prepared according to a method reported elsewhere [28]. Pluronic F-127 (Sigma Aldrich) (1.6 g) as a nonionic surfactant and 1,3,5-trimethylbenzene (Kishida Chemical, ≥ 98.0%) (1.1 mL) as a swelling agent were dissolved in 90 mL of 0.2 molL$^{-1}$ hydrochloric acid, which was prepared by diluting concentrated hydrochloric acid (Kishida Chemical, 35%) with deionized water. Tetraethoxysilane (Kishida Chemical, ≥ 99.0%) (7.1 mL) was added to the solution and stirred at 35°C for 24 h, followed by hydrothermal treatment at 140°C for 24 h using a Teflon bottle in a sealed brass vessel. The precipitates formed were collected by suction filtration, washed with deionized water and ethanol, dried at 80°C for 12 h, then finally calcined at 600°C for 4 h under a flow of air (15 mL min$^{-1}$). Ce$_{0.64}$Zr$_{0.16}$Fe$_{0.20}$O$_{2−δ}$/SBA-16 was synthesized using a co-precipitation technique. Solutions of 1.0 molL$^{-1}$ Ce(NO$_3$)$_3$, 0.10 molL$^{-1}$ ZrO(NO$_3$)$_2$, and 0.10 molL$^{-1}$ Fe(NO$_3$)$_3$ were prepared by dissolving Ce(NO$_3$)$_3$·6H$_2$O (Kojundo, 99.9%), Zr(NO$_3$)$_2$·2H$_2$O (Kishida Chemical, ≥ 99.0%), and Fe(NO$_3$)$_3$·9H$_2$O (FUJIFILM Wako Pure Chemical, 99.9%) in deionized water, respectively. The SBA-16 powder (0.4 g) was dispersed in a 1.0 molL$^{-1}$ Ce(NO$_3$)$_3$·aq., 0.10 molL$^{-1}$ ZrO(NO$_3$)$_2$·aq., and 0.10 molL$^{-1}$ Fe(NO$_3$)$_3$·aq. in the stoichiometric ratio, followed by the addition of 30 mL of deionized water. After stirring at room temperature for 30 min, an aqueous solution of ammonia (5vol%), prepared by diluting ammonia solution (Kishida Chemical, 28%) with deionized water, was added dropwise into the solution with vigorous stirring until pH = 11. This was followed by further stirring at room temperature for 12 h. The precipitates were filtered by suction filtration, dried at 80°C for 12 h, and then calcined at 900°C for 1 h in atmospheric air. The Ce$_{0.64}$Zr$_{0.16}$Fe$_{0.20}$O$_{2−δ}$ loading amount (x) varied from 0 to 60 wt%, and the samples were denoted as xwt%CeF/SBA. Pt loading onto xwt% CZFe/SBA was carried out by the impregnation method. The xwt%CZFe/SBA powder (0.4 g) was suspended on a platinum colloid stabilized with polyvinylpyrrolidone (Pt: 4.0wt%; Tanaka Kikinzoku Kogyo) and 40 mL of ethanol (Kishida Chemical, 99.5%) was added, where the Pt amount was adjusted to 7 wt%. The solution was evaporated at 90°C for 2 h, and the resulting powder was calcined at 500°C for 4 h in atmospheric air. Hereafter, 7 wt%Pt/xwt%Ce$_{0.64}$Zr$_{0.16}$Fe$_{0.20}$O$_{2−δ}$/SBA-16 are represented as Pt/xwt%CZFe/SBA.

The crystalline phase was identified with an X-ray powder diffraction (XRD; SmartLab, Rigaku) using a Cu-Kα radiation (40 kV, 30 mA). The XRD data
were analyzed by whole powder pattern fitting using PDXL software (Rigaku) to estimate the crystallite size. The lattice constant was calculated by refining the XRD peak angles using α-alumina as an internal standard. The Brunauer–Emmett–Teller (BET) specific surface area was measured at −196°C using N₂ (Micromeritics Tristar 3000, Shimadzu). The morphology and particle sizes were observed by transmission electron microscopy (TEM; H-800, Hitachi) and scanning electron microscopy (SEM; SSX-550, Shimadzu). X-ray photoelectron spectroscopy (XPS; PHI5000 VersaProbe II, ULVAC-PHI) was measured using an Al-Kα radiation to investigate the valence state of Pt. The acidity was evaluated using a temperature-programmed desorption method using ammonia (NH₃-TPD). After the sample (0.1 g) was preheated at 800°C for 1 h under a helium flow at 50 mL·min⁻¹, it was exposed to ammonia (0.5vol% ammonia–99.5vol% helium, 50 mL·min⁻¹) at 50°C for 30 min, followed by purging at the same temperature for 15 min under a helium flow (50 mL·min⁻¹). Subsequently, the temperature was increased at a rate of 10°C·min⁻¹ under a helium flow of 30 mL·min⁻¹ (BELCAT-B, MicrotracBEL). The oxygen release ability was evaluated by temperature-programmed reduction measurement using hydrogen (H₂-TPR), performed with 0.2 g of the sample at a heating rate of 5°C·min⁻¹ under a reducing gas (5vol% hydrogen–95vol% argon) flow at 50 mL·min⁻¹ (BELCAT-B, MicrotracBEL). After the H₂-TPR analysis, the oxygen storage capacity (OSC) was examined using the pulse injection method at 500°C. The sample composition was determined using X-ray fluorescence spectrometry (XRF; Supermini200, Rigaku).

The catalytic glycerol oxidation test was conducted in an open-air system. An aqueous solution of 1 wt% glycerol was prepared by dissolving glycerol (Kishida Chemical, 99.0%) in deionized water. The catalyst (0.3 g) and 1 wt% glycerol aqueous solution (10 mL) were mixed in a flask equipped with a condenser (4°C) and stirred in an oil bath at 30°C under the base-free condition (pH = 7) without applying pressure of gas bubbling. After the reaction, the liquid-phase (10 μL) was analyzed using a high-performance liquid chromatography (HPLC, JASCO), where the product was separated by a Shodex Sugar SH-1011 column operating at 50°C with 5 mmol·L⁻¹ dilute sulfuric acid as the eluent (prepared by diluting concentrated sulfuric acid (Kishida Chemical, 98%) in deionized water) (0.75 mL·min⁻¹) and detected by a refractive index (RI) and a photodiode array (PDA). The glycerol conversion, product yield, and product selectivity were estimated as follows:

\[
\text{Glycerol conversion} = 1 - \left( \frac{[\text{Glycerol}]}{[\text{Glycerol}]_0} \right)
\]

\[
\text{Product yield} = \left( \frac{[\text{Product}] \times n_{\text{product}}}{[\text{Glycerol}]_0 \times n_{\text{glycerol}}} \right)
\]

\[
\text{Product selectivity} = \left( \frac{[\text{Product}] \times n_{\text{product}}}{[\text{Glycerol}]_0 \times n_{\text{glycerol}}} \right) / \left( \frac{[\text{Glycerol}]_0}{[\text{Glycerol}]_0} \right)
\]

where [Glycerol]₀ and [Glycerol] are the glycerol concentrations (mol·L⁻¹) before and after the reaction, respectively. [Product] is the product concentration (mol·L⁻¹) and \( n_{\text{product}} \) and \( n_{\text{glycerol}} \) are the number of carbon atoms in the product and glycerol (\( n_{\text{glycerol}} = 3 \)), respectively. Each concentration was determined using the calibration curve method, in which standard solutions were prepared by diluting DL-glyceric acid (Tokyo Chemical Industry, 20% in water) with deionized water, by dissolving 1,3-dihydroxyacetone dimer (Sigma-Aldrich, 97%), DL-glyceraldehyde (Sigma-Aldrich, ≥ 90%), glycolic acid (FUJIFILM Wako Pure Chemical, 97%), oxalic acid dihydrate (Kishida Chemical, 99.5%), and tartronic acid (Alfa Aesar, 98%) in deionized water, and by dissolving sodium β-hydroxypropyruvate hydrate (Sigma-Aldrich, ≥ 97%) and sodium mesoxalate monohydrate (Sigma-Aldrich, ≥ 98%) in dilute sulfuric acid (5 mmol·L⁻¹).

### 3. Results and discussion

#### 3.1. Characterization

Figure 1 shows the XRD patterns of xwt% CZFe/SBA and SBA [26]. The peaks corresponding to SBA-16 and the cubic fluorite-type structure of \( \text{Ce}_{0.64} \text{Zr}_{0.16} \text{Fe}_{0.20} \)
O_{2−δ} (CZFe) were observed for xwt% CZFe/SBA. The crystallite size of CZFe (D_{CZFe}) was estimated, and the relationship between the D_{CZFe} and the CZFe loading amount (x) is shown in Figure 2. The D_{CZFe} increased with the increase in x, indicating the crystallite growth.

To investigate the effects of the aggregation of CZFe on the surface area, the theoretical specific surface area (S_{cal}) was calculated as follows [29,30]:

\[ S_{cal} = (1 - x) S_{SBA,0} + x S_{CZFe} \]

where S_{SBA,0} is the measured surface area of the SBA (S_{SBA,0} = 560 m^2 g^{-1} [26]). S_{CZFe} is the theoretical surface area of CZFe calculated from D_{CZFe} using the following equations under the assumption that CZFe crystallites and SBA are ideally separated from each other.

\[ S_{CZFe} = \frac{6}{D_{CZFe} \times \rho_{CZFe}} \]

where \( \rho_{CZFe} \) is the density of CZFe. The \( \rho_{CZFe} \) value was calculated to be 6.21 g·cm\(^{-3}\) using the feed composition of CZFe and the lattice constant (0.538 nm), which was estimated from the XRD result of 40 wt% CZFe/SBA. Figure 3 shows the compositional dependence of the S_{cal} values as well as the observed data (S_{obs}) measured by the BET method. As the S_{obs} decreased with an increase in x, the specific surface area of CZFe was lower than that of SBA-16. For the same CZFe loading amount, each S_{obs} value was lower than the theoretical value (S_{cal}), indicating that the CZFe crystallites formed aggregates, and the mesopores of the SBA-16 support were partially covered by CZFe. A similar effect has been reported in previous studies [30].

For CZFe/SBA, as low acidity is necessary to produce GA effectively, NH\textsubscript{3}-TPD measurements were carried out. Figure 4 shows the NH\textsubscript{3}-TPD profiles of the xwt% CZFe/SBA samples. The profile of SBA showed two small peaks at ca. 150°C and ca. 300°C, assigned to the weak and strong acidic sites on the SBA-16 support, respectively. For the CZFe-loaded samples, three peaks were observed at ca. 150°C, ca. 300°C, and ca. 400°C, corresponding to the weak, medium, and strong acidic sites on the CZFe promoter, respectively. From these profiles, the total number of acidic sites was calculated, and the results are shown in Figure 5. The number of acidic sites increased up to x = 16, indicating that the CZFe promoter exhibits a high acidity. The CZFe system was reported to have oxygen vacancies formed by the replacement of the Ce\(^{4+}\) and Zr\(^{4+}\) sites for lower-valent Fe\(^{2+/3+}\) [25], which might
work as Lewis acidic sites. For \( x > 16 \), the number of acidic sites decreased with increasing \( x \). To exclude the effect of the CZFe loading amount, the number of acidic sites per gram of CZFe was estimated (Figure 5 (b)). As \( x \) increased, the number of acidic sites per CZFe significantly decreased, as these acidic sites were intrinsically related to the surface area and impacted by the crystallite growth and particle aggregation. Thus, the lowering of the acidity for \( x > 16 \) was predominantly affected by the CZFe surface compared to the CZFe loading amount. Therefore, the increase in the CZFe loading amount successfully lowered the acidity of CZFe in the range of \( x > 16 \).

To compare the relative oxygen release and storage abilities of xwt% CZFe/SBA, H\(_2\)-TPR measurements using 5vol%H\(_2\)-95vol%Ar, followed by the OSC examination, were carried out. The profiles of the xwt% CZFe/SBA samples are presented in Figure 6 along with the SBA data. Although SBA demonstrated no reduction peak, the profiles of xwt% CZFe/SBA could be fitted to three reduction peaks. Hereafter, the peaks at ca. 400, ca. 440, and ca. 500°C are denoted as the \( \alpha \)-peak, \( \beta \)-peak, and \( \gamma \)-peak, respectively. The \( \alpha \) - and \( \beta \)-peaks might be respectively attributed to the release of the surface and bulk oxygen species involved with the synergistic reduction of Ce\(^{4+}\) to Ce\(^{3+}\) with Fe\(^{3+}\) to Fe\(^{2+}\) [31,32]. The \( \gamma \)-peak is probably assigned to the reduction of Fe\(^{2+}\) to Fe\(^{0}\) [33], while only its shoulder was observed. The peak top temperatures of the \( \alpha \)- and \( \beta \)-peaks, related to the valence change of Ce\(^{3+/4+}\) and Fe\(^{2+/3+}\), and the peak area ratios of \( \alpha \)-peak/(\( \alpha \)-peak + \( \beta \)-peak) are listed in Table 1. While the reduction temperatures of the \( \alpha \)- and \( \beta \)-peaks were essentially unchanged, the \( \alpha \)-peak/(\( \alpha \)-peak + \( \beta \)-peak) ratio decreased with increasing CZFe loading amount. In other words, the increase in \( x \) decreases the effects of the surface oxygen release and increases the effects of the bulk oxygen release. This behavior is caused by the crystallite growth and particle aggregation of the CZFe promoter. Table 1 shows the total amount of hydrogen consumed. The total amount of hydrogen consumption increased monotonically with increasing \( x \). Figure 7(a) shows the OSC values for xwt% CZFe/SBA. Each OSC value was consistent with that of the total amount of oxygen released in the H\(_2\)-TPR measurements. The OSC improved linearly with the increase in \( x \), similar to the tendency exhibited by the total hydrogen consumption amount (Table 1). Therefore, the oxygen release and storage abilities were continuously enhanced with an increase in \( x \). For further investigation, the OSC per gram of CZFe was estimated, and the results are presented in Figure 7(b). Only a slight decrease in OSC per CZFe was observed.

**Figure 5.** Effect of the CZFe loading amount (\( x \)) on (a) number of acidic sites and (b) number of acidic sites per CZFe for xwt% CZFe/SBA.

**Figure 6.** H\(_2\)-TPR profiles of xwt% CZFe/SBA.

**Table 1.** Reduction temperatures of \( \alpha \)- and \( \beta \)-peaks, peak area ratio of \( \alpha \)-peak/(\( \alpha \)-peak + \( \beta \)-peak), and total amount of H\(_2\) consumption for xwt% CZFe/SBA.

| Sample | Reduction temperature/°C | \( \alpha \)-peak \( \beta \)-peak | \( \alpha \)-peak/(\( \alpha \)-peak + \( \beta \)-peak) ratio/% | Total amount of H\(_2\) consumption/μmol·g\(^{-1}\) |
|--------|--------------------------|-----------------|----------------------|---------------------|
| \( x = 0 \) | - | - | - | 0 |
| \( x = 10 \) | 381 | 440 | 80 | 119 |
| \( x = 16 \) | 398 | 441 | 66 | 224 |
| \( x = 20 \) | 397 | 436 | 51 | 260 |
| \( x = 30 \) | 398 | 436 | 39 | 370 |
| \( x = 40 \) | 400 | 436 | 35 | 450 |
| \( x = 50 \) | 405 | 435 | 32 | 481 |
| \( x = 60 \) | 402 | 441 | 25 | 628 |
likely due to the crystallite growth and particle aggregation. However, in comparison with that of the acidic sites (Figure 5(b)), the change in OSC per CZFe can be ignored, indicating that the oxygen species could be stored inside the lattice [34]. Thus, the continuous increase in OSC was predominantly affected by the CZFe loading amount compared to the CZFe surface. Therefore, the high loading amount of CZFe contributed to the lowering of the acidic sites as well as the improvement of the oxygen release and storage abilities as expected.

From the XRD measurements of Pt-loaded xwt% CZFe/SBA (Figure S1), all the peaks were indexed as metallic Pt, the fluorite-type structure of CZFe, and SBA-16. The crystallite sizes of Pt and CZFe were estimated from the XRD patterns, and the results are shown in Figure 8. The CZFe crystallite sizes in Pt/xwt %CZFe/SBA were almost the same as those in the case of xwt%CZFe/SBA (d_{CZFe}): that is, the Pt loading process did not change the CZFe crystallite size. As for the Pt crystallite size, the value decreased with increasing x. This phenomenon indicates that the oxygen supply from the CZFe promoter facilitated the oxidation of Pt, which contributed to the suppression of the Pt particle growth, similar to that reported by a previous study [35].

The compositions of Pt/xwt%CZFe/SBA measured by XRF analysis were in good agreement with their feed values within the range of experimental error (Table 2). The specific surface area, estimated by the BET method (Table 2), decreased with an increase in x. In addition, the Pt loading of Pt/xwt%CZFe/SBA caused a decrease in the specific surface area compared to that of the xwt%CZFe/SBA (Figure 3).

![Figure 7. Effect of the CZFe loading amount (x) on (a) OSC and (b) OSC per CZFe for xwt%CZFe/SBA.](image)

![Figure 8. Crystallite sizes of CZFe and Pt as a function of the CZFe loading amount (x) for Pt/xwt%CZFe/SBA.](image)

| Catalyst | Measured composition | Specific surface area/m²·g⁻¹ |
|----------|----------------------|-----------------------------|
| Pt/SBA   | 7.1 wt%Pt/SBA-16     | 476 [26]                    |
| Pt/10 w% | 7.9 wt%Pt/9.9 wt%Zr₂O₃·ZrO₂/SBA-16 | 285 |
| CZFe/SBA | 6.7 wt%Pt/15.3 wt%CeO₂·ZrO₂/SBA-16 | 276 [26] |
| Pt/20 w% | 7.0 wt%Pt/19.6 wt%CeO₂·ZrO₂/SBA-16 | 200 |
| Pt/30 w% | 7.2 wt%Pt/30.8 wt%CeO₂·ZrO₂/SBA-16 | 181 |
| Pt/40 w% | 6.9 wt%Pt/41.1 wt%CeO₂·ZrO₂/SBA-16 | 169 |
| CZFe/SBA | 0.21               | 75                          |

TEM images and ED patterns of Pt/xwt%CZFe/SBA (x = 0, 16, 40, 60) are displayed in Figure 9. For Pt/SBA, in addition to the regular arrangement of mesopores with ca. 13 nm diameter, the Pt particles with diameters from 10 to 40 nm were observed as dark spots in and/or on the mesopores. On the other hand, Pt/xwt%CZFe/SBA (x = 16, 40, 60) contains small Pt particles with ca. 10 nm diameter compared to the Pt/SBA case, similar to the Pt crystallite size (Figure 8). While it is difficult to distinguish between CZFe and SBA, the ED patterns can be assigned to the Pt metal and the fluorite-type structure derived from CZFe (insets of Figure 9(b-d)). In the case of x = 60, aggregates were clearly observed outside the mesopores, likely due to the particle aggregation of CZFe. The morphology of Pt/xwt%CZFe/SBA was also investigated using SEM observation (Figure S2). The primary particles with diameters from 0.1 to 5 μm agglomerated together, which formed large secondary particles with 10–20 μm.
The XPS spectra of the Pt 4f core-levels of Pt/xwt% CZFe/SBA (x = 0, 16 [26], 40, 60) are depicted in Figure 10, where the fitting parameters are listed in Table S1. The peaks were identified as Pt2⁺ and Pt⁰, and the Pt2⁺/(Pt2⁺+Pt⁰) ratio is shown in parentheses in the figure. The Pt2⁺/(Pt2⁺+Pt⁰) ratios of Pt/16 xwt%CZFe/SBA (52% [26]) was significantly higher than that of Pt/SBA (26%), indicating that the oxygen supply from CZFe led to the generation of Pt2⁺. The x = 40 sample showed the slightly high Pt2⁺/(Pt2⁺+Pt⁰) ratio compared to the x = 16 case, likely due to the further improvement of the oxygen release and storage abilities. On the other hand, the Pt2⁺/(Pt2⁺+Pt⁰) ratio of x = 60 was decreased compared to that of x = 40 regardless of the further increase of oxygen release and storage abilities. This phenomenon can be explained by the decrease of the CZFe surface for the Pt loading.

3.2. Catalytic activity

The catalytic liquid-phase oxidation of glycerol was carried out for Pt/xwt%CZFe/SBA at 30°C in an atmospheric open-air system. After 4 h of reaction, GA, GLA, dihydrox-yacetone (DHA), hydroxypyruvic acid (HA), tartronic acid (TA), mesoxalic acid (MA), glycolic acid (GLOA), and oxalic acid (OA) were identified using HPLC. Figure 11 depicts the proposed reaction scheme of glycerol oxidation, which includes the obtained products, based on previous studies [2–5,36]. Figure 12 shows the glycerol conversion and product yields as a function of the CZFe loading amount. The glycerol conversion increased with increasing x up to the catalyst with x = 40, while the specific surface area decreased. This behavior indicates that the increase in OSC mainly affected the improvement of the catalytic activity. On the other hand, for x > 40, glycerol conversion decreased because the low specific surface area decreased the catalytic active sites. Therefore, the highest glycerol conversion was obtained for the x = 40 catalyst.

For all the prepared catalysts, the predominant product was GA, which was generated by the oxidation of the primary OH group in glycerol via the intermediate compound of GLA. In addition, the GA yield was higher than that of DHA, which was formed by the oxidation of the secondary OH group in glycerol. This indicates that the primary OH group in glycerol is predominantly oxidized compared to the secondary OH group.
GLA production, the yield increased with increasing $x$ up to $x = 16$, whereas the GLA yield decreased in the range of $x > 16$. This behavior is related to the number of acidic sites and indicated that the high acidity of CZFe facilitated the GLA desorption, resulting in the suppression of the further oxidation of GLA. As a result, the highest GLA yield of 22.1% was obtained for $x = 16$ catalyst [26]. For GA production, the yield continuously increased until $x = 40$, and the $x = 40$ catalyst showed the highest GA yield of 40.9%. This high GA yield might be caused by the lowering of the acidity and the increase in the oxygen release and storage abilities. In contrast, the GA yield for $x > 40$ decreased because of the decrease in glycerol conversion. The yields of the other organic products (HA, TA, MA, GLOA, and OA) were lower than 10%.

Figure 13 shows the catalytic activity for the $x = 40$ catalyst (Pt/40 wt%CZFe/SBA) as a reaction time function at 30°C in an atmospheric open-air system. The glycerol conversion continuously increased with increasing reaction time and reached up to 99.2% after 10 h. The GA yield was higher than that of GLA even after 1 h of reaction, indicating that the further oxidation of GLA was accelerated due to the high oxygen release and storage abilities and the suppression of the desorption of GLA due to the low acidity. Although the DHA yield was constant (ca. 9%) and lower than that of GA, the further oxidized products of GA or DHA (HA, TA, MA, GLOA, and OA) gradually increased. The predominant product was GA, and its yield increased to 68.2% after 10 h of reaction, where the GA selectivity was estimated to be 68.8%. Although the previous Pt/C catalyst [21] could generate GA with
4. Conclusions

This study demonstrated the effective production of GA from glycerol using Pt/CeO$_2$–ZrO$_2$–Fe$_2$O$_3$/SBA-16 under mild conditions in an atmospheric open-air system at room temperature without additives, such as base or oxygen gas flow. In the catalysts, the CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ promoter supported on SBA-16 facilitated the oxidation of the Pt activator. The increase in the CeO$_2$–ZrO$_2$–Fe$_2$O$_3$ loading amount led to crystallite growth and particle aggregation. As a result, the number of acidic sites of CeO$_2$–ZrO$_2$–Fe$_2$O$_3$/SBA-16 decreased with increasing loading amount in the range over 16 wt%. Conversely, the oxygen release and storage abilities increased continuously even at a high loading amount of CeO$_2$–ZrO$_2$–Fe$_2$O$_3$. The low acidity and high oxygen release and storage abilities successfully improved the GA yield, and the highest activity was obtained for 7 wtPt/40 wt%Ce$_{0.64}$Zr$_{0.16}$Fe$_{0.20}$O$_{2.8}$/SBA-16, which exhibited a high GA yield (68.2%) and selectivity (68.8%) with glycerol conversion (99.2%) even under mild conditions after 10 h of reaction in an open-air system at 30°C.

**Acknowledgments**

A part of the experiments were carried out using a facility in the Research Center for Ultra-High Voltage Electron Microscopy at Osaka University, and we thank Dr. Takao Sakata and Prof. Dr. Jun Yamasaki (Research Center for Ultra-High Voltage Electron Microscopy, Osaka University) for helping us with the TEM observation. We thank Dr. Hirokazu Izumi (Hyogo Prefectural Institute of Technology) for his assistance during XPS measurement. This work was supported in part by the Iwatani Corporation, JSPS KAKENHI Grant Number JP19H02435, Steel Foundation for Environmental Protection Technology, and JFE 21st Century Foundation.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by the Iwatani Corporation, the Japan Society for the Promotion of Science [JP19H02435], Steel Foundation for Environmental Protection Technology, and JFE 21st Century Foundation.

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