Selective oxidation of glycerol to dihydroxyacetone using CeO$_2$-ZrO$_2$-Bi$_2$O$_3$-SnO$_2$-supported platinum catalysts

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ABSTRACT

The effects of the Bi$^{3+}$ introduction and the oxygen release and storage abilities on selective oxidation of glycerol into dihydroxyacetone (DHA) were demonstrated using Pt/CeO$_2$-ZrO$_2$-Bi$_2$O$_3$-SnO$_2$/SBA-16 (SBA-16: Santa Barbara Amorphous No. 16) catalysts. By introducing Bi$^{3+}$ or Sn$^{4+/2+}$ ions into the CeO$_2$-ZrO$_2$ promoter, the oxygen release and storage abilities were enhanced, which led to increased glycerol conversion. The improvement in the DHA yield was affected by the introduction of Bi$^{3+}$, which might accelerate selective oxidation of a secondary hydroxy group in glycerol caused by the geometric effect. The highest activity was obtained for Pt/CeO$_{0.64}$Zr$_{0.16}$Bi$_{0.15}$Sn$_{0.05}$O$_{2}/$SBA-16, which showed high oxygen release and storage abilities and a high number of Bi$^{3+}$ ions, with the DHA yield increasing to 53% and high rates of glycerol conversion (74%) and DHA selectivity (72%) after reaction at a moderate temperature of 30 °C for 4 h in atmospheric air.

1. Introduction

Biodiesel has received attention as a promising renewable fuel produced from lipids such as vegetable oils, animal fats, and waste fats. Biodiesel is generally produced by a process of transesterification of glyceride and methanol, generation of glycerol as a byproduct. The recent increase in biodiesel production has contributed to a glycerol oversupply, making utilization of the excess glycerol an important issue. One effective approach is transformation of glycerol into valuable chemical compounds such as dihydroxyacetone (DHA), glycolic acid, lactic acid, and acrolein [1–3]. Of these, DHA is especially important to our lives because of its skin tanning effect without UV irradiation; that is to say, its sunless tanning effect. Since this tanning is nontoxic and poses no risk of skin cancer due to UV rays, DHA has found applications in cosmetics, clinical use for camouflaging vitiligo, etc. DHA is currently produced from glycerol by a fermentation method (87–94% yield after ca. 32 h); it requires a long processing time, however, and strict control of the pH, temperature, and dissolved oxygen concentration to protect against bacteria [4].

From the standpoint of production efficiency, catalytic transformation using a heterogeneous catalyst is an ideal method of producing DHA [5–12]. Several studies reported that a Pt-Bi bimetallic catalyst can effectively convert glycerol to DHA due to a geometric effect of active sites, which may suppress primary hydroxy group oxidation of glycerol owing to a blocking effect and accelerate secondary hydroxy group oxidation. To date, Pt-Bi/MCM-41 (MCM-41: Mobile Composition of Matter No. 14) has been reported to show a high glycerol conversion rate (85%), a high DHA yield (55%), and high DHA selectivity (65%), while it requires the severe operating conditions including high oxygen pressure of 0.3 MPa (3 atm) and a high temperature of 75°C for 4 h [11]. Under atmospheric pressure conditions, high selectivity of 64% has been reported for Pt/NCNT (NCNT: N-doped carbon nanotubes) with a bismuth nitrate additive in a reaction solution at 60°C for 6 h; the values for glycerol conversion (29%) and the DHA yield (19%) are still low, however, and the process requires an oxygen gas flow [12]. As concerns glycerol oxidation under moderate conditions of room temperature in atmospheric air without a gas flow, since the solubility of oxygen gas in water is extremely low, it is important to apply promoters which supply the activator with active oxygen species from inside the lattice. We have previously found that the introduction of Bi$_2$O$_3$ into a CeO$_2$-ZrO$_2$ solid solution improved its oxygen release and storage abilities, because the formation of oxygen vacancies through low-valent Bi$^{3+}$ substitution facilitated the supply of oxygen species [13–16]. By inserting the CeO$_2$-ZrO$_2$-Bi$_2$O$_3$ promoter and a Pt activator into the pores of mesoporous silica SBA-16 (Santa Barbara Amorphous No. 16) with a large surface area, we demonstrated that Pt/CeO$_2$-ZrO$_2$-Bi$_2$O$_3$/SBA-16 effectively converted glycerol to DHA [15]. This high efficiency is considered to be affected by the oxygen...
supply from the promoter and by geometric effects among glycerol, Pt, and surface Bi\(^{3+}\) ions in the promoter. However, the exact reason for the high DHA yield still remains unclear.

The aim of this study was to clarify the effects of Bi\(^{3+}\) introduction and oxygen release and storage abilities on DHA yields obtained using CeO\(_2\)-ZrO\(_2\)-based catalysts. To this end, Sn\(^{4+/2+}\) was selected as a dopant to improve the oxygen release and storage abilities owing to the facile Sn\(^{4+/2+}\) redox cycle [16-18]; therefore, Bi\(^{3+}\) and Sn\(^{4+/2+}\)-doped CeO\(_2\)-ZrO\(_2\) promoters were synthesized, and the catalytic activities of Pt/CeO\(_2\)-ZrO\(_2\)-Bi\(_{3}O\(_2\)/SBA-16 for selective glycerol oxidation were investigated.

2. Experimental

SBA-16 was prepared via a hydrothermal reaction similar to that in the previous study [19]. Pluronic F-127 (1.6 g) and 1,3,5-trimethylbenzene (1.1 mL) were dissolved in 0.2 mol\(\text{L}^{-1}\) hydrochloric acid (90 mL), to which tetramethyl orthosilicate (7.1 mL) was then added. The solution was poured into a Teflon bottle in a sealed brass vessel and heated at 140°C for 24 h. The obtained solid was collected by filtration, dried, and calcined at 600°C for 4 h under an air flow. Ce\(_{0.2}\left\{1-x-y\right\}Zr\(_{0.2}\left\{1-x-y\right\}Bi\_{x}\Sn\_{y}O_{2-δ} /SBA-16 (CZBi(x)Sn(y)/SBA) were synthesized by a co-precipitation process. Stoichiometric amounts of 1 mol\(\text{L}^{-1}\) Ce(NO\(_3\))\(_3\), 1 mol\(\text{L}^{-1}\) Zr(NO\(_3\))\(_2\), and 0.5 mol\(\text{L}^{-1}\) Bi(NO\(_3\))\(_3\) aqueous solutions and SnC\(_2\)O\(_4\) powder were mixed with distilled water (ca. 30 mL). The SBA-16 powder (0.8 g) was dispersed in the solution, and stirred at room temperature for 30 min. The pH of the mixture was adjusted to 11 by dropwise addition of 6% ammonia aqueous solution. After stirring at room temperature for 12 h, the precipitation was collected by filtration, dried and then calcined at 600°C for 1 h in atmospheric air. Supported platinum catalysts (Pt/CZBi(x)Sn(y)/SBA) were prepared by the impregnation method. The obtained CZBi(x)Sn(y)/SBA samples were added to platinum colloid stabilized with PVP (Tanaka Kikinzoku Kogyo). After vaporization of the solvent, the mixture was dried at 80°C for 12 h and then calcined at 500°C for 4 h. The amounts of Pt and CZBi(x)Sn(y) were adjusted to 7 wt% and 16 wt%, respectively.

The composition of the catalysts was determined by X-ray fluorescence analysis (XRF; ZSX1000e, Rigaku). The Brunauer-Emmett-Teller (BET) specific surface area was analyzed by nitrogen adsorption at −196°C (TriStar 3000, Shimadzu). X-ray powder diffraction (XRD; SmartLab, Rigaku) measurements were performed with Cu Ka radiation (40 kV, 30 mA) in the 2θ range from 10 to 70 deg. The crystallite size of the platinum was calculated by the Scherrer equation. Temperature-programmed reduction (TPR) measurements were performed under a flow of 5 vol% hydrogen-95 vol% argon at 50 mL\(\text{min}^{-1}\) and a heating rate of 5 °C\(\text{min}^{-1}\) (BELCAT-B, MicrotracBEL), and each TPR spectrum was fit using a Gaussian-Lorentzian shape. Following TPR, the total OSC values were determined using the pulse-injection method at 427°C (BELCAT-B, MicrotracBEL). X-ray photoelectron spectroscopy (XPS; PHI5000 VersaProbe II, ULVAC-PHI) was carried out at room temperature using Al Kα radiation.

The oxidation of glycerol was carried out using a three-necked flask equipped with an ethanol-water-cooled condenser in an open system. The catalyst (0.3 g) and 1 wt% glycerol aqueous solution (10 mL) were entered into the flask and stirred at 30°C for 4 h. After the reaction, the catalyst and liquid phase were separated by centrifugation (Allegra 64 R centrifuge, Beckman Coulter). The liquid phase sample was mixed with 0.2 wt% naphthalene methanol solution as an internal standard in a volume ratio of 1:1, and this sample was then analyzed using gas chromatograph mass spectrometry (GC-MS; GCMS-QP2010 Plus, Shimadzu) to evaluate the glycerol and DHA concentrations. For each analysis, 1 μL of the sample was injected, and the flow rate of helium was set to 1.1 mL\(\text{min}^{-1}\). Mass spectra were recorded in the mass range from 15 to 150 amu. The temperature of the injector was set to 240°C, and the column (Rtx-624, Restek) temperature program was set in the range of 100–190°C. The glycerol conversion, DHA yield, and DHA selectivity were estimated from the following equations:

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

\[
\text{(DHA yield)} = \frac{[\text{DHA}]}{[\text{Glycerol}]}_0
\]

\[
\text{(DHA selectivity)} = \frac{[\text{DHA yield}]}{(DHA conversion)}
\]

where [Glycerol] and [Glycerol]\(_0\) are the glycerol concentration before and after the reaction. [DHA] is the DHA concentration after the reaction. The glyceraldehyde (GLA) yield and selectivity were also estimated using similar equations. The used catalyst was heated at 200°C for 1 h under an air flow prior to the reusability test. The catalytic performance under nitrogen gas bubbling was also examined at 30°C for 4 h. The metal leaching during the catalytic reaction was analyzed by XRF (Rayny EDX-720, Shimadzu).

3. Results and discussion

The measured compositions of Pt/CZBi(x)Sn(y)/SBA were confirmed to be in good agreement with the feed compositions within the range of experimental error (Table S1). The BET surface areas of Pt/CZBi(x)Sn(y)/SBA are listed in Table 1. Introducing Pt and CZBi(x)Sn(y) reduced the surface areas compared to that of SBA, suggesting that Pt and CZBi(x)Sn(y) were successfully loaded on the SBA-16 support. In addition, the surface area decreased with increases in the Bi or Sn contents, likely due to the lower melting points of Bi\(_2\)
O$_3$ (817°C) [20] and SnO$_2$ (1630°C) [21] compared to those of CeO$_2$ (2445°C) [22] and ZrO$_2$ (2710°C) [22]. From the XRD measurements of Pt/CZBi(x)Sn(y)/SBA (Figure S1), the diffraction peaks were indexed to Pt, a cubic fluorite-type structure, and SBA-16, where no impurity phase was observed. The platinum crystallite sizes, estimated using the XRD patterns, were almost the same for the Pt/CZBi(x)Sn(y)/SBA catalysts (Table 1).

Catalytic glycerol oxidation was carried out for the Pt/CZBi(x)Sn(y)/SBA catalysts at 30°C in an air atmosphere for 4 h. Figure 1 shows the glycerol conversion, DHA yield, and DHA selectivity as functions of the Bi content (x) in the Pt/CZBi(x)/SBA and Pt/CZBi(x)Sn(0.05)/SBA series, for which typical GC-MS results are shown in Figure S2. For Pt/CZBi(x)/SBA (x ≤ 0.15), increases in both the glycerol conversion and the DHA yield were clearly observed with increases in x. Furthermore, the DHA selectivity was obviously improved. These increases might be attributed to both an increase in the oxygen storage abilities and the introduction of the Bi$^{3+}$ ions, much as in our previous study [15]. The excess Bi$^{3+}$ introduction (x = 0.20) in Pt/CZBi(x)/SBA caused a decrease in DHA selectivity, while the glycerol conversion was still increased, suggesting that DHA was further oxidized. In the Pt/CZBi(x)Sn(y)/SBA series, the glycerol conversion, DHA yield, and DHA selectivity were increased with increases in x up to [x = 0.15; y = 0.05], although the glycerol conversion and DHA yield of the sample with [x = 0.20; y = 0.05] were lower than in the [x = 0.15; y = 0.05] cases, possibly due to the small surface area. The highest DHA yield was obtained for the sample with [x = 0.15; y = 0.05], in which the value rose to 53% with DHA selectivity of 72%.

Figure 2 shows the Sn content (y) dependences of the glycerol conversion, DHA selectivity, and DHA yield for the Pt/CZBi(x)Sn(y)/SBA and Pt/CZBi(0.15)Sn(y)/SBA series. When y increased from 0 to 0.05, the glycerol conversion increased for both series. On the other hand, the conversion was decreased for both samples with [x = 0, 0.15; y = 0.10], likely due to their small surface areas (Table 1). Remarkably, the DHA selectivities were almost constant irrespective of the Sn content (y). Pt/CZBi(0.15)Sn(0.05)/SBA exhibited high

### Table 1. BET surface area and Pt crystallite size of the Pt/CZBi(x)Sn(y)/SBA catalysts.

| Catalyst                     | BET surface area/m$^2$·g$^{-1}$ | Pt crystallite size/nm |
|------------------------------|----------------------------------|------------------------|
| Pt/CZ/SBA                    | 377                              | 8.1                    |
| Pt/CZBi(0.05)/SBA            | 370                              | 8.7                    |
| Pt/CZBi(0.10)/SBA            | 347                              | 7.3                    |
| Pt/CZBi(0.15)/SBA            | 326                              | 7.7                    |
| Pt/CZBi(0.20)/SBA            | 314                              | 7.4                    |
| Pt/CZBi(0.05)Sn(0.05)/SBA    | 344                              | 7.4                    |
| Pt/CZBi(0.05)Sn(0.05)/SBA    | 333                              | 7.8                    |
| Pt/CZBi(0.10)Sn(0.05)/SBA    | 322                              | 7.0                    |
| Pt/CZBi(0.15)Sn(0.05)/SBA    | 315                              | 7.8                    |
| Pt/CZBi(0.20)Sn(0.05)/SBA    | 312                              | 8.2                    |
| Pt/CZSn(0.10)/SBA            | 279                              | 8.1                    |
| Pt/CZBi(0.15)Sn(0.10)/SBA    | 304                              | 7.7                    |
| Pt/SBA                       | 432                              | 13.2                   |
| CZBi(0.15)Sn(0.05)/SBA       | 330                              | -                      |
| SBA                          | 500                              | -                      |

Figure 1. Glycerol conversion, DHA selectivity, and DHA yield as functions of Bi(x) for Pt/CZBi(x)Sn(0.05)/SBA (closed circle) and Pt/CZBi(x)/SBA (open circle).

Figure 2. Glycerol conversion, DHA selectivity, and DHA yield as functions of Sn(y) for Pt/CZBi(0.15)Sn(y)/SBA (closed square) and Pt/CZSn(y)/SBA (open square).
selectivities of over 60%, moreover, while the selectivities of Pt/CZSn(y)/SBA without the Bi$^{3+}$ ion were below 15%. These results indicate that DHA selectivity might be affected by the introduction of the Bi$^{3+}$ ion, rather than by Sn$^{4+/2+}$ doping.

In order to investigate the effect of the oxygen release and storage abilities of the promoter on catalytic activity, TPR and OSC measurements were carried out. The TPR profiles of CZ/SBA, CZBi(0.15)/SBA, CZSn(0.05)/SBA, and CZBi(0.15)Sn(0.05)/SBA samples are presented in Figure 3. While CZ/SBA showed no obvious reduction peak below 450°C, reduction peaks appeared with the introduction of Bi$^{3+}$ and/or Sn$^{4+/2+}$ ions. For CZBi(0.15)/SBA and CZBi(0.15)Sn(0.05)/SBA, two reduction peaks at ca. 350°C and ca. 400°C were observed, likely due to surface and bulk reduction, respectively [23], whereas peak separation for the CZSn(0.05) profile was difficult because of its low, broad shape. The first reduction peak temperature of CZBi(0.15)Sn(0.05)/SBA was lower than that of CZBi(0.15)/SBA, owing to the synergistic effect of the introduction of Bi$^{3+}$ and Sn$^{4+/2+}$. Thus, the oxygen release was facilitated by the introduction of Bi and/or Sn. After the TPR measurement, the total OSC value was measured, yielding the following results: CZBi(0.15)Sn(0.05)/SBA (135 μmol·g$^{-1}$) > CZBi(0.15)/SBA (122 μmol·g$^{-1}$) > CZSn(0.05)/SBA (70 μmol·g$^{-1}$) > CZ/SBA (17 μmol·g$^{-1}$), which indicated that the introduction of Bi and/or Sn increased the oxygen storage ability. These results demonstrated that the introduction of Bi and/or Sn improved the oxygen release and storage abilities. These tendencies correspond to the findings of our previous study [16], where we revealed the effect of introducing Bi or Sn on oxygen release and storage abilities from the viewpoint of the oxide ion and electronic conductivities. Bi introduction considerably increased oxide ion conductivity via the oxide ion vacancies formed by low-valent Bi$^{3+}$ substitution into the Ce$^{4+}$ and Zr$^{4+}$ sites, while Sn introduction significantly affected the increase in electronic conductivity due to the valence change of Sn$^{4+/2+}$ [16]. Both oxide ion and electronic conductivities improved the oxygen release and storage abilities. The high oxide ion conductivity might accelerate oxide ion migration from inside the lattice toward the surface. Electronic conduction occurs during oxide ion migration to maintain the charge valence. Also, oxygen release and storage are generally involved with the respective reduction and oxidation of the constituent cations. Among the promoters, CZBi(0.15)Sn(0.05)/SBA showed the highest oxygen release and storage abilities, because co-doping with Bi and Sn might lead to an increase in both oxide ion and electronic conductivities.

The effective oxygen supply from the promoter might lead to oxidation of the Pt activator, and the XPS results (Figure S3) revealed that the Pt$^{2+}$/Pt$^{3+}$ ratio in Pt/CZBi(0.15)Sn(0.05)/SBA (0.21) was slightly higher than that in Pt/CZ/SBA (0.17). The tendency of the oxygen release and storage abilities of the promoter is similar to glycerol conversion, Pt/CZBi(0.15)Sn(0.05)/SBA (74%) > Pt/CZBi(0.15)/SBA (65%) ≈ Pt/CZSn(0.05)/SBA (61%) > Pt/CZ/SBA (42%), rather than to DHA selectivity, Pt/CZBi(0.15)Sn(0.05)/SBA (72%) > Pt/CZBi(0.15)/SBA (60%) > Pt/CZSn(0.05)/SBA (8%) = Pt/CZ/SBA (10%). Thus, the oxygen release and storage abilities predominantly affected glycerol conversion as opposed to DHA selectivity.

The effects of Bi and Sn on DHA selectivity were investigated in detail using Pt/CZBi(0.15)/SBA and Pt/CZSn(0.05)/SBA, which showed almost the same rates of glycerol conversion. In the reaction process, oxidation of the primary hydroxy group in glycerol is also considered to have proceeded, as shown in Figure 4. Based on the GC-MS measurements of Pt/CZBi(0.15)/SBA and Pt/CZSn(0.05)/SBA, glyceraldehyde (GLA) was observed in addition to DHA and residual glycerol, while the other compounds were not detected. For Pt/CZBi(0.15)/SBA, the GLA yield (19%) was lower than the DHA yield (39%), indicating that a geometric effect among glycerol, Pt, and Bi$^{3+}$ in CZBi(0.15) facilitated selective oxidation of the secondary hydroxy group in glycerol [12]. By contrast, no such selectivity was confirmed for Pt/CZSn(0.05)/SBA, because the GLA yield (5%) was the same as the DHA yield (5%). Here, both the GLA and DHA yields of Pt/CZSn(0.05)/SBA were low values (5%) compared to those of Pt/CZBi(0.15)/SBA case (GLA yield: 19%, DHA yield: 39%), while the glycerol conversion of Pt/CZSn(0.05)/SBA (61%) was comparable to that of Pt/CZBi(0.15)/SBA.

Figure 3. TPR profiles of CZ/SBA, CZBi(0.15)/SBA, CZSn(0.05)/SBA, and CZBi(0.15)Sn(0.05)/SBA.
(65%), suggesting that further oxidation had proceeded in the case of Pt/CZnSn(0.05)/SBA. Based on these results, it was considered that the high DHA selectivity of Pt/CZBi(0.15)/SBA was caused by the geometric effect of oxidizing the secondary hydroxy group in glycerol.

The activities of SBA, CZBi(0.15)Sn(0.05)/SBA, and Pt/SBA were investigated to clarify the effects of the promoter and the Pt activator on their selective oxidation ability, and the results are tabulated in Table 2 with data for Pt/CZBi(0.15)Sn(0.05)/SBA. For CZBi(0.15)Sn(0.05)/SBA without Pt, no catalytic reaction appears to have proceeded, because the conversion and yield were similar to those for SBA. For Pt/SBA, the glycerol conversion and DHA yield were considerably lower than those for Pt/CZBi(0.15)Sn(0.05)/SBA; therefore, the CZBi(0.15)Sn(0.05) promoter successfully accelerated selective oxidation of glycerol to yield DHA. To investigate the role of the promoter, a catalytic reaction was carried out under nitrogen gas bubbling using Pt/CZBi(0.15)Sn(0.05)/SBA. The results showed that glycerol conversion (8%) and the DHA yield (6%) were drastically decreased compared to those recorded in atmospheric air (glycerol conversion: 74%, DHA yield: 54%), indicating that the promoter continuously supplied oxygen species from the solution to the activator inside the promoter lattice. In other words, after the lattice oxygen in the promoter was released toward the Pt catalyst, the promoter stored oxygen species inside its lattice from the oxygen soluted in the liquid phase. Therefore, both the Pt activator and the CZBi(0.15)Sn(0.05) promoter are indispensable materials for realizing high DHA yields and selectivity.

After the catalytic reaction, no metal leaching from Pt/CZBi(0.15)Sn(0.05)/SBA was observed using XRF measurements of the solution. In addition, the measured composition of the Pt/CZBi(0.15)Sn(0.05)/SBA catalyst after the reaction (6.4 wt% Pt/14 wt% Ce0.63Zr0.16Bi0.15Sn0.06O2−δ/SBA-16) was almost the same as that of the fresh sample (6.7 wt% Pt/14 wt% Ce0.63Zr0.17Bi0.14Sn0.06O2−δ/SBA-16). Figure 5 shows the results of a reusability test for the used Pt/CZBi(0.15)Sn(0.05)/SBA catalyst after heat treatment (200°C, 1 h). The glycerol conversion and DHA yield maintain high values of over 79% and 54%, respectively.

4. Conclusion

This study demonstrated the effects of promoters on selective oxidation of glycerol to dihydroxyacetone under moderate reaction conditions (room temperature and atmospheric air) using novel synthesized Pt/CeO2-ZrO2-Bi2O3-SnO2/SBA-16 catalysts. Introducing both Bi3+ and Sn4+/2+ to CeO2-ZrO2 clearly increased its oxygen release and storage abilities, which led to improvement of the glycerol conversion for Pt/CeO2-ZrO2-Bi2O3-SnO2/SBA-16. The DHA selectivity was affected by the amount of Bi3+ content in the CeO2-ZrO2-Bi2O3-SnO2, likely due to a geometric effect facilitating the oxidation of a secondary hydroxy group in glycerol. Among the samples prepared, 6.7 wt% Pt/14 wt% Ce0.63Zr0.17Bi0.14Sn0.06O2−δ/SBA-16 exhibited the highest DHA yield of 54% after reaction at 30°C for 4 h in atmospheric air, where the glycerol conversion and the

Table 2. Glycerol conversion, DHA yield, and DHA selectivity of SBA, CZBi(0.15)Sn(0.05)/SBA, Pt/SBA, and Pt/CZBi(0.15)Sn(0.05)/SBA.

| Catalyst | Glycerol conversion/% | DHA yield/% | DHA selectivity/% |
|----------|-----------------------|-------------|------------------|
| SBA      | 21                    | 0           | 0                |
| CZBi(0.15)Sn(0.05)/SBA | 15                  | 0           | 0                |
| Pt/SBA   | 48                    | 4           | 8                |
| Pt/CZBi(0.15)Sn(0.05)/SBA | 74                | 54          | 72               |

Figure 4. Reaction route of selective glycerol oxidation.

Figure 5. Glycerol conversion and DHA yield obtained via reused Pt/CZBi(0.15)Sn(0.05)/SBA.
DHA selectivity reached high levels of 74% and 72%, respectively.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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