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Oxidative dehydrogenation of n-butene to buta-1,3-diene with novel iron oxide-based catalyst: Effect of iron oxide crystalline structure

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	We investigate the effect of the crystalline structure of iron oxide catalysts on oxidative dehydrogenation (ODH) of n-butene. ODH reactions of n-butene were carried out with a fixed-bed flow reactor at 450 °C under a but-1-ene (1-C ₄ H ₈) or <i>cis</i> -but-2-ene (<i>cis</i> -2-C ₄ H ₈)(mL/min)/O ₂ (mL/min) flow ratio of 5/2.5. Of the various iron oxide-based catalysts (α , β -, γ -, ε -Fe ₂ O ₃ , Fe ₃ O ₄ , ZnFe ₂ O ₄), ε -Fe ₂ O ₃ showed the highest ODH activity. To the best of our knowledge, ε -Fe ₂ O ₃ has never been used for the ODH of n-butene. Moreover, the catalytic performance of ε -Fe ₂ O ₃ was improved by adding SiO ₂ , which is related to the maintenance of its structure and improves its redox property. A high BD selectivity of 65 % and BD yield of 18 % were then obtained for 4 h without deactivation. This catalyst can be applied to the ODH of <i>cis</i> -2-C ₄ H ₈ and is proposed as the noble high catalytic performance catalyst for the ODH of n-butene.	

1. Introduction

One of the principal intermediate products in the petrochemical industry is buta-1,3-diene (BD). The demand for BD is increasing, as it is as a major building block in the industry and can be mostly produced by the steam cracking of naphtha. However, this process must be operated at temperatures over 700 °C, and the endothermic reaction thus requires a lot of energy. In addition, the steam cracking of naphtha shows the low BD selectively because light olefins such as ethene and propylene were produced. Due to the shale gas revolution, ethane can be cheaply supplied; the substrate used in cracking to produce ethylene transfers from naphtha to ethane derived from the shale gas. Therefore, in terms of a near-future supply of BD, an alternative production process is needed.

Recently, the oxidative dehydrogenation (ODH) of C4 fraction (Eq. (1)), which is an exothermic reaction, has attracted attention. This reaction is very useful from the viewpoint of energy conservation, and it has been proposed as a process for the efficient production of BD.

$$C_4H_8 + 1/2O_2 \rightarrow C_4H_6 + H_2O \quad \Delta H^o = -132.1 \text{ kJ/mol}$$
 (1)

However, ODH has a serious problem in that the complete oxidation of reactant and product to CO_2 proceeds easily (Eqs. (2) and (3)).

$$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O \quad \Delta H^o = -2540.8 \text{ kJ/mol}$$
 (2)

$$C_4H_8 + 4O_2 \rightarrow 4CO + 4H_2O \quad \Delta H^\circ = -1409.0 \text{ kJ/mol}$$
 (3)

In order to inhibit complete oxidation, the ODH of n-butene has been carried out under an O₂ flow with a large amount of steam [1]. However, since the latent heat of steam is large, this requires a lot of energy. The ODHs of n-butene and propane have also been performed using the lattice oxygen of a catalyst in order to prevent the complete oxidation of the substrates (Eqs. (4) and (5)) [2,3]. However, this approach has not been suitable for the continuous BD production over a long duration because it requires the regeneration of the catalyst used.

$$C_4H_8 + MO_x \rightarrow C_4H_6 + H_2O + MO_{x-1}$$
 (4)

$$MO_{x-1} + 1/2O_2 \to MO_x \tag{5}$$

For effective and continuous BD production, it would be preferable to conduct the ODH of n-butane and n-butene under O2 flow without steam.

Various effective catalysts such as Bi-Mo composite oxide [4-13], ferrite type [14-27], and V-containing [28-30] have been proposed for the ODH of n-butene and n-butane. Among these catalysts, the Bi-Mo composite oxide and ferrite type catalysts have been widely studied. It has been reported that the ODH reaction with these catalysts proceeds

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through the Mars-van Krevelen mechanism [4,5]. This mechanism is a redox cycle with the lattice oxygen in the metal oxide, and the reactivity of lattice oxygen in the metal oxide during the ODH reaction is a crucial factor in determining the catalytic performance.

On the other hand, the effect of the crystalline structure of the catalyst on the ODH has often been discussed [7,17,19]. The Bi-Mo complex oxide has α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉, and γ -Bi₂MoO₆. Generally, the catalytic activity for the ODH of n-butene is on the order of $\gamma > \alpha$ [7]. β -Bi₂Mo₂O₉ is therefore inappropriate for the ODH, because it decomposes to α and γ at the reaction temperature of 400–550 °C [6]. It is suggested that this order is consistent with lattice oxygen reactivity [31]. In the case of an iron oxide catalyst, it is reported that ferrite type catalysts with a spinel structure can exhibit high ODH activity, and the presence of α -Fe₂O₃ leads to low ODH performance [17,19].

Thus, extensive study of the effect of the crystallite structure on the ODH is important to the development of a catalyst with high catalytic performance. Iron oxide has various crystalline structures, including α -, β -, γ -, and ϵ -Fe₂O₃, and each the single phase can be easily synthesized. Meanwhile, detailed investigation of the crystalline phase of iron oxide in various ODH reactions has not yet been conducted.

Therefore, in this study we examined the effect of the crystalline structure of iron oxide on the ODH of n-butene. We were able to propose an effective iron oxide catalyst for the ODH reaction. In order to achieve efficient BD production, the ODH of butenes was carried out under O_2 flow without steam, and catalytic performance stability during the ODH was also investigated.

2. Experimental

2.1. Materials

Fe(NO₃)₃·9H₂O (assay = min. 99.0 %), FeSO₄·7H₂O (assay = 99–102 %), Fe₂(SO₄)₃·nH₂O (assay = 60–80 %), Zn(NO₃)₂·6H₂O (assay = min. 99.0 %), NaOH (assay = min. 97.0 %), 28 %NH₃ solution, n-octane (assay = min. 98 %), butan-1-ol (assay = min. 99 %), acetone (assay = min. 99.5 %), methanol (assay = min. 99.8 %), NaCl (assay = 99.5 %), cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS) (assay = min. 95.0 %), and Fe₃O₄ were purchased from Wako Pure Chemical Industries, and used for the preparation of iron oxide catalysts. But-1-ene (1-C₄H₈) (assay = min. 99.0 %) was supplied by Sumitomo Seika Chemical. *Cis*-but-2-ene (*cis*-2-C₄H₈) (assay = min. 99.0 %) was supplied by Takachiho Chemical Industrial Co., Ltd.

2.2. Preparation of various iron oxide catalysts

 α -Fe₂O₃ was prepared by the precipitation method. Fe(NO₃)₃·9H₂O (10 mmol) was dissolved in 100 mL of pure water. The solution was stirred at room temperature for 1 h. After stirring, 1 mol/L of NaOH solution was added to the solution under vigorous stirring until the pH reached 10. After stirring for 1 h, the resultant precipitate was separated by centrifugation, and the solid was washed with a large amount of pure water until the pH reached 7–8. It was then dried at 110 °C overnight in an oven. The solid was calcined at 500 °C for 2 h in air. γ -Fe₂O₃ was prepared by the same method. FeSO₄·7H₂O (10 mmol) was used as a precursor, and the calcination was carried out at 400 °C.

 β -Fe₂O₃ was prepared as described in previous reports [32,33]. First, Fe₂(SO₄)₃ was prepared by calcining Fe₂(SO₄)₃·nH₂O at 400 °C under N₂ flow. Fe₂(SO₄)₃ and NaCl at a molar ratio of 1:2 were mixed in a mortar for 30 min. The mixed material was calcined at 550 °C for 2 h in air. The calcined product was added to pure water, and stirred at room temperature overnight. After stirring, the solid was filtered, washed with a large amount of pure water, and dried at 110 °C overnight in an oven.

 ϵ -Fe₂O₃-SiO₂ was first prepared with reference to previous reports [34–36]. That is, ϵ -Fe₂O₃-SiO₂ was prepared by the reverse micelle method. Fe(NO₃)₃·9H₂O was dissolved in a mixed solution of pure

water, n-octane, and butan-1-ol. CTAB at $H_2O/CTAB = 30/1$ (mol/mol) was added to the mixed solution containing Fe(NO₃)₃.9H₂O, and stirred until dissolved (Solution 1). Next, the solution was changed from Fe (NO₃)₃·9H₂O to 28 % NH₃ aq, prepared with the same method as Solution 1 (Solution 2). Solution 2 was added drop-wise to Solution 1, and the slurry obtained was stirred for 30 min. TEOS was added to the slurry to yield a weight ratio of $(Fe_2O_3)/(SiO_2+Fe_2O_3) = 0.1, 0.2, and 0.5, and$ stirred overnight. After stirring, slurries were separated by centrifugation. Obtained solids were washed with a mixed solvent of acetone and methanol (volume ratio = 1/1), and then dried at 60 °C in an oven for 5 h. The solid was calcined at 1050 $^\circ \text{C}$ for 4 h in air. The different Fe₂O₃-containing catalysts were prepared by varying the amount of Fe $(NO_3)_3$ ·9H₂O. Here, the notation is ε -Fe₂O₃(X)-SiO₂, where X is Fe₂O₃ content (wt%). Pure ε -Fe₂O₃ was obtained by the following process. SiO₂ in ɛ-Fe2O3(50)-SiO2 was dissolved in 1 mol/L NaOH solution at 60 °C overnight, and the solid was filtered, washed with a large amount of pure water, and dried at 110 °C overnight in an oven.

 $ZnFe_2O_4$ was prepared as previously reported [19]. Briefly, Fe $(NO_3)_3$ ·9H₂O and $Zn(NO_3)_2$ ·6H₂O were dissolved in 100 mL of pure water. The mixed solution was stirred at room temperature for 1 h. After stirring, 3 mol/L of NaOH solution was added to the solution under vigorous stirring to reach pH 9. After stirring at room temperature for 12 h, it was aged overnight. The resultant precipitate was separated by centrifugation, the solid was washed with a large amount of pure water until pH was 7–8, and then it was dried at 175 °C for 16 h. The solid was calcined at 650 °C for 2 h in air.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of iron oxide catalysts were obtained by the powder method using a Rigaku RINT-TTRIII diffractometer with monochromatic CuK α radiation under the following conditions: tube voltage 40 kV, tube current 30 mA, scan step 0.02 degrees, scan region 10–80 degrees, and scan speed 4.0 degrees/min.

2.4. Catalyst test

2.4.1. ODH of n-butene with iron oxide catalyst under O_2 atmosphere

The ODH of 1-C₄H₈ was carried out using a fixed-bed flow quartz reactor at 450 °C under atmospheric pressure. After 200 mg of the catalyst was placed in the reactor, it was preheated to a reaction temperature of 450 °C under 22.5 mL/min (STP) of Ar flow. Oxygen, 1-C₄H₈ or *cis*-2-C₄H₈, and Ar were introduced at a flow rate of O₂/1-C₄H₈ or *cis*-2-C₄H₈/Ar = 2.5/5/22.5 mL/min (STP). Total gas flow rate was fixed at 30 mL/min.

The C4 fractions $(1-C_4H_8, cis-2-C_4H_8, trans-2-C_4H_8, and C_4H_6)$ were analyzed using a flame ionization detector (FID) gas chromatograph (Shimadzu GC14B, column: Unicarbon A-400). CH₄, CO, and CO₂ were also analyzed with a thermal conductivity detector (TCD) gas chromatograph (column: activated carbon). O₂ and H₂ were analyzed by TCD gas chromatograph (Shimadzu GC8A, column: molecular sieves 5A).

2.4.2. ODH of but-1-ene with lattice oxygen in iron oxide catalyst

The ODH of 1-C₄H₈ was carried out using the fixed-bed flow quartz reactor at 450 °C under atmospheric pressure. After 200 mg of the catalyst was placed in the reactor, it was preheated to a reaction temperature of 450 °C under 25 mL/min (STP) of Ar flow. Then, 5 mL/min of 1-C₄H₈ and 25 mL/min of Ar were introduced for 5 min. Reoxidation was carried out after the reaction under 5 mL/min of O₂ and 25 mL/min of Ar for 10 min at 450 °C. Quantification of the products was carried out using the same equipment as in Section 2.4.1.



Fig. 1. XRD patterns of various iron oxides.



Fig. 2. Effect of crystal phase of iron oxide on ODH of but-1-ene under O2 flow. Catalyst: 200 mg.

Flow rate: 1-C4H8/O2/Ar = 5/2.5/22.5 mL/min. Reaction temperature: 450 °C. Reaction time: 30 min.

3. Results and discussion

3.1. Effect of crystal phase of iron oxide on the ODH

Fig. 1 presents the XRD patterns of various iron oxide catalysts. α -Fe₂O₃ and γ -Fe₂O₃ showed α -Fe₂O₃ and γ -Fe₂O₃ diffraction peaks, respectively (Fig. 1(a), (d)). Formation of ϵ -Fe₂O₃ and β -Fe₂O₃ in the single phase could be confirmed with diffraction peaks matching those reported in the literature (Fig. 1(b), (c)) [33,36,37].

Fig. 2 shows the effect of the crystallite structure of various iron oxides on the ODH of 1-C₄H₈. Although all the iron oxide catalysts showed a high O₂ conversion of more than 95 % (data not shown in Fig. 2), we give the different catalytic performances in each iron oxide catalyst. The α -Fe₂O₃ catalyst mainly progressed the complete oxidation, because a high CO₂ selectivity of 47.6 % and the lowest BD yield of 2.8 % were given. When γ - and β -Fe₂O₃ were used for the ODH, these catalysts exhibited a high 1-C₄H₈ conversion of more than 20 %, and BD yields of



Fig. 3. Effect of crystal phase of iron oxide on ODH of but-1-ene with lattice oxygen.

Catalyst: 200 mg.

ODH: 30 mL/min (1-C4H8 /Ar = 5/25 mL/min).

ODH temperature: 450 °C, ODH time: 5 min.

Table 1Specific sureface area of various iron oxide catalysts.		
Catalyst	Specific surface are m^2/g	
α-Fe ₂ O ₃	38	
β -Fe ₂ O ₃	n.d.	
γ -Fe ₂ O ₃	129	
e-Fe ₂ O ₂	67	

more than 10 %. In the case of ε -Fe₂O₃, this catalyst showed the highest 1-C₄H₈ conversion of 43.5 % and lower CO₂ selectivity of 16.6 % than other iron oxides; the highest BD yield of 17.1 % was also obtained. Moreover, ε -Fe₂O₃ showed higher catalytic activity compared to Fe₃O₄ and ZnFe₂O₄ that were already reported here (Fig. S1). Among various iron oxide catalysts, ε -Fe₂O₃ exhibited the highest ODH activity.

To the best of our knowledge, this is the first successful result showing the high activity of $\epsilon\text{-}Fe_2O_3$ for the ODHs of various substrates, such as propane and but-1-ene. In order to understand the effect of the crystalline structure of iron oxide on the ODH in the absence of molecular O_2 , we carried out ODH with lattice oxygen in iron oxide. Fig. 3 presents our results. $\alpha\text{-}Fe_2O_3$ showed a low $1\text{-}C_4H_8$ conversion of 9.9 % and low BD selectivity of 15.6 %. While $\gamma\text{-}Fe_2O_3$ showed a high conversion of 24.4 %, this catalyst exhibited high CO_2 selectivity of 22.1 %. Therefore, $\gamma\text{-}Fe_2O_3$ progressed the complete oxidation. Although $\beta\text{-}Fe_2O_3$ indicated low conversion of 13.8 %, it produced the highest BD selectivity of 56.9 %. Surprisingly, $\epsilon\text{-}Fe_2O_3$ showed the highest conversion of 46.4 %, and the high BD selectivity of 49.9 %.

The order of BD yield was thus: ε -Fe₂O₃ (23.2 %) > β -Fe₂O₃ (7.9 %) > γ -Fe₂O₃ (5.5 %) > α -Fe₂O₃ (1.6 %). These results clarified that the lattice oxygen in ε -Fe₂O₃ was effectively used for the ODH of 1-C₄H₈. The unique performance of ε -Fe₂O₃ appeared to be related to the ODH of 1-C₄H₈ in the presence of O₂. When the specific surface area of various iron oxide catalysts was measured (Table 1), the order of specific surface area was following: γ -Fe₂O₃> ε -Fe₂O₃> α -Fe₂O₃. Generally, the specific surface area depends on the particle size or the controlled pore structure. The order of particle size may be α -Fe₂O₃> ε -Fe₂O₃> γ -Fe₂O₃ because the pore structure is not controlled. On the other hand, the order of ODH activity was ε -Fe₂O₃> γ -Fe₂O₃> α -Fe₂O₃. Therefore, it is considered that the specific surface area of the catalyst is not related to ODH activity. This fact indicated that the ODH activity strongly depends on the crystallite structure of iron oxide rather than the specific surface area and particle size.

On the other hand, it is reported that the α -Fe₂O₃/ZnFe₂O₄ biphasic catalyst showed the high ODH performance. According to the research, n-butene was interacted with ZnFe₂O₄ and ZnAl₂O₄ which have the spinel structure, and the activated butene reacted with the lattice





(b) XRD patterns of fresh and used catalyst.



Fig. 5. Evaluation of redox property for ϵ -Fe2O3.

(a) Repeated ODH of but-1-ene and re-oxidation with $\epsilon\text{-}Fe2O3.$

(b) XRD patterns of ε-Fe2O3 after the ODH with lattice oxygen and re-oxidation with O2. Catalyst: 200 mg.

ODH: 30 mL/min (1-C4H8 /Ar = 5/25 mL/

min). ODH temperature: 450 °C, ODH time: 5 min. Re-oxidation: O2/Ar = 5/25 mL/min. Re-oxidation temperature: 450 °C, Re-oxidation time: 10 min.

oxygen in α -Fe₂O₃ to produce BD [38]. In other words, this result indicated that iron-based catalyst combined corundum structure and spinel structure is more effective for the ODH of n-butene. When ϵ -Fe₂O₃ was focused, ϵ -Fe₂O₃ has the crystalline structure that combine corundum structure (α -Fe₂O₃) and spinel structure (γ -Fe₂O₃). Therefore, it is considered that ϵ -Fe₂O₃ catalyst could show the particularly high ODH activity.

3.2. Stability of ε -Fe₂O₃ catalyst for ODH

Catalytic performance stability for the ODH reaction is an important factor for the efficient production of BD. Therefore, we conducted a stability test of ε -Fe₂O₃. Fig. 4 shows the result of ODH and XRD analysis before and after the reaction. Although ε -Fe₂O₃ showed the high BD yield of 17.1 % for 30 min, after 60 min, the 1-C₄H₈ conversion decreased from 34.3 to 27.8 %, while CO₂ selectivity increased from 20.5 to 25.5%. Unfortunately, the BD yield decreased from 17.1 % to 13.7 % (Fig. 4(a)).

To examine the reason for the decrease in the ODH activity, XRD analyses of the catalyst before and after the ODH were conducted. As shown in Fig. 4(b), ε -Fe₂O₃ diffraction peaks observed before the ODH disappeared after the reaction, and Fe₃O₄ diffraction peaks appeared after the reaction for 2 h. In the ODH of 1-C₄H₈, it has been reported that the ODH activity of the iron oxide-based catalyst declined due to the formation of divalent iron oxide species during the reaction [26,27]. Actually, the Fe₃O₄ catalyst showed low ODH activity (Fig. S1). Therefore, it is considered that the catalytic performance was decreased due to it changing from ε -Fe₂O₃ to a reduced iron oxide such as Fe₃O₄ during the ODH.

On the other hand, Wan et al. reported that catalytic activity for the ODH of n-butene is related to the oxidation and reduction cycle (redox cycle) through the lattice oxygen in the metal oxide [11]. Hence, the ODH with the lattice oxygen in the catalyst and regeneration with O_2 were carried out using ε -Fe₂O₃. The crystallite phase of ε -Fe₂O₃ after the ODH with lattice oxygen and regeneration with O_2 were then also analyzed by XRD. The results are shown in Fig. 5. In the first ODH reaction (Fig. 5(a)), a high BD yield of 23 % was obtained. Although the 1-C₄H₈ conversion (53.7 %) of the second reaction was higher than that (46.4 %) of the first reaction, low BD selectivity of 19.2 % and BD yield of 10.3 % were observed.

These results indicated that the lattice oxygen in ε -Fe₂O₃ could be used to produce BD, but could not be regenerated with O₂. Thus, BD yield decreased in the second ODH. According to XRD analysis of ε -Fe₂O₃ after the ODH using the lattice oxygen and the regeneration using O₂ (Fig. 5(b)), diffraction peaks attributable to Fe₃O₄ were shown in the catalyst (Fig. 5(b-2)), and those of γ -Fe₂O₃ in the catalyst after regeneration with O₂ (Fig. 5(b-3)). This result clearly indicates that ε -Fe₂O₃ was reduced to Fe₃O₄, and could not be regenerated to ε -Fe₂O₃ by molecular O₂.

This suggested that keeping the redox property of the lattice oxygen of the ϵ -Fe₂O₃ phase is very important to maintaining ODH activity under O₂ flow.

3.3. Effect of addition of SiO_2 to the catalyst on the ODH

As mentioned above, the ϵ -Fe₂O₃ catalyst showed the highest ODH activity among the iron oxide catalysts and was proposed as a novel catalyst. However, it was deactivated due to changes in the crystalline



Fig. 6. Stability test of ε -Fe2O3(50)-SiO2 catalyst during ODH reaction. (a) ODH under O2 flow.

(b) XRD patterns of fresh and used catalyst.



Fig. 7. Evaluation of Redox property for ε-Fe2O3 containing SiO2.

(a) Repeated ODH of but-1-ene and re-oxidation with $\epsilon\text{-}Fe2O3(50)\text{-}SiO2.}$

(b) XRD patterns of $\epsilon\mbox{-Fe2O3(50)-SiO2}$ after the ODH with lattice oxygen and re-oxidation with O2.

Catalyst: 200 mg.

ODH: 30 mL/min (1-C4H8 /Ar = 5/25 mL/min).

ODH temperature: 450 °C, ODH time: 5 min. Re-oxidation: O2/Ar = 5/25 mL/min. Re-oxidation temperature: 450 °C, Re-oxidation time: 10 min.

structure during the reaction and failure of the redox cycle. Therefore, we attempted to improve catalytic performance stability.

Studies have proposed Fe₂O₃/SiO₂ as a good catalyst with high catalytic performance for high-temperature sulfuric acid decomposition [37,39]. According to the literature, the redox property of metal oxide is an important factor in determining the reaction rate, and it has been reported that Fe₂O₃/SiO₂ showed the better redox property among various iron oxide-based catalysts. It was also reported that Fe₂O₃ containing Al₂O₃, CaO, and SiO₂ showed high redox cycle stability for the cyclic water gas shift process. Thus, SiO₂ seems to be related to inhibition of iron species sintering by physical blocking [40]. We therefore expected that the redox property could be improved by including SiO₂ in the iron oxide.

On the other hand, $\epsilon\text{-}Fe_2O_3$ can be formed by calcining iron oxide ($\gamma\text{-}Fe_2O_3$) coated with SiO₂ at 1050 °C [36]. Hence, to maintain the catalytic activity during the ODH, we investigated the effect of $\epsilon\text{-}Fe_2O_3$ containing SiO₂ on the ODH of 1-C₄H₈ under O₂ flow. $\epsilon\text{-}Fe_2O_3(50)$ wt %)-containing SiO₂ catalyst ($\epsilon\text{-}Fe_2O_3(50)\text{-}SiO_2$) was used for the reaction.

Fig. 6(a) shows the results of ODH with an ϵ -Fe₂O₃(50)-SiO₂ catalyst. Although the ϵ -Fe₂O₃(50)-SiO₂ catalyst showed a high 1-C₄H₈ conversion of 22.5 %, and a BD yield of 13.0 % was obtained in the reaction for 30 min, after 60 min, this catalyst showed a higher BD yield (ca.18 %) than that of pure ϵ -Fe₂O₃. In addition, no deactivation was observed during the reaction for 4 h. Therefore, the ϵ -Fe₂O₃ containing SiO₂ catalyst had a higher catalytic performance than pure ϵ -Fe₂O₃.

In order to understand the effect of adding SiO₂ on the ODH reaction, N₂ adsorption, XRD and FT-IR analyses were conducted. From N₂ adsorption, the both ε -Fe₂O₃ and ε -Fe₂O₃-SiO₂ catalysts showed almost the same value (Table S1). This result indicated that pore property in

catalyst was not related to the catalytic activity and the stability of catalyst. When XRD analyses of the ε -Fe₂O₃(50)-SiO₂ catalyst before and after the ODH were conducted, ε -Fe₂O₃ diffraction peaks were observed in the catalyst even after the ODH (Fig. 6(b)). Moreover, from the result of FT-IR, although all ε -Fe₂O₃ phase in pure ε -Fe₂O₃ catalyst was converted to Fe₃O₄ phase after reaction, ε -Fe₂O₃(50)-SiO₂ catalyst contained only ε -Fe₂O₃ phase without the formation of Fe₃O₄ (Fig. S2). Thus, this result is indicated that the amorphous iron oxide species other than ε -Fe₂O₃ phase, which cannot confirm with XRD analysis, did not exist in the used ε -Fe₂O₃(50)-SiO₂.

Unlike pure ε -Fe₂O₃, we found that the stability of the ε -Fe₂O₃ phase could be improved by SiO₂, and that maintenance of the ε -Fe₂O₃ phase led to increased ODH activity and stability during the reaction.

We also examined the redox property of the lattice oxygen in the ε -Fe₂O₃(50)-SiO₂ catalyst through repeated ODH. The results are shown in Fig. 7. The low 1-C₄H₈ conversion of 22.4 %, high BD selectivity of 49.2 %, and low BD yield of 11 % were obtained in the first ODH reaction (Fig. 7(a)). The result showed lower lattice oxygen reactivity than that of pure ε -Fe₂O₃. This is because the amount of lattice oxygen that could be used for the ODH was probably half that of pure ε -Fe₂O₃. Meanwhile, when the ODH with the lattice oxygen in the reoxidized ε -Fe₂O₃(50)-SiO₂ was carried out, the 1-C₄H₈ conversion of 23.3 %, BD selectivity of 45.7 %, and BD yield of 10.7 % were similar to the results in the first ODH. This indicated that the used lattice oxygen in ε -Fe₂O₃ containing SiO₂ could be easily regenerated by molecular O₂.

XRD analysis (Fig. 7(b)) revealed that ε -Fe₂O₃ diffraction peaks were not evident in ε -Fe₂O₃(50)-SiO₂ after the reaction with the lattice oxygen, and the small diffraction peaks related to Fe₃O₄ were also observed (Fig. 7(b-2)). Surprisingly, after reoxidation with molecular O₂, the catalyst showed ε -Fe₂O₃ diffraction peaks (Fig. 7(b-3)). Therefore, after



Fig. 8. XRD patterns of ε-Fe2O3 catalysts containing SiO2.

the ODH with the lattice oxygen, ε -Fe₂O₃(50)-SiO₂ could be restructured to the ε -Fe₂O₃ phase by O₂. Results of the XRD analyses and repeated ODH showed that SiO₂ improved the redox property of the lattice oxygen in ε -Fe₂O₃ compared to pure ε -Fe₂O₃.

As above the results, the fact, that the other iron oxide species such as Fe_3O_4 in ε - $Fe_2O_3(50)$ -SiO₂ after the ODH under O₂ flow were not seen, seems to be related to improvement of the redox property. In addition, improvement of redox property led to the high catalytic activity and stability during the ODH under O₂ flow.

3.4. Effect of ε -Fe₂O₃ content on the ODH

The usefulness of ε -Fe₂O₃ in SiO₂ for the ODH was suggested. Therefore, we investigated the effect of ε -Fe₂O₃ content on the ODH. We tested ε -Fe₂O₃(10, 20, 50)-SiO₂ and pure ε -Fe₂O₃ for the ODH. XRD analyses were carried out, and the results are shown in Fig. 8. The ε -Fe₂O₃ diffraction peaks appeared in all the catalysts, and amorphous SiO₂ peaks were observed in ε -Fe₂O₃(10, 20, 50)-SiO₂.

Fig. 9 shows the results of the ODH using ε -Fe₂O₃(10, 20, 50)-SiO₂. As mentioned in Sections 3.2 and 3.3, the pure ε -Fe₂O₃ catalyst gave the high 1-C4H8 conversion of 34.3 % and high BD yield of 17.1 % for 30 min. However, after 30 min, a decrease in BD selectivity and increase in CO₂ selectivity were observed, and the BD yield declined to 13.7 %. Meanwhile, although the E-Fe₂O₃(50)-SiO₂ catalyst showed lower 1-C₄H₈ conversions and lower BD yield than pure ε-Fe₂O₃ until 30 min, after 60 min, the BD yield increased to about 18.0 % over 4 h. In the ODH with the ε -Fe₂O₃(20)-SiO₂ catalyst, the CO₂ selectivity of about 14 % was lower than that of ε -Fe₂O₃(50)-SiO₂. In addition, the high BD yield of ca.18 % was obtained, and the ODH activity of the ε -Fe₂O₃(20)-SiO₂ catalyst was maintained during the reaction for 4 h, similar to the ε-Fe₂O₃(50)-SiO₂ catalyst. The ε-Fe₂O₃(10)-SiO₂ catalyst showed the lowest CO₂ selectivity of 11 % in this study. Low O₂ conversion of about 60 % (data not shown in Fig. 9) and 1-C₄H₈ conversion of 22 % were exhibited, producing a lower BD yield of ca.14 % compared to the other ε-Fe₂O₃ containing SiO₂ catalysts. However, the catalytic performance was the most stable for the ε -Fe₂O₃(10)-SiO₂ catalyst.

As shown in these results, all ε -Fe₂O₃ containing SiO₂ exhibited high stability compared to pure ε -Fe₂O₃. Although the BD yield improved with increasing ε -Fe₂O₃ content, the BD yield plateaued over 20 wt% of ε -Fe₂O₃. In addition, the CO₂ selectivity did not increase in the reaction with the catalyst containing ε -Fe₂O₃ over 20 wt%. Therefore, we determined that 20 wt% of ε -Fe₂O₃ was the best content percentage.

Finally, *cis*- or *trans*-but-2-ene is also important as a raw material for producing BD by the ODH. When the ODH of *cis*-2-C₄H₈ with ϵ -Fe₂O₃(20)-SiO₂ catalyst was carried out (Fig. 10), high ODH activity was obtained similar to the case of ODH of 1-C₄H₈. In addition, the ODH activity was again maintained for 4 h. These results indicated that *cis*-2-



Fig. 9. Effect of ɛ-Fe2O3 containing level on ODH of but-1-ene under O2 flow.



Fig. 10. ODH of *cis*-but-2-ene under O2 flow with ε -Fe2O3(20)-SiO2. Catalyst: 200 mg, Flow rate: 30 mL/min (*cis*-2-C4H8 /O2/Ar = 5/2.5/22.5). Reaction temperature: 450 °C.

 C_4H_8 can also be used as a new material for BD with the $\epsilon\text{-}Fe_2O_3(20)\text{-}SiO_2$ catalyst. We propose the $\epsilon\text{-}Fe_2O_3$ catalyst containing SiO_2 as a novel iron oxide catalyst that shows high catalytic performance for the ODH of n-butene.

4. Conclusions

In this study, we investigated the effect of the crystalline structure of iron oxide catalyst on the ODH of $1-C_4H_8$. The ε -Fe₂O₃ catalyst showed the highest ODH activity (BD yield of 17.1 %) among various iron oxide catalysts, and we therefore present it as a novel and excellent catalyst. Moreover, when ε -Fe₂O₃ containing SiO₂ (ε -Fe₂O₃-SiO₂) was used for this reaction, the catalyst showed high BD yield, and deactivation was not seen over 4 h. We found that SiO₂ improved the maintenance of the crystalline structure and the redox property of lattice oxygen in ε -Fe₂O₃. The optimum ε -Fe₂O₃ content was 20 wt%, because a high BD yield of 18 % for 4 h was obtained. This catalyst could also be used for the ODH of *cis*-2-C₄H₈ with the same BD yield (17 %) and high stability as for 1-C₄H₈. This suggested that *cis*- and *trans*-2-C₄H₈ could be recycled, which means the substantial selectivity of BD is higher than those indicated in the Tables and Figures in this report.

CRediT authorship contribution statement

Takayasu Kiyokawa: Conceptualization, Validation, Investigation, Writing - original draft, Visualization. Naoki Ikenaga: Resources, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

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