1. Introduction

Buta-1,3-diene (BD) is an important intermediate product in the petrochemical industry. BD is a raw material used in synthesizing rubbers such as polybutadiene rubber and styrene-butadiene rubber. BD is mainly produced through the purification of the C4 fraction, which is the main by-product in the production of ethylene by the steam cracking of naphtha. The steam cracking of naphtha, however, is associated with certain problems. One of these is that this reaction is an endothermic reaction and requires high temperatures of 700-800 °C. Another problem with this process is that has relatively low BD selectivity.

An attractive alternative to the steam cracking of naphtha is the oxidative dehydrogenation (ODH) of but-1-ene (1-C4H8) to buta-1,3-diene (BD). This exothermic reaction can proceed at a lower temperature than that required for the steam cracking of naphtha. Moreover, this process can produce BD more selectively. It has been reported that Bi2Mo6, ZnFe11, and FeSb12 oxide catalysts have the high activity for the ODH of n-C4H8, yet the complete oxidation of the reactant and the products can proceed easily (Eqs. (2), (3)).

In our laboratory, the ODH of propane using the lattice oxygen of the VOx/SiO2 catalyst has been investigated as a means of preventing the complete oxidation of the substrates. As a result, it was found that the lattice oxygen of V contributes to the high propylene yield. On the other hand, the ODH of the C4 fraction is similar to the ODH of ethylbenzene in terms of the reaction mechanism. V/MgO catalyst shows high activity for the ODH of ethylbenzene with carbon dioxide because higher-valence V species are reduced to lower-valence V species during the dehydrogenation of ethylbenzene. Furthermore, it has been reported that metal complex oxide catalysts such as Fe–Al15,16), Fe–Al–Zn–Mg17–22), and Fe–Co–Mg–Al23–26) have high activity for the ODH of ethylbenzene. It is expected that these metal oxides can be applied to the ODH of 1-C4H8 as well.

In the present study, we aimed to develop catalysts that enable high performance for the ODH of 1-C4H8 using the lattice oxygen by adding metal oxides such as Al2O3, Fe2O3, and Co2O3 to V-Mg complex oxide catalysts. In addition, given that the ODH of 1-C4H8 using molecular O2 is required for the continuous production of BD, we examined whether these catalysts can main-
tain the activity of the ODH of 1-C₄H₈ under an O₂ atmosphere.

2. Experimental

2.1. Materials
NH₄VO₃ (assay = min. 99.0 %), Mg(NO₃)₂·6H₂O (assay = min. 99.0 %), Al(NO₃)₃·9H₂O (assay = min. 99.0 %), Fe(NO₃)₃·9H₂O (assay = min. 99.0 %), Zn(NO₃)₂·6H₂O (assay = min. 99.0 %), Co(NO₃)₂·6H₂O (assay = min. 99.0 %), and citric acid (assay = min. 98.0 %) were purchased from Wako Pure Chemical Industries, Ltd. But-1-ene (1-C₄H₈, assay = min. 99.0 %) was purchased from Sumitomo Seika Chemicals Co., Ltd.

2.2. Catalyst Preparation by Citric Acid Complex Method
V-Mg(20 : 30), V-Mg-Al(20 : 30 : 10), V-Mg-Fe(20 : 30 : 1-15), V-Mg-Zn(20 : 30 : 10), V-Mg-Co(20 : 30 : 1-30), V-Co(20 : 30), and V-Co-Mg(20 : 30 : 1-20) oxide catalysts were prepared according to the citric acid complex method. When these catalysts were prepared, NH₄VO₃ (1.17 g, 0.010 mol), Mg(NO₃)₂·6H₂O (3.85 g, 0.015 mol), and Al(NO₃)₃·9H₂O (1.87 g, 0.005 mol), Fe(NO₃)₃·9H₂O (2.02 g, 0.005 mol), Zn(NO₃)₂·6H₂O (1.50 g, 0.005 mol), or Co(NO₃)₂·6H₂O (0.17-4.38 g, 0.0005-0.015 mol) were dissolved in 30 mL of the citric acid (4.80-7.68 g) aqueous solution. After standing for 24 h at a room temperature, the water was slowly evaporated from the mixed solution in an oil bath at 80 °C. The catalysts were then calcined at 600 °C for 15 h in air.

2.3. Characterization of Catalysts
In order to analyze the crystalline structure of the catalysts before and after the reaction, X-ray diffraction (XRD) analysis was carried out according to the powder method with a Shimadzu XRD-6000 diffraction meter with monochromatic CuKα radiation (tube voltage 40 kV, tube current 30 mA, scan step 0.02 °, scan region 10-80 °, scan rate 1.0 °/min). X-ray photoelectron spectra (XPS) analysis was carried out with a JEOL model JPS-9010 MX using MgKα radiation as the energy source. Surface areas of the catalysts were determined by the BET method using N₂ adsorption equipment (MicrotracBEL Corp., BELSORP-miniII-ISP). Samples were dried at 200 °C for 1 h prior to the measurement. Temperature programmed reaction with 1-C₄H₈ (1-C₄H₈-TPR) was conducted with an online quadrupole mass spectrometer (Hiden Analytical Ltd., HAL 201) fitted with an outlet of a fixed-bed quartz reactor (4 mmøx 200 mm). After placing 200 mg of the catalyst in the reactor, the catalyst was preheated at 200 °C for 1 h under Ar to eliminate adsorbed H₂O. Then, 5 mL/min of 1-C₄H₈ or O₂ and 25 mL/min of Ar were introduced. The reactor was heated to 800 °C at the heating rate of 5 °C/min. Mass spectrometer was scanned corresponding parent peaks of following products, C₄H₈, C₄H₆, H₂, H₂O, CO, CO₂, and CH₄ within 1 s. The repeated scans were collected in a personal computer.

2.4. Catalyst Test
2.4.1. ODH of 1-C₄H₈ without Molecular O₂
ODH of 1-C₄H₈ was carried out with a fixed-bed flow-type quartz reactor (10 mmøx 350 mm) at 480 °C under atmospheric pressure. Typical reaction conditions were as follows: after placing 200 mg of the catalyst in the reactor, the catalyst was heated to 480 °C under 25 mL/min of Ar. The reaction was carried out with 5 mL/min of 1-C₄H₈ and 25 mL/min of Ar for 0.5-8 min. The re-oxidation was carried out with 5 mL/min of O₂ and 25 mL/min of Ar at 480 °C for 8 min. The C4 products (1-C₄H₈, cis-2-C₄H₈, trans-2-C₄H₈, and C₄H₆) were analyzed with a GC-FID (Shimadzu GC-14B, column: Unicarbon A-400). CO and CO₂ were also analyzed with a GC-FID (Shimadzu GC-14B, column: active carbon) equipped with a methanizer (Shimadzu MTN-1). H₂ was analyzed with a GC-TCD (Shimadzu GC-8A, column: active carbon).

2.4.2. ODH of 1-C₄H₈ under O₂ Flow
ODH of 1-C₄H₈ under an O₂ atmosphere was carried out with a fixed-bed flow-type quartz reactor (10 mmøx 350 mm) at 480 °C under atmospheric pressure. Typical reaction conditions were as follows: after placing 200 mg of the catalyst in the reactor, the catalyst was heated to 480 °C under 22.5 mL/min of Ar. The flow gas was switched to 5 mL/min of 1-C₄H₈, 22.5 mL/min of Ar, and 2.5 mL/min of O₂. The reactor was kept at 480 °C for 100 min or 600 min. The C4 products (1-C₄H₈, cis-2-C₄H₈, trans-2-C₄H₈, and C₄H₆), CO, and CO₂ were analyzed with a GC-FID as described in 2.4.1. H₂ was analyzed with a GC-TCD as described in 2.4.1.

2.4.3. Pulse Reaction
Pulse reaction was carried out with the fixed-bed flow-type quartz reactor (10 mmøx 350 mm) at 480 °C under an atmospheric pressure. Typical reaction conditions are as follows: After placing 200 mg of the catalyst in the reactor, the catalyst was heated to 480 °C under 25 mL/min of N₂. Then, 1 mL of 1-C₄H₈ and ¹⁸O₂ mixed gas (1-C₄H₈/¹⁸O₂ = 2/1) was introduced into the reactor with 25 mL/min of N₂. H₂O (m/z = 18 and 20), ¹⁸CH₄ (m/z = 41), C₁H₆ (m/z = 54), O₂ (m/z = 32 and 36), and CO₂ (m/z = 44 and 48) were detected with the on-line quadrupole mass spectrometer.

3. Results and Discussion
3.1. Activity of V–Mg Catalysts for ODH of 1-C₄H₈
3.1.1. Effect of Adding Metal Oxides to V–Mg Catalysts
Table 1 shows the results of 1-C₄H₈ ODH in the presence of V-Mg(20 : 30), V-Mg-Al(20 : 30 : 10), V-
Mg-Fe(20 : 30 : 10), V-Mg-Zn(20 : 30 : 10), and V-Mg-Co(20 : 30 : 10) catalysts without molecular O2. The numerical values in parentheses indicate molar ratios. V-Mg(20 : 30) enabled high CO and CO2 selectivity of 5.2 % and 10.2 %, respectively, and a low BD yield of 10.9 % (Run 1). When metal oxide-added V-Mg catalysts were used, CO and CO2 selectivity were decreased to 1-4 % (Runs 2-5). V-Mg-Al(20 : 30 : 10) and V-Mg-Fe(20 : 30 : 10) enabled high BD yields of 16.8 % and 18.9 %, respectively (Runs 2, 3). V-Mg-Zn(20 : 30 : 10) resulted in a low BD yield of 12.9 % (Run 4) in contrast to other metal oxide-added V-Mg catalysts. The highest BD yield of 22.9 % was obtained with V-Mg-Co(20 : 30 : 10) (Run 5). V-Mg-Co(20 : 30 : 10) was the best catalyst for ODH without molecular O2.

To clarify these results, we next measured the specific surface areas and XRD of the catalysts. Figure 1 illustrates the specific surface areas and the XRD patterns of V-Mg(20 : 30), V-Mg-Al(20 : 30 : 10), V-Mg-Fe(20 : 30 : 10), V-Mg-Zn(20 : 30 : 10), and V-Mg-Co(20 : 30 : 10). The specific surface area of V-Mg (20 : 30) and V-Mg-Al(20 : 30 : 10) are smaller than those of other catalysts at 18 m²/g. V-Mg-Zn(20 : 30 : 10) has a specific surface area of 19 m²/g, and those of V-Mg-Fe(20 : 30 : 10) and V-Mg-Co(20 : 30 : 10) are nearly the same at 27 m²/g and 26 m²/g, respectively. These results suggest that among these catalysts, those with large specific surface areas exhibit relatively high activity. Yet while this rule appear to be generally true, we noted that V-Mg-Co(20 : 30 : 10) enabled a higher BD yield than V-Mg-Fe(20 : 30 : 10) did. To explore this phenomenon, we next examined the crystalline structures of the catalysts.

V-Mg(20 : 30), V-Mg-Al(20 : 30 : 10), and V-Mg-Fe(20 : 30 : 10) have the crystalline structure of Mg₃V₂O₈ only. The XRD patterns of Mg₃V₂O₈ and Zn₃V₂O₈ can be seen within V-Mg-Zn(20 : 30 : 10). It has been reported that the crystalline structure of Mg₃V₂O₈ contributes to the ODH of n-pentane. Therefore, V-Mg-Zn(20 : 30 : 10) has low activity for the ODH of 1-C₄H₈ because the crystalline structure of Mg₃V₂O₈ does not grow. V-Mg-Co(20 : 30 : 10) exhibits not only the diffraction peaks of Mg₃V₂O₈ but also those of Mg₂V₂O₇, CoO₃, and Co₃V₂O₈, which do not exist in V-Mg-Fe(20 : 30 : 10). It appears that the difference in ODH activity between V-Mg-Fe(20 : 30 : 10) and V-Mg-Co(20 : 30 : 10) is due to the crystalline structures of Mg₂V₂O₇, CoO₃, or Co₃V₂O₈. In other words, the crystalline structures of Mg₂V₂O₇, CoO₃, or Co₃V₂O₈ seem to contribute significantly to BD production in the ODH of 1-C₄H₈.

### Table 1: Effect of Metal (Al, Fe, Zn, and Co) Oxides Addition to V-Mg Catalysts on the ODH of 1-C₄H₈ without Molecular O₂

| Run | Catalyst | 1-C₄H₈ conv. [%] | Selectivity [%] | Yield [%] |
|-----|----------|----------------|---------------|---------|
|     |          | C₄H₆ cis | C₄H₆ trans | CO | CO₂ |
| 1   | V-Mg(20 : 30) | 33.3       | 40.0         | 23.8 | 20.9 | 5.2 | 10.2 | 10.9 |
| 2   | V-Mg-Al(20 : 30 : 10) | 47.6      | 35.3         | 31.1 | 29.0 | 0.8 | 3.8  | 16.8 |
| 3   | V-Mg-Fe(20 : 30 : 10) | 60.5      | 32.2         | 31.7 | 32.0 | 0.8 | 2.5  | 18.9 |
| 4   | V-Mg-Zn(20 : 30 : 10) | 61.7      | 23.3         | 35.3 | 36.2 | 1.0 | 3.1  | 12.9 |
| 5   | V-Mg-Co(20 : 30 : 10) | 60.7      | 39.7         | 28.9 | 27.5 | 0.5 | 3.4  | 22.9 |

Catalyst: 200 mg. Flow rate: 1-C₄H₈/Ar = 5 (mL/min)/25 (mL/min). Reaction temp.: 480 °C. Reaction time: 8 min.
ous work\textsuperscript{28}).

Figure 2 shows the XRD patterns and the specific surface areas of V-Mg and V-Mg-Fe catalysts. The crystalline structures of Mg\textsubscript{3}V\textsubscript{2}O\textsubscript{8} and Mg\textsubscript{2}V\textsubscript{2}O\textsubscript{7} were observed for all the catalysts. However, MgFe\textsubscript{2}O\textsubscript{4} diffraction peaks were seen in the V-Mg-Fe(20 : 30 : 15). This fact suggested that Fe could be incorporated into the V-Mg structure up to V : Mg : Fe (molar ratio) = 20 : 30 : 10. Specific surface area increased with increasing the amount of iron oxide, indicating the largest specific surface area of 32 m\textsuperscript{2}/g with the V-Mg-Fe(20 : 30 : 10). However, that of the V-Mg-Fe(20 : 30 : 15) decreased to 18 m\textsuperscript{2}/g.

Table 2 presents the results of the ODH of 1-C\textsubscript{4}H\textsubscript{8} with V-Mg and V-Mg-Fe catalysts in the absence of molecular O\textsubscript{2}. As noted in section 3.1.1, the V-Mg (20 : 30) showed a low BD yield of 10.9\%. The BD yield increased up to V : Mg : Fe = 20 : 30 : 10 (20.3\%) and decreased to 19.1\% with the V-Mg-Fe(20 : 30 : 15). These results suggested that the improvement of the BD yield could be attributed to an increase in the specific surface area of the V-Mg-Fe catalysts.

Table 2 | Effect of Fe Addition Amount on the ODH of 1-C\textsubscript{4}H\textsubscript{8} without Molecular O\textsubscript{2}

| Run | Catalyst | 1-C\textsubscript{4}H\textsubscript{8} conv. [%] | Selectivity [%] | Yield [%] | C\textsubscript{4}H\textsubscript{6} | cis-2-C\textsubscript{4}H\textsubscript{8} | trans-2-C\textsubscript{4}H\textsubscript{8} | CO | CO\textsubscript{2} |
|-----|----------|------------------|----------------|----------|---------|----------------|-----------------|-----|-------|
| 1   | V-Mg(20 : 30) | 33.3 | 40.0 | 23.8 | 20.9 | 5.2 | 10.2 | 10.9 |
| 6   | V-Mg-Fe(20 : 30 : 1) | 45.9 | 40.4 | 27.8 | 26.0 | 1.1 | 4.7 | 18.6 |
| 7   | V-Mg-Fe(20 : 30 : 5) | 53.6 | 35.5 | 27.9 | 29.2 | 1.2 | 6.1 | 19.1 |
| 8   | V-Mg-Fe(20 : 30 : 10) | 53.9 | 37.7 | 29.2 | 27.1 | 1.2 | 4.8 | 20.3 |
| 9   | V-Mg-Fe(20 : 30 : 15) | 56.3 | 33.9 | 31.1 | 28.2 | 1.5 | 5.4 | 19.1 |

In order to evaluate the relationship between the ODH activity and reactivity of the lattice oxygen, 1-C\textsubscript{4}H\textsubscript{8}-TRP measurements of the V-Mg(20 : 30) and the V-Mg-Fe(20 : 30 : 10) were carried out. The results are illustrated in Fig. 3. Although the V-Mg catalyst formed H\textsubscript{2}O (m/z = 18), BD (m/z = 54), and CO\textsubscript{2} (m/z = 44) at around 430 °C, the V-Mg-Fe(20 : 30 : 10) formed H\textsubscript{2}O and BD at around 300 °C. Therefore, it is clear that the V-Mg-Fe(20 : 30 : 10) could progress the ODH of 1-C\textsubscript{4}H\textsubscript{8} at a lower temperature than the V-Mg(20 : 30). These results suggest that the reactivity of the lattice oxygen in the catalyst increased with increasing iron oxide, and it is considered that the high reactivity of the lattice oxygen contributes to higher BD yield.

To investigate the state of the V-Mg-Fe(20 : 30 : 10) after the ODH without molecular O\textsubscript{2}, XPS analyses of the V-Mg-Fe(20 : 30 : 10) before and after the reaction were carried out. Figure 4 shows XPS spectra of the V-Mg-Fe(20 : 30 : 10). Only V\textsuperscript{5+} existed in a fresh catalyst (Fig. 4a). After the ODH in the absence of molecular O\textsubscript{2}, the V\textsuperscript{5+} oxidation state of the V-Mg-Fe(20 : 30 : 10) was observed (Fig. 4b).
molecular O2, however, all V species were reduced to V4+. Meanwhile, Fe3+ existed in the fresh catalyst and were reduced to Fe2+ after the reaction (Fig. 4b). These results suggest that the lattice oxygen of Mg3V2O8 and the incorporated iron oxide species can be used for the ODH.

We also examined whether the V-Mg-Fe(20 : 30 : 10) could be repeatedly reused. ODHs and re-oxidation with molecular O2 were repeated. The result is shown in Fig. 5. The 1-C4H8 conversion and the BD yield were decreased up to 3 times, but after that, the catalyst exhibited the constant catalytic performance up to 8 times. Therefore, it is clear that the re-oxidation of used V-Mg-Fe(20 : 30 : 10) is possible and the regenerated catalyst could be reused for the ODH of 1-C4H8.

3.1.3 Effects of Different Amounts of Co Added to V-Mg-Co Catalyst on ODH of 1-C4H8

In order to examine how different amounts of Co added to V-Mg-Co affect the ODH of 1-C4H8, V-Mg-Co catalysts were prepared with various Co content ratios. Table 3 shows the ODH of 1-C4H8 using V-Mg-Co catalysts without molecular O2. V-Mg-Co(20 : 30 : 5) indicated the best activity, giving a high BD yield of 22.5 % and a low CO2 selectivity of 3.2 % (Run 10). As the Co content ratio increased, however, the BD selectivity and the BD yield significantly decreased. We next investigated whether V-Mg-Co catalysts can maintain the activity of the ODH of 1-C4H8 under O2 flow. Table 4 shows the ODH of 1-C4H8 using V-Mg-

![Fig. 4 XPS Spectra of V-Mg-Fe(20 : 30 : 10) Catalyst before and after ODH without Molecular O2](image)

![Fig. 5 Repeated Runs of But-1-ene ODH and Re-oxidation Cycle with V-Mg-Fe(20 : 30 : 10)](image)

| Run | Catalyst | 1-C4H8 conv. [%] | Selectivity [%] | Yield [%] |
|-----|----------|------------------|-----------------|-----------|
|     |          |                  | C4H6 | cis-2-C4H6 | trans-2-C4H6 | CO | CO2 | C4H6 |
| 1   | V-Mg(20 : 30) | 33.3             | 40.0 | 23.8      | 20.9        | 5.2 | 10.2 | 10.9 |
| 10  | V-Mg-Co(20 : 30 : 5) | 65.6             | 36.7 | 28.1      | 31.3        | 0.7 | 3.2  | 22.5 |
| 11  | V-Mg-Co(20 : 30 : 10) | 60.7             | 39.6 | 28.9      | 27.4        | 0.6 | 3.6  | 22.9 |
| 12  | V-Mg-Co(20 : 30 : 20) | 63.8             | 33.9 | 30.2      | 31.1        | 0.7 | 4.2  | 19.4 |
| 13  | V-Mg-Co(20 : 30 : 30) | 72.4             | 26.1 | 31.7      | 40.1        | 0.6 | 1.5  | 17.6 |

Catalyst: 200 mg. Flow rate: 1-C4H8/Ar = 5 (mL/min)/25 (mL/min). Reaction temp.: 480 °C. Reaction time: 8 min.

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3. 2. Activity of V–Co Catalysts for the ODH of 1-C₄H₈

3. 2. 1. Effect of Various Proportions of Mg Added to V–Co–Mg Catalyst

In order to examine whether Co₃V₂O₈ and CoV₂O₄ are capable of high activity for ODH, V-Co(20 : 30) was prepared. In addition, to investigate the possibility that the difference in the activity was related to the amount of Mg, V-Co-Mg(20 : 30 : 5-20) were prepared. The ODH of 1-C₄H₈ was conducted using these catalysts under an O₂ atmosphere. As shown in Table 5, V-Co(20 : 30) enabled a 1-C₄H₈ conversion of 38.2 % and a BD yield of 12.7 % (Run 19). V-Co-Mg(20 : 30 : 5), in contrast, enabled a 1-C₄H₈ conversion of 31.8 % and a BD yield of 18.1 % (Run 20). However, both the 1-C₄H₈ conversion and the BD yield decreased as the amount of added Mg decreased.

To interpret these results, we performed XRD analyses to investigate the effects of differences in the crystallite structures of catalysts, which contribute significantly more to the ODH of 1-C₄H₈ than Mg₃V₂O₈ does.

V-Mg-Co(20 : 30 : 5) exhibits high activity for the ODH of 1-C₄H₈ with the lattice oxygen but low activity for the same ODH process under O₂ flow. To explore the reasons for this, we conducted XRD analyses of V-Mg-Co(20 : 30 : 5) and V-Mg-Co(20 : 30 : 30) after the reaction. As shown in Fig. 7, the crystallite structure of V-Mg-Co(20 : 30 : 5) changed from Mg₃V₂O₈ to MgO during the reaction, both without molecular O₂ and under O₂ flow. In the XRD patterns of V-Mg-Co(20 : 30 : 30), the crystallite structure transformed to that of MgO and CoV₂O₄ during both reactions. It was expected that Mg₃V₂O₈ would yield high 1-C₄H₈ conversion and high BD selectivity in the early stage, but in practice, Mg₃V₂O₈ could not be maintained because the crystallite structure changed to that of MgO during the reactions. On the other hand, V-Mg-Co(20 : 30 : 30), which has the crystallite structures of Co₃V₂O₈ and CoV₂O₄, showed high activity for ODH under O₂ flow. Therefore, we concluded that Co₃V₂O₈ and CoV₂O₄ have high activity for the ODH of 1-C₄H₈.

### Table 4  Effect of Co Addition Amount on the ODH of 1-C₄H₈ under O₂ Flow

| Run | Catalyst | 1-C₄H₈ conv. [%] | Selectivity [%] | Yield [%] |
|-----|----------|-----------------|-----------------|----------|
|     |          | C₄H₄ | cis-2-C₄H₈ | trans-2-C₄H₈ | CO | CO₂ | C₄H₈ |
| 14  | V-Mg(20 : 30) | 32.9 | 22.5 | 25.9 | 22.1 | 7.7 | 21.8 | 7.4 |
| 15  | V-Mg-Co(20 : 30 : 5) | 25.2 | 44.4 | 16.0 | 12.3 | 4.3 | 22.9 | 11.4 |
| 16  | V-Mg-Co(20 : 30 : 10) | 27.2 | 44.0 | 15.3 | 11.7 | 5.0 | 24.0 | 12.2 |
| 17  | V-Mg-Co(20 : 30 : 20) | 28.5 | 41.4 | 17.8 | 13.7 | 3.6 | 23.5 | 12.5 |
| 18  | V-Mg-Co(20 : 30 : 30) | 33.0 | 41.2 | 21.1 | 17.3 | 3.1 | 17.3 | 13.4 |

Catalyst: 200 mg. Flow rate: 1-C₄H₈/O₂/Ar = 5 (mL/min)/2.5 (mL/min)/22.5 (mL/min). Reaction temp.: 480 °C. Reaction time: 100 min.
ses of the catalysts before and after the reactions. Figure 8 depicts XRD patterns of V-Co and V-Co-Mg catalysts before the reaction. All the catalysts have the crystalline structure of Co$_3$V$_2$O$_8$. When Mg was added, the diffraction peaks of Mg$_2$V$_2$O$_7$ and Co$_3$O$_4$ appeared. The intensity of these peaks increased as we increased the amount of Mg. Figure 9 shows the XRD patterns of V-Co and V-Co-Mg catalysts after the reactions. The crystalline structure of V-Co(20 : 30) changed to that of CoV$_2$O$_4$, and that of V-Co-Mg(20 : 30 : 5, 7.5, 10, 20) changed to that of CoV$_2$O$_4$ and MgO. The intensity of the diffraction peaks of MgO increased as we increased the amount of Mg. Both the 1-C$_4$H$_8$ conversion and the BD yield, however, decreased as the peak intensity of Mg$_2$V$_2$O$_7$ and MgO increased. Therefore, V-Co-Mg(20 : 30 : 5) is the best catalyst for ODH under O$_2$ flow.

In order to investigate what makes V-Co-Mg(20 : 30 : 5) the best catalyst for ODH, we conducted XPS analyses of the catalysts before and after the reactions. Figure 10 shows the XPS spectra of V-Co(20 : 30) and V-Co-Mg(20 : 30 : 5-20). Only V$^{5+}$ was observed in these fresh catalysts. After the reactions, certain portions of this V$^{5+}$ were reduced to V$^{4+}$ and V$^{3+}$. After the reaction with V-Co(20 : 30), 30.6 % of the V$^{5+}$, which shows high activity for the ODH of ethylbenzene$^{10}$, maintained in the catalyst. After the reaction with V-Co-Mg(20 : 30 : 5), which gave the highest activity, however, the percentage of V$^{5+}$ remaining was the highest at 42.2 %. Figure 11 shows the relationship between the percentage of V$^{5+}$ and the BD yield. The BD yield increased as the percentage of V$^{5+}$ increased. V$^{3+}$ is believed to exist mainly in bulk form, because our XRD analysis revealed that the crystalline structure of the catalyst after the reaction was that of CoV$_2$O$_4$. Yet the results of our XPS analysis revealed that V$^{5+}$, V$^{4+}$, and V$^{3+}$ were present on the catalyst surface (Fig. 10). These results indicate that the oxidation state of the V species.

| Run | Catalyst          | 1-C$_4$H$_8$ conv. [%] | Selectivity [%] | Yield [%] | C$_4$H$_6$ | cis-2-C$_4$H$_8$ | trans-2-C$_4$H$_8$ | CO | CO$_2$ |
|-----|-------------------|------------------------|----------------|----------|---------|----------------|-------------------|----|-------|
| 19  | V-Co(20 : 30)     | 38.2                   | 33.2           | 22.3     | 19.4    | 4.0            | 21.1               | 12.7|
| 20  | V-Co-Mg(20 : 30 : 5) | 31.8                  | 55.1           | 13.9     | 10.4    | 2.6            | 18.0               | 18.1|
| 21  | V-Co-Mg(20 : 30 : 7.5) | 31.3                  | 53.5           | 12.8     | 9.3     | 2.4            | 22.0               | 17.2|
| 22  | V-Co-Mg(20 : 30 : 10) | 29.2                  | 53.3           | 12.8     | 9.5     | 2.3            | 22.0               | 15.6|
| 23  | V-Co-Mg(20 : 30 : 20) | 27.3                  | 51.9           | 13.1     | 9.8     | 2.5            | 22.6               | 14.3|

Catalyst: 200 mg. Flow rate: 1-C$_4$H$_8$/O$_2$/Ar = 5 (mL/min)/2.5 (mL/min)/22.5 (mL/min). Reaction temp.: 480 °C. Reaction time: 100 min.
of catalyst contributes to the BD production in the ODH of 1-C₄H₈. In addition, V-Co-Mg(20 : 30 : 5) showed high activity for ODH because the V species of the catalysts can maintain high oxidation states.

To investigate the difference in the reactivity of the catalysts for the ODH due to Mg adding to V-Co catalyst, 1-C₄H₈-TPRs were conducted. Figure 12 shows the results of 1-C₄H₈-TPR measurements of V-Co (20 : 30) and V-Co-Mg(20 : 30 : 5). In 1-C₄H₈-TPR profile of V-Co-Mg(20 : 30 : 5), H₂O was produced at a lower temperature of 280 °C than that of V-Co(20 : 30) catalyst (370 °C). This fact suggests that the ODH of 1-C₄H₈ could proceed at a lower temperature by means of the adding of Mg. Therefore, oxygen mobility seems to be increased by the Mg addition.

3.2.2. Effect of Reaction Time on the ODH of 1-C₄H₈

The crystalline structure of V-Co-Mg(20 : 30 : 5) changed during a 100 min reaction (Fig. 9). Therefore, it is expected that the reactivity of the catalyst for the ODH may change with a change in the crystalline structure. To confirm this expectation, the effect of reaction time on the ODH of 1-C₄H₈ using the V-Co-Mg(20 : 30 : 5) catalyst under an O₂ atmosphere was examined. As shown in Fig. 13 (Fig. 13a: 0-20 min, Fig. 13b: 20-600 min), the extremely high 1-C₄H₈ conversion of 66.1 % and a BD yield of 42.5 % were obtained during a 0.5 min reaction. As the reaction time increased up to 20 min, however, the 1-C₄H₈ conversion and the BD yield decreased. In particular, significant decreases in 1-C₄H₈ conversion and BD yield were observed between 0.5 min and 5 min. In order to explore the reasons for this, we conducted XRD analyses. Figure 14 shows the XRD patterns of V-Co-Mg(20 : 30 : 5) before and after the reactions. During the 5 min reaction, the crystalline structure changed completely from that of Co₃V₂O₈, Mg₂V₂O₇, and Co₃O₄ to that of CoV₂O₄ and MgO. It appears that this change in the crystalline structure of Co₃V₂O₈ is a cause of the significant decrease in activity over time. As the results in Fig. 13a and Fig. 14 reveal, the crystalline structure of Co₃V₂O₈ can exhibit excellent activity for the ODH of 1-C₄H₈, but the stability of Co₃V₂O₈ is low, resulting in a decreased activity over time.

Although the 1-C₄H₈ conversion decreased until 100 min (Fig. 13b), the BD yield was maintained at
17.5% throughout the 100 min reaction. The 1-C4H8 conversion was suppressed because the isomerization reaction of 1-C4H8 was decreased. The cis-2-C4H8/trans-2-C4H8 ratio in the reaction remained stable at 1.3 for 600 min. According to our XPS analysis, no metals such as V, Co, and Mg were present on the catalyst surface after the reaction. These results suggest that the surface of this catalyst was acidic. During the 20 min reaction, the deposited carbon calculated from the TG analysis was 53.1 μmol (0.32 wt%). During the 100 min reaction, the deposited carbon increased to 169.1 μmol (1.01 wt%). The carbon was deposited on the acid sites of the catalyst during the ODH of 1-C4H8 under O2 flow, decreasing its activity for isomerization. The BD selectivity, however, increased between 20 min and 100 min. The 1-C4H8 conversion and the BD yield were maintained at 28.5% and 17.5%, respectively, even during a 600 min reaction. During this 600 min reaction, notably, the crystalline structure of the catalyst remained as it was during the 100 min reaction (Fig. 14). These results suggest that the crystalline structure of CoV2O4 can produce BD continuously in the ODH of 1-C4H8 under O2 flow. In addition, to explore how V-Co-Mg(20 : 30 : 5) can maintain its activity for 600 min, we conducted XPS analyses of the catalyst after a 600 min reaction. Figure 15 shows the XPS spectra of V-Co-Mg(20 : 30 : 5). During the 600 min reaction, the percentage of V5+ was 42.3%, which is almost identical to the percentage of V5+ in the catalyst used for the ODH for 100 min (42.2%). Thus V-Co-Mg(20 : 30 : 5) can maintain its activity because its percentage of V5+ stays constant whether the reaction lasts 100 min or 600 min.

3.2.3. Pulse Reaction of 1-C4H8 and 18O2

A pulse reaction of 1-C4H8 and 18O2 was carried out to clarify the reaction mechanism of ODH on V-Co-Mg(20 : 30 : 5). As shown in Fig. 16, at the moment when the pulse was sent, BD (m/z = 54), CO2 (m/z = 44), and H2O (m/z = 18) were observed, but H18O (m/z = 20) was not produced. Therefore, the fresh V-Co-Mg(20 : 30 : 5) catalyst could induce the ODH of 1-C4H8 using the lattice oxygen of the catalyst. The intensity of the C18O2 (m/z = 48) peak increased as the number of pulses increased. Thus 18O2 must be used...
for the oxidation of the deposited carbon or the re-oxidation of the catalyst, because H$_2^{18}$O (m/z = 20) was not observed. Therefore, the lattice oxygen of Co$_3$V$_2$O$_8$ might be used for the ODH of 1-C$_4$H$_8$ at the first stage of the reaction.

The pulse reaction was carried out with V-Co-Mg(20 :
30 : 5) that had been used in the ODH of 1-C₄H₈ under an O₂ atmosphere for 100 min. As shown in Fig. 17, ¹⁸O₂ must have been used for the ODH of 1-C₄H₈ or the complete oxidation of the substrates, because BD (m/z = 54), H₂¹⁸O (m/z = 20), and C¹⁸O₂ (m/z = 48) were produced. After the 100 min reaction, the crystalline structure of the catalyst was CoV₂O₄ as opposed to Co₃V₂O₈ (Fig. 14). Therefore, we concluded that molecular O₂ was not used for the re-oxidation of the catalyst. Rather, molecular O₂ was assumed to absorb and react on the surface of the catalyst. To support this assumption, ODH using V-Co-Mg(20 : 30 : 5) that had been used in the ODH under an O₂ atmosphere for 100 min was carried out without molecular O₂. This
reaction produced 136.4 μmol of BD, which is almost identical to the amount of produced H₂ (133.3 μmol). This result suggests that only the simple dehydrogenation of 1-C₄H₈ occurred. In other words, the lattice oxygen of CoV₂O₄ was not used for ODH under these conditions. It is likely, therefore, that ODH can proceed with the oxygen adsorbed on the surface of CoV₂O₄.

From these results, we concluded that the reaction mechanism is depicted in Scheme 1. In the first stage of the reaction, the ODH of 1-C₄H₈ progresses using the lattice oxygen of Co₃V₂O₈. During the production of BD, H₂O, and CO₂, Co₃V₂O₈ rapidly changes to CoV₂O₄ (Fig. 14). At the next stage, the ODH reaction transfers to the catalyst cycle as shown in Scheme 1. A portion of the 1-C₄H₈ that was adsorbed on the catalyst is deposited as carbon on the surface of CoV₂O₄, then oxidized into CO₂ by molecular O₂ which had been adsorbed on the surface of CoV₂O₄. The ODH of 1-C₄H₈ can thus progress using the O₂ adsorbed on the catalyst surface. In the reaction cycle, it is likely that these reactions occur almost simultaneously, because BD (m/z = 54), H₂¹⁸O (m/z = 20), and C¹⁸O₂ (m/z = 48) were observed at the same time (Fig. 17).

4. Conclusions

We have found that introducing iron oxide to the V-Mg catalyst increased the specific surface area of the catalyst while maintaining the Mg₃V₂O₈ structure. Therefore, the V-Mg-Fe(20 : 30 : 10) catalyst could give a higher BD yield of 20.3 % in the ODH of 1-C₄H₈ without molecular O₂. The V-Co catalysts, which have the crystalline structure of Co₃V₂O₈ and CoV₂O₄, were more active than the V-Mg catalysts for the ODH under O₂ flow. The V-Co-Mg(20 : 30 : 5) catalyst has the highest activity for the ODH of 1-C₄H₈ under O₂ flow, maintaining a 1-C₄H₈ conversion of 28.5 % and a BD yield of 17.5 % for 600 min. The percentage of V⁵⁺ on the surface of the catalyst affects the 1-C₄H₈ conversion and the BD yield. Preserving high valence of the V species is important to maintain their capacity for ODH over the long term. It is likely that CoV₂O₄ is highly active in the early stage of ODH, whereas in the later stages, ODH proceeds using oxygen adsorbed on the surface of CoV₂O₄.

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