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Efficient production of 1,3-butadiene in the catalytic dehydration of 2,3-butanediol

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ABSTRACT

Vapor-phase catalytic dehydration of 2,3-butanediol (2,3-BDO) was investigated over rare earth oxide catalysts and In_2O_3 at around 400 °C. In the dehydration of 2,3-BDO over Sc_2O_3, 1,3-butadiene was mainly produced together with butanone, 2-methyl-propanal, 2-methyl-propanol, 3-buten-2-ol, and butene isomers. Sc_2O_3 calcined at 800 °C showed the highest 1,3-butadiene yield of 88.3% at 411 °C in H_2 carrier gas flow. Since 3-buten-2-ol is produced selectively from 2,3-BDO over Sc_2O_3 at a low temperature of 325 °C, 3-buten-2-ol rather than butanone is a probable intermediate from 2,3-BDO to 1,3-butadiene. 3-Buten-2-ol is readily converted into 1,3-butadiene at temperatures lower than 411 °C over Sc_2O_3 and Al_2O_3. In addition, double-bed catalysts composed of an upper catalyst bed of Sc_2O_3 and a lower of Al_2O_3 successfully converted 2,3-BDO directly into 1,3-butadiene with a stable selectivity higher than 94% at 318 °C and 100% conversion of 2,3-BDO.

1. Introduction

1,3-Butadiene (BD) is one of the most important chemicals for manufacturing polymers such as styrene-butadiene rubber (SBR) [1–5], polybutadiene rubber (BR) [6,7], acrylonitrile-butadiene-styrene resins, and adiponitrile [1,8]. The major products such as SBR and BR are in great demand to produce tires of automobiles. More than 95% BD is produced in the steam cracking of petroleum over the global world [8]. However, the supply of BD depends on the production of ethylene, so that it is not stable under the situation changing the supply of chemical resources in recent years.

Ethanol [9–11] and 2,3-butanediol (2,3-BDO) [12–18] can be derived from potential resources of "bio-carbon" such as glucose and cellulose converted from corn and sugar cane. The bio-based chemicals have the possibility to take the place of naphtha to produce BD. Catalytic conversion of ethanol into BD has been considered as a possible route [19–25]: a high BD selectivity of 72% has been reported [23]. In either the direct process using pure ethanol [19] or the two-step process using a mixture of ethanol and acetaldehyde [25], a complexed reaction sequence of different types of reactions such as dehydrogenation, aldol condensation, hydrogenation, and dehydration is required to produce BD directly. Unfortunately, sufficient catalysts for the ethanol route have not been developed yet.

On the other hand, 2,3-BDO is an alternative resource to produce BD because of its C4 structure, and the dehydration of 2,3-BDO to BD has been also investigated since 1940s [26–28]. Great attention had been paid to the exploitation of renewable resources to produce BD. Winfield disclosed that BD was obtained with a yield of 62% over ThO_2 at 500 °C [26]. ThO_2 has the catalytic activities to produce BD from 2,3-BDO. Winfield also described that the dehydration product of 3-buten-2-ol (3B2OL) was obtained with a yield of 70% at a low temperature of 350 °C [26]. It is reasonable that 2,3-BDO can be dehydrated into 3B2OL and further dehydrated into BD at a higher temperature. However, it is difficult to use ThO_2 as a commercial catalyst for its radioactive properties. Although several catalysts were proposed in the production of BD from 2,3-BDO, most of the process resulted in high yields of butanone (MEK) [28,14,29]. Recently, the probability of the synthesis of BD from bio-based ethanol and butanediols has been discussed in review papers [30,31].

In our previous work, we have investigated the dehydration of 2,3-BDO over all the rare earth oxide (REO) catalysts [32]. It has been found that Sc_2O_3 calcined at 800 °C shows an excellent catalytic activity with the highest 3B2OL selectivity of 85.0% at a 2,3-BDO conversion of 99.9% in an average of the initial 5 h at a low reaction temperature of 325 °C. In addition, In_2O_3 calcined at 400 °C also showed the dehydration activity with a 3B2OL selectivity of

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Table 1
Dehydration of 2,3-BDO over REOs calcined at 800 °C[a]

Catalyst	R_i[b] (nm)	SA[c] ($m^2\ g^{-1}$)	CP[d]	Conv. (mol%)	Selectivity (mol%)					
					BD	3B2OL	MEK	IBA	IBO	Others[e]
Sc_2O_3	0.0745	51.5	C	100.0	58.2	1.9	12.8	1.6	1.7	23.8
Sc_2O_3[f]	0.0745	51.5	C	100.0	88.3	0.8	1.1	0.1	0.3	9.4
$Sc_{1.5}Yb_{0.5}O_3$[f]	0.0776	53.2	C	98.8	42.6	10.6	14.9	2.1	4.7	25.1
$Sc_{1.0}Yb_{1.0}O_3$[f]	0.0807	35.9	C	99.1	27.1	10.9	15.3	2.6	6.2	37.9
$Sc_{0.5}Yb_{1.5}O_3$[f]	0.0837	26.2	C	99.2	9.2	35.3	14.9	6.3	5.9	28.4
In_2O_3	0.0800	13.2	C	99.0	2.5	0.6	22.8	1.8	0.6	70.7
Lu_2O_3	0.0861	27.8	C	99.4	23.2	5.0	23.1	1.8	0.8	46.1
Yb_2O_3	0.0868	28.8	C	97.2	0.5	20.5	20.2	5.4	11.2	42.2
Tm_2O_3	0.0880	27.0	C	78.4	0.8	6.5	34.1	17.6	16.2	24.8
Er_2O_3	0.0890	21.5	M+C	100.0	2.4	20.0	21.1	7.2	7.2	42.1
Y_2O_3	0.0900	29.3	M+C	99.3	0.3	19.3	22.8	7.0	7.0	43.6
Ho_2O_3	0.0901	23.7	M	92.3	1.7	24.6	23.9	4.4	8.2	37.2
Dy_2O_3	0.0912	19.1	M	99.1	0.5	13.0	15.7	5.9	9.2	55.7
Tb_4O_7	0.0923	17.7	C_F	83.6	0.0	20.0	19.8	6.1	9.9	44.2
Gd_2O_3	0.0938	20.6	M	96.1	0.0	20.6	18.2	4.6	6.4	50.2
Eu_2O_3	0.0947	19.8	M	99.2	0.6	17.5	32.9	6.1	3.7	39.2
Sm_2O_3	0.0958	20.3	M	99.5	1.2	21.3	21.7	7.1	6.2	42.5
CeO_2	0.0970	53.7	C_F	100.0	0.5	0.5	39.2	2.4	0.6	56.8
Nd_2O_3	0.0983	18.2	H	87.8	0.0	35.2	16.9	4.0	6.0	37.9
Pr_6O_{11}	0.0990	22.7	C_F	95.6	0.7	9.6	34.7	8.6	9.3	37.1
La_2O_3	0.1032	18.0	H	92.5	0.5	8.1	23.2	9.2	11.8	47.2

BD, 1,3-butadiene; 3B2OL, 3-buten-2-ol; MEK, butanone; IBA, 2-methylpropanal; IBO, 2-methyl-1-propanol.

[a] Reaction temperature: 425 °C, catalyst weight: 1 g, feed rate: 1.06 g h^{-1}, flow rate of H_2: 45 $cm^3\ min^{-1}$, conversion and selectivity were averaged in the initial 5 h.

[b] Ionic radius of trivalent rare earth cation with coordination number 6, except Ce^{4+} with coordination number 8, the data cited from Refs. [33,38].

[c] The data cited from Ref. [33].

[d] CP: crystal phase; H, A-type hexagonal; M, B-type monoclinic; C, C-type cubic bixbyite; C_F, cubic fluorite. The data cited from Ref. [33].

[e] Others included 3-hydroxy-2-butanone, 2,3-butanedione, 2-butanol, *trans*-2-butene, 1-butene, isobutene, propylene, ethylene, etc.

[f] Reaction temperature: 411 °C.

79.6% and a conversion of 51.9% at 305 °C [32]. In this work, we investigated the dehydration of 2,3-BDO over Sc_2O_3 and In_2O_3 at high reaction temperatures to produce BD directly from 2,3-BDO, and also investigated the dehydration of 3B2OL and MEK over Sc_2O_3 and Al_2O_3 to establish the direct reaction route.

2. Experimental

2.1. Catalyst preparation

All the REO catalysts and In_2O_3 were purchased from KANTO CHEMICAL CO., INC., and they were calcined in air at a prescribed temperature for 3 h, while the samples are the same as the previous work [32,33] and the physical properties are reported elsewhere [33]. Al_2O_3 (JRC-ALO-6) with a specific surface area of 180 $m^2\ g^{-1}$ [34] was supplied by the Reference Catalyst Division, the Catalysis Society of Japan. The Al_2O_3 catalyst was used for the reaction without further heat treatment. Composite oxide of $Sc_{2-x}Yb_xO_3$ with $x = 0.5$, 1.0, and 1.5, namely $Sc_{1.5}Yb_{0.5}O_3$, $Sc_{1.0}Yb_{1.0}O_3$, and $Sc_{0.5}Yb_{1.5}O_3$, were supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan [35].

2.2. Catalytic reaction

The dehydration of 2,3-BDO was carried out in a fixed-bed tubular flow reactor under atmospheric pressure of H_2 with a flow rate of 45 $cm^3\ min^{-1}$ at a prescribed temperature. Prior to the reaction, a catalyst (1.0 g) was preheated in an H_2 flow at the prescribed temperature for 1 h. After the catalyst bed had been preheated, 2,3-BDO was fed through the reactor top at a feed rate of 1.06 g h^{-1} (11.8 mmol h^{-1}). The liquid effluent collected every hour was analyzed by gas chromatography (GC-8A, Shimadzu, Japan) with a 60-m capillary column (DB-WAX). The products were identified by gas chromatography with a mass spectrometer (GCMS-QP5050A, Shimadzu) and a 30-m capillary column (DB-WAX). Gaseous products such as BD and butene isomers were analyzed by on-line gas chromatography (GC-8A, Shimadzu) with a 6-m packed column (VZ-7). The catalytic activity was evaluated by averaging the conversion and selectivity data in the initial 5 h. Both the conversion of 2,3-BDO and the selectivity to each product were defined as mol%. The above-mentioned description is essentially the same as those described in the previous work [32,36,37].

In Section 3.4, the dehydration of MEK and 3B2OL was also examined in the same way as the 2,3-BDO dehydration in order to confirm an intermediate product in the dehydration from 2,3-BDO to BD. In Section 3.5, the dehydration of 2,3-BDO was also investigated over two different catalysts packed in the tubular reactor, which consisted of 1.0 g of Al_2O_3 placed in a lower bed with 6 mm height and 1.0 g of Sc_2O_3 placed in an upper bed with 4 mm height, to establish the efficient BD formation.

3. Results

3.1. Dehydration of 2,3-BDO catalyzed by REOs calcined at 800 °C

Winfield reported that in the dehydration of 2,3-BDO over ThO_2: 3B2OL was mainly obtained with a selectivity of 70% at 350 °C, and BD was mainly obtained with a selectivity of about 62% together with 3B2OL selectivity of only 8% at 500 °C [26]. This indicates that 3B2OL and BD can be obtained as stepwise dehydration products of 2,3-BDO at low and high reaction temperatures, respectively. In our previous reports, we have synthesized 3B2OL at high yields from 2,3-BDO over monoclinic ZrO_2 modified with alkaline earth metal oxides [37] as well as monoclinic ZrO_2 [36] at 350 °C. Neither monoclinic ZrO_2 nor the modified ones showed their activities to produce BD even at high reaction temperatures. We have also found that In_2O_3 and Sc_2O_3 show excellent catalytic activity to produce 3B2OL at 325 °C [32]. In the REO catalysts, Sc_2O_3 shows the highest selectivity to 3B2OL. However, the possibility of the REO catalysts was not evaluated in the BD formation from 2,3-BDO at high temperatures.

Table 1 summarizes the results in the catalytic reaction of 2,3-BDO over the REO catalysts at 425 °C. In the dehydration of

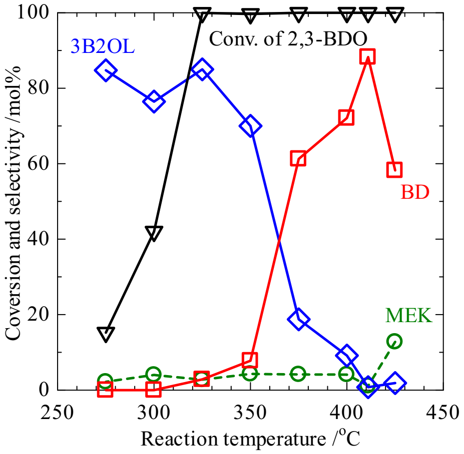


Fig. 1. Changes in the dehydration ability of Sc_2O_3 in the dehydration of 2,3-BDO into BD, 3B2OL, and MEK with reaction temperature. Calcination temperature of Sc_2O_3, 800 °C; catalyst, 1.0 g; feed rate of 2,3-BDO, 1.06 g h^{-1}; flow rate of H_2 carrier gas, 45 cm^3 min^{-1}.

2,3-BDO, BD was mainly produced only over Sc_2O_3, together with by-products such as 3B2OL, MEK, 2-methyl-propanal, 2-methyl-propanol, and butene isomers. In particular, Sc_2O_3 calcined at 800 °C showed a high BD yield of 88.3% at 411 °C. In the composite oxides of $Sc_{2-x}Yb_xO_3$ (x = 0.5, 1.0, and 1.5), the selectivity to BD simply decreased with increasing Yb content. Nd_2O_3 and Lu_2O_3 showed almost the same ability for the formation of BD and MEK. The other REOs such as Yb_2O_3, Er_2O_3, Y_2O_3, Ho_2O_3, Dy_2O_3, Tb_4O_7, Gd_2O_3 and Sm_2O_3 displayed similar catalytic activities to form 3B2OL and MEK, but BD was not produced.

3.2. Dehydration of 2,3-BDO over In_2O_3 and Sc_2O_3 calcined at different temperatures

In_2O_3 calcined at 800 °C (Table 1) shows a quite low selectivity to BD, although it shows a 3B2OL selectivity of 68.5% at a 2,3-BDO conversion of 72.9% at 305 °C [32]. In the case of In_2O_3 catalyst, calcination at 400 °C is preferable to obtain a 3B2OL-selective In_2O_3 catalyst [32]. Table 2 shows the catalytic activity of In_2O_3 calcined at 400 and 800 °C. The 3B2OL selectivity was 84.1% at 280 °C, and it decreased steeply with increasing the reaction temperature. At 425 °C, BD and 3B2OL were hardly obtained over In_2O_3. It was also found that 2,3-BDO was converted into MEK and some gaseous by-products such as *trans*-2-butene, 1-butene, isobutene, and propylene over In_2O_3 but not BD at high temperatures.

Table 3 shows the dehydration ability of Sc_2O_3 calcined at different temperatures in the dehydration of 2,3-BDO at 411 °C. Under the conditions, the conversion of 2,3-BDO reached ca. 100%. It is obvious that Sc_2O_3 calcined at 800 °C showed the highest BD selectivity, which exceeded 88%. The change in the selectivity had no correlation with the specific surface area, which decreased with increasing the calcination temperature.

In our previous report, we have already investigated the dehydration activities of Sc_2O_3 at reaction temperatures up to 350 °C in the formation of 3B2OL from 2,3-BDO. Over Sc_2O_3 calcined at 800 °C, the highest yield of 3B2OL was obtained at 325 °C with a selectivity of 85% and the selectivity declined rapidly at 350 °C with only a little BD detected [32]. In the present work, the dehydration ability of Sc_2O_3 calcined at 800 °C was further investigated at higher reaction temperatures. Fig. 1 shows the changes in the catalytic activity of Sc_2O_3 calcined at 800 °C. 3B2OL was mainly obtained at low reaction temperatures, and the formation of BD was increased at high temperatures. Sc_2O_3 showed the maximum BD yield of 88.3% at 411 °C. However, the selectivity to BD declined rapidly at 425 °C. At 425 °C, BD dimers such as octenes were also detected along with MEK. It indicates that the appropriate reaction temperature is 411 °C for a high yield of BD.

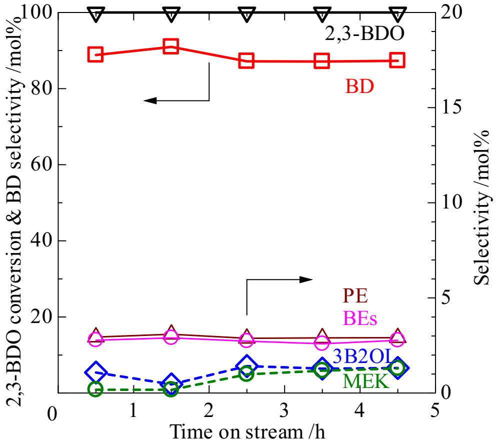


Fig. 2. Changes in conversion and selectivities to BD, 3B2OL and MEK in the dehydration of 2,3-BDO over Sc_2O_3 with time on stream. Calcination temperature of Sc_2O_3, 800 °C; Reaction temperature, 411 °C; catalyst weight, 1.0 g; feed rate of 2,3-BDO, 1.06 g h^{-1}; flow rate of H_2, 45 cm^3 min^{-1}.

Fig. 2 shows the changes in catalytic activity of Sc_2O_3 calcined at 800 °C in the dehydration of 2,3-BDO with time on stream. Stable catalytic activity was obtained in the initial 5 h: the conversion of 2,3-BDO kept 100% with BD selectivity of 88% in H_2 flow at 411 °C. The selectivity to propylene was ca. 3% while the selectivity to the sum of butene isomers such as *trans*-2-butene, 1-butene, and isobutene was ca. 3%. Both the selectivities of 3B2OL and MEK were as low as 1%.

3.3. Effects of carrier gas on the dehydration of 2,3-BDO over Sc_2O_3 calcined at 800 °C

Fig. 3 shows the catalytic activity of Sc_2O_3 in N_2 carrier gas. The trend in the catalytic activity of Sc_2O_3 in N_2 flow resembled that in H_2 flow (Fig. 1). However, even at the same reaction temperature, the selectivities to both 3B2OL and BD in N_2 flow were lower than those in H_2 flow, as being compared with Fig. 1. In addition, it was observed that less coke on the catalyst used in H_2 flow was accumulated than in N_2 flow, judging from the color of the catalyst used: gray in H_2 in contrast to dark brown in N_2.

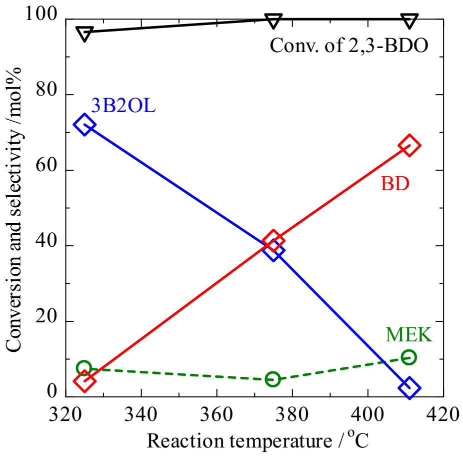


Fig. 3. Dehydration ability of Sc_2O_3 in the dehydration of 2,3-BDO in N_2 flow. Calcination temperature of Sc_2O_3, 800 °C; catalyst weight, 1.0 g; feed rate of 2,3-BDO, 1.06 g h^{-1}; flow rate of N_2, 45 cm^3 min^{-1}.

Table 2
Dehydration of 2,3-BDO over In_2O_3 calcined at different temperatures.[a]

Reaction temp. (°C)	Conv. (mol%)	Selectivity (mol%)								
		BD	3B2OL	MEK	IBA	IBO	BEs	PE	EE	Others
280[b]	11.6	0	84.1	2.3	2.7	0.4	0	0.1	0	9.4
305[b]	51.9	0.1	79.6	1.5	0	0.9	1.4	0.7	0	15.8
325[b]	85.4	4.6	64.8	3.2	0.6	0.1	6.9	0.7	0	19.1
325[c]	59.4	0.3	65.8	4.0	0.3	0.4	2.3	0.5	0	26.4
350[b]	89.9	2.9	58.0	9.0	1.3	0.2	6.7	0.5	0	21.4
355[c]	87.4	1.9	44.3	8.8	0.5	0.3	11.0	1.2	0	36.0
375[b]	90.0	1.3	36.2	22.4	2.0	0.5	5.2	0.3	0	32.1
375[c]	97.0	4.7	32.5	13.6	1.3	0.3	16.2	1.1	0	30.3
404[c]	95.1	0.9	15.9	30.8	1.6	1.1	12.2	1.5	0.1	35.9
425[c]	99.0	2.5	0.9	20.8	1.8	0.6	49.1[d]	11.0	1.3	13.1

BD, 1,3-butadiene; 3B2OL, 3-buten-2-ol; MEK, butanone; IBA, 2-methylpropanal; IBO, 2-methyl-1-propanol; BEs included *trans*-2-butene, 1-butene, and isobutene; PE, propylene; EE, ethylene; others included 3-hydroxy-2-butanone, 2,3-butanedione, 2-butanol, etc.

[a] Catalyst weight: 1 g, feed rate: 1.06 g h^{-1}, flow rate of H_2: 45 cm^3 min^{-1}, conversion and selectivity were averaged in the initial 5 h.

[b] In_2O_3 calcined at 400 °C.

[c] In_2O_3 calcined at 800 °C.

[d] BEs included *trans*-2-butene (20.8%), 1-butene (14.8%), and isobutene (13.5%).

Table 3
Dehydration of 2,3-BDO over Sc_2O_3 calcined at different temperatures.[a]

Calcination temp.(°C)	SA[b] (m^2 g^{-1})	Conv. (mol%)	Selectivity (mol%)								
			BD	3B2OL	MEK	IBA	IBO	BEs	PE	EE	Others
As-received	98.4	99.9	50.4	4.4	11.9	1.8	4.0	3.9	6.1	2.2	15.3
600	72.1	99.9	66.5	0.8	8.3	1.2	2.0	4.6	7.5	2.2	6.9
700	66.2	100.0	83.0	0.9	1.9	0.1	0.6	3.8	4.5	2.8	2.4
800	51.5	100.0	88.3	0.8	1.1	0.1	0.3	2.8	2.9	1.6	2.1
900	45.4	100.0	62.4	1.9	11.8	1.7	3.1	6.2	4.8	1.5	6.6
1000	30.9	100.0	62.6	2.5	7.6	0.9	1.5	4.1	8.7	4.2	7.9

Abbreviations are the same as those in Table 2.

[a] Reaction temperature: 411 °C, catalyst weight: 1 g, feed rate: 1.06 g h^{-1}, flow rate of H_2: 45 cm^3 min^{-1}, conversion and selectivity were averaged in the initial 5 h.

[b] The data cited from Ref. [33].

Fig. 4 shows the changes in the selectivities to BD, 3B2OL, and MEK in the dehydration of 2,3-BDO over Sc_2O_3 with the flow rate of H_2 carrier gas at 411 °C. Under all the conditions at different H_2 flow rates, the conversion of 2,3-BDO reached 100%. At a H_2 flow rate of 80 cm^3 min^{-1}, a stable BD selectivity over 90% was obtained. At a H_2 flow rate of 100 cm^3 min^{-1}, however, by-products such as butene isomers increased so that they resulted in a decreased BD selectivity. At a low H_2 flow rate of 20 cm^3 min^{-1}, 3B2OL and MEK were observed together with BD. Because the feed rate of 2,3-BDO is constant in Fig. 4, the low H_2 flow rate means a high partial pressure of 2,3-BDO, at which 3B2OL and MEK are observed as by-products. Therefore, the proper flow rate of H_2 carrier gas can be considered as 80 cm^3 min^{-1}.

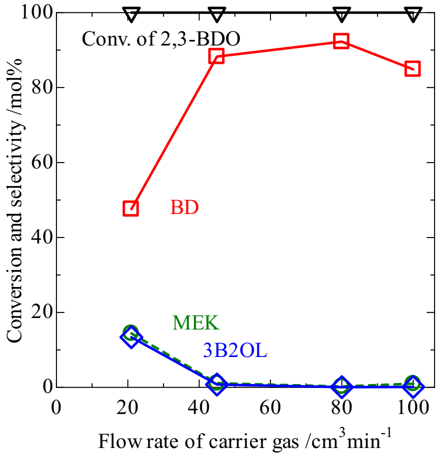


Fig. 4. Changes in the dehydration of 2,3-BDO at different flow rates of H_2 carrier gas over Sc_2O_3. Calcination temperature of Sc_2O_3, 800 °C; reaction temperature, 411 °C; catalyst, 1.0 g; feed rate of 2,3-BDO, 1.06 g h^{-1}.

3.4. Dehydration of MEK and 3B2OL

MEK is one of the products in the dehydration of 2,3-BDO, so that it could be an intermediate in the BD formation. Table 4 summarizes the dehydration of MEK over Sc_2O_3 and Al_2O_3 catalysts. However, the reactant MEK was rarely reacted at 325 °C over Al_2O_3 catalyst. Even at 550 °C, the decomposition of MEK proceeded over Al_2O_3 to produce mainly butene isomers, propylene, and ethylene, while BD with a selectivity of 8.6% was detected. On the other hand, the reaction proceeded at 425 °C over Sc_2O_3 but little BD was detected from MEK. Therefore, MEK would not be the major intermediate in the BD formation from 2,3-BDO over Sc_2O_3.

3B2OL could also be an intermediate in the BD formation from 2,3-BDO. Fig. 5 shows the dehydration of 3B2OL over Sc_2O_3 and Al_2O_3 catalysts as well as a blank test without using catalysts. It is obvious that even at 425 °C the thermal decomposition of 3B2OL hardly proceeded without catalysts. Sc_2O_3 showed the dehydration ability at temperatures between 300 and 400 °C. Over Sc_2O_3, both the conversion of 3B2OL and the BD selectivity increased with increasing the reaction temperature and they reached the highest at 372 °C. In addition, the BD selectivity from 3B2OL (91.5%) is higher than that directly from 2,3-BDO even at the same reaction temperature in comparison with Fig. 1. This indicates that the formation of BD from 3B2OL is much easier than that from 2,3-BDO.

Fig. 5 also indicates that Al_2O_3 is more active than Sc_2O_3 on the formation from 3B2OL to BD. Although their catalytic activities showed a similar trend over the reaction temperature, the highest BD yield was obtained over Al_2O_3 at 250 °C: 3B2OL conversion, 95.4%; BD selectivity, 91.2%. Al_2O_3 showed the similar trend

Table 4
Dehydration of MEK over Sc_2O_3 and Al_2O_3.[a]

Catalyst (1 g)	Temp. (°C)	Conv. (mol%)	Selectivity (mol%)							
			BD	3B2OL	IBA	IBO	BEs	PE	EE	Others
Al_2O_3	325	2.7	0	0	4.2	0	22.9	23.4	1.6	47.9
Al_2O_3	550	39.7	8.6	0	7.2	0	34.3	12.5	21.0	16.4
Sc_2O_3[b]	425	40.2	0	0	2.2	6.9	15.7	18.5	4.6	52.1

Abbreviations are the same as those in Table 2.

[a] Feed rate: $1.06\,g\,h^{-1}$, flow rate of H_2: $45\,cm^3\,min^{-1}$, conversion and selectivity were averaged in the initial 5 h.

[b] Sc_2O_3 calcined at 800 °C.

to Sc_2O_3 in the catalytic performance at a temperature which is 127 °C lower than Sc_2O_3 did. It is reasonable that the dehydration of 3B2OL into BD can be easily catalyzed by solid acid catalyst such as Al_2O_3 at a low temperature. Although Al_2O_3 catalyzes the dehydration of 2,3-BDO into MEK and 2-methylpropanal as well as into BD [36], it is expected as a catalyst in the dehydration of 3B2OL into BD.

3.5. Efficient formation of BD in the dehydration of 2,3-BDO with a combination of acid catalyst

Al_2O_3 catalyzes the dehydration of 3B2OL at 250 °C (Fig. 5), and 3B2OL has been obtained with a yield of 85% from 2,3-BDO over Sc_2O_3 at 325 °C [32]. Thus, 2,3-BDO could be effectively converted to BD using Al_2O_3 as a dehydration catalyst for 3B2OL at a low temperature. In order to obtain BD directly from 2,3-BDO at a low temperature, the dehydration was investigated over two catalyst beds packed in the tubular reactor, which composed of Sc_2O_3 loaded in the upper bed to convert 2,3-BDO into 3B2OL and Al_2O_3 placed in the lower bed to convert 3B2OL into BD. Fig. 6 shows the catalytic activities at 318 °C with time on stream. The flow rate of H_2 carrier gas was $80\,cm^3\,min^{-1}$, and all the other conditions were the same as the dehydration of 2,3-BDO over the single-bed Sc_2O_3 catalyst (Fig. 2). The average of the BD selectivity was 94% with the complete conversion of 2,3-BDO at 318 °C during the initial 5 h. Butene isomers with the total selectivity less than 5% and propylene with less than 1% were observed whereas little MEK and 3B2OL were detected. In contrast, MEK and 3B2OL were observed over the single-bed Sc_2O_3 catalyst at 411 °C (Fig. 2). It is obvious that the double-bed catalysts had stable catalytic activity, and that the selectivity to BD was higher than that of the single-bed Sc_2O_3 catalyst tested at 411 °C. Therefore, the double-bed catalysts consisted of Sc_2O_3 and Al_2O_3 efficiently work to produce BD directly from 2,3-BDO.

4. Discussion

4.1. Correlation between ionic radii and catalytic activity of REOs

Relationships between the ionic radii of rare earth cations [33,38] and the selectivities to unsaturated alcohols similar to Fig. 7 have also been observed in the dehydration of other

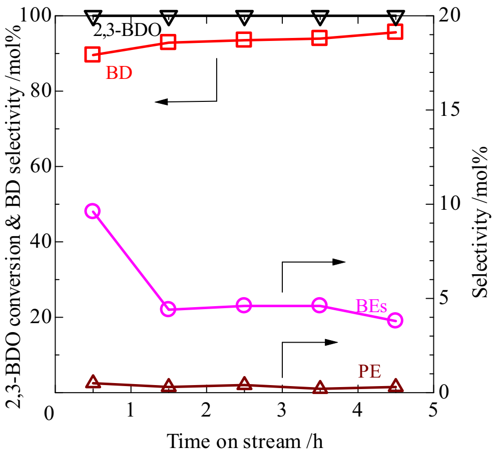


Fig. 6. Changes in conversion and selectivities to BD, BEs, and PE in the dehydration of 2,3-BDO at 318 °C over the double-bed catalysts of Sc_2O_3 and Al_2O_3 with time on stream. Reaction conditions: catalyst weight: Sc_2O_3 (calcined at 800 °C) placed in the upper bed, 1.0 g; Al_2O_3 located in the lower bed, 1.0 g; feed rate of 2,3-BDO, $1.06\,g\,h^{-1}$; flow rate of H_2 carrier gas, $80\,cm^3\,min^{-1}$. BEs included *trans*-2-butene, 1-butene, and isobutene; PE, propylene.

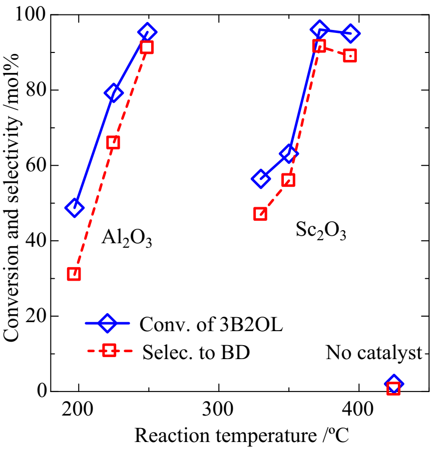


Fig. 5. Changes in the dehydration of 3B2OL into BD with reaction temperature over Al_2O_3 and Sc_2O_3. Calcination temperature of Sc_2O_3, 800 °C; catalyst weight, 1.0 g; flow rate of H_2 carrier gas, $45\,cm^3\,min^{-1}$.

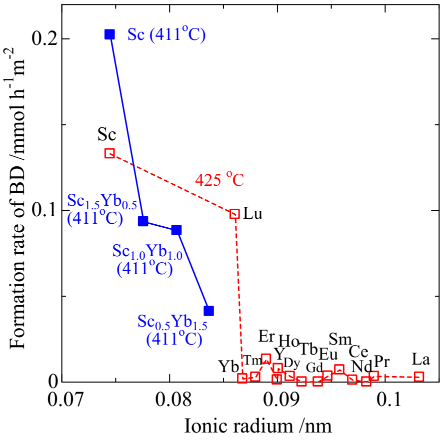
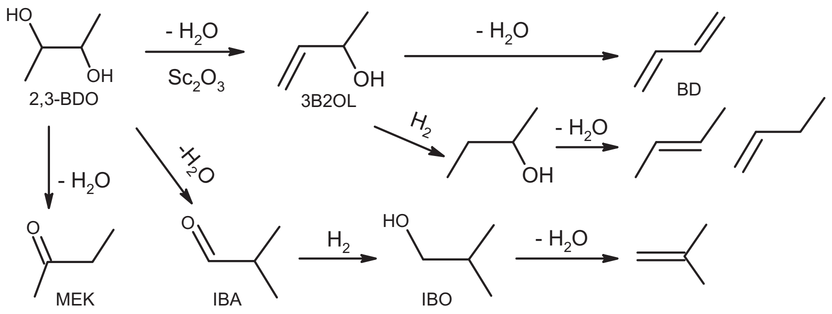


Fig. 7. Formation rate of BD at 425 °C over REO catalysts with different ionic radii of rare earth cations. Calcination temperature, 800 °C; flow rate of H_2, $45\,cm^3\,min^{-1}$. The formation rate was averaged in the initial 5 h. The reaction temperature over $Sc_{2-x}Yb_xO_3$ catalysts was 411 °C.



Scheme 1. Probable reaction pathway to various products from 2,3-BDO over REOs.

diols [35,39–43]. Terminal diols such as 1,5-pentanediol [35,42], 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, and 1,12-dodecanediol [41] were converted into the corresponding unsaturated alcohols with sufficient selectivity over Sc_2O_3 catalyst. In the formation of 4-penten-1-ol from 1,5-pentanediol [42], $Sc_{0.5}Yb_{1.5}O_3$ with the average ionic radius of 0.0837 nm shows the highest formation rate, so that there must be the most proper lattice parameter between that of Sc_2O_3 and Lu_2O_3. As a result, $Sc_{0.5}Yb_{1.5}O_3$ was confirmed to be more active than Sc_2O_3 and Lu_2O_3. Except CeO_2, Lu_2O_3 is the most active in the dehydration of 1,3-butanediol, and 1,4-butanediol [43]. In the dehydration of 1,3-butanediol, CeO_2 is exceptionally the most active catalyst [40].

In the dehydration of 2,3-BDO at 325 °C, high selectivities to 3B2OL have also been obtained over In_2O_3 [32] and ZrO_2 [36], in which the ionic radii of In_2O_3 (0.0800 nm) and ZrO_2 (0.0840 nm) are between that of Sc_2O_3 (0.0745 nm) and Lu_2O_3 (0.0861 nm). Sc_2O_3 and Lu_2O_3 show the BD selectivities of 58.2 and 28.2 mol% at 425 °C, respectively (Table 1), while ZrO_2 shows the 2,3-BDO conversion of 98.6% and the selectivities to BD, 3B2Ol, and MEK of 13.9, 19.6, and 33.3 mol% at 400 °C, respectively [36]. In_2O_3, however, shows at most 4.7% for the BD selectivity (Table 2), because In_2O_3 has an ability of hydrogenation of BD to butene isomers. In_2O_3 actually has redox catalytic property: 1,4-butanediol is dehydrogenated into γ-butyrolactone and 1-butanol can be dehydrogenated to butanal [44].

Fig. 7 summarizes the relationship between the ionic radii of REOs and their formation rate of BD. Sc_2O_3, $Sc_{2-x}Yb_xO_3$, and Lu_2O_3 have the same cubic crystal phase, as shown in Table 1. Among the REO catalysts, Sc_2O_3 with the smallest ionic radius showed the highest BD selectivity. Lu_2O_3 also showed the selectivity to BD while the others with larger ionic radii showed no catalytic abilities to produce BD. It can be said that only Sc_2O_3 is selective to BD. In this study, the highest formation rate of BD is obtained over Sc_2O_3 at 411 °C (Fig. 7). Thus, Sc_2O_3 with the smallest ionic radius of Sc^{3+} would provide a suitable adsorption site of 2,3-BDO on the surface for the formation of 3B2OL and BD.

There are several examples that well-crystallized oxide surface calcined at high temperatures shows high selectivity to a specific product in the dehydration of diols [32,36,39–43]. In the dehydration of 1,4-butanediol over REO catalysts [39], we have reported that a high calcination temperature results in high selectivity to 3-buten-1-ol in spite of growth of REO particles with a well-crystallized cubic phase. A proper calcination temperature could lead to the well-crystallized monoclinic ZrO_2 for the adsorption of the reactant 2,3-BDO [36]. In our previous work, it is confirmed that Sc_2O_3 calcined at 800 °C with better crystallized cubic phase has high selectivity to 3B2OL from 2,3-BDO [32] as well as the high selectivity to BD from 2,3-BDO (Table 3).

In the dehydration of 1,4-butanediol into 3-buten-1-ol over rare earth oxides such as Er_2O_3, we have already investigated the adsorption of 1,4-butanediol on Er_2O_3 using density functional theory (DFT) and paired interacting orbitals (PIO) calculations [45]. The adsorption of 1,4-butanediol proceeds via tridentate coordination: three attractive interactions between a position-2 hydrogen atom of 1,4-butanediol and an oxygen anion on Er_2O_3 surface and between each OH group of 1,4-butanediol and erbium cations on Er_2O_3 are observed. We also speculate that similar interactions could be formed between 2,3-BDO and Sc_2O_3. In order to prove the speculation, DFT and PIO calculations of adsorption of 2,3-BDO on Sc_2O_3 are executed to discuss the issue. The results and the related discussion will be presented in the near future.

4.2. Intermediates during the dehydration of 2,3-BDO to BD

In the pioneering work of Winfield, 3B2OL is mainly obtained in the dehydration of 2,3-BDO over ThO_2 at 350 °C while the main product shifts to BD at a high temperature of 500 °C [26]. However, other research groups also disclosed their results with high MEK selectivity but rare or no 3B2OL [28,14,29]. Some researchers believed that MEK had been the intermediate from the dehydration of 2,3-BDO [27]. Bouns reported that MEK was obtained with a yield of 86% in the dehydration of 2,3-BDO over mineral acids such as bentonite at 225 °C, and it was converted into BD of 20% at 700 °C with water as a diluent [27]. It seems that both MEK and 3B2OL can be considered as the intermediates for the formation of BD from 2,3-BDO.

Table 4 and Fig. 5 clearly indicate that BD is formed from 3B2OL but not from MEK over Sc_2O_3. Therefore, it is obvious that 3B2OL is the intermediate from 2,3-BDO to BD over Sc_2O_3, whereas MEK is not appropriate to be the intermediate to BD. Scheme 1 summarizes the probable reaction routes to the major products over Sc_2O_3. Butene isomers could come from butanols via dehydration. 2-Butanol and 2-methyl-1-propanol are actually detected in the products (Tables 2 and 3). It is speculated that propylene could be formed via the dehydration of 1-propanol through propanal, which can be produced via pinacol rearrangement with the elimination of methanol instead of water.

Winfield has also pointed out that the equilibrium constant for the dehydration of 2,3-BDO to MEK is 10^5 times greater than that for the reaction to 3B2OL at 500 °C, and that the equilibrium constant for the dehydration of 3B2OL to BD is 10^4 times greater than that for the reaction of MEK to BD at 500 °C [26]. Thus, it is considerable that the formation of MEK from 2,3-BDO readily proceeds but the formation of BD from MEK is difficult. The BD formation from MEK needs a high reaction temperature. Winfield has already considered that 3B2OL rather than MEK is probably the intermediate in the dehydration from 2,3-BDO to BD [26]. These are also well consistent with the results of Table 4 and Fig. 5.

In Fig. 6, we have demonstrated that the dehydration of 2,3-BDO to produce BD proceeds over the double-bed catalysts at 318 °C in order to overcome the decomposition of the intermediates. The main by-products such as MEK and propylene observed in Fig. 2 are greatly reduced in the double-bed catalysts (Fig. 6). BD is obtained with a selectivity higher than 94%. This is probably because Al_2O_3 catalyst in the lower bed converted 3B2OL into BD efficiently. The present double-bed catalyst system consisting of Sc_2O_3 and Al_2O_3 would be a candidate in the manufacture of BD from bio-based 2,3-BDO. In our previous report, on the other hand, 3B2OL and 2-buten-1-ol are readily dehydrated to produce BD over acidic catalysts such as silica-alumina, while 3-buten-1-ol is preferably decomposed into propylene [46]. Therefore, it can be proposed that 3B2OL and 2-buten-1-ol are preferable intermediates in a selective production of BD rather than 3-buten-1-ol. Since 1,3-butanediol can be selectively dehydrated into 3B2OL and 2-buten-1-ol over CeO_2 catalyst [40,43], 1,3-butanediol is also introduced to be a potential reactant for the production of BD [30,31].

5. Conclusions

Vapor-phase catalytic dehydration of 2,3-BDO was investigated over all the REO catalysts and In_2O_3 at high temperatures around 425 °C. In the dehydration of 2,3-BDO, BD was mainly produced, together with MEK, 2-methyl-propanal, 2-methyl-propanol, 3B2OL, and butene isomers over Sc_2O_3. It was only Sc_2O_3 catalyst among the REO catalysts showed catalytic activities for the formation of BD from 2,3-BDO. Sc_2O_3 calcined at 800 °C exhibited the highest BD yield of 88.3% at 411 °C in the initial 5 h in H_2 flow with a flow rate of 45 cm^3 min^{-1}. BD yield exceeded 90% at the carrier gas up to 80 cm^3 min^{-1}. Sc_2O_3 calcined at 800 °C also showed a great yield of 3B2OL at 325 °C. 3B2OL, rather than MEK, is considered to be the probable intermediate from 2,3-BDO to BD.

The dehydration of 3B2OL was also investigated over Sc_2O_3 and Al_2O_3 catalysts. Over Sc_2O_3 and Al_2O_3, 3B2OL was easily converted into BD at temperatures lower than 411 °C. Thus, the dehydration of 2,3-BDO was also investigated over two catalyst beds that consisted of an upper catalyst bed of Sc_2O_3 and a lower of Al_2O_3. The double-bed catalysts converted 2,3-BDO directly into BD, and they efficiently worked with a complete conversion of 2,3-BDO and a stable BD selectivity of 94% at a low temperature of 318 °C. Although 3B2OL and MEK were detected in the dehydration of 2,3-BDO over Sc_2O_3, 3B2OL is regarded as the intermediate in the formation of BD because MEK did not react under the conditions.

References

[1] M. Macaluso, R. Larson, E. Delzell, N. Sathiakumar, M. Hovinga, J. Julian, D. Muir, P. Cole, Toxicology 113 (1996) 190–202.
[2] S. Choi, J. Anal. Appl. Pyrolysis 62 (2002) 319–330.
[3] V.K. Srivastava, M. Maiti, R.V. Jasra, Eur. Polym. J. 47 (2011) 2342–2350.
[4] A. Ventura, T. Chenal, M. Bria, F. Bonnet, P. Zinck, Y. Ngono-Ravache, E. Balanzat, M. Visseaux, Eur. Polym. J. 49 (2013) 4130–4140.
[5] X. Liu, S. Zhao, X. Zhang, X. Li, Y. Bai, Polymer 55 (2014) 1964–1976.
[6] J. Lynch, Chem. Biol. Interact. 135–136 (2001) 147–153.
[7] M. Maiti, V. Srivastava, S. Shewale, R. VirJasra, A. Chavda, S. Modi, Chem. Eng. Sci. 107 (2014) 256–265.
[8] W.C. White, Chem. Biol. Interact. 166 (2007) 10–14.
[9] G.G. McBee, R.A. Creelman, F.R. Miller, Biomass 17 (1988) 203–211.
[10] C. Reyes Valle, A.L. Villanueva Perales, F. Vidal-Barrero, A. Gómez-Barea, Appl. Energy 109 (2013) 254–266.
[11] R. Singh, A. Shukla, S. Tiwari, M. Srivastava, Renew. Sustain. Energy Rev. 32 (2014) 713–728.
[12] K.B. Ramachandran, G. Goma, J. Biotechnol. 9 (1988) 39–46.
[13] E. Celińska, W. Grajek, Biotechnol. Adv. 27 (2009) 715–725.
[14] L.Y. Zhang, Y.L. Yang, J.A. Sun, Y.L. Shen, D.Z. Wei, J.W. Zhu, J. Chu, Bioresour. Technol. 101 (2010) 1961–1967.
[15] X.J. Ji, H. Huang, P.K. Ouyang, Biotechnol. Adv. 29 (2011) 351–364.
[16] L. Li, Y. Wang, L. Zhang, C. Ma, A. Wang, F. Tao, P. Xu, Bioresour. Technol. 115 (2012) 111–116.
[17] H. Shin, S. Yoon, J.R. Wu, C. Rutter, S. Kim, R.R. Chen, Bioresour. Technol. 118 (2012) 367–373.
[18] Q.Z. Wang, T. Chen, X.M. Zhao, J. Chamu, Biotechnol. Bioeng. 109 (2012) 1610–1621.
[19] B.B. Corson, H.E. Jones, C.E. Welling, J.A. Hinckley, E.E. Stahly, Ind. Eng. Chem. 42 (1950) 359–373.
[20] S.K. Bhattacharyya, N.D. Ganguly, J. Appl. Chem. 12 (1962) 97–104.
[21] S.K. Bhattacharyya, N.D. Ganguly, J. Appl. Chem. 12 (1962) 105–110.
[22] H. Niiyama, S. Morii, E. Echigoya, Bull. Chem. Soc. Jpn. 45 (1972) 655–659.
[23] Y. Kitayama, A. Michishita, J. Chem. Soc., Chem. Commun. 9 (1981) 401–402.
[24] V. Gruver, A. Sun, J.J. Fripiat, Catal. Lett. 34 (1995) 359–364.
[25] M.D. Jones, C.G. Keir, C.D. Iulio, R.A.M. Robertson, C.V. Williams, D.C. Apperley, Catal. Sci. Technol. 1 (2011) 267–272.
[26] M.E. Winfield, J. Counc. Sci. Ind. Res. 18 (1945) 412–423.
[27] A.N. Bouns, Can. J. Res. 25B (1947) 80–89.
[28] R.R. Emerson, M.C. Flickinger, G.T. Tsao, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 473–477.
[29] W.G. Zhang, D.H. Yu, X.J. Jia, H. Huang, Green Chem. 14 (2012) 3441–3450.
[30] P. Lanzafame, G. Centi, S. Perathoner, Chem. Soc. Rev. 43 (2014) 7562–7580.
[31] E.V. Makshina, M. Dusselier, W. Janssens, J. Degrève, P.A. Jacobs, B.F. Sels, Chem. Soc. Rev. 43 (2014) 7917–7953.
[32] H. Duan, Y. Yamada, S. Sato, Chem. Lett. 43 (2014) 1773–1775.
[33] S. Sato, R. Takahashi, M. Kobune, H. Gotoh, Appl. Catal. A: Gen. 356 (2009) 57–63.
[34] H. Matsuhashi, S. Nishiyama, H. Miura, K. Eguchi, K. Hasegawa, Y. Iizuka, A. Igarashi, N. Katada, J. Kobayashi, T. Kubota, T. Mori, K. Nakai, N. Okazaki, M. Sugioka, T. Umeki, Y. Yazawa, D. Lu, Appl. Catal. A: Gen. 272 (2004) 329–338.
[35] F. Sato, S. Sato, Catal. Commun. 27 (2012) 129–133.
[36] H. Duan, D. Sun, Y. Yamada, S. Sato, Catal. Commun. 48 (2014) 1–4.
[37] H. Duan, Y. Yamada, S. Sato, Appl. Catal. A: Gen. 487 (2014) 226–233.
[38] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751–767.
[39] S. Sato, R. Takahashi, M. Kobune, H. Inoue, Y. Izawa, H. Ohno, K. Takahashi, Appl. Catal. A: Gen. 356 (2009) 64–71.
[40] H. Gotoh, Y. Yamada, S. Sato, Appl. Catal. A: Gen. 377 (2010) 92–98.
[41] K. Abe, Y. Ohishi, T. Okada, Y. Yamada, S. Sato, Catal. Today 164 (2011) 419–424.
[42] F. Sato, H. Okazaki, S. Sato, Appl. Catal. A: Gen. 419–420 (2012) 41–48.
[43] S. Sato, F. Sato, H. Gotoh, Y. Yamada, ACS Catal. 3 (2013) 721–734.
[44] M. Segawa, S. Sato, M. Kobune, T. Sodesawa, T. Kojima, S. Nishiyama, N. Ishizawa, J. Mol. Catal. A: Chem. 310 (2009) 166–173.
[45] F. Sato, S. Sato, Y. Yamada, M. Nakamura, A. Shiga, Catal. Today 226 (2014) 124–133.
[46] N. Ichikawa, S. Sato, R. Takahashi, T. Sodesawa, J. Mol. Catal. A: Chem. 256 (2006) 106–112.