



# 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<sub>2</sub>O<sub>3</sub> at around 400 °C. In the dehydration of 2,3-BDO over Sc<sub>2</sub>O<sub>3</sub>, 1,3-butadiene was mainly produced together with butanone, 2-methyl-propanal, 2-methyl-propanol, 3-buten-2-ol, and butene isomers. Sc<sub>2</sub>O<sub>3</sub> calcined at 800 °C showed the highest 1,3-butadiene yield of 88.3% at 411 °C in H<sub>2</sub> carrier gas flow. Since 3-buten-2-ol is produced selectively from 2,3-BDO over Sc<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. In addition, double-bed catalysts composed of an upper catalyst bed of Sc<sub>2</sub>O<sub>3</sub> and a lower of Al<sub>2</sub>O<sub>3</sub> 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.

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## 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 C<sub>4</sub> 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<sub>2</sub> at 500 °C [26]. ThO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sup>a</sup>

Catalyst	$R_i^b$ (nm)	SA <sup>c</sup> (m <sup>2</sup> g <sup>-1</sup> )	CP <sup>d</sup>	Conv. (mol%)	Selectivity (mol%)					
					BD	3B2OL	MEK	IBA	IBO	Others <sup>e</sup>
Sc <sub>2</sub> O <sub>3</sub>	0.0745	51.5	C	100.0	58.2	1.9	12.8	1.6	1.7	23.8
Sc <sub>2</sub> O <sub>3</sub> <sup>f</sup>	0.0745	51.5	C	100.0	88.3	0.8	1.1	0.1	0.3	9.4
Sc <sub>1.5</sub> Yb <sub>0.5</sub> O <sub>3</sub> <sup>f</sup>	0.0776	53.2	C	98.8	42.6	10.6	14.9	2.1	4.7	25.1
Sc <sub>1.0</sub> Yb <sub>1.0</sub> O <sub>3</sub> <sup>f</sup>	0.0807	35.9	C	99.1	27.1	10.9	15.3	2.6	6.2	37.9
Sc <sub>0.5</sub> Yb <sub>1.5</sub> O <sub>3</sub> <sup>f</sup>	0.0837	26.2	C	99.2	9.2	35.3	14.9	6.3	5.9	28.4
In <sub>2</sub> O <sub>3</sub>	0.0800	13.2	C	99.0	2.5	0.6	22.8	1.8	0.6	70.7
Lu <sub>2</sub> O <sub>3</sub>	0.0861	27.8	C	99.4	23.2	5.0	23.1	1.8	0.8	46.1
Yb <sub>2</sub> O <sub>3</sub>	0.0868	28.8	C	97.2	0.5	20.5	20.2	5.4	11.2	42.2
Tm <sub>2</sub> O <sub>3</sub>	0.0880	27.0	C	78.4	0.8	6.5	34.1	17.6	16.2	24.8
Er <sub>2</sub> O <sub>3</sub>	0.0890	21.5	M+C	100.0	2.4	20.0	21.1	7.2	7.2	42.1
Y <sub>2</sub> O <sub>3</sub>	0.0900	29.3	M+C	99.3	0.3	19.3	22.8	7.0	7.0	43.6
Ho <sub>2</sub> O <sub>3</sub>	0.0901	23.7	M	92.3	1.7	24.6	23.9	4.4	8.2	37.2
Dy <sub>2</sub> O <sub>3</sub>	0.0912	19.1	M	99.1	0.5	13.0	15.7	5.9	9.2	55.7
Tb <sub>4</sub> O <sub>7</sub>	0.0923	17.7	C <sub>F</sub>	83.6	0.0	20.0	19.8	6.1	9.9	44.2
Gd <sub>2</sub> O <sub>3</sub>	0.0938	20.6	M	96.1	0.0	20.6	18.2	4.6	6.4	50.2
Eu <sub>2</sub> O <sub>3</sub>	0.0947	19.8	M	99.2	0.6	17.5	32.9	6.1	3.7	39.2
Sm <sub>2</sub> O <sub>3</sub>	0.0958	20.3	M	99.5	1.2	21.3	21.7	7.1	6.2	42.5
CeO <sub>2</sub>	0.0970	53.7	C <sub>F</sub>	100.0	0.5	0.5	39.2	2.4	0.6	56.8
Nd <sub>2</sub> O <sub>3</sub>	0.0983	18.2	H	87.8	0.0	35.2	16.9	4.0	6.0	37.9
Pr <sub>6</sub> O <sub>11</sub>	0.0990	22.7	C <sub>F</sub>	95.6	0.7	9.6	34.7	8.6	9.3	37.1
La <sub>2</sub> O <sub>3</sub>	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.

<sup>a</sup> Reaction temperature: 425 °C, catalyst weight: 1 g, feed rate: 1.06 g h<sup>-1</sup>, flow rate of H<sub>2</sub>: 45 cm<sup>3</sup> min<sup>-1</sup>, conversion and selectivity were averaged in the initial 5 h.

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

<sup>c</sup> The data cited from Ref. [33].

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

<sup>e</sup> Others included 3-hydroxy-2-butanone, 2,3-butanedione, 2-butanol, *trans*-2-butene, 1-butene, isobutene, propylene, ethylene, etc.

<sup>f</sup> 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<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> at high reaction temperatures to produce BD directly from 2,3-BDO, and also investigated the dehydration of 3B2OL and MEK over Sc<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> to establish the direct reaction route.

## 2. Experimental

### 2.1. Catalyst preparation

All the REO catalysts and In<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> (JRC-ALO-6) with a specific surface area of 180 m<sup>2</sup> g<sup>-1</sup> [34] was supplied by the Reference Catalyst Division, the Catalysis Society of Japan. The Al<sub>2</sub>O<sub>3</sub> catalyst was used for the reaction without further heat treatment. Composite oxide of Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> with  $x=0.5, 1.0,$  and  $1.5,$  namely Sc<sub>1.5</sub>Yb<sub>0.5</sub>O<sub>3</sub>, Sc<sub>1.0</sub>Yb<sub>1.0</sub>O<sub>3</sub>, and Sc<sub>0.5</sub>Yb<sub>1.5</sub>O<sub>3</sub>, 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<sub>2</sub> with a flow rate of 45 cm<sup>3</sup> min<sup>-1</sup> at a prescribed temperature. Prior to the reaction, a catalyst (1.0 g) was preheated in an H<sub>2</sub> 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<sup>-1</sup> (11.8 mmol h<sup>-1</sup>). 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<sub>2</sub>O<sub>3</sub> placed in a lower bed with 6 mm height and 1.0 g of Sc<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>: 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<sub>2</sub> modified with alkaline earth metal oxides [37] as well as monoclinic ZrO<sub>2</sub> [36] at 350 °C. Neither monoclinic ZrO<sub>2</sub> nor the modified ones showed their activities to produce BD even at high reaction temperatures. We have also found that In<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> show excellent catalytic activity to produce 3B2OL at 325 °C [32]. In the REO catalysts, Sc<sub>2</sub>O<sub>3</sub> 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

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