

Dehydrogenative cyclization of 1,4-butanediol over copper-based catalyst

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Abstract

Synthesis of γ -butyrolactone (GBL) from 1,4-butanediol (BDO) over copper-based catalysts with ZnO, Al₂O₃ and ZrO₂ was investigated. Catalytic activity of copper was greatly affected by the additive oxides. The highest activity was obtained at a catalyst molar ratio of CuO:ZnO:ZrO₂:Al₂O₃ = 6:1:2:2. ZrO₂ showed the highest additive effect for the GBL synthesis with enhancing dehydrogenation ability of metallic Cu and enlarging Cu surface area. Al₂O₃ enlarged Cu surface area, whereas a large amount of tetrahydrofuran (THF) was formed over the acid sites of Al₂O₃ surface, and ZnO reduced the THF yield. The reaction pathway from BDO to GBL was also clarified: BDO was initially dehydrogenated to 4-hydroxybutanal, which was immediately hemiacetalized to 2-hydroxytetrahydrofuran, followed by the dehydrogenation to GBL over metallic Cu.

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1. Introduction

γ -Butyrolactone (GBL) is known as a versatile solvent and a raw material of 2-pyrrolidone derivatives. GBL is manufactured via two methods: hydrogenation of maleic anhydride and dehydrogenative cyclization of 1,4-butanediol (BDO). The process via the hydrogenation of maleic anhydride was explored extensively because of the reasonable price of maleic anhydride [1–4]. This process, however, has some disadvantages. In the process, CO₂ emission is inevitable because maleic anhydride is manufactured by oxidation of benzene or *n*-butane, and two hydrogen molecules are consumed to produce GBL stoichiometrically.

BDO had been manufactured by a classical Reppe process in which two formaldehydes were added to acetylene. However, acetylene is expensive and difficult to handle because of its explosive character. Recently, a new process of

BDO production employing 1,3-butadiene and acetic acid as feedstocks was developed [5]. In the process, BDO is manufactured via diacetoxylation of 1,3-butadiene followed by hydrogenation and hydrolysis. Also, the environmental stress in the BDO production is less than that in the maleic anhydride production because of low CO₂ emission.

Several research groups investigated the dehydrogenative cyclization of BDO to GBL in homogeneous [6–8] and heterogeneous catalyst systems [9–12]. In the homogeneous systems, transition metal complexes were employed to dehydrogenate BDO to GBL. The heterogeneous systems are found in patent literatures: the non-oxidative dehydrogenation over copper-based catalysts such as alkali-doped Cu-Zn [9], Cu/Cr/Mn/Ba/Na [10] and Cu/SiO₂-CaO [11], and the oxidative dehydrogenation over Bi-doped Pt catalyst [12] were employed.

In this paper, we investigated the effects of composition of copper-based catalyst on the catalytic activity, and discussed reaction pathway from BDO to GBL using reactions of several substrates such as tetrahydrofuran (THF), 2-hydroxytetrahydrofuran (2HTHF), and succindialdehyde (SDA), which are possible intermediates.

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2. Experimental

2.1. Catalyst preparation

Catalyst samples were prepared by a conventional co-precipitation method. Three metal oxides, ZnO, ZrO₂ and Al₂O₃, were employed as additives. The detailed procedure was described elsewhere [13]. Hereafter, the catalyst composition of CuO:ZnO:ZrO₂:Al₂O₃ = *a*:*b*:*c*:*d* was abbreviated as A-*abcd*. For example, a catalyst name of “A-6122” means its molar ratio of CuO:ZnO:ZrO₂:Al₂O₃ = 6:1:2:2.

Tables 1–3 list the physical property of specific surface area and copper metal surface area [13]. The details of the

measurement of Cu surface area are described elsewhere [14].

2.2. Preparation procedure of 2HTHF and SDA

2HTHF was synthesized as referring [15,16]. The details are as follows. A mixture of 2,3-dihydrotetrahydrofuran and the four-fold volume of 0.1 mol dm⁻³ of HCl solution was heated at 60 °C for 1 h with reflux-condenser. Heating at higher temperature and longer reaction period lowered the yield of 2HTHF probably because of oligomerization. After the reaction, the mixture was cooled to ambient temperature and neutralized with 0.2 mol dm⁻³ of NaOH solution.

Table 1
Effect of additive on physical property and catalytic activity in the dehydrogenative cyclization of BDO^a

Catalyst	S _{BET} ^b (m ² g ⁻¹)	S _{A_{Cu}} ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (mol%)		
				GBL	THF	2HTHF
A-3000	1.2	1.2	27.6	88.9	0	9.6
A-3100	5.5	5.6	25.7	66.4	0.5	31.3
A-3010	53.8	16.6	65.2	96.4	0.2	3.1
A-3001	113.6	39.5	43.8	70.1	11.9	4.0

^a Average conversion and selectivity between 1 and 5 h, catalyst weight 0.150 g, BDO feed rate 1.8 cm³ h⁻¹, He flow rate 30 cm³ min⁻¹ at 240 °C.

^b Specific surface area cited from [13].

^c Cu surface area cited from [13].

Table 2
Effect of additive to A-3001 sample on physical and catalytic property in the dehydrogenative cyclization of BDO^a

Catalyst	S _{BET} ^b (m ² g ⁻¹)	S _{A_{Cu}} ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (mol%)		
				GBL	THF	2HTHF
A-6002 ^d	113.6	39.5	43.8	70.1	11.9	4.0
A-6202	101.0	52.7	71.0	96.1	<0.1	3.3
A-6022	134.4	36.0	62.0	95.1	0.4	3.7
A-6220	51.8	20.7	50.6	86.7	0	10.1
A-6222	120.1	39.7	67.4	92.6	0.1	3.6
A-6122	131.2	40.3	84.0	97.7	0.2	1.6

^a Average conversion and selectivity between 1 and 5 h, catalyst weight 0.150 g, BDO feed rate 1.8 cm³ h⁻¹, He flow rate 30 cm³ min⁻¹ at 240 °C.

^b Specific surface area cited from [13].

^c Cu surface area cited from [13].

^d Equals A-3001.

Table 3
Physical property and catalytic activity of A-*a*122 (*a* = 0–95) sample in the dehydrogenative cyclization of BDO^a

<i>a</i>	S _{BET} ^b (m ² g ⁻¹)	S _{A_{Cu}} ^c (m ² g ⁻¹)	Conversion (%)	Selectivity (mol%)		
				GBL	THF	2HTHF
0	183.3	–	43.5	0.6	95.0	0.3
1	161.3	36.3	57.7	75.2	1.3	4.0
3	144.7	35.5	67.5	95.9	0.1	2.3
6	131.2	40.3	84.0	97.7	0.2	1.6
12	99.7	38.7	84.1	94.9	0.1	1.5
18	83.2	45.1	74.9	96.1	<0.1	2.1
95	37.3	31.6	56.1	93.2	0.2	3.9

^a Average conversion and selectivity between 1 and 5 h, reaction temperature 240 °C, catalyst weight 0.150 g, BDO feed rate 1.8 cm³ h⁻¹, He flow rate 30 cm³ min⁻¹.

^b Specific surface area cited from [13].

^c Cu surface area cited from [13].

2HTHF was distilled under reduced pressure and remaining water was removed by drying over anhydrous Na_2SO_4 . The purity of 2HTHF exceeded 94% in GC.

SDA was synthesized as modifying the procedure described in the literature [17]. The details are as follows. 2,5-Dimethoxytetrahydrofuran and the four-fold volume of 0.1 mol dm^{-3} of HCl solution were mixed in a flask and heated at 95°C for 3 h with reflux-condenser. The reaction mixture was cooled to ambient temperature and neutralized with 0.2 mol dm^{-3} of NaOH solution. SDA was distilled under reduced pressure. Since high concentrated SDA solution was solidified, SDA was collected by distillation in aqueous solution at low concentration. The concentration of SDA in the solution was 21 wt.%.

2.3. Catalytic reaction

The reaction of BDO to GBL was performed in a fixed-bed down-flow glass reactor at $200\text{--}300^\circ\text{C}$ under atmospheric pressure in He flow of $30 \text{ cm}^3 \text{ min}^{-1}$. Prior to the reaction, the catalyst was reduced by H_2 at the flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ at 300°C for 1 h. After the reduction, the catalyst bed was cooled to the reaction temperature, and the carrier gas was switched to He. The reactant BDO was fed into the reactor and the effluent was collected periodically at every hour for 5 h at 0°C , and analyzed by FID-GC (Shimadzu GC-8A) using a 30 m capillary column of TC-WAX (GL Science, Japan). No gaseous products except H_2 were detected during the reaction with on-line TCD-GC. A typical reaction was carried out under the conditions at 240°C and $W/F = 0.083 \text{ g h cm}^{-3}$ where W and F are catalyst weight and reactant feed rate, respectively.

The reactions of 2HTHF and SDA over several catalyst samples were carried out at 240°C with the same procedure described above. Either 2HTHF with 94% purity or SDA 21 wt.% solution was introduced over the reduced catalyst for 1 h in the reactions because of small quantity of produced 2HTHF and SDA.

3. Results

Table 1 summarizes the effects of additives on both the physical and catalytic properties of copper-based catalysts. Both specific surface area and Cu surface area decreased as following order: A-3001 > A-3010 > A-3100 [13]. All the samples were slightly deactivated during the initial reaction for 5 h. Thus, the catalytic data were average activity between 1 and 5 h. Over A-3001 sample, for example, the conversion of BDO and selectivity to GBL in the initial period for 1 h was 71.8 and 97.3 mol%, respectively. At the final period between 4 and 5 h, they decreased to 63.3 and 96.1 mol%, respectively. The cause of deactivation would be the deposition of carbon species onto the catalyst surface, because the deactivated catalyst recovered its initial activity after the oxidizing treatment at 500°C . In addition to the

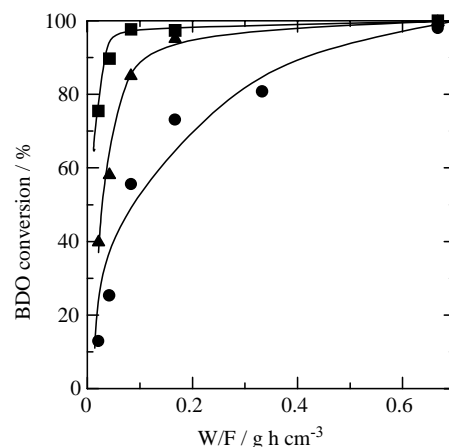


Fig. 1. Change in the conversion of BDO with W/F at (●) 200°C , (▲) 240°C and (■) 300°C over A-6122 sample.

majority of GBL, THF, 2HTHF and some unidentified products were detected in the effluent. However, we should note that 4-hydroxybutanal and SDA were not detected within the detection limit. GBL was formed even in the reaction over A-3000, which is pure Cu without additives. As shown in Table 1, no clear correlation between catalytic activity and Cu surface area was observed in the binary system. Over A-3001, the conversion of BDO was not so high in spite of its high surface area, and THF was observed with relatively high selectivity. A-3010 showed the highest conversion of BDO and selectivity to GBL in the binary systems. A-3100 was less active than A-3000, and 2HTHF was observed with high selectivity.

Table 2 summarizes the effects of ZnO and/or ZrO_2 added to A-3001 on both the physical and catalytic properties. Both specific surface area and Cu surface area were maintained their high values after the addition of ZnO and ZrO_2 to A-3001. It was also observed that the addition of ZnO and ZrO_2 increased the conversion of BDO and it decreased

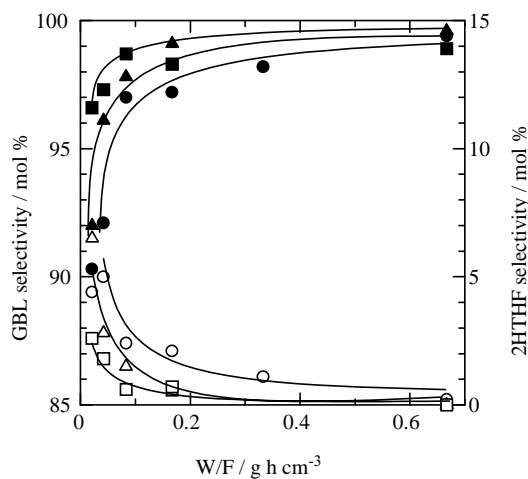


Fig. 2. Changes in the selectivity to GBL (closed symbols) and 2HTHF (open symbols) with W/F at (circle) 200°C , (triangle) 240°C , (square) 300°C over A-6122 sample.

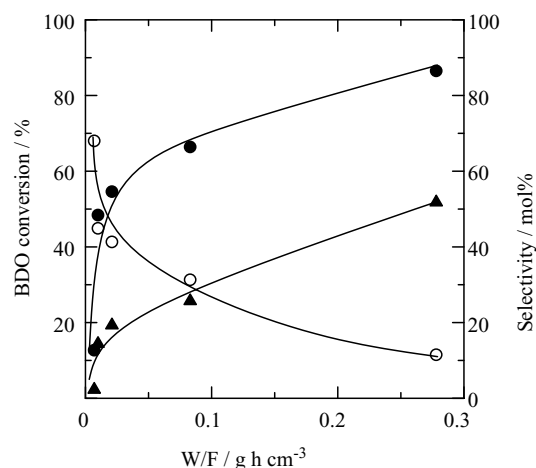


Fig. 3. Changes in the conversion of BDO (▲), the selectivity to GBL (●) and 2HTHF (○), with W/F over A-3100 sample at 240 °C.

the selectivity to THF together with increasing GBL yield. A-6222, containing both ZnO and ZrO₂, showed similar activity to that of A-6022, while A-6122 showed much higher activity than A-6222.

Table 3 summarizes the physical and catalytic properties of A-*a*122 ($a = 0-95$). Specific surface area decreased monotonically with increasing the copper content. Cu content did not affect Cu surface area around 40 m² g⁻¹. THF was selectively produced at $a = 0$, where there is no copper. The production of THF, however, drastically suppressed at $a = 1$ and the selectivity to GBL increased. The catalytic activity was enhanced with increasing Cu content, and the highest catalytic activity, 84.0% BDO conversion and 97.7 mol% GBL selectivity, was obtained at $a = 6$ (A-6122).

Figs. 1 and 2 show changes in the conversion of BDO and in the selectivity to GBL and 2HTHF with W/F over A-6122 at reaction temperature range between 200 and 300 °C, respectively. At any reaction temperature, the BDO conversion and the GBL selectivity increased with increasing W/F value, while the 2HTHF selectivity decreased. Fig. 3 shows changes in the conversion of BDO and the selectivity to GBL and 2HTHF with W/F value over a less active A-3100 at 240 °C. It was confirmed that high selectivity to 2HTHF was attained at low BDO conversion. The GBL selectivity increased with decreasing the 2HTHF selectivity.

Table 4 summarizes the dehydrogenation of 2HTHF over several copper-based catalysts and support (A-0122). 2HTHF was dehydrogenated to GBL over all the samples we tested. The catalytic activity was quite different: the

Table 4
Dehydrogenation of 2HTHF^a

Catalyst	Conversion (%)	Selectivity (mol%)	
		GBL	BDO
A-0122	25.6	18.2	12.0
A-3000	12.1	35.7	1.8
A-3100	12.1	27.5	7.0
A-3010	76.9	80.3	13.9
A-3001 (A-6002)	79.6	84.8	6.0
A-3111 (A-6222)	88.4	66.7	3.9

^a Each data were obtained by the reaction results of initial 1 h, reaction temperature 240 °C, catalyst weight 0.150 g, 2HTHF feed rate 1.8 cm³ h⁻¹, He flow rate 30 cm³ min⁻¹.

Table 5
Transformation of SDA^a

Catalyst	Carrier gas	Conversion (%)	Selectivity (mol%)		
			GBL	2HTHF	BDO
A-0122	He	14.4	69.2	30.8	0
A-0122	H ₂	14.9	77.8	21.4	0.8
A-3010	He	2.7	93.8	0	6.2
A-3010	H ₂	89.9	95.6	4.0	0.4
A-3111	He	0.5	100	0	0
A-3111	H ₂	88.4	92.0	5.6	2.4

^a Each data were obtained by the reaction results of initial 1 h, reaction temperature 240 °C, catalyst weight 0.150 g, carrier gas flow rate 30 cm³ min⁻¹. SDA solution of 21 wt.% was fed at 1.8 cm³ h⁻¹.

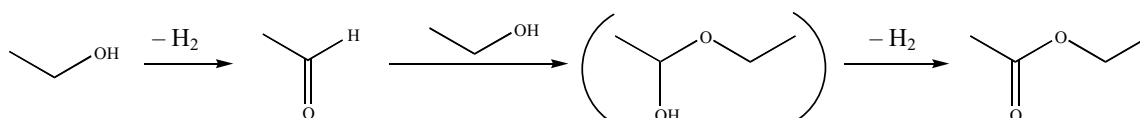
A-3001, A-3010 and A-3111 samples showed much higher activity than A-0122, A-3000 and A-3100 samples.

Table 5 summarizes the transformation of SDA in different atmospheres of He and H₂. Over the non-copper sample (A-0122), a small amount of SDA was transformed to GBL in both atmospheres, and the catalytic activity was not affected by carrier gas. Other products, 2HTHF and BDO, were also observed. In contrast, copper-based catalysts had little activity in He flow, whereas they effectively transformed SDA to GBL in H₂ flow. This result implies that the formation of GBL from SDA requires hydrogenation at the first step of the transformation.

4. Discussion

4.1. Effects of additives on the physical and catalytic property

A-3000 catalyst, pure copper, showed ability of dehydrogenative cyclization (Table 1). On the other hand, A-0122 containing no copper was active to dehydrative cyclization



Scheme 1. Reaction pathway from ethanol to ethyl acetate over the copper-based catalyst. A compound in the parenthesis is not observed in the ethyl acetate formation.

to THF. Therefore, metallic Cu is active center of dehydrogenation of BDO to GBL. However, no simple correlation between catalytic activity and Cu surface area was observed (Tables 1–3). Hence, the catalytic activity would be greatly influenced by the additives.

In the reaction of ethanol to ethyl acetate over the same catalyst systems [13,18], the reaction pathway was considered as shown in Scheme 1. Ethanol was initially dehydrogenated to acetaldehyde, followed by hemiacetalization with ethanol. The hydroxyl group of hemiacetal compound, which was not detected in the reaction effluent, was dehydrogenated to ethyl acetate.

In the previous work, we summarized the effects of additives in the direct synthesis of ethyl acetate from ethanol [13]. Al₂O₃ increased Cu surface area, and enhanced the catalytic activity. The high dispersion of Cu species would be attributed to the insertion of aluminum ions into CuO lattice to decrease CuO particle size. However, a large amount of diethyl ether was observed in Cu-Al₂O₃ system such as A-3001. ZrO₂ greatly increased the catalytic activity. ZnO did not affect both the Cu surface area and catalytic activity. The addition of ZnO and ZrO₂ to A-3001 suppressed the diethyl ether formation. This decrease in the selectivity to diethyl ether would be attributed to neutralization of acid sites of Al₂O₃ surface with ZnO and ZrO₂. In the reaction of ethanol to ethyl acetate over the quaternary system, A-a122, diethyl ether was observed at low copper content, whereas it disappeared at high copper content. The formation of diethyl ether was attributed to the isolated Al₂O₃ species, which was not incorporated into CuO lattice. At low copper content, aluminum ion was not incorporated into CuO lattice completely. Thus, the isolated Al₂O₃ species existing over catalyst surface catalyze the etherification of ethanol to diethyl ether. The content of copper in A-a122 sample affects the catalytic activity, and the highest activity is observed at $a = 12$.

In the present reaction of BDO to GBL, effects of additives on catalytic activity are similar to those observed in the ethyl acetate formation (13). While ZnO did not affect the catalytic activity, ZrO₂ drastically enhanced it. THF was formed over A-3001 sample in place of diethyl ether formed in the reaction of ethanol. Subba Rao et al. reported that BDO interacted with Brønsted acid site of CrZSM-5 and was dehydrated to THF [19]. It is probable that THF would be formed over acidic sites of Al₂O₃. The formation of THF over A-3001 sample was greatly suppressed by the addition of ZnO and ZrO₂. The catalytic activity was enhanced in the quaternary system. In the A-a122 systems, THF was preferentially formed at $a = 0$, whereas it was greatly suppressed by the addition of copper, which would reduce acidic property. The highest activity was obtained at $a = 6$.

4.2. Kinetic consideration

In the reaction of BDO to GBL, the reaction pathway would be similar to that of ethanol to ethyl acetate

(Scheme 1). The variations in the selectivity to GBL and 2HTHF shown in Figs. 1–3 suggest that 2HTHF is the intermediate in the GBL synthesis from BDO. The reaction of BDO to GBL is simply regard as the consecutive reaction via 2HTHF as following:



The reaction rate constants of the steps, BDO to 2HTHF and 2HTHF to GBL, were denoted as k_1 and k_2 , respectively. We simulated the relation between conversion and selectivity, assuming that the elementary reaction of each step has first order. In general, the change in the composition of BDO, 2HTHF and GBL in the consecutive reaction can be expressed as follows [20]:

$$\begin{aligned} X_A &= \exp(-k_1 t), \\ X_B &= \left[\frac{k_1}{k_1 - k_2} \right] [\exp(-k_2 t) - \exp(-k_1 t)], \\ X_C &= 1 - X_A - X_B \end{aligned}$$

where t , X_A , X_B and X_C are the time factor, the composition of BDO, that of 2HTHF and that of GBL, respectively. Eliminating the time factor, we obtained the selectivity to 2HTHF as the function of the conversion of BDO, as the following equation:

$$y = \left(\frac{1/x}{1 - k_2/k_1} \right) [(1 - x)^{k_2/k_1} - (1 - x)]$$

where x and y represent the conversion of BDO, $x = 1 - X_A$, and the selectivity to 2HTHF, $y = X_B/(1 - X_A)$, respectively. The selectivity to GBL is expressed as $1 - y$.

We can calculate the theoretical selectivity–conversion curve at appropriate ratio of k_2 to k_1 , k_2/k_1 , which is the variable. Figs. 4 and 5 show the relation between the conversion and selectivity over A-6122 and A-3100, respectively, together with the theoretical curves at several k_2/k_1 values.

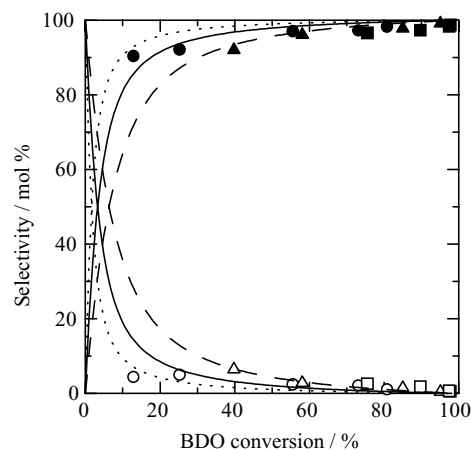


Fig. 4. The theoretical selectivity–conversion curves simulated at several k_2/k_1 over A-6122 sample: broken curve, $k_2/k_1 = 24$; solid, $k_2/k_1 = 48$; dotted, $k_2/k_1 = 96$. Symbols are the same as those in Fig. 2.

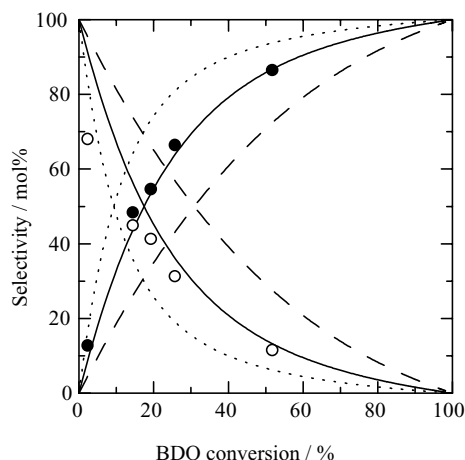


Fig. 5. The theoretical selectivity–conversion curves simulated at several k_2/k_1 over A-3100 sample: broken curve, $k_2/k_1 = 4$; solid, $k_2/k_1 = 8$; dotted, $k_2/k_1 = 16$. Symbols are the same as those in Fig. 3.

The curves calculated with the k_2/k_1 value at 48 and 8 well fit with the plotted data of Figs. 4 and 5, respectively. The results indicate that the reaction rate of the second step is 48 times faster than that of the first step over A-6122, whereas it is eight times faster over A-3100. Therefore, the addition of ZnO into Cu catalyst decreased the dehydrogenation ability, especially in the second step. In the reduction of A-3100, ZnO could be partially reduced with Cu, to be bimetal solid solution. This would be the reason for the deactivation over A-3100. This consideration is consistent with the result shown in Table 4: A-3100 is less active than the others in the dehydrogenation of 2HTHF to GBL.

The initial step, the reaction from BDO to 2HTHF, includes two elementary reactions, which involve the dehydrogenation of BDO to 4-hydroxybutanal and hemiacetalization of 4-hydroxybutanal to 2HTHF. In the step, the hemiacetalization would much faster than dehydrogenation because

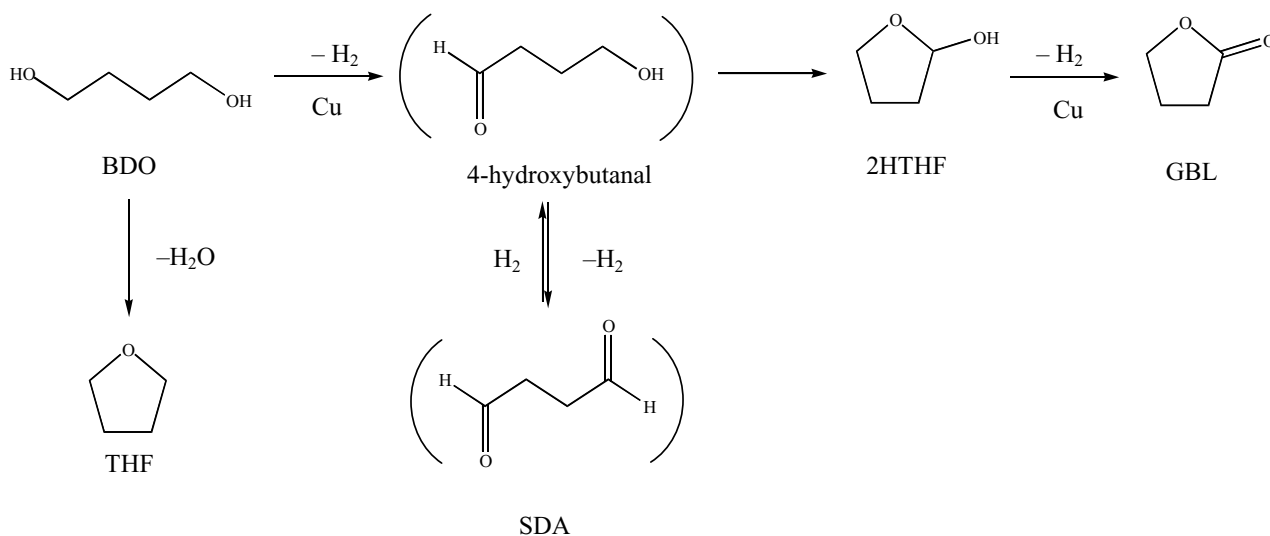
4-hydroxybutanal was not observed in the reaction of BDO to GBL. Therefore, we insist that the dehydrogenation of BDO to 4-hydroxybutanal is the rate-determination-step in the total GBL formation.

4.3. Reaction pathway from BDO to GBL

As shown in Table 4, 2HTHF was dehydrogenated to GBL over any samples. The catalytic activity, however, is quite different among the samples. In the A-0122 and A-3000 samples, the yield of GBL is almost the same in spite of specific surface area of A-0122 sample being more than 150 times higher than the Cu surface area of A-3000 (Table 1). This means that the dehydrogenation of 2HTHF mainly proceeds over metallic Cu surface. In the binary systems, A-3100 is less active than A-3010 and A-3001 samples. This is probably caused by not only their Cu surface area but also effects of additive mentioned in the Section 4.1.

Although we elucidate that 2HTHF is the intermediate in the reaction of BDO to GBL, other possible reaction pathways, partial oxidation of THF and Tishchenko reaction of SDA, are still remained. In the partial oxidation of THF, the oxygen source would be bulk oxygen in metal oxide of additives and/or oxygen in H_2O , which was generated during the dehydration of BDO to THF. Neither pure THF nor 50 mol% aqueous THF solution was reacted even over the most reactive A-6122 in He flow. Hence, the possibility of partial oxidation of THF to GBL is denied in the present system.

Then, we employed SDA as feedstock and examined whether Tishchenko reaction would proceed over the samples or not. The fact that a small amount of SDA is transformed to GBL in both atmospheres of He and H_2 over A-0122 (Table 5) indicates that Tishchenko reaction could proceed over the mixed metal oxides. However, Tishchenko reaction did not occur over the copper-based catalysts in He



Scheme 2. Reaction pathway from BDO to GBL over copper-based catalyst. Compounds in the parenthesis are not observed in the BDO reaction.

flow. It is reported that Tishchenko reaction required both acidic and basic sites [21], and we previously mentioned that Cu addition to A-0122 would suppress the surface acidity [13]. Thus, we speculated that similar suppression would inhibit Tishchenko reaction of SDA to GBL over A-0122 except for A-0122. On the other hand, SDA was transformed to GBL over the copper-based catalyst in H₂ flow. In H₂, one of formyl groups in SDA would be hydrogenated to be 4-hydroxybutanal. This can be converted to GBL through 2HTHF. In the reaction of SDA in H₂, BDO would be formed by the further hydrogenation of 4-hydroxybutanal.

In Scheme 2, we summarize the reaction pathway. BDO is initially dehydrogenated over metallic Cu surface to 4-hydroxybutanal. Since we did not observe the existence of 4-hydroxybutanal within the detection limit, 4-hydroxybutanal is so unstable that it is rapidly hemiacetalized to 2HTHF. 2HTHF is further dehydrogenated to GBL over metallic Cu surface. 2HTHF is the intramolecular hemiacetal compound of 4-hydroxybutanal. In the reaction of ethanol to ethyl acetate (Scheme 1), the existence of hemiacetal was not confirmed, while acetaldehyde was observed in the possible reaction pathway [13]. Here, we can confirm that hemiacetal is the intermediate in the dehydrogenative esterification of alcohol.

5. Conclusions

Synthesis of γ -butyrolactone (GBL) from 1,4-butanediol (BDO) was investigated over Cu-Zn-Zr-Al-O catalyst. The relation between catalyst composition and catalytic activity for the GBL synthesis from BDO and the reaction pathway were examined. GBL was effectively formed over the copper-based catalyst. The catalytic activity was greatly affected by additives, and the mixing of metal oxide additives increased catalytic activity, the maximum activity was obtained at catalyst composition of CuO:ZnO:ZrO₂:Al₂O₃ = 6:1:2:2.

The reaction pathway was clarified as follows; BDO was initially dehydrogenated to 4-hydroxybutanal, which was rapidly hemiacetalized to 2HTHF. 2HTHF was further dehydrogenated to GBL. All the dehydrogenation occurred over metallic Cu species. The pathways through the partial oxidation of THF and Tishchenko reaction of SDA were denied over the copper-based catalysts.

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