

Dehydrogenation of 1,3-butanediol over Cu-based catalyst

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Abstract

Vapor-phase dehydrogenation of 1,3-butanediol into 4-hydroxy-2-butanone was examined over copper catalysts modified with ZnO, ZrO₂, Al₂O₃, and MgO. 4-Hydroxy-2-butanone was efficiently produced by the dehydrogenation of 1,3-butanediol over pure Cu and Cu/ZnO catalysts. However, the selectivity to 4-hydroxy-2-butanone decreases with increasing conversion of 1,3-butanediol, while the selectivity to butanone increases. Addition of Al₂O₃ and ZrO₂ to the catalysts decreases the selectivity to 4-hydroxy-2-butanone because of the enhancement of dehydration of 4-hydroxy-2-butanone into 3-buten-2-one and the following hydrogenation into butanone. An addition of basic MgO increases the formation of propanone via the retro-aldol reaction of 4-hydroxy-2-butanone.

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1. Introduction

Dehydrogenation of diols produces important chemicals that can be used as intermediates in the synthesis of medicines. Under oxidative conditions, 1,2-diols such as ethylene glycol [1,2] and 1,2-propanediol [3] were dehydrogenated to 1,2-diones such as glyoxal and 2-oxopropanal, respectively. Under non-oxidative conditions, α -hydroxyketones are produced in the dehydrogenation of 1,2- and 2,3-diols over Cu catalysts [4–6].

β -Hydroxyketones such as 4-hydroxy-2-butanone (4HB) are also expected to be formed from 1,3-butanediol (1,3-BDO) by dehydrogenation. The dehydrogenation of 1,3-diols was studied over Pt [7], Rh [8,9] and Cu catalysts [10]. 1,3-BDO is converted into butanone over supported Rh and Cu catalysts [9,10]. It has been reported that 4HB is produced with the yield of 70% in the liquid-phase oxidative dehydrogenation of 1,3-BDO using hydrogen peroxide and tungsten-containing mesocellular silica foam catalyst at 65 °C [11]. 4HB is an important raw material of 3-buten-2-one, and we have developed an effective TiO₂ cat-

alyst for vapor-phase selective dehydration of 4HB to produce 3-buten-2-one [12].

We have recently reported effective copper catalysts modified with ZnO, ZrO₂ and Al₂O₃ (Cu–Zn–Zr–Al–O) for the vapor-phase dehydrogenative dimerization of ethanol into ethyl acetate [13–15]. ZrO₂ as an additive increases Cu surface area, effectively promoting the formation of ester. Al₂O₃ enlarges Cu surface area, and the acid sites of Al₂O₃ catalyze the formation of diethyl ether. ZnO reduces the yield of ether and butanone in the presence of Al₂O₃ [13]. In the dehydrogenative cyclization of 1,4-butanediol over the Cu–Zn–Zr–Al–O catalysts, the reaction pathway is clarified [16]: 1,4-butanediol is initially dehydrogenated to 4-hydroxybutanal, which is hemiacetalized within the molecule to 2-hydroxytetrahydrofuran, followed by the dehydrogenation to γ -butyrolactone over metallic Cu. Thus, the additives can create multifunctional catalysis in the copper catalyst. Vapor-phase dehydrogenation of 1,2-butanediol has also been investigated over the Cu–Zn–Zr–Al–O catalysts [6]: the selectivity to 1-hydroxy-2-butanone exceeds 98 mol%, and the catalytic activity is stable at 210 °C. The secondary OH group in 1,2-diol is dehydrogenated to the carbonyl group more readily than the primary OH group. We consider that the support effect on catalysis is also important in the formation of 4HB from 1,3-BDO.

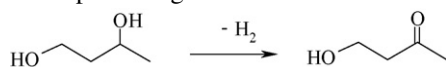
In this paper, we investigated vapor-phase dehydrogenation of 1,3-BDO catalyzed by several copper-based catalysts with

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ZnO, ZrO₂, Al₂O₃, and MgO, and discussed the catalytic reaction of 1,3-BDO producing 4HB.



2. Experimental

2.1. Catalyst samples

Commercial catalysts such as N-211 (CuO–ZnO, supplied by Nikki Chemicals, Japan) and Raney Cu (purchased from Aldrich) were used in the reaction. The N-211 CuO–ZnO has CuO and ZnO with the weight % of 49.3 and 45.1, respectively. The Raney Cu has already been developed and stored in water. Wet Raney Cu samples were used without further treatment in the reaction and the characterization.

The Cu–Zn–Zr–Al–O catalysts were prepared by a conventional coprecipitation method. The catalyst composition of CuO:ZnO:ZrO₂:Al₂O₃ = *a*:*b*:*c*:*d* was abbreviated as A-*abcd*. For example, a catalyst name of “A-3110” means its molar ratio of CuO:ZnO:ZrO₂:Al₂O₃ = 3:1:1:0. They are the same catalysts that we reported previously [6,13–16], and the detailed preparation procedure was described elsewhere [13]. A Cu/MgO sample with a Cu content of 40 mol% was prepared by the citrate process using copper(II) nitrate, magnesium nitrate, and citric acid. The detailed preparation procedure was described elsewhere [17,18].

The physical properties such as specific surface area and Cu metal surface area of copper-based catalysts used in this study are listed in Table 1, where some of the data were cited from the previous papers [6,13]. The details of the measurement of Cu surface area was described elsewhere [18].

2.2. Catalytic reaction

The catalytic reaction of 1,3-BDO was performed in a fixed-bed down-flow glass reactor at 200–260 °C. Prior to the reaction, a catalyst was reduced by H₂ at the flow rate of 30 cm³ min⁻¹ at 300 °C for 1 h. After the reduction, the catalyst bed was cooled

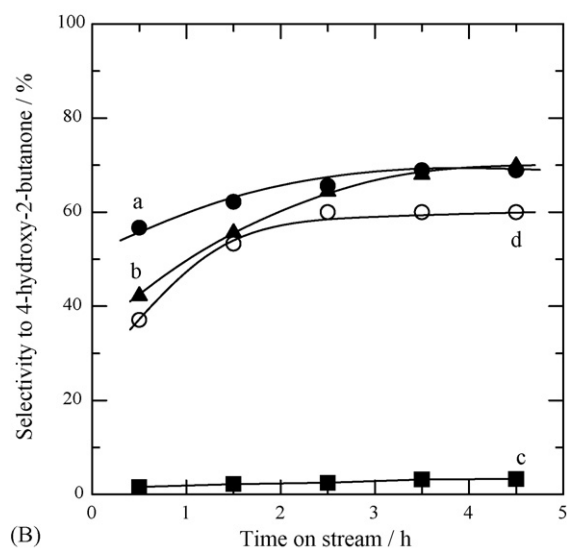
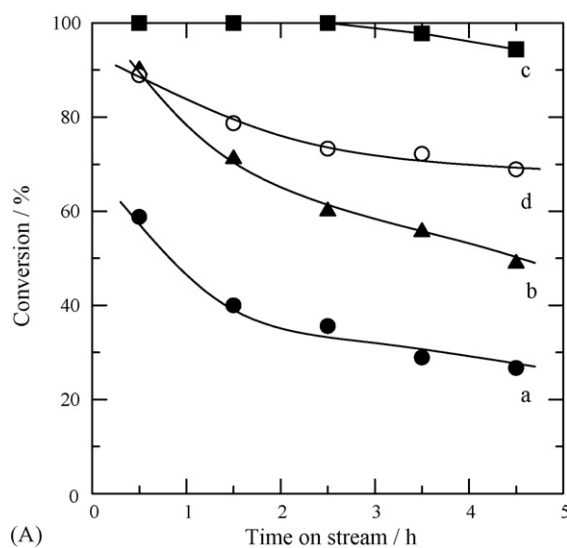


Fig. 1. Changes in 1,3-BDO conversion and selectivity to 4HB with reaction time over (a) A-3000, (b) A-3100, (c) A-3001, and (d) N-211 samples at 240 °C. Catalyst weight, 0.10 g; liquid 1,3-BDO feed rate, 1.8 cm³ h⁻¹; He carrier gas flow rate, 30 cm³ min⁻¹.

Table 1
Catalytic activity in the dehydrogenation of 1,3-BDO over copper-based catalysts^a

Catalyst ^b	Cu content (mol%)	S _{BET} ^c (m ² g ⁻¹)	S _{A_{Cu}} ^d (m ² g ⁻¹)	Conversion (%)	Selectivity (mol%)			
					4HB	MEK	AcH	AcMe
A-3000	100	1.2	1.2	40.8	55.9	6.1	2.7	17.8
A-3100	75	5.5	5.6	66.3	55.5	19.9	1.7	9.2
A-3010	75	53.8	16.6	99.4	7.1	50.1	3.9	19.6
A-3001	60	113.6	39.5	98.4	2.6	51.5	3.6	15.5
A-3110	60	51.8	20.7	91.9	20.2	44.0	5.6	14.9
Cu/MgO	40	55.0	–	89.8	22.8	22.0	7.3	28.6
Raney Cu	100	34.6	31.0	88.3	43.7	23.3	3.7	14.5
N-211 ^e	49	38.0	7.7	77.7	51.4	24.8	3.8	7.6

^a Average conversion and selectivity between 1 and 5 h, catalyst weight 0.10 g, 1,3-BDO feed rate 1.8 cm³ h⁻¹, He flow rate 30 cm³ min⁻¹ at 240 °C. 4HB, 4-hydroxy-2-butanone; MEK, butanone; AcH, ethanal; AcMe, propanone.

^b Sample name, A-*abcd*, shows the composition of CuO:ZnO:ZrO₂:Al₂O₃ = *a*:*b*:*c*:*d*.

^c Specific surface area.

^d Cu surface area.

^e N-211 is a commercial CuO–ZnO sample.

Table 2
Effect of reaction temperature in the dehydrogenation of 1,3-BDO over N-211 catalyst^a

Reaction temperature (°C)	Conversion (mol%)	Selectivity (mol%)			
		4HB	MEK	AcH	AcMe
200	44.2	64.5	18.9	1.4	3.3
220	53.3	61.4	20.5	1.7	5.3
240	77.7	51.4	24.8	3.8	8.0
260	85.7	50.3	23.0	3.9	7.7

^a The reaction conditions and abbreviations are the same as those in Table 1.

to the prescribed reaction temperature, and the carrier gas was switched to He. 1,3-BDO was fed through the reactor top at the liquid feed rate ranging from 1.8 to 7.2 cm³ h⁻¹ under atmospheric pressure of He flow at 30 cm³ min⁻¹. An effluent was collected periodically for 5 h at 0 °C, and analyzed by GC–MS (Shimadzu GCMS-QP5050) and FID–GC (Shimadzu GC-8A) using a 30-m capillary column of TC-WAX (GL Science, Japan).

3. Results and discussion

Fig. 1 shows changes in the conversion of 1,3-BDO with time on stream over typical Cu samples, A-3000, A-3100, A-3001, and commercial Cu/ZnO (N-211). For each catalyst, the conversion of 1,3-BDO decreased with increasing time on stream during the initial 5 h. Pure copper (A-3000) and Cu/ZnO (A-3100 and N-211) were selective to 4HB, and the selectivity slightly increased with time on stream. Cu/Al₂O₃ (A-3001) was less selective to 4HB, whereas the conversion was high. Hereafter, the catalytic activities are presented as the average for those after 1 and 5 h time on stream.

Table 1 summarizes the catalytic activity of Cu-based catalysts at 240 °C, together with physical properties of specific surface area and copper surface area. Pure copper (A-3000 and Raney copper) and Cu/ZnO catalysts were selective to

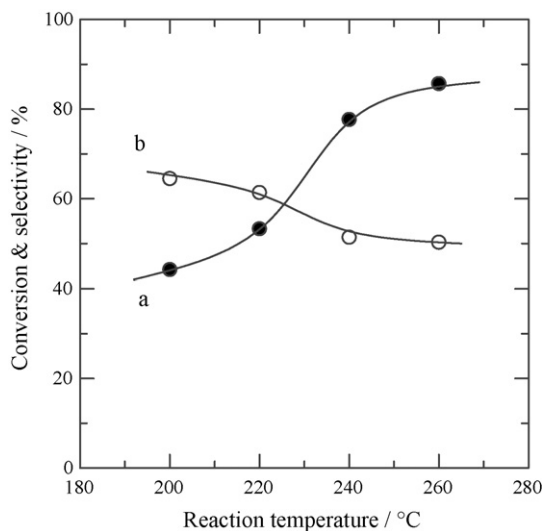


Fig. 2. Changes in (a) 1,3-BDO conversion and (b) selectivity to 4HB with reaction temperature over N-211 sample. The reaction conditions are the same as those in Fig. 1.

Table 3
Effect of W/F in the dehydrogenation of 1,3-BDO over N-211 catalyst at 240 °C^a

W/F (g h cm ⁻³)	Conversion (mol%)	Selectivity (mol%)			
		4HB	MEK	AcH	AcMe
0.014	38.7	71.6	13.2	1.8	3.7
0.028	55.9	64.3	12.9	1.2	7.4
0.056	77.7	51.4	24.8	3.8	7.6
0.111	94.8	35.8	27.9	2.9	20.8

^a The reaction conditions and abbreviations are the same as those in Table 1 other than catalyst weight (0.10–0.20 g) and total feed rate (1.8–7.2 cm³ h⁻¹).

4HB while major by-products were butanone, propanone, and ethanal. In contrast, over Cu/ZrO₂ (A-3010), Cu/Al₂O₃ (A-3001), and Cu/ZnO–ZrO₂ (A-3110), the major product was butanone. Propanone was competitively produced with the formation of 4HB and butanone over Cu/MgO.

Table 2 summarizes the catalytic activities of N-211 catalysts at temperatures of 200–260 °C. Fig. 2 shows temperature-dependence of 1,3-BDO conversion over the N-211 catalyst. The

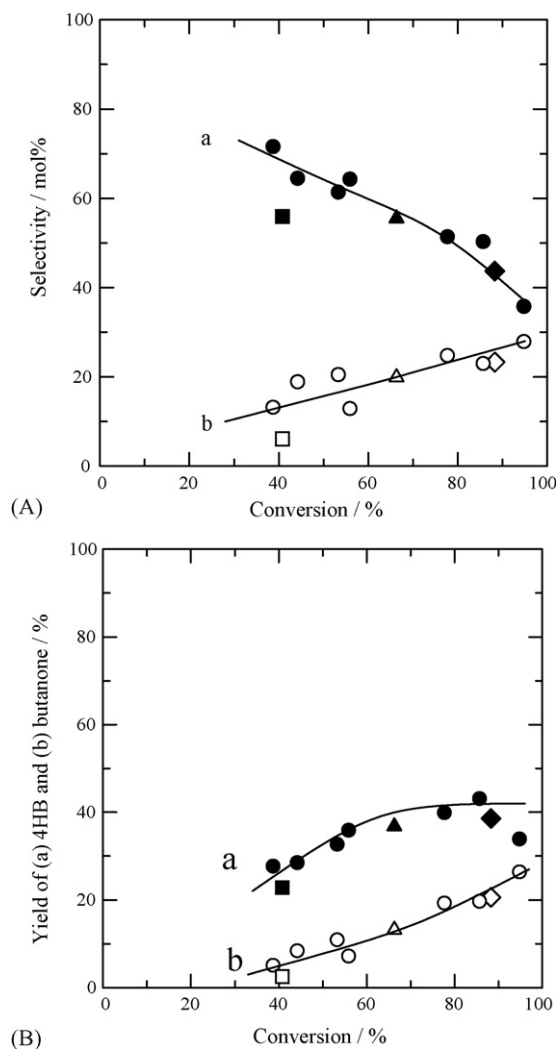


Fig. 3. Curves of (A) selectivity-conversion and (B) yield-conversion over Cu and Cu/ZnO catalysts. (a) 4HB; (b) butanone. Circle, data for N-211; triangle, A-3100; square, A-3000; diamond, Raney copper.

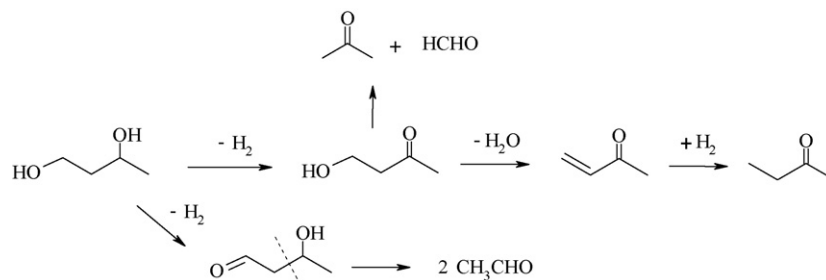


Fig. 4. Reaction route in the reaction of 1,3-butanediol.

conversion of 1,3-BDO increased with increasing the reaction temperature, while the selectivity to 4HB decreased. The selectivity to butanone increased with increasing temperature. Table 3 shows dependence of activity on contact time in the reaction of 1,3-BDO over N-211 at 240 °C. The contact time is expressed by W/F , where W and F are the catalyst weight and the reactant feed rate, respectively. The 1,3-BDO conversion increased with increasing contact time, while the selectivity to 4HB decreased and the selectivity to butanone increased.

In Fig. 3A, we plotted the selectivity-conversion data for the Cu and Cu/ZnO catalysts listed in Tables 1–3 in order to clarify the formation route. The selectivity to 4HB decreased with increasing 1,3-BDO conversion, while the selectivity to butanone increased. In Fig. 3B, we added plots of yields of 4HB and of butanone, which are defined as a product of the conversion and the selectivity: 4HB yield (%) = (1,3-BDO conversion/%) (4HB selectivity/%) / 100. The curve shows plateau at high conversion. The results indicate that 4HB is an intermediate, which forms butanone through the dehydration and the following hydrogenation, as shown in Fig. 4.

In the dehydrogenation of 1,2-butanediol, a good correlation has been observed between Cu surface area and the conversion of 1,2-butanediol [6]. The additives do not affect the selectivity to 1-hydroxy-2-butanone, which is higher than 90%. In the reaction of 1,4-butanediol into γ -butyrolactone, however, there is no clear correlation between Cu surface area and catalytic activity [16]; the reaction is complex in the mechanism. In addition to the dehydrogenation ability of metallic Cu, appropriate acid–base catalysis is required for the formation of hemiacetal as an intermediate in the ester formation. In Table 1, there is no correlation between Cu surface area and the selectivity to 4HB, while good correlation also seems to be observed between Cu surface area and the conversion of 1,3-BDO. This indicates that additives to the catalysts greatly affect the side reactions such as the formation of butanone, ethanal, and propanone.

In the present reaction of 1,3-BDO over A-3010 and A-3001, the selectivity to 4HB is low, and butanone is the major product because of the dehydration ability of zirconia and alumina, although the conversion of 1,3-BDO is high owing to their high Cu surface area. Actually, alumina component catalyzes the formation of ethers in the reactions of ethanol [13] and 1,4-butanediol [16,19]. In contrast, the major product is

propanone in the present reaction of 1,3-BDO over Cu/MgO. This indicates that basic MgO catalyzes retro-aldol reaction of 4HB to form propanone and formaldehyde. Ethanal, which is invariably produced in a small amount, can be formed via retro-aldol reaction of acetoalcohol, 3-hydroxybutanal, produced by the dehydrogenation in the primary OH group of 1,3-BDO. The formation route to ethanal and propanone is also depicted in Fig. 4.

In the dehydrogenation of 1,2-butanediol [6], we have found that the conversion of 1,2-butanediol is limited by chemical equilibrium between 1,2-butanediol and 1-hydroxy-2-butanone. The conversion increases with increasing W/F and the conversion levels off at ca. 60% at 210 °C, while the selectivity to 1-hydroxy-2-butanone exceeds 90%. In an H_2 flow instead of the N_2 flow, the conversion level decreases to ca. 30%. The equilibrium value increases with increasing temperature from 190 to 230 °C.

In Fig. 3B, we observe plateau in the yield of 4HB and steeply increase in butanone yield at high 1,3-BDO conversion. Since 4HB is readily dehydrated into 3-buten-2-one even on the surface of silica [12], it could be dehydrated on the copper surface at high concentration of 4HB. Then, 3-buten-2-one is hydrogenated to butanone in the hydrogen produced in the dehydrogenation of 1,3-BDO. Thus, the plateau in Fig. 3B is probably due to the fact that the H_2 consumption in the hydrogenation of 3-buten-2-one shifts the dehydrogenation equilibrium. There is a solution to overcome the equilibrium limitation: oxidative conditions are efficient for the production of 4HB. The yield of 4HB higher than 70% was obtained in the liquid-phase oxidative dehydrogenation of 1,3-BDO [11].

4. Conclusions

Dehydrogenation of 1,3-BDO was examined over Cu-based catalysts. Over Cu/Al₂O₃ and Cu/ZrO₂, the selectivity to 4HB is low because they catalyze dehydration of 4HB into 2-buten-2-one, followed by hydrogenation into butanone. Cu/MgO with basic support catalyzes retro-aldol reaction of 4HB into propanone and formaldehyde. Pure copper and Cu/ZnO are effective for the dehydrogenation into 4HB. However, 4HB is decomposed into butanone or propanone at high conversion even over pure copper catalysts. It is reasonable that equilibrium of the dehydrogenation of 1,3-BDO to 4HB would limit the yield of 4HB to 40%.

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