

Effective formation of ethyl acetate from ethanol over Cu-Zn-Zr-Al-O catalyst

Kanichiro Inui^{a,b,*}, Toru Kurabayashi^b, Satoshi Sato^{c,1}, Naoki Ichikawa^a

^a Graduate School of Science and Technology, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan

^b Chisso Petrochemical Corporation, 5-1 Goi-kaigan, Ichihara 290-8551, Japan

^c Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan

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Abstract

Post-treatment of reduced copper catalyst, which contains Zn, Zr, and Al, with alkaline solution is effective in improving the selectivity to ethyl acetate in the dehydrogenative dimerization of ethanol. The treatment with Na₂CO₃ and K₂CO₃ greatly suppressed the formation of by-products such as butanone and 2-butanol, and resulted in the improvement of the selectivity to ethyl acetate. The suppression of butanone and 2-butanol is caused by the neutralization of surface acid sites that are active for the dehydration from 1,3-butanediol, into which acetaldehyde is hydrogenated. These acid-sites are formed after reduction of the Cu-Zn-Zr-Al-O mixed oxide precursor, and thus the post-treatment is effective. We also discuss the reaction routes in the side reactions.

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1. Introduction

In the manufacture of ethyl acetate, dehydrogenative dimerization of ethanol to ethyl acetate has many advantages over the conventional methods such as esterification of ethanol and acetic acid. For example, it uses only ethanol, which is non-corrosive and less toxic. We investigated the ester formation, and developed a quaternary copper catalyst Cu-Zn-Zr-Al-O being the most promising catalyst, which has the composition of Cu:ZnO:ZrO₂:Al₂O₃ = 12:1:2:2 [1]. The selectivity to ethyl acetate greatly increased under pressured conditions [2]. The conversion of ethanol and the selectivity to ethyl acetate achieved 51% and 96 mol%, respectively, at 473 K and 0.8 MPa. Although some researchers speculated the reaction routes to the by-products [3,4], it is not confirmed experimentally.

In this process, however, butanone (MEK) is formed as a by-product. It causes serious problem in the following purification process. MEK and ethyl acetate form azeotropic

mixture, and MEK is never removed from ethyl acetate in any distillation methods, even by pressurized distillation. A manufacturer of ethyl acetate using the dimerization of ethanol removes MEK from ethyl acetate by the selective hydrogenation of MEK as a form of 2-butanol [5]. Clarification of the formation route of the by-products and development of the reduction of the by-products based on the formation route are important in the industrial process. This helps us to improve the selectivity to ethyl acetate.

The metallic character of copper and the acid–base property of the additives of metal oxides surely affect both the catalytic activity and the product selectivity over the Cu-Zn-Zr-Al-O catalyst. It is reasonable that acid–base property varies with the reduction of CuO because a portion of CuO forms solid solution with other oxide [1]. Therefore, we expected the post-treatment after reduction being effective in the dehydrogenative dimerization of ethanol to ethyl acetate. We preliminarily found that treatment of the Cu-Zn-Zr-Al-O catalyst with alkaline increased the selectivity to ethyl acetate in the reaction; the post-treatment was more effective than the pre-treatment.

In this paper, we examined the catalytic performance by the post-treatment of the Cu-Zn-Zr-Al-O catalyst with alkaline metal compounds to reduce the by-products, MEK

* Corresponding author. Tel.: +81-436-235625; fax: +81-436-231157.

E-mail addresses: inui@chisso.co.jp (K. Inui),

satoshi@faculty.chiba-u.jp (S. Sato).

¹ Co-corresponding author.

and 2-butanol, and we discussed the reaction routes to the by-products in the dehydrogenative dimerization of ethanol to ethyl acetate comparing with other reactions of various substrates, which are regarded to be intermediates.

2. Experimental

2.1. Catalysts

Several copper-based catalysts were prepared by co-precipitation with the corresponding nitrate solution. Typical component in the catalysts has an atomic ratio of Cu:ZnO:ZrO₂:Al₂O₃ = 12:1:2:2. Pure copper and mixed metal oxide catalysts were prepared by the same procedure with copper nitrate and the corresponding nitrates, respectively. The mixed metal oxide catalyst has the atomic ratio of ZnO:ZrO₂:Al₂O₃ = 1:2:2. The details of the catalyst preparation were described elsewhere [1]. The catalyst was reduced with a flow of mixture of H₂ and N₂ (H₂/N₂ = 10/90) at 0.1 dm³ min⁻¹ at temperatures up to 443 K.

The post-treatment of catalyst after reduction was carried out by soaking the reduced catalyst into 0.189 mol dm⁻³ of a solution of alkaline metal compounds (except for Li₂CO₃), NaCl, and boric acid. The treatment was carried out with saturated solution of Li₂CO₃ and Ca(OH)₂ in the post-treatment with Li₂CO₃ and Ca(OH)₂, respectively. The wet catalysts were put into the reactor, and then flushed with 1 dm³ of deionized water. The pre-treatment of catalyst before reduction was carried out by soaking precursor of the catalyst into 0.189 mol dm⁻³ of potassium carbonate solution, and then the sample was reduced at 443 K.

Loading of alkaline metal supported on the reduced catalysts was measured by HCl titration of the filtered solution. It was determined from the difference of alkaline concentration in the solution after the treatment. The amount of alkaline metals loaded on the catalysts measured by HCl titration were 0.66, 0.17, 0.19, and 0.06 mmol g_{catalyst}⁻¹ in the post-treatment with Li₂CO₃, Na₂CO₃, K₂CO₃, and Cs₂CO₃, respectively.

2.2. Catalytic reaction

All the reactants were supplied by Wako Pure Chemical Corp. and used without further purification. Dehydrogenative dimerization of ethanol was carried out at atmospheric pressure using a conventional fixed-bed down-flow glass reactor. The reactant of ethanol, which contained 0.5 wt% of water, was introduced into the reactor at a temperature of 473–533 K and at $W/F = 1.6$ h, where W and F are catalyst weight (g) and flow rate of ethanol (g h⁻¹), respectively. The reactant was heated and vaporized in the preheating zone equipped above the catalyst bed. After the reactant had passed through the catalyst bed, the effluent of the products was recovered by cooling at 195 K. The effluent collected periodically was analyzed by gas chromatography

Table 1
Abbreviations of compounds

13BD	1,3-Butanediol
1BO	1-Butanol
1PO	1-Propanol
2BO	2-Butanol
2PN	2-Pentanone
2PO	2-Propanol
AcH	Acetaldehyde
AcMe	Propanone
AcOEt	Ethyl acetate
AcOH	Acetic acid
BA	Butanal
BE	Butyl acetate
CA	2-Butenal
DEE	Diethyl ether
EB	Ethyl butyrate
EtOH	Ethanol
KB	4-Hydroxy-2-butanone
MEK	Butanone
MVC	3-Buten-2-ol
MVK	3-Buten-2-one
PA	Propanal
PB	Propyl butyrate

(Shimadzu GC-14A) with a capillary column (G-100 and G-300, Kagakuin Kensa Kyoukai) with toluene as an internal standard. The gaseous products that did not condense at 195 K were collected in a plastic bag and analyzed by gas chromatography (Shimadzu GC-9A) with a column filled with active carbon. The reaction of 1-propanol and butanal was also carried out in the glass reactor.

Reactions of other reactants, which are considered to be possible intermediates, are carried out by the same procedure as the ethanol reaction described above. All the abbreviations of chemicals used in this paper are listed in Table 1.

3. Results

3.1. Treatment after reduction

Table 2 shows the influence of pre- and post-treatment of catalyst with potassium carbonate solution on the dehydrogenative dimerization of ethanol. Selectivity to ethyl acetate increases in both the pre- and post-treatment with potassium carbonate while the conversion of ethanol is not affected. It is obvious that the selectivity to MEK is greatly decreased by the post-treatment with potassium carbonate. Formation of 2-butanol (2BO), a hydrogenated MEK, is also suppressed by the post-treatment. In addition, diethyl ether (DEE) is completely suppressed by the potassium carbonate treatment. However, other by-products, such as propanone and 1-butanol (1BO), are not affected by the alkaline treatment.

3.2. Treatment with alkaline carbonate

Fig. 1 shows changes in the conversion of ethanol with reaction temperature in the alkaline carbonate treatment.

Table 2

Typical results of catalyst treatment before and after the reduction in the dehydrogenative dimerization of ethanol over the Cu-Zn-Zr-Al-O catalyst

Treatment	X (%)	Selectivity to (mol%)											
		AcOEt	AcH	MEK	2BO	AcMe	2PO	1BO	2PN	EB	BE	AcOH	DEE
None	67.6	78.0	6.4	7.3	1.1	1.5	0.3	0.4	0.2	1.0	0.5	0.2	0.1
Pre	66.5	81.3	6.3	6.5	1.1	1.6	0.4	0.4	0.2	1.0	0.6	0.2	0.0
Post	66.0	85.0	5.7	3.9	0.6	1.7	0.4	0.4	0.1	1.1	0.7	0.1	0.0

Reaction conditions: 493 K; $W/F = 1.6$ h. Pre, treatment before reduction; Post, treatment after reduction; X, conversion of ethanol. Abbreviations are listed in Table 1.

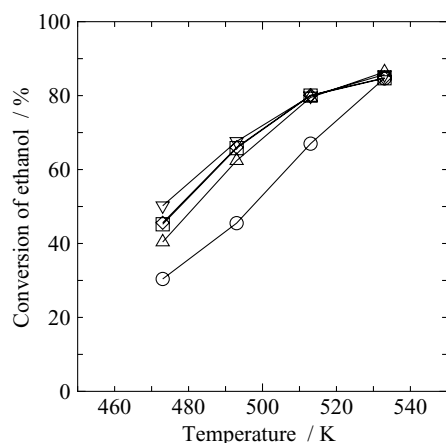


Fig. 1. Changes in the conversion of ethanol with reaction temperature ($W/F = 1.6$ h). Treatment with (circle) Li₂CO₃; (square) Na₂CO₃; (rhombus) K₂CO₃; (triangle) Cs₂CO₃; and (reverse triangle) none treatment.

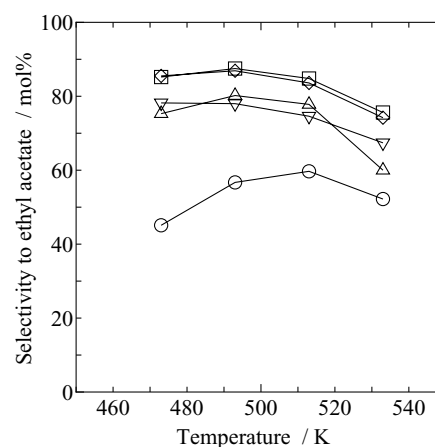


Fig. 2. Changes in the selectivity to ethyl acetate with reaction temperature. Symbols and reaction conditions are the same as those in Fig. 1.

Treatment with Na₂CO₃, K₂CO₃ and Cs₂CO₃ does not affect the conversion of ethanol at the temperatures higher than 493 K. On the other hand, Li₂CO₃ greatly depresses the ethanol conversion. Fig. 2 shows changes in the selectivity to ethyl acetate with reaction temperature. Treatment with Na₂CO₃ and K₂CO₃ shows higher the selectivity than the none treatment. Treatment with Li₂CO₃ decreases the selectivity to ethyl acetate.

Table 3 also summarizes the selectivity to other by-products. The low selectivity to ethyl acetate in the

Li₂CO₃ treatment is due to the formation of acetaldehyde. The level of selectivity to ethyl acetate in the Cs₂CO₃ treatment is similar to the non-treated catalyst. The treatment with Li₂CO₃ and Cs₂CO₃ especially increases the formation of propanone, 2-propanol, and 2-pentanone together with 1BO and ethyl butyrate. DEE formation, however, is completely suppressed by the alkaline carbonate treatment. Treatment with basic material such as NaOH and Ca(OH)₂ is also effective in the suppression of MEK formation. Treatment with boric acid decreases both the conversion of ethanol and the selectivity to ethyl acetate, while it

Table 3

Typical results of post-treatment of reduced catalyst in the dehydrogenative dimerization of ethanol over the Cu-Zn-Zr-Al-O catalyst

Post-treatment	X (%)	Selectivity to (mol%)											
		AcOEt	AcH	MEK	2BO	AcMe	2PO	1BO	2PN	EB	BE	AcOH	DEE
None	67.6	78.0	6.4	7.3	1.1	1.5	0.3	0.4	0.2	1.0	0.5	0.2	0.1
Li ₂ CO ₃	45.5	56.7	21.8	4.4	0.3	6.3	1.0	1.4	0.6	1.7	0.5	0.1	0.0
Na ₂ CO ₃	65.8	85.8	5.5	3.9	0.7	1.5	0.3	0.4	0.1	0.9	0.5	0.1	0.0
K ₂ CO ₃	66.0	85.0	5.7	3.9	0.6	1.7	0.4	0.4	0.1	1.1	0.7	0.1	0.0
Cs ₂ CO ₃	62.4	80.2	6.3	2.2	0.2	3.0	0.7	0.7	0.4	2.0	1.0	0.0	0.0
NaOH	62.2	81.9	7.1	4.0	0.6	1.7	0.4	0.4	0.1	0.8	0.5	0.1	0.0
NaCl	66.0	76.1	5.9	7.2	1.1	1.6	0.4	0.7	0.3	1.7	0.8	0.2	0.1
H ₃ BO ₃	60.3	68.0	10.4	9.5	1.3	1.7	0.4	0.6	0.5	1.1	0.8	0.2	0.3
Ca(OH) ₂	66.4	80.9	6.2	4.8	0.8	1.8	0.4	0.4	0.2	1.0	0.6	0.2	0.0

Reaction conditions: 493 K; $W/F = 1.6$ h. Abbreviations are listed in Table 1.

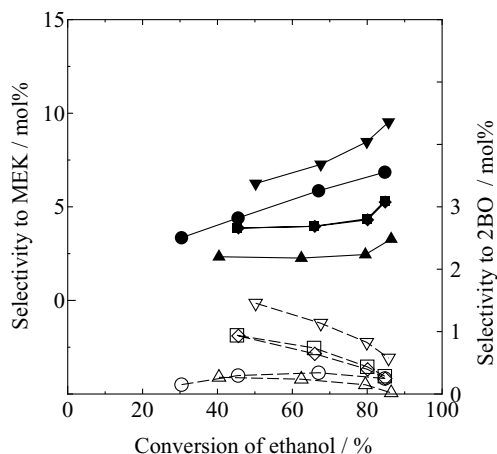


Fig. 3. Changes in the selectivity to butanone and 2-butanol with the conversion of ethanol. Closed symbols with solid line and opened symbols with dash line represent the selectivity to butanone and 2-butanol, respectively. Symbols and reaction conditions are the same as those in Fig. 1.

increases the selectivity to MEK and DEE. Treatment with neutral salt NaCl shows no distinct effect.

Fig. 3 shows changes in the selectivity to MEK and 2BO with the conversion of ethanol. All the catalysts treated with alkaline metal carbonate show lower selectivity than the non-treated catalyst. The selectivity to MEK increases with increasing the conversion of ethanol, while the selectivity to 2BO decreases except for the treatment with Li_2CO_3 . The Li_2CO_3 -treated catalyst shows a broad maximum of the selectivity to 2BO in the vicinity of 50–70% of the conversion.

Fig. 4 shows changes in the selectivity to propanone and 2-propanol with the conversion of ethanol. Both the selectivity to propanone and to 2-propanol increase with increasing the conversion of ethanol in all the catalysts.

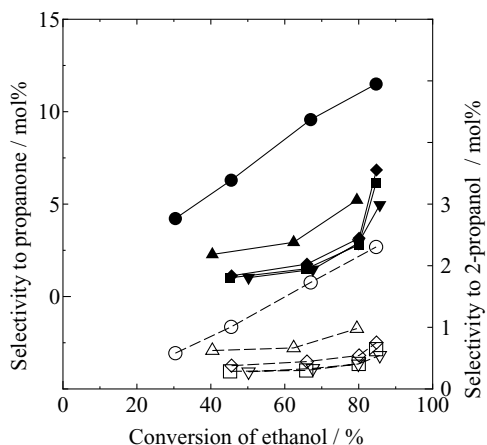


Fig. 4. Changes in the selectivity to propanone and 2-propanol with the conversion of ethanol. Closed symbols with solid line and opened symbols with dash line represent the selectivity to propanone and 2-propanol, respectively. Symbols and reaction conditions are the same as those in Fig. 1.

Table 4

Influence of the concentration of water in ethanol in the reaction of ethanol over Cu-Zn-Zr-Al-O catalyst

H ₂ O content (wt.%)	Conversion of ethanol (%)	Selectivity to (wt.%)		
		Ethyl acetate	Acetic acid	Propanone
0.5	67.6	78.0	0.2	1.5
5	49.2	76.7	1.7	0.6
10	44.4	70.0	5.4	0.5
15	43.5	62.7	9.1	0.5

Reaction conditions: 493 K, $W/F = 1.6$ h.

3.3. Effect of water in the reaction of ethanol

Table 4 lists the effect of the concentration of water in ethanol feedstock over non-treated Cu-Zn-Zr-Al-O catalyst. The reactant of ethanol originally contains 0.5% of water. The selectivity to acetic acid increases with increasing water content in ethanol. Thus, an increase in water concentration in the reactor causes high selectivity to acetic acid. It is noticed that the selectivity to propanone decreases with increasing the selectivity to acetic acid.

3.4. Coupling of alcohol and aldehyde

Table 5 shows the results of the catalytic reaction of 1-propanol and butanal over pure Cu, Zn-Zr-Al-O without Cu, and Cu-Zn-Zr-Al-O catalysts under conditions at a very short contact time ($W/F = 0.01$ h). In the reaction over pure Cu catalyst, the products are propene (dehydrated 1-propanol), propanal (dehydrogenated 1-propanol), and 1BO (hydrogenated butanal). The products increase with increasing reaction temperature. No esters such as propyl butyrate are observed in the products over the pure Cu catalyst. Over the Zn-Zr-Al-O with the molar ratio of $\text{ZnO}:\text{ZrO}_2:\text{Al}_2\text{O}_3 = 1:2:2$ without metallic state of the components, the products are propene and a small amount of propanal and 1-butanol, in addition to propyl butyrate. At longer contact time, propyl propionate, butyl propionate, and butyl butyrate are observed in addition to the formation of propyl butyrate (data not shown). In the reaction over the Cu-Zn-Zr-Al-O catalyst with the molar ratio of $\text{Cu}:\text{ZnO}:\text{ZrO}_2:\text{Al}_2\text{O}_3 = 1:1:2:2$, the products are propanal and 1-butanol together with a small amount of propene and propyl butyrate. The product distribution over the Zn-Zr-Al-O and the Cu-Zn-Zr-Al-O catalyst is similar to each other. In a similar way, butyl propionate is observed as the primary ester product at low conversion in another reaction of 1-butanol and propanal over the catalyst.

3.5. Reaction of other reactants

Table 6 summarizes the results in the reaction of acetaldehyde (AcH), acetaldehyde with ethanol (AcH + EtOH), and ethyl acetate (AcOEt) together with the reference ethanol (EtOH) over the non-treated Cu-Zn-Zr-Al-O catalyst un-

Table 5
Coupling of 1-propanol and butanal

Catalyst	Temperature (K)	Composition of effluent (wt.%)						
		IPO	BA	Propene	PA	1BO	PB	Others
Cu	473	53.3	43.5	0.3	0.4	0.1	0.0	2.4
	493	51.3	44.8	0.1	1.3	0.3	0.0	2.2
	513	49.1	39.3	0.2	5.0	3.7	0.0	2.7
Zn-Zr-Al-O	473	53.1	45.8	0.3	0.2	0.1	0.1	0.4
	493	52.8	45.0	0.5	0.7	0.5	0.1	0.4
	513	51.7	44.4	0.2	1.4	1.5	0.2	0.6
Cu-Zn-Zr-Al-O	473	51.1	43.1	0.6	1.5	1.2	0.1	2.4
	493	48.1	42.7	0.6	3.5	2.6	0.1	2.4
	513	45.9	35.9	0.5	6.9	4.6	0.1	6.1

$W/F = 0.01$ h. Abbreviations are listed in Table 1.

Table 6
Reaction of acetaldehyde and ethanol in a flow of N_2 and H_2 over Cu-Zn-Zr-Al-O catalyst

Reactant(s)	Carrier gas	Composition of products (wt.%)												
		EtOH	AcH	AcOEt	MEK	2BO	AcMe	CA	BA	1BO	2PN	EB	BE	Others
AcH	N_2	2.1	<u>83.0</u>	3.3	0.3	0.0	1.6	3.3	3.9	0.1	0.3	0.7	0.3	1.1
AcH	H_2	16.9	<u>10.6</u>	46.8	2.9	0.3	5.0	0.0	0.6	1.6	1.9	4.1	4.1	5.5
AcH + EtOH	N_2	<u>30.7</u>	<u>14.8</u>	31.1	6.3	0.4	1.4	0.0	0.0	1.8	0.5	1.8	1.9	9.7
AcOEt	H_2	37.1	0.9	<u>61.1</u>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
EtOH	N_2	<u>33.7</u>	4.3	<u>51.6</u>	4.0	0.6	0.7	0.0	0.0	0.2	0.1	0.6	0.3	3.9

Reaction conditions: 493 K, $W/F = 1.6$ h. Others contain a small number of unidentified products. Underline represents the reactant(s) in the reaction. Abbreviations are listed in Table 1.

der different atmospheric conditions. In a N_2 flow reaction, acetaldehyde is hardly converted to ethyl acetate, and acetaldehyde derivatives such as 2-butenal and butanal are observed. In contrast, the reaction of acetaldehyde in a H_2 flow is accompanied by the formation of ethyl acetate as a major product. Hydrogenated products such as ethanol and 1-butanol are also observed in a H_2 flow, whereas no 2-butenal is detected. In addition, propanone is observed in the reaction. The product distribution in the H_2 flow reac-

tion is similar to that observed in the reaction of ethanol in a N_2 flow. In the reaction of an equimolar mixture of acetaldehyde and ethanol in a N_2 flow, the product distribution is also similar to that observed in the reaction of ethanol. The reaction of ethyl acetate in H_2 is a reverse reaction of the dehydrogenative dimerization of ethanol to ethyl acetate.

Table 7 summarizes the results of other reactants such as acetic acid (AcOH), 1,3-butanediol (13BD),

Table 7
Reaction of other reactants in a flow of N_2 and H_2 over Cu-Zn-Zr-Al-O catalyst

Reactant(s)	Carrier gas	Composition of products (wt.%)											
		EtOH	AcH	AcOH	AcOEt	MEK	MVK	2BO	AcMe	2PO	1BO	2PN	Others
AcOH	H_2	5.0	1.9	<u>90.0</u>	2.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.5
13BD	N_2	5.1	2.4	0.8	1.0	59.0	0.0	1.9	3.4	0.1	4.4	0.2	21.7
13BD ^a	N_2	4.9	4.2	1.6	0.8	52.2	0.0	0.4	2.7	0.0	6.4	0.3	26.4
13BD	H_2	6.8	1.4	0.4	1.0	55.6	0.0	4.2	3.3	0.3	4.5	0.2	22.4
KB	N_2	0.0	0.0	0.0	0.0	26.5	61.8	0.3	8.2	0.0	0.0	0.0	3.2
KB	H_2	0.0	0.7	0.0	0.0	62.4	0.4	13.8	7.6	1.3	0.0	0.0	13.8
MVK	H_2	0.0	0.0	0.0	0.0	67.7	<u>trace</u>	25.0	0.0	0.0	0.0	0.0	7.3
MVC	H_2	0.0	0.0	0.0	0.0	58.4	<u>trace</u>	17.4	0.0	0.0	0.0	0.0	24.2
MEK	H_2	0.4	4.9	0.0	0.0	<u>39.7</u>	0.0	24.6	0.0	0.0	0.0	0.0	30.4
2BO	H_2	0.0	0.0	0.0	0.0	56.8	0.0	<u>33.7</u>	0.0	0.0	0.0	0.0	9.5
AcH + AcMe	H_2	49.0	<u>0.7</u>	0.0	8.9	0.0	0.0	0.6	<u>31.6</u>	0.2	3.2	1.1	4.7 ^b

Reaction conditions: 493 K, $W/F = 1.6$ h. Underline represents the reactant(s) in the reaction. Abbreviations are listed in Table 1.

^a Reacted over the catalyst post-treated with K_2CO_3 solution.

^b Others in the reaction of AcH + AcMe contains 2-pentanol (3.3%) and 3-penten-2-one (0.4%).

4-hydroxy-2-butanone (KB), 3-buten-2-one (MVK), 3-buten-2-ol (MVC), 2BO, MEK, and acetaldehyde with propanone (AcH + AcMe) over the Cu-Zn-Zr-Al-O catalyst under different atmospheric conditions. Acetic acid is hardly converted over the catalyst. Small amounts of ethanol, acetaldehyde, ethyl acetate, and propanone are observed in the reaction of acetic acid in a H₂ flow. In the reactions of 13BD and KB, the reactants are completely consumed. In the reaction of KB, the major product is MVK in a flow of N₂, and MEK in a flow of H₂. The major product of the 13BD reaction is MEK, and small amounts of acetaldehyde, 1BO, ethanol, ethyl acetate, propanone, and KB are detected. The products of the reaction of KB in a N₂ flow are MVK, MEK, propanone, and a small amount of 2BO, while those in a H₂ flow are MEK, 2BO, propanone, 2-propanol, together with a small amount of acetaldehyde and MVK. The product distribution in the reaction of MVK, MVC, 2BO, and MEK in a H₂ flow is very similar to each other. MEK and 2BO are observed as main products in the reactions. Reactions irreversibly proceed in the reactions of MVK and MVC: MVK and MVC are completely consumed in the reactions. These results probably originate from the equilibrium of 2BO and MEK. The reaction of equimolar mixture of acetaldehyde and propanone in a flow of H₂ shows a formation of ethanol, ethyl acetate, 2-pentanone, 1BO, 2BO, 2-pentanol, and 3-penten-2-one. In addition, the selectivity to MEK and 2BO in the reaction of 13BD over the alkaline-treated Cu-Zn-Zr-Al-O catalyst is relatively low comparing with the non-treated one.

4. Discussion

4.1. Effect of treatment with alkaline after reduction

Iwasa and Takezawa reported that the doping of KOH on a Cu/Al₂O₃ catalyst decreased the formation of C₄-species such as butanal, MEK, and 1BO [6]. They concluded that the C₄-species were produced by acid-catalyzed reaction. Judging from the results of the treatment with K₂CO₃ solution after and before reduction (Table 2), the post-treatment affects the acid–base sites that formed after reduction. Especially, the alkaline treatment suppresses the formation of MEK and 2BO. This result is probably caused by masking of surface acid sites, and the treatment decreases the dehydration ability. This assumption is supported by complete suppression of DEE formation in the alkaline treatment (Table 3). Actually, the formation of MEK and 2BO decreased with the alkaline treatment in the reaction of 13BD (Table 7). The treatment with boric acid increases the formation of MEK and DEE (Table 3). The distribution of the products in the dehydrogenative dimerization of ethanol is surely affected by the surface acid–base property. We insist that the post-treatment of the copper catalyst with Na₂CO₃ and K₂CO₃ is effective in improving the selectivity to ethyl acetate.

The initial reaction of aldol addition is abstraction of α -hydrogen from aldehyde to form carbanion, followed by attacking a carbon of carbonyl in another aldehyde. It is well known that aldol addition is catalyzed by base catalysts. Chang and Ko [7], and Climent et al. [8] reported that surface acidities promoted aldol addition, and Di Cosimo et al. [9] reported that aldol addition of propanone proceeded over a pair of the acid–base on a catalyst surface. In addition, acid sites also catalyze dehydration during aldol reaction [7]. In this step, an acid site on a metal oxide probably promotes activation of acetaldehyde. Actually, MEK and 2BO in the acetaldehyde derivatives decrease in the reaction of ethanol over Na₂CO₃- and K₂CO₃-treated catalysts (Table 3).

In the dehydrogenative dimerization of ethanol, we can summarize the roles of acid sites on the metal oxide surface, which are to: (a) assist the formation of ethyl acetate via hemiacetal, which is deactivated by Li₂CO₃-treatment (Fig. 5A), (b) promote the aldol addition, which may be deactivated by all the alkaline treatments (Fig. 5B), and (c) perform the dehydration of alcohols (Fig. 5C).

The treatment with Na₂CO₃ and K₂CO₃ did not affect the formation of butanal and 1BO (Table 3). The increase in the selectivity to ethyl acetate is caused by the decrease in the selectivity to MEK, 2BO, and DEE. The suppression of the dehydration of 13BD into MVC shifts the equilibrium of aldol addition to the acetaldehyde side. This attributes the high selectivity to ethyl acetate. The results indicate that the treatment with Na₂CO₃ and K₂CO₃ has no effect on the roles (a) and (b), and that affects only the role (c), especially the dehydration of primary alcohols such as ethanol, 13BD, and KB. Although the alkaline treatment may mask the acid sites of all the roles (a)–(c), an optimum amount of Na and K could mask only the acid sites on which 13BD and KB can be dehydrated. It is necessary that the acid sites formed after reduction of the catalyst should be masked to suppress the side reactions.

4.2. Active center in the coupling of ethanol and acetaldehyde

The reaction route in the formation of ethyl acetate has been already discussed [3,10–12]. We have also proposed the reaction route from ethanol to ethyl acetate [2]. The reaction proceeds via hemiacetal as an intermediate (second row of Fig. 6), whereas hemiacetal has not been detected in the reaction of ethanol. In contrast, we have recently detected 2-hydroxy-tetrahydrofuran, a hemiacetal form of 4-hydroxybutanal, in the dehydrogenative cyclization of 1,4-butanediol [13]. Fig. 7 shows the reaction scheme of 1,4-butanediol to gamma-butyrolactone over Cu-Zn-Zr-Al-O catalyst. However, it is not clarified where the active sites for the coupling of alcohol and aldehyde are.

The results in Table 5 suggest that the coupling of alcohol with aldehyde occurs over the mixed metal-oxides surface not over the Cu metal surface. In addition, the carboxylate part and the alkoxy part in the product ester

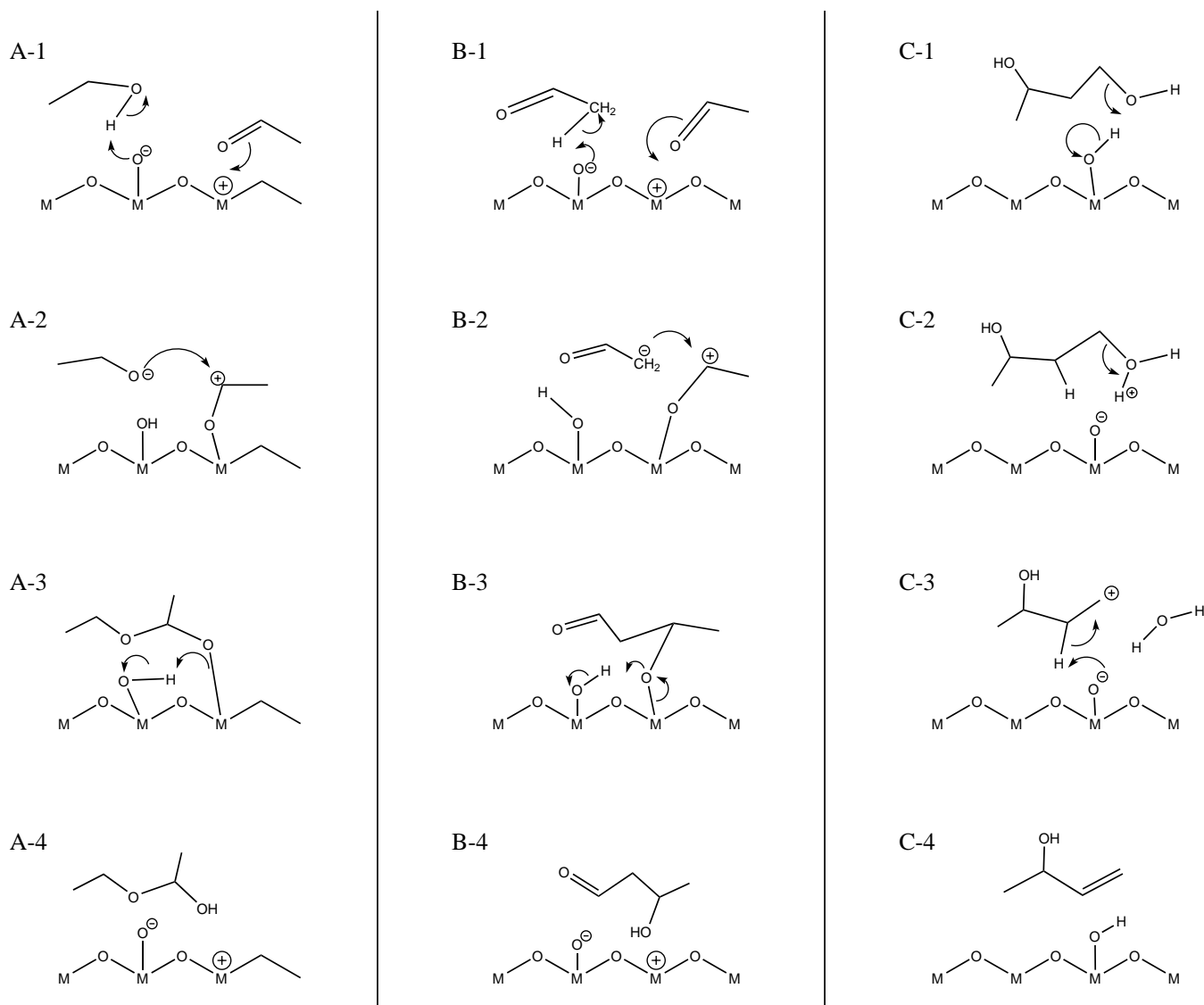


Fig. 5. Models of surface reaction over the metal oxide surface for: (A) the formation of ethyl acetate, (B) aldol addition, and (C) dehydration.

originate from aldehyde and alcohol, respectively. The dehydrogenated ethanol, namely acetaldehyde, was adsorbed on the acid site, while a hydrogen of the OH group in ethanol was abstracted by surface base site forming surface alkoxide. Then, a hemiacetal is formed from the surface alkoxide and the adsorbed aldehyde (Fig. 5A). The hemiacetal would be dehydrogenated immediately and produce ethyl acetate. Since the hemiacetal was not detected in our investigation, hemiacetal could exist as unstable adsorbed species. The assistance of acid site to activate the acetaldehyde are observed in similar role of active center in the Tishchenko reaction of benzaldehyde [14] and in the aldol condensation of benzaldehyde and heptanal [8]. In the similar way, we insist that the formation of ethyl butyrate and butyl acetate (Tables 2 and 3) would proceed via hemiacetals of ethanol–butanal and 1-butanol–acetaldehyde, respectively.

4.3. Formation mechanism of by-products

We have found many kinds of by-products (Tables 2 and 3), and try to explain the formation route of each by-products in this section. Fig. 6 depicts the reaction scheme from ethanol to by-products in the dehydrogenative dimerization of ethanol over Cu–Zn–Zr–Al–O catalyst.

First, diethyl ether and acetic acid depicted in the first and the second rows of Fig. 6 are derived from ethanol and ethyl acetate, respectively. Diethyl ether is formed from inter-molecular dehydration of ethanol. This reaction is a typical acid-catalyzed reaction. The formation of diethyl ether is completely suppressed in the alkaline-treated catalyst (Table 3). It is known that Cu–Al–O catalyzes the formation of dimethyl ether as well as methyl formate in the reaction of methanol [15]. Thus, the formation of diethyl ether is probably attributed to surface acidity on

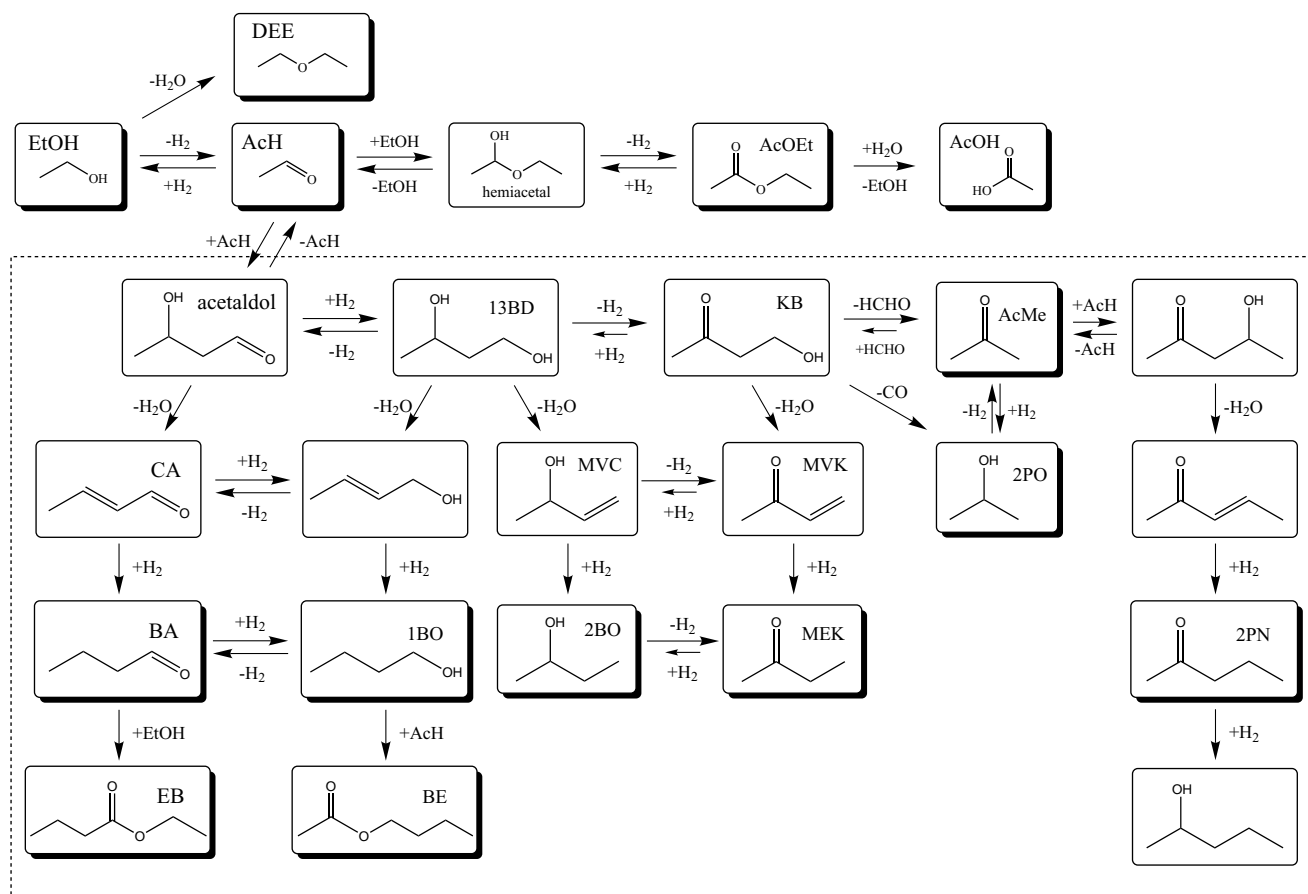


Fig. 6. Probable reaction scheme in the dehydrogenative dimerization of ethanol. All the abbreviations in the scheme are listed in Table 1. Substrates shown by squares with shadows are eventually detected in the reaction of ethanol dehydrogenation.

alumina. Acetic acid is mainly formed by hydrolysis of ethyl acetate. This pathway needs water. Actually, water concentration in ethanol feedstock affects the selectivity to acetic acid (Table 4). Acetic acid itself was hardly reacted (Table 7).

The key materials of major by-products in the reaction are acetaldehyde and its hydrogenated product, namely 1,3BD. Acetaldehyde is formed by aldol addition of acetaldehyde. Thus, the formation of acetaldehyde and 1,3BD would be reduced by suppression of the formation of isolated acetaldehyde. The pressurized reaction effectively suppressed the formation of isolated acetaldehyde resulted in the selective formation of ethyl acetate [2]. All the products surrounded by broken line in Fig. 6 are derived from acetaldehyde.

4.3.1. Propanone and 2-propanol

The formation of propanone may have two routes, ketonization of acetic acid and reverse aldol addition of KB. Although we cannot deny the route of ketonization, it is probably minor. The reasons are: (1) the formation of propanone in the reaction of acetic acid in H_2 is very small (Table 6); and (2) the propanone formation does not increase with increasing the concentration of acetic acid in the reactor (Table 4). Actually, the ketonization proceeds at higher temperature (higher than 673 K [18,19]) than the present reaction temperature [16,17]: the ketonization of acetic acid needs the temperature above 673 K [18]. Kamimura et al. [19] and Wrzyszc et al. [20] proposed the ketonization of esters to form symmetric ketone. Nevertheless, the

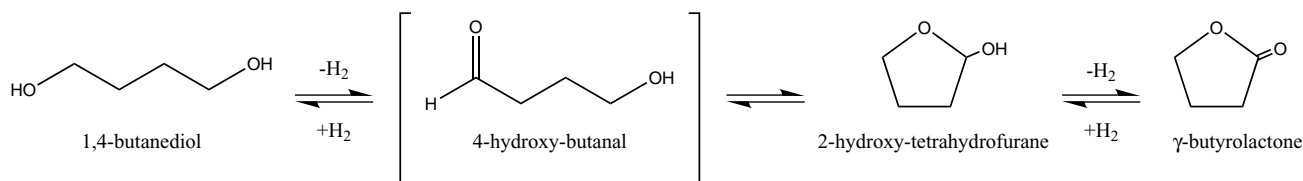


Fig. 7. Reaction scheme of 1,4-butanediol to gamma-butyrolactone over Cu-Zn-Zr-Al-O catalyst.

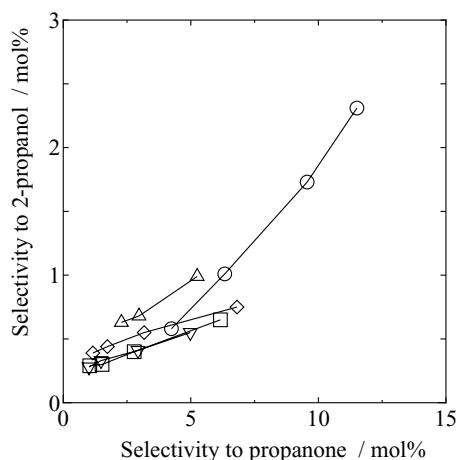


Fig. 8. Changes in the selectivity to 2-propanol with the selectivity to propanone. Symbols are the same as those in Fig. 1.

ketonization in the system is denied by the reaction of ethyl acetate (Table 6). The propanone formation in the reaction of KB (Table 7) suggests that an intermediate of propanone is KB. Therefore, propanone is probably formed through reverse aldol addition.

The formation of 2-propanol proceeds only in the existence of H_2 (Table 7). This may show that 2-propanol is formed by the hydrogenation of propanone, but it is not simple. Fig. 8, in which the data in Fig. 4 are replotted, shows changes in the selectivity to 2-propanol with the selectivity to propanone in the reaction of ethanol over the Cu-Zn-Zr-Al-O catalyst. The selectivity to 2-propanol increases with increasing propanone. Fig. 8 indicates that propanone and 2-propanol could be simultaneously formed in the decomposition of KB in the presence of H_2 , which is produced by dehydrogenation of ethanol. Actually, propanone was hardly hydrogenated into 2-propanol in the reaction of propanone with acetaldehyde (Table 7). In addition, KB is formed from 13BD via dehydrogenation. The alkaline treatment causes increase of KB because the dehydration of 13BD is suppressed by the treatment. KB would be immediately converted into propanone and formaldehyde. They are confirmed by a slight increase of propanone in the treatment with alkaline (Tables 2 and 3).

Therefore, the most probable route of the formation of propanone is the reverse aldol addition of KB, and 2-propanol is simultaneously formed via decomposition of KB with H_2 .

4.3.2. Butanone and 2-butanol

We have already clarified that MEK and 2BO are formed via dehydration of 13BD [2]. In this section, we discuss the formation route from 13BD to MEK.

A large amount of MEK was observed in the reactions of 13BD and KB in both flow of N_2 and H_2 (Table 7). MVK was dominant in the reaction of KB in N_2 because of a lack of hydrogen. The reaction between 2BO and MEK is

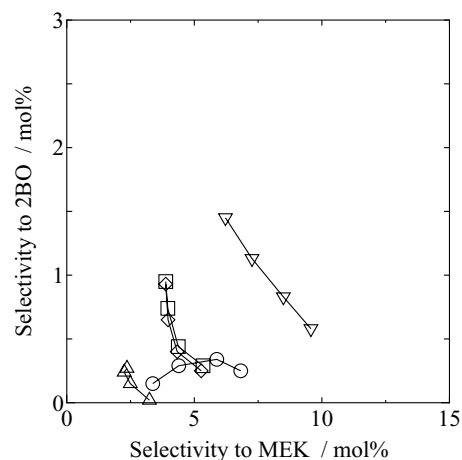


Fig. 9. Changes in the selectivity to 2-butanol with the selectivity to butanone. Symbols are the same as those in Fig. 1.

probably controlled by its equilibrium. Moreover, we did not observe MVK, MVC, and KB in the reaction of ethanol over the catalyst. Thus, we can list the considerable reaction routes from 13BD to MEK in Fig. 6. The following three routes are possible; they are reaction sequences: (A) 13BD–MVC–2BO–MEK; (B) 13BD–KB–MVK–MEK; and (C) 13BD–MVC–MVK–MEK. They occur simultaneously, so that we cannot distinguish among them. The dehydration step catalyzed by acid in the reactions, 13BD to MVC and KB to MVK, are irreversible. Here, in Fig. 9, we replotted the data shown in Fig. 3. Fig. 9 shows changes in the selectivity to 2BO with the selectivity to MEK. The selectivity to 2BO decreases with increasing MEK except for the treatment with Li_2CO_3 . Figs. 3 and 9 suggest that the formation of MEK proceeds step-wise via 2BO. Therefore, the most probable route is the sequence (A) 13BD–MVC–2BO–MEK.

4.3.3. 2-Pentanone

A small amount of 2-pentanone was detected in the reaction of ethanol (Table 3). It is reasonable that 2-pentanone is formed through aldol reaction of acetaldehyde and propanone, followed by dehydration and hydrogenation [2]. We observed 2-pentanone in the reaction of equimolar mixture of acetaldehyde and propanone (Table 7). We also observed 2-pentanol and 3-penten-2-one in the reaction of the mixture. Thus, it is concluded that 2-pentanone forms via aldol addition of acetaldehyde and propanone.

5. Conclusion

Effective treatment of Cu-Zn-Zr-Al-O catalyst for the production of ethyl acetate was investigated in the dehydrogenative dimerization of ethanol. The post-treatment of the reduced Cu-Zn-Zr-Al-O catalyst with alkaline carbonate solution greatly suppressed the formation of butanone and 2-butanol. This is achieved by masking of the acid sites that

catalyzes the dehydration of 1,3-butanediol to 3-buten-2-ol. The acid sites are formed after reduction. The treatment with sodium carbonate and potassium carbonate is the most effective in the selective production of ethyl acetate.

An active center of the formation of hemiacetal of acetaldehyde and ethanol exists on metal oxides not on copper metal. We clarified the formation route of propanone, 2-propanol, butanone, and 2-butanol. Propanone and 2-propanol are formed by reverse aldol reaction of 4-hydroxy-2-butanone. Butanone and 2-butanol are formed from 1,3-butanediol. We summarized the reaction scheme from ethanol to ethyl acetate and other by-products in the dehydrogenative dimerization of ethanol over Cu-Zn-Zr-Al-O catalyst, as shown in Fig. 6.

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