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Effect of Ag loading on Cu/Al_2O_3 catalyst in the production of 1,2-propanediol from glycerol

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ABSTRACT

The vapor-phase hydrogenolysis of glycerol was performed at a gradient temperature and ambient hydrogen pressure over a commercial Cu/Al_2O_3 catalyst modified with silver. Addition of Ag into Cu/Al_2O_3 catalysts was found to be efficient in inhibiting the decomposition of glycerol to produce ethylene glycol and gave a yield of 1,2-propanediol higher than that of the original Cu/Al_2O_3 without Ag. To minimize the ethylene glycol formation, the suitable loading of Ag was 1 wt.%. Since the Ag loading decreases the hydrogenation ability of the Cu/Al_2O_3 catalyst, 1 wt.% Ag-loaded Cu/Al_2O_3 catalyst was placed on the upper layer of the fixed catalyst bed and the Cu/Al_2O_3 catalyst was placed on the bottom layer for achieving much higher 1,2-propanediol yield. The effect of temperatures of the top, the interlayer, and the bottom of the catalyst bed on the yield was also examined: a high 1,2-propanediol yield of 98.3%, which is the highest value under ambient H_2 pressure conditions, was achieved at a gradient temperature from 170 to 105 °C and a glycerol concentration of 15 wt.%.

1. Introduction

The application of renewable biomass provides a facile route to alleviate the shortage of fossil fuels and reduce CO_2 emission [1,2]. Glycerol, as a biomass derivate, is currently produced in the biodiesel production process which brings a huge amount of glycerol close to 10 wt.% of the overall biodiesel production [3–5]. Nowadays, a large surplus of crude glycerol is directly incinerated, although the crude glycerol must be a potential raw material [6]. Many kinds of value-added chemicals [1–5], such as acrolein [6–9], lactic acid [10,11], 1,2-propanediol (1,2-PDO) [12–19], and 1,3-propanediol (1,3-PDO) [20–23], can be derived from glycerol.

1,2-PDO is a valuable chemical, which is mainly used for producing polymers [24]. In the liquid-phase processes, hydrogenolysis of glycerol into 1,2-PDO proceeds over various metal catalysts such as Rh [25,26], Ru [27,28], Ni [29,30], Pt [31,32], Ag [33], and Cu [12,19]. Huang et al. reported 98% selectivity to 1,2-PDO with a conversion of ca. 82% over Cu/SiO_2 catalyst at 180 °C and an H_2 pressure of 6.0 MPa, while ethylene glycol (EG) as a by-product increases with increasing the reaction temperature [12]. In the liquid phase, the formation of 1-propanol is preferable over Cu/boehmite at 200 °C and an H_2 pressure of 4.0 MPa, so that the stepwise hydrogenolysis of 1,2-PDO decreases the selectivity to 1,2-PDO at high conversion [19].

In the vapor phase, copper metal works in the formation of 1,2-PDO from glycerol at H_2 atmosphere [13–18]. Zhu et al. also reported 98% selectivity to 1,2-PDO with a complete conversion over boron oxide-loaded Cu/SiO_2 catalyst at 200 °C at an H_2 pressure of 5.0 MPa [18]. It is known that this reaction proceeds through two steps: the first step is glycerol dehydration to produce hydroxyacetone (HA) [34,35], and the second step is HA hydrogenation to produce 1,2-PDO [15,16]. In our previous research, we performed the reaction at a gradient temperature, which was efficient for both endothermic dehydration of glycerol at high temperature and the exothermic hydrogenation of HA at low temperature: the selectivity to 1,2-PDO higher than 95% with a complete conversion was obtained even at ambient pressure [15]. Under an H_2 pressure of 5.0 MPa at 220 °C, Ag supported on porous manganese oxide exhibits the stable glycerol hydrogenolysis activity with the 1,2-PDO selectivity above 65% at the glycerol conversion of 60% [33].

In the vapor-phase processes, a major by-product, EG, reduces the 1,2-PDO selectivity [14–18,33], while another by-product, HA, can be hydrogenated into 1,2-PDO because of the shift of equilibrium in the hydrogenation [14,15]. Furthermore, the reduction of the EG yield is also important from the view of industrial application because the separation of EG from 1,2-PDO is difficult due to the similar properties of 1,2-PDO and EG. Therefore, inhibiting EG formation is regarded as the key for achieving a complete yield of 1,2-PDO from glycerol. Recently, we have reported the dehydration of glycerol into HA over Ag/SiO_2 catalyst: the selectivity to HA is 91.1 mol% in H_2 flow at 240 °C [36], while the selectivity to EG was only 1.6%, which is much lower than 5.4% over Cu/Al_2O_3 without Ag

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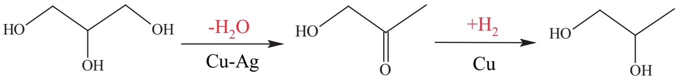
at 230 °C [15]. It is expected that the modification of Cu/Al_2O_3 catalyst with silver inhibits the generation of EG and increases 1,2-PDO yield.

In this study, a commercial Cu/Al_2O_3 catalyst was modified with Ag for the glycerol dehydration–hydrogenation reaction, and optimum reaction conditions for the 1,2-PDO formation were also studied at gradient temperatures and ambient hydrogen pressure.



2. Experimental

2.1. Sample preparation

Glycerol and silver nitrate were purchased from Wako Pure Chemical Industries Ltd. Cu/Al_2O_3 (N242) purchased from Nikki Chemical Co., Ltd. has the CuO content of 55.1% and the surface area of 118 $m^2\,g^{-1}$ [15]. Supported silver catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of silver nitrate as the precursor of Ag and N242 as a support. After the impregnation process, the catalyst was dried at 110 °C for 12 h, and finally calcined at 400 °C for 3 h. The percentage of Ag in the Ag-loaded N242 catalyst was calculated based on the weight of Ag metal. For comparison, unloaded N242 was also calcined at 400 °C for 3 h prior to the reaction. The sample name is denoted by "N242-x%Ag", where x is weight percentage of Ag loaded on N242 catalyst. For example, 1 wt.% Ag-containing N242 catalyst, hereafter denoted as N242-1%Ag.

2.2. Catalytic reaction

The catalytic reaction of glycerol was performed in a fix-bed down-flow glass reactor with an inner diameter of 17 mm at ambient H_2 pressure: a detail procedure is described elsewhere [15]. A catalyst (weight, 8.7 g; volume, 7.2 cm^3; height, 3.4 cm) was placed in the catalyst bed. When two types of catalysts such as N242 and N242-2%Ag catalysts were used, the Ag-loaded N242 catalyst was placed over the N242 catalyst bed where the total weight of the catalysts was 8.7 g. Prior to the reaction, the catalysts were reduced by H_2 at 250 °C for 1 h. After the temperature of the catalysts bed had been kept at the prescribed temperature, an aqueous solution of glycerol was fed through the top of the reactor at the liquid feed rate of 1.32 $cm^{-3}\,h^{-1}$ with an H_2 flow of 360 $cm^{-3}\,min^{-1}$. The liquid effluents collected in a dry ice-acetone trap (−78 °C) every hour were analyzed by a FID–GC (GC-2014, Shimadzu) with a 30 m capillary column of TC-WAX (GL-Science, Japan). A GC–MS (QP5050A, Shimadzu) was used for identification of the products in the effluent. The conversion and selectivity were calculated as follows [15]:

$$conversion(\%) = \frac{sum\ of\ moles\ of\ all\ products}{mole\ of\ the\ reactant} \times 100$$

$$selectivity(\%) = \frac{moles\ of\ carbon\ in\ specific\ product}{moles\ of\ carbon\ in\ all\ products} \times 100$$

2.3. Characterization of catalysts

Temperature-programmed reduction (TPR) measurements were performed for characterizing metal state of the catalysts in a mixed flow of H_2/N_2 (=1/9) at a flow rate of 10 $cm^3\,min^{-1}$ at a heating rate of 5 °C min^{-1} from 25 to 900 °C, the details are described elsewhere [15,37]. The XRD patterns of the samples were recorded on a D8 ADVANCE (Bruker, Japan) using Cu Kα radiation.

3. Results

3.1. Reaction of 1,2-PDO over different loading of Ag–Cu/Al_2O_3 catalysts

Prior to the temperature-gradient experiment, the reaction was performed at a constant temperature of 200 °C and short contact time in order to clarify the effect of Ag loading on the catalytic performance of N242 catalyst. Table 1 demonstrates catalytic data at conversion level lower than 100% using a catalyst of 1 g and an aqueous glycerol solution with the concentration of 30 wt.% as the reactant. The glycerol conversion decreased with increase in Ag loading. In addition, the selectivity to 1,2-PDO was decreased with increase in Ag loading while the selectivity to HA was significantly increased by Ag loading. The Ag loading on N242 catalyst clearly indicates the decrease in the catalytic activities of N242 catalyst for both the dehydration of glycerol and the hydrogenation of HA. It should be noticed that the selectivity to EG was significantly reduced by Ag loading.

Since the gradient temperature conditions have been proved to be efficient in achieving high yields of 1,2-PDO even at ambient pressure in our previous study [15], the additive effect of Ag into N242 catalyst was examined at the gradient temperatures of 200–130 °C in the following section. Table 1 also shows the results of glycerol hydrogenolysis over Ag-loaded N242 catalysts with different Ag contents. Glycerol was completely converted in all the reactions. 1,2-PDO was the major product while HA, EG, and methanol were the main by-products with a small amount of 1-propanol. The Ag-loaded catalysts show the selectivity to EG lower

Table 1
Effect of Ag loading over N242 on the catalytic reaction of glycerol[a].

Ag content/%	Conversion/%[b]	Selectivity/%[b]			
		1,2-PDO	HA	EG	1-Propanol
0[c]	94.3	70.5	23.7	3.6	0.2
1.0[c]	93.2	69.9	25.9	2.1	0.1
5.0[c]	84.1	59.9	35.6	2.8	0.1
0[d]	100	94.1	1.2	3.4	0.1
0.5[d]	100	93.8	1.0	2.8	0.1
1.0[d]	100	96.2	1.2	1.6	0.1
1.5[d]	100	95.7	1.1	1.7	0.1
2.0[d]	100	95.1	1.2	2.3	0.1
5.0[d]	100	92.7	3.2	2.7	0

[a] Reaction conditions: feed rate, 1.32 $cm^3\,h^{-1}$; H_2 flow rate, 360 $cm^3\,min^{-1}$; H_2/glycerol = 700. An aqueous solution of glycerol at a concentration of 30 wt.% was used as the reactant.
[b] Average activity between 1 and 5 h.
[c] Reaction temperature, 200 °C; catalyst weight, 1.0 g (0.4 cm).
[d] Gradient temperature, 200 to 130 °C.; catalyst weight, 8.7 g (3.4 cm).

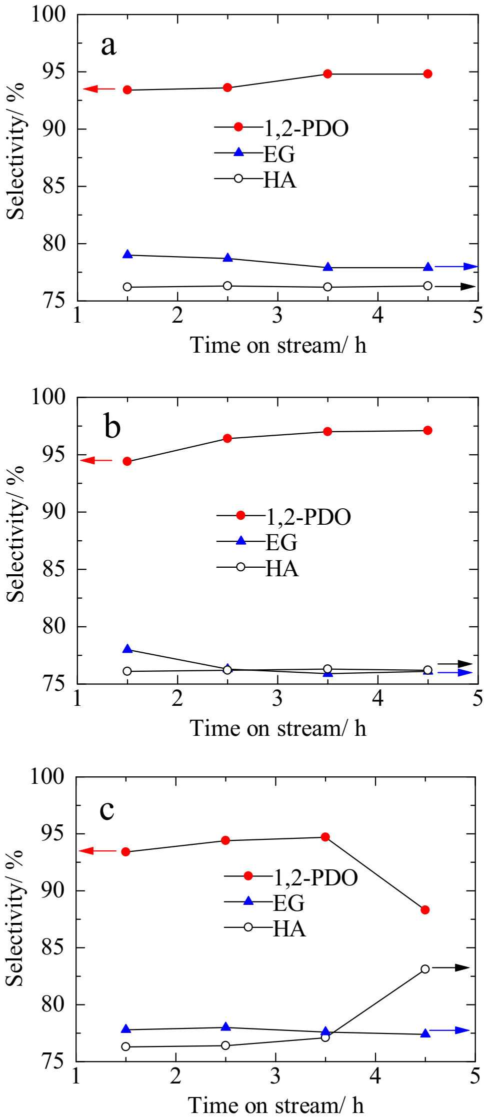


Fig. 1. Changes in selectivity with time on stream over (a) N242, (b) N242-1%Ag, and (c) N242-5%Ag. Reaction conditions: gradient temperature, 200 to 130 °C; feed rate, 1.32 $cm^3\ h^{-1}$; H_2 flow rate, 360 $cm^3\ min^{-1}$; H_2/glycerol = 700; catalyst weight, 8.7 g (3.4 cm). An aqueous solution of glycerol at a concentration of 30 wt.% was used as the reactant.

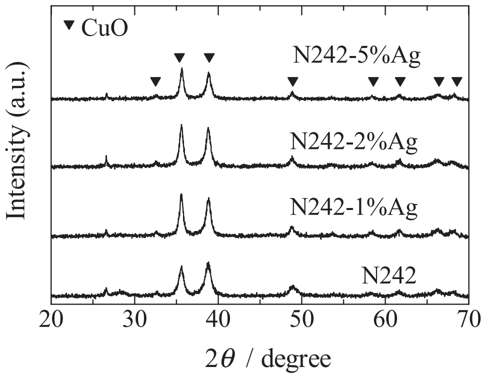


Fig. 2. XRD patterns of N242 and Ag-loaded N242 catalysts.

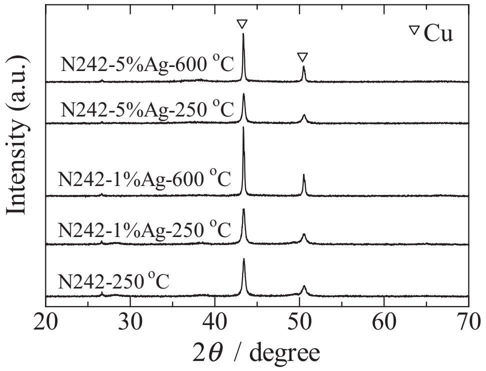


Fig. 3. XRD patterns of N242 and Ag-loaded N242 catalysts reduced at different temperatures.

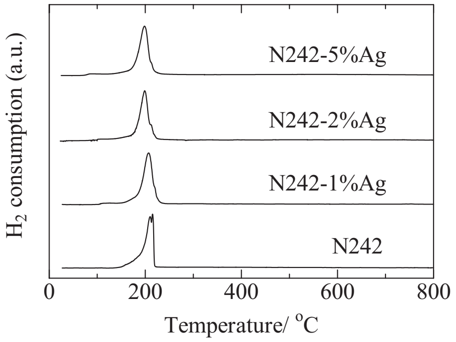


Fig. 4. TPR profiles of N242 and Ag-loaded N242 catalysts.

than that of N242. The selectivity to EG decreased with increasing the loading of Ag at Ag loading lower than 1 wt.%. The lowest selectivity to EG of 1.6% was obtained over N242-1%Ag catalyst, which gave the highest 1,2-PDO selectivity of 96.2%.

Fig. 1 shows the changes in the catalytic activities of N242 and Ag-loaded N242 catalysts with time on stream. It is obvious that the decrease in the selectivity to EG and the increase in the selectivity to 1,2-PDO are achieved by 1 wt.% Ag loaded on N242 (Fig. 1a and b). However, at Ag loading higher than 1 wt.%, the selectivity to 1,2-PDO decreased and the selectivity to EG increased with increasing the Ag loading. The selectivity to HA increases to 3.2% and the selectivity to 1,2-PDO decreases to 92.7% at Ag content of 5 wt.%. The changes in the catalytic activity with time on stream over N242-5%Ag is shown in Fig. 1c. The increase of the selectivity to HA is observed after 3 h of the reaction.

Fig. 2 shows the XRD patterns of modified N242 catalysts with different Ag loading. The unloaded N242 without Ag showed typical diffraction peaks of CuO at $2\theta = 35.5$ and 38.7° [JCPDS file 5-0661]. All the Ag-loaded N242 catalysts showed the same diffraction patterns of N242 and no peak attributed to Ag and/or AgO was detected. The loaded Ag is not agglomerated on the N242 catalyst because only peaks of CuO were observed. Fig. 3 shows the XRD patterns of Ag-loaded N242 catalysts reduced at different temperatures for 1 h. N242 reduced at 250 °C shows typical diffraction peaks of Cu at $2\theta = 43.5$ and 50.1° [JCPDS file 4-0836]. The diffraction patterns of N242-1% Ag and N242-5%Ag reduced at 250 °C are the same as those of reduced N242. Even at a high reduction temperature of 600 °C, the Ag-loaded samples had no diffraction peaks attributed to Ag metal, while they show higher crystallinity of Cu than those reduced at 250 °C.

Fig. 4 shows TPR profiles of N242 and Ag-loaded N242 catalysts with different Ag loading. N242 had two reduction peaks at 210 °C and 215 °C. The reduction peaks of 0, 1, 2, and 5 wt.% Ag-loaded N242 catalysts are observed at 210, 207, 199, and 198 °C, respectively. The reduction peak shifts from the high temperature to the low temperature with increasing Ag loading.

Table 2
Effect of calcination temperature of N242-1%Ag[a].

Calcined temperature/°C	Conversion/%[b]	Selectivity/%[b]			
		1,2-PDO	HA	EG	1-Propanol
400	100	96.2	1.2	1.6	0.1
500	100	95.3	1.0	1.7	0.2
600	100	92.0	1.0	1.8	1.1

[a] Reaction conditions: gradient temperature, 200 to 130 °C; feed rate, 1.32 cm^3 h^{-1}; H_2 flow rate, 360 cm^3 min^{-1}; H_2/glycerol = 700; catalyst weight, 8.7 g (3.4 cm). An aqueous solution of glycerol at a concentration of 30 wt.% was used as the reactant.

[b] Average activity between 1 and 5 h.

3.2. Effect of calcination temperature of N242-1%Ag catalysts

Table 2 summarizes the catalytic performance of N242-1%Ag catalysts calcined at different temperatures. The conversion of 1,2-PDO is 100% in these reactions. The calcination temperature clearly affected HA and EG formation. The selectivities to HA and EG increased with increasing the calcination temperature while the selectivity to 1,2-PDO decreased. 1-Propanol and some unidentified products were formed over the catalysts calcined at high temperatures.

Fig. 5 shows the XRD patterns of N242-1%Ag calcined at different temperatures. The intensity of the diffraction peaks of CuO in N242-1%Ag increased with increasing the calcination temperature. The crystallinity of CuO increases with increasing the calcination temperature. This tendency indicates that large particles of CuO were formed at high temperatures.

3.3. Hydrogenolysis of glycerol over double-layered catalysts

Since the addition of Ag decreased the hydrogenation ability, the selectivity to 1,2-PDO decreased and that to HA increased (5 wt.% Ag loading, Table 1). Catalytic reactions, in which N242-1%Ag in the bottom layer of the catalyst bed was replaced by N242 catalyst with powerful hydrogenation ability, was performed to shift the equilibrium to the 1,2-PDO side in the hydrogenation. The effect of reaction temperatures in the top, the interlayer, and the bottom position of the catalyst bet on the selectivity to 1,2-PDO was also examined (Table 3). In the single-layered N242-1%Ag catalyst at the same gradient temperature (Entry 1 of Table 3), the selectivity to 1,2-PDO and EG were 96.2 and 1.6%, respectively, at a gradient temperature from 200 to 130 °C. In the double-layered catalyst bed, where the total weight of N242-1%Ag and N242 was 8.7 g, the interlayer temperature was controlled by the charged amounts of N242-1%Ag and N242. The selectivity to 1,2-PDO and EG were 95.5 and 2.1%, respectively, at a gradient temperature from 200 to 130 °C with an interlayer temperature of 185 °C (Entry 2). The selectivity to the by-product EG decreased with decreasing the interlayer temperature: when the interlayer temperature decreased to 170 °C (Entry 3), the EG selectivity was similar to that of single-layered N242-1%Ag catalyst bed (Entry 1). In Entry 2, the EG selectivity was higher than that of Entry 1.

The reaction was also performed at a gradient temperature from a top temperature of 200 °C to a low bottom temperature of 120 °C, and the selectivity to HA decreased to 0.5% and the selectivity to 1,2-PDO significantly increased to 96.8% (Entry 4). However, the conversion decreased to 99.7% and the HA selectivity increased to 1.8% at the gradient temperature from 190 to 130 °C (Entry 5).

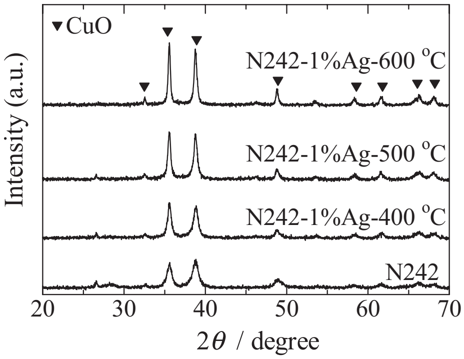


Fig. 5. XRD patterns of N242 and N242-1%Ag calcined at different temperatures.

3.4. Reaction using aqueous glycerol solution at a concentration of 15 wt.% over double-layered catalysts

When an aqueous glycerol solution at the concentration of 30 wt.% was used as the reactant (Entry 5, Table 3), the HA hydrogenation to 1,2-PDO was not completed and the conversion of glycerol decreased at a top temperature of 190 °C. Thus, further study for achieving high 1,2-PDO yield was performed using an aqueous glycerol solution at a concentration of 15 wt.%. Table 4 shows the catalytic reaction results. The selectivity to 1,2-PDO was 97.5% with a complete conversion at a gradient temperature from 185 °C to 120 °C (Entry 1). The selectivity to EG slightly decreased with decreasing the top temperature, and the selectivity to 1,2-PDO was 98.0% at a gradient temperature from 170 to 120 °C (Entry 2). The selectivity to HA was only 0.2% and the selectivity to 1,2-PDO increased to 98.3% in the reaction performed at a gradient temperature from 170 °C to a low bottom temperature of 105 °C (Entry 3). Fig. 6 shows the changes of the catalytic activity with time on stream: the catalytic activity was stable during the initial 5 h we tested. For comparison, the reaction at a gradient temperature from 170 to 120 °C over the unloaded N242 catalyst was performed: the selectivity to 1,2-PDO was 96.0% (Entry 4), which was lower than 98.3% over double-layered catalysts (Entry 3).

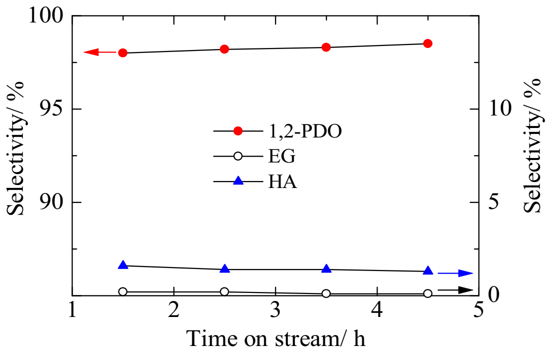


Fig. 6. Changes in selectivity with time on stream over double-layered catalysts at a gradient temperature from 170 °C to 105 °C (Table 4, Entry 3). Reaction conditions: feed rate, 1.32 cm^3 h^{-1}; H_2 flow rate, 360 cm^3 min^{-1}; H_2/glycerol = 1400; catalyst weight, 8.7 g (3.4 cm). An aqueous solution of glycerol at a concentration of 15 wt.% was used as the reactant.

Table 3
Hydrogenolysis of glycerol over double-layered catalysts[a].

Entry	Catalyst (g)	Temperature/°C		Conversion/%[b]	Selectivity/%[b]		
		Top	Bottom		1,2-PDO	HA	EG
1	A(8.7)	200	130	100	96.2	1.2	1.6
2	A(1.9)	200	185	100	95.5	1.0	2.1
	B(6.8)	185	130				
3	A(3.7)	200	170	100	96.1	1.0	1.7
	B(5.0)	170	130				
4	A(3.3)	200	170	100	96.8	0.5	1.6
	B(5.4)	170	120				
5	A(3.6)	190	165	99.7	96.1	1.8	1.5
	B(5.1)	165	130				

[a] Reaction conditions: feed rate, 1.32 $cm^3 h^{-1}$; H_2 flow rate, 360 $cm^3 min^{-1}$; H_2/glycerol = 700; catalyst weight, 8.7 g (3.4 cm). An aqueous solution of glycerol at a concentration of 30 wt.% was used as the reactant. Catalyst A and B are N242-1%Ag and N242, respectively.
[b] Average activity between 1 and 5 h.

Table 4
Hydrogenolysis of glycerol at a concentration of 15 wt.% over double-layered catalysts[a].

Entry	Catalyst	Temperature/°C		Conversion/%[b]	Selectivity/%[b]		
		Top	Bottom		1,2-PDO	HA	EG
1	A(3.5 g)	185	164	100	97.5	0.5	1.6
	B(5.2 g)	164	120				
2	A(3.5 g)	170	150	100	98.0	0.5	1.4
	B(5.2 g)	150	120				
3	A(3.5 g)	170	144	100	98.3	0.2	1.4
	B(5.2 g)	144	105				
4	B(8.7 g)	170	105	100	96.0	0.2	3.0

[a] Reaction conditions: feed rate, 1.32 $cm^3 h^{-1}$; H_2 flow rate, 360 $cm^3 min^{-1}$; H_2/glycerol = 1400; catalyst weight, 8.7 g (3.4 cm). An aqueous solution of glycerol at a concentration of 15 wt.% was used as the reactant. Catalyst A and B are N242-1%Ag and N242, respectively.
[b] Average activity between 1 and 5 h.

4. Discussion

4.1. Effect of the loading of Ag on the catalytic activity of Cu/Al_2O_3

Bimetallic catalysts have been found to be effective for many kinds of reactions such as CO oxidation over TiO_2 supported Au–Cu bimetallic catalysts [38]. Cu–Ag bimetallic catalyst was found to be effective for the epoxidation of propylene [39] and ethylene [40–42]. The synergistic effect between Ag and Cu was found to be beneficial to produce more active sites where electrophilic oxygen species can be absorbed and increase the propylene oxide selectivity [39]. DFT calculations also proved that Cu in Cu–Ag bimetallic surfaces altered the chemical and electronic properties of the surface, which affected the ethylene oxide formation [41]. Cu–Ag bimetallic catalysts were also applied for the glycerol hydrogenolysis in liquid phase [43]. A high 1,2-PDO selectivity of 99% with a low conversion of 21% was obtained over alumina supported Cu–Ag with a mole ratio of 95:5 at 200 °C under an H_2 pressure of 1.5 MPa. The maximum conversion of glycerol was 27% at a Cu/Ag mole ratio of 7:3, whereas the selectivity to 1,2-PDO decreased to 96%. It was found that the addition of Ag to the Cu-based catalyst facilitates the reduction of the Cu species that generates low valence Cu species in situ under mild reaction conditions [43].In this study, the comparison of catalytic activity at a constant temperature clarifies the effect of Ag in the N242 catalyst (Table 1). The role of Ag loaded on N242 is to reduce the ability of Cu for the decomposition of glycerol into EG with sacrificing the ability of Cu for both the dehydration of glycerol and the hydrogenation of HA into 1,2-PDO. Since no diffraction peak attributed to Ag in the samples was observed in XRD patters of Figs. 2 and 3, Ag seems to be highly dispersed on N242. The TPR results that the reduction peak shifts from the high temperature to low temperature side with increasing Ag loading (Fig. 4) indicate the existence of the interaction between Cu and Ag. Our previous work elucidates that EG is formed by C—C bond cleavage of glycerol over Cu metal at high temperatures [15,16]. Thus, we propose that the loading of Ag in N242 alters the chemical and electronic properties of the surface, which reduces the cracking ability of Cu in N242 and thus inhibits the EG formation. However, it is difficult to explain why the EG formation increases at high Ag loading. We speculate that high Ag loading results in agglomeration of Ag into large Ag particles, which could be ineffective for inhibiting the EG formation because of small interaction between Cu and Ag. Although we observed the samples using TEM, there is no significant difference in the morphologies observed in TEM images among the Ag-loaded and unloaded N242 catalysts (TEM images not shown). This is probably caused by the large amount of Cu in the catalyst compared to 1 wt.% Ag: Ag can be solved or absorbed in Cu particles because Ag metal has the same crystal structure of face-centered cubic as Cu.

The high Ag loading leads an obvious increase of the HA formation (N242-5%Ag, Table 1 and Fig. 1c). Since Ag has hydrogenation ability lower than that of Cu [36], it is reasonable that high Ag loading decreases the hydrogenation ability of the catalyst, especially, under ambient H_2 pressure conditions. The hydrogenation of HA, as the intermediate of 1,2-PDO, cannot proceed sufficiently when the Ag loading is high, that results in the increase in the selectivity to HA.

Calcination temperature also affects the catalytic property of Ag-loaded N242 catalyst (Table 2). Large CuO particles were generated at high calcination temperatures, which agrees with the results reported by Gu et al. [44]. Large Cu particles formed from the reduction of CuO would not be efficient for 1,2-PDO formation because of low specific surface area of Cu metal. Therefore, we judge that the calcination temperature of 400 °C is suitable for the 1,2-PDO formation.

4.2. Hydrogenolysis of glycerol over double-layered catalysts

The selectivity to EG is 2.1% in the double-layered catalysts at a gradient temperature from 200 to 130 °C with an interlayer temperature of 185 °C (Entry 2 in Table 3), which is a little higher than 1.6% over N242-1%Ag in the single-layered catalyst at the same gradient temperature (Entry 1 in Table 3). The interlayer temperature could be still high for the inhibition of the EG formation through the decomposition of glycerol. The selectivity to EG decreased to 1.7% at an interlayer temperature of 170 °C (Entry 3 in Table 3). This indicates that EG would be generated at high temperatures, and that the unloaded N242 decomposes much glycerol to EG at temperatures between 170 and 185 °C. The selectivity to HA decreased to 0.5% at a gradient temperature from 200 °C to a low bottom temperature of 120 °C (Entry 4 in Table 3), which indicates the exothermic hydrogenation of HA to 1,2-PDO prefers low reaction temperatures and agrees with our previous reports [15,16]. The conversion decreased to 99.7% and the HA selectivity increased to 1.8% at the top temperature of 190 °C (Entry 5 in Table 3). This means that the top temperature must be higher than 190 °C for keeping the complete glycerol conversion to HA when an aqueous glycerol solution with the concentration of 30 wt.% was used as the reactant.

The concentration of aqueous glycerol solution is also an important parameter in the glycerol hydrogenolysis into 1,2-PDO. High concentration of glycerol always leads to low glycerol conversion and low 1,2-PDO selectivity in the liquid-phase reaction [24,45,46]. The decrease in the glycerol conversion and the increase in the selectivity to 1,2-PDO (Entry 4 in Table 3) indicate that the active sites are not enough at the low gradient temperatures from 190 to 130 °C when the concentration of glycerol is 30 wt.%. At a low glycerol concentration of 15 wt.%, the low top temperature is effective in inhibiting the cracking products such as EG and methanol, and the low bottom temperature is effective for the HA hydrogenation to 1,2-PDO, the highest 1,2-PDO yield of 98.3% was obtained over double-layered catalysts at a gradient temperature from 170 to 105 °C (Entry 3 in Table 4). On the other hand, the yield of 1,2-PDO is at most 96% over the unloaded N242 at the same reaction conditions (Entry 4 in Table 4), which demonstrates the superiority of the Ag-loaded Cu/Al_2O_3 catalyst on the inhibition of the EG formation.

5. Conclusions

Ag-loaded Cu/Al_2O_3 catalysts were studied for the glycerol hydrogenolysis into 1,2-PDO. It was found that the addition of Ag onto a commercially available Cu/Al_2O_3 was efficient in inhibiting the EG formation via the decomposition of glycerol and thus increased the 1,2-PDO selectivity. The suitable Ag loading onto Cu/Al_2O_3 was 1 wt.%. The calcination temperature of the catalyst also affected the reaction: 400 °C was the favorable calcination temperature for the 1,2-PDO formation. The role of Ag is reduction of the ability of Cu/Al_2O_3 for the decomposition of glycerol into EG at the expense of the catalytic ability of Cu for both the dehydration of glycerol and the hydrogenation of HA into 1,2-PDO.

Since the addition of Ag decreases the hydrogenation ability, the catalytic reaction test with double-layered catalysts, 1% Ag-containing Cu/Al_2O_3 loaded on the upper layer of catalyst bed and Cu/Al_2O_3 loaded on the bottom, was performed. The effect of the top, the interlayer, and the bottom temperatures of the catalyst bed was also examined. Cu/Al_2O_3 with 1 wt.% Ag was found to mainly inhibit the EG formation in the first step of glycerol dehydration to HA over the upper-layer catalyst, while the bottom-layer catalyst could be replaced by Cu/Al_2O_3 catalyst with high hydrogenation ability. Because the selectivity to cracking products is low at low top temperatures and the hydrogenation of HA prefers the low bottom temperatures, the highest 1,2-PDO yield of 98.3%, was obtained at ambient hydrogen pressure and a low gradient temperature from 170 °C to 105 °C using aqueous glycerol solution at the concentration of 15 wt.%.

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