Selective Conversion of Glycerol into 1,2-Propanediol at Ambient Hydrogen Pressure

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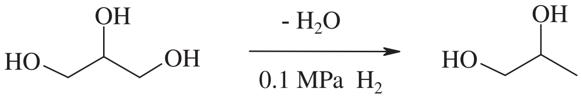
The vapor-phase reaction of glycerol was performed over a copper–alumina catalyst at ambient hydrogen pressure. Glycerol was converted into 1,2-propanediol (PDO) through dehydration–hydrogenation via hydroxyacetone (HA). We also found that 1,2-PDO was produced at the selectivity higher than 93 mol % in hydrogen flow at gradient temperatures: the dehydrogenation into HA was catalyzed at around 180–200 °C, while the following hydrogenation into 1,2-PDO was catalyzed by Cu–alumina catalyst at around 145–160 °C.

The catalytic conversion of carbon-neutral biomass into useful chemicals is expected to be a potential solution to the severe global environmental pollution problem.[1,2] Renewable biomass fuels, such as bioethanol and biodiesel fuel (BDF), i.e., fatty acid methyl esters, are attracting much attention worldwide. Glycerol, a by-product of BDF production for ca. 10 mass % of BDF produced, is one of such promising renewable resources. Its quantity increases as the amount of BDF produced is increased.

Recently, quite a number of studies on the reaction of glycerol have appeared in reviews[2–4] and research papers.[5–16] In liquid-phase hydrogenolysis under hydrogen pressure, glycerol is converted into 1,2-PDO and 1,3-PDO in the presence of supported Rh,[5] Ru,[6–8] or Pt.[8,9] In the vapor-phase hydrogenolysis of glycerol, Cu catalyzes 1,2-PDO formation in the presence of high hydrogen pressure.[10–13] Since the hydrogenolysis requires elevated hydrogen pressure,[5–11] side reactions occur to form several by-products, including ethylene glycol (EG), propanol, lactic acid, and propanoic acid. Hydroxyacetone (HA) is an intermediate product in the conversion of glycerol into 1,2-PDO through the dehydration–hydrogenation reactions. Over Cu catalysts, however, 1,2-PDO selectivity higher than 90 mol % is attained:[12,13] low temperatures and high hydrogen pressures favor the shift of equilibrium from HA to 1,2-PDO and reduce the formation of by-products resulting from HA side reactions.[13] One effective operation is a two-step process composed of dehydration under vacuum and hydrogenation under hydrogen pressure.[13,15]

It is known that copper works as a dehydrogenation catalyst for polyols, such as 1,2-[17] and 1,3-diols.[18] However, glycerol can be dehydrated into HA over copper metal catalysts.[14–16] It should be noted that copper metal catalyzes the dehydration of glycerol to produce HA with selectivity higher than 90 mol % at 250 °C, and that no dehydrogenation proceeds to form dihydroxyacetone.[14,16] 1,2-PDO is dehydrogenated to form HA in the presence of inert carrier gas over copper catalysts, and the dehydrogenation is controlled by equilibrium.[17] This reminds us that 1,2-PDO is favored at high hydrogen partial pressure even at ambient pressure. As copper metal works as a catalyst for the dehydrogenation of 1,2-PDO into HA at 210 °C,[17] it is expected to be an efficient catalyst for the reverse hydrogenation at temperatures lower than 210 °C.



Scheme 1.

In this paper, we report that the transformation of glycerol into 1,2-PDO was performed over alumina-supported copper catalyst at ambient hydrogen pressure, and that 1,2-PDO was selectively formed from glycerol at gradient temperatures (Scheme 1).

A commercially available catalyst, such as Cu/Al_2O_3 (N242) with CuO content of 55 wt %, was purchased from Nikki Chemical Co., Ltd., Japan. The reaction of glycerol was performed in a fixed-bed down-flow reactor with an inner diameter of 17 mm at ambient hydrogen pressure and temperatures between 135 and 250 °C. A catalyst with 75 to 650-µm granule size was placed in the reactor. After the temperature of the catalyst bed had been maintained at a prescribed temperature in hydrogen flow for 1.0 h, a 30 wt % aqueous solution of glycerol was fed into the reactor at the feed rate of $1.8\ cm^3\ h^{-1}$, which corresponded to 5.9 mmol of glycerol per hour. The liquid product that was collected in a dry ice–acetone trap (at −80 °C) every hour was analyzed on a gas chromatograph (FID-GC, Shimadzu GC-8A) using a 60-m capillary column (TC-WAX, GL Science, Japan).

Figure 1 shows changes in the catalytic conversion of glycerol with reaction temperature. The conversion attained 100% at temperatures higher than 190 °C. The selectivity to 1,2-PDO was maximum at 190 °C, while that to HA was minimum at the same temperature. The selectivity to EG increased slowly with increasing reaction temperature. The highest yield of 1,2-PDO was attained at 190 °C. The changes in the selectivities to HA and 1,2-PDO suggest that the hydrogenation of HA into 1,2-PDO is favored at low temperatures.

Figure 2 shows changes in the catalytic conversion of glycerol with H_2 flow rate at 210 °C and ambient pressure. The results indicate that 1,2-PDO is favored at high H_2 flow rate even at ambient pressure. The selectivity to 1,2-PDO became constant at H_2 flow rates above $360\ cm^3\ min^{-1}$, which corresponded to $glycerol/H_2 = 1/141$. The selectivity to EG increased slowly with increasing H_2 flow rate. Therefore, the hydrogenation of HA into 1,2-PDO should be operated at temperatures lower than 190 °C to shift the equilibrium to the right side.

Hydrogenation of carbonyl compounds, such as acetone and propanal, is an exothermic reaction.[19] Thus, in the hydrogenolysis of glycerol, the second-step hydrogenation would favor low temperatures thermodynamically. Actually, the reverse reaction,

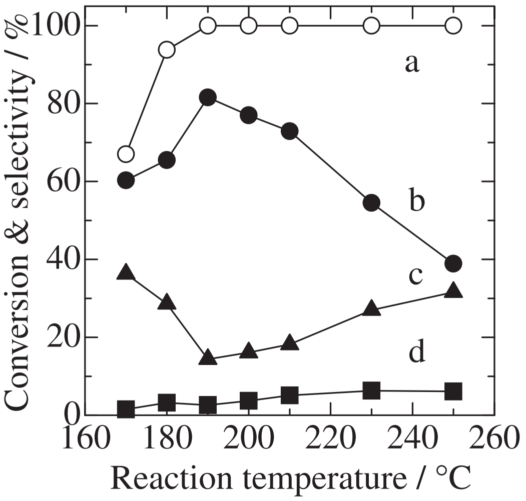


Figure 1. Changes in catalytic activity of Cu/Al_2O_3 with reaction temperature for the reaction of glycerol. (a) Conversion of glycerol, (b) selectivity to 1,2-PDO, (c) selectivity to HA, (d) selectivity to EG. Reaction conditions: catalyst weight, 2.9 g ($2.4\,cm^3$); feed rate of 30 wt % glycerol solution, $1.8\,cm^3\,h^{-1}$; H_2 flow rate, $360\,cm^3\,min^{-1}$.

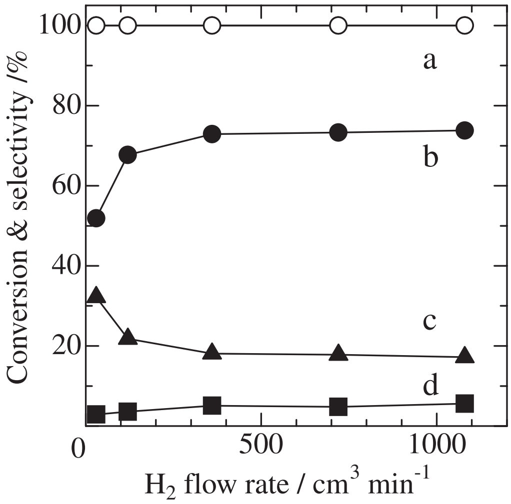


Figure 2. Changes in catalytic activity of Cu/Al_2O_3 with H_2 flow rate at 210 °C. Symbols and reaction conditions are the same as those in Figure 1.

i.e. the dehydrogenation of 1,2-butenediol into 1-hydroxy-2-butanone, is favorable at high temperatures.[17] Therefore, in order to achieve high equilibrium conversion in the hydrogenation, the second-step hydrogenation should be operated at temperatures lower than the temperature favorable for the dehydration of glycerol. Then, we carried out the reaction in a 3-cm-high catalyst bed at gradient temperatures.

Table 1 lists the results of the gradient temperature experiment. The highest yield of 1,2-PDO was attained at 180–145 °C: selectivity to 1,2-PDO was higher than 93 mol %. At 170–135 °C, the top temperature is too low to produce HA from glycerol. Catalyst deactivation was observed: unreacted glycerol was recovered in the initial reaction after 5 h. The selectivity to EG decreased with decreasing top temperature.

Table 1. Catalytic conversion of glycerol at gradient temperatures[a]

Top temp /°C	Bottom temp /°C	Selectivity/mol %		
		1,2-PDO	HA	EG
210	170	81.9	5.9	3.8
200	160	91.7	2.7	3.0
180	145	93.7	2.6	2.4
170	135	92.3	5.7	0

[a] Catalyst, Cu/Al_2O_3 (N242) 8.7 g ($7.2\,cm^3$); H_2, $360\,cm^3\,min^{-1}$. Conversion of glycerol, 100%. Other by-products are methanol and 1-propanol.

We have previously reported that copper metal catalyzes the dehydration of glycerol into HA: copper supported on alumina showed the highest catalytic activity with HA selectivity higher than 90 mol % at an ambient pressure of N_2 and 250 °C.[16] Thus, the first-step dehydration of glycerol favors high temperature. However, C–C bond cleavage proceeds in H_2 flow at 250 °C, as shown in Figure 1. Therefore, a low temperature is favorable for the selective formation of 1,2-PDO in H_2 flow, as long as catalyst deactivation does not proceed.

We concluded that the dehydration of glycerol into HA and the following hydrogenation into 1,2-PDO were efficiently performed at gradient temperatures between 180 and 145 °C. The molar composition in the vapor phase was $glycerol/H_2/H_2O = 1/141/12$. The highest yield of 1,2-PDO exceeded 93% even at ambient hydrogen pressure in the operation at gradient reaction temperatures.

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