



# Efficient production of propylene in the catalytic conversion of glycerol



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## ABSTRACT

Vapor-phase catalytic conversion of glycerol into propylene was performed over Cu/Al<sub>2</sub>O<sub>3</sub> and acid-loaded Cu/Al<sub>2</sub>O<sub>3</sub> catalysts in an H<sub>2</sub> flow at ambient pressure. Acidic substances such as WO<sub>3</sub>, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> and H<sub>3</sub>PO<sub>4</sub> were loaded on a commercial Cu/Al<sub>2</sub>O<sub>3</sub>. The addition of WO<sub>3</sub> was found to be effective for promoting the formation of 1-propanol and propylene from glycerol, and 9.3 wt% WO<sub>3</sub>-loaded Cu/Al<sub>2</sub>O<sub>3</sub> (WO<sub>3</sub>/Cu/Al<sub>2</sub>O<sub>3</sub>) catalyst showed the best catalytic performance. WO<sub>3</sub>/Cu/Al<sub>2</sub>O<sub>3</sub> calcined at a low temperature of 320 °C had the largest number of acid sites and gave a 1-propanol selectivity of 38.2% and a propylene selectivity of 47.4% in an H<sub>2</sub> flow at 250 °C. The catalytic reaction of glycerol was performed over double-bed catalysts, in which WO<sub>3</sub>/Cu/Al<sub>2</sub>O<sub>3</sub> was charged in the upper bed and a commercial silica–alumina was charged in the lower bed, to promote the conversion of 1-propanol into propylene. A high propylene selectivity of 84.8% was obtained over the double-bed catalysts at 100% glycerol conversion. An efficient catalytic process for the production of propylene from glycerol was proposed.

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## 1. Introduction

In recent years, there is an increasing interest on the use of biodiesel as an alternative fuel [1,2]. The production of biodiesel is 22.7 million metric tons in 2012, and is forecasted increasing to 36.9 million metric tons in 2020 [2]. The rapid increase in biodiesel production has led to an oversupply of crude glycerol, and the effective utilization of glycerol has attracted much attention in the past decade [1,2]. Numerous efforts have been reported on the conversion of glycerol into value-added products, such as acrolein [1–6], acrylic acid [7–10], lactic acid [11,12], glycidol [13,14], hydroxyacetone (HA) [15–17], 1,2-propanediol (1,2-PDO) [18–38], 1,3-propanediol [36–42], and 1-propanol (1-PO) [43,44].

Hydrogenolysis of glycerol into 1,2-PDO, which is a valuable chemical mainly used for producing polymers, has been intensively reported over various metal catalysts such as Cu [18–26], Rh [27,28], Ru [29,30], Ni [31,32], Pt [33,34], and Ag [26,35]. In this reaction, HA is primarily generated in the dehydration of glycerol, and then hydrogenated into 1,2-PDO [15,16]. In our latest paper, a high 1,2-PDO yield of 98.3% was obtained over Ag-modified Cu/Al<sub>2</sub>O<sub>3</sub>

catalyst in vapor phase at a gradient temperature from 170 to 105 °C under ambient hydrogen pressure flow conditions [26].

Because of the availability of 1,2-PDO from glycerol, several research groups investigated the conversion of 1,2-PDO to form 1-PO [43–45] and propanal (PA) [46–49]. In the hydrogenolysis of 1,2-PDO using iridium complex catalyst, Foskey et al. reported that the presence of water in the reaction mixture gave improved selectivity to 1-PO, and that a 95% yield of 1-PO was achieved at 125 °C and 0.7 MPa [45]. Amada et al. also reported that the selectivity to 1-PO reached 74% with a conversion of 86.6% at 120 °C and 8 MPa together with the competitive formation of 2-propanol in the hydrogenolysis of 1,2-PDO in a liquid phase using Rh-ReOx/SiO<sub>2</sub> catalyst [43]. They also performed a reaction using glycerol as the reactant, and a 76% yield of 1-PO was obtained over Rh-ReOx/SiO<sub>2</sub> at 120 °C and 8 MPa. We have recently developed a new type of solid acid catalyst such as silica-supported WO<sub>3</sub> for the 1,2-PDO dehydration into PA [49]. The silica-supported WO<sub>3</sub> catalyst calcined at 320 °C had a large number of acid sites, and 93.5% selectivity to PA was achieved with a complete conversion at a reaction temperature of 250 °C.

The production of propylene which is an important starting chemical in the petrochemical industry, from renewable resources has also attracted much attention in recent years. Glycerol is an abundant renewable resource for C3 chemicals, and it is beneficial that propylene is produced from glycerol *via* the further dehydration of 1-PO derived from glycerol *via* 1,2-PDO and PA. In the

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**Table 1**  
Hydrogenolysis of glycerol over Cu/Al<sub>2</sub>O<sub>3</sub>, T317 and N242.<sup>a</sup>

Catalyst	Temp. (°C)	Conv. <sup>b</sup> (%)	Selectivity (%) <sup>b</sup>										
			Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
T317	190	98.3	0.5	0	2.5	0	32.1	54.3	0	0.2	0	0	0.2
	220	100	1.5	0	1.7	0.1	25.6	35.5	0	6.2	12.1	0.5	18.3
	250	100	4.1	2	0.7	3.2	10.7	6.1	1.7	22.6	27.8	1	50.4
N242	190	79.5	0	0	2.9	0	42.6	51.2	0	0	0	0	0
	220	99.2	2.1	0.1	4.5	0	37.6	46.9	0	0.1	0	0	0.1
	250	100	5.2	0.9	8.1	0.9	41	30.8	0	1.3	0	0	1.3

<sup>a</sup> Reaction conditions: catalyst weight, 1 g; H<sub>2</sub> flow rate, 60 cm<sup>3</sup> min<sup>-1</sup>; feed rate of glycerol solution, 1.32 cm<sup>3</sup> h<sup>-1</sup>. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

<sup>b</sup> Average value in 2–5 h. (EG, ethylene glycol; HA, hydroxyacetone; 1,2-PDO, 1,2-propanediol; PA, propanal; 1-PO, 1-propanol.)

latest report, propylene has been produced with a selectivity of 85% in the 100% conversion of glycerol in a flow reactor loaded double-bed catalysts of Ir/ZrO<sub>2</sub> and HZSM-5 at 250 °C and 1 MPa, in which 1-PO was an intermediate of propylene [50]. In this study, the catalytic conversion of glycerol into propylene was investigated over acid-loaded commercial Cu/Al<sub>2</sub>O<sub>3</sub> catalysts at ambient H<sub>2</sub> pressure, and the optimum reaction conditions were also studied for the production of propylene.

## 2. Experimental

### 2.1. Samples

Glycerol was purchased from Wako Pure Chemical Industries, Japan. Glycerol was used for the catalytic reaction without further purification. Two types of CuO/Al<sub>2</sub>O<sub>3</sub> catalysts, N242 and T317, were purchased from Nikki Chemical Co., Ltd. and Nissan Girdler Co., respectively. The weight percentage of CuO in N242 and T317 is 55.1 and 14.9%, respectively [21]. The specific surface areas of N242 and T317 are 118 and 166 m<sup>2</sup> g<sup>-1</sup>, respectively [21]. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (N631L) was purchased from Nikki Chemical. The specific surface of N631L is 440 m<sup>2</sup> g<sup>-1</sup> and the Al<sub>2</sub>O<sub>3</sub> content in N631L is ca. 15 wt%. The precursors of the acidic substances such as (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, NH<sub>4</sub>VO<sub>3</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> were purchased from Wako Pure Chemical Industries.

Supported catalysts were prepared by an incipient-wetness impregnation method. As an example, an acid precursor of 0.586 g (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O was dissolved in 15 cm<sup>3</sup> of 30% hydrogen peroxide water for preparing a 9.3 wt% WO<sub>3</sub>-loaded T317 catalyst. The solution with an amount of ca. 0.3 cm<sup>3</sup> was dropped onto 5.088 g T317 catalyst for once, and the water was evaporated at an ambient pressure and 70 °C by being illuminated by a 350-W electric light bulb. After impregnation, the obtained solid was dried at 110 °C for 24 h, and then calcined at a prescribed temperature for 3 h. Hereafter, the catalysts are expressed as x%A/B, where x indicates the weight percentage of A; A indicates the species of the loaded acidic substance, and B indicates the support material. For example, 9.3%WO<sub>3</sub>/T317 indicates 9.3 wt% WO<sub>3</sub> loaded on a T317 catalyst.

### 2.2. Catalytic reaction

The catalytic reaction of glycerol was performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at an ambient H<sub>2</sub> pressure. Prior to the reaction, 1.0 g of a catalyst placed in the catalyst bed was reduced at 250 °C for 1 h in an H<sub>2</sub> flow of 60 cm<sup>3</sup> min<sup>-1</sup>. After that, 20 wt% aqueous glycerol solution was fed through the top of the reactor at a liquid feed rate of 1.32 cm<sup>3</sup> h<sup>-1</sup> together with H<sub>2</sub>. The liquid effluent collected in a dry ice-acetone trap (-78 °C) every hour was analyzed by a FID-GC (GC-2014, Shi-

madzu) with a 30-m capillary column of TC-WAX (GL-Science, Japan). The gaseous products were identified by on-line gas chromatography (GC-8A, Shimadzu, Japan) with a 6-m packed column (VZ-7, 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:

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

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

### 2.3. Characterization of catalysts

Temperature-programmed desorption (TPD) of adsorbed NH<sub>3</sub> was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution of H<sub>2</sub>SO<sub>4</sub> to estimate acidity of the catalysts, as has been described in the TPD experiment of adsorbed NH<sub>3</sub> [48]. X-ray diffraction (XRD) patterns of the samples were recorded on a D8 ADVANCE (Bruker, Japan) using Cu K $\alpha$  radiation. Temperature-programmed reduction (TPR) measurements were performed for characterizing metal state of the catalysts in a mixed flow of H<sub>2</sub>/N<sub>2</sub>(=1/9) at a flow rate of 10 cm<sup>3</sup> min<sup>-1</sup> from 25 to 900 °C at a heating rate of 5 °C min<sup>-1</sup>, and the details are described elsewhere [21,51].

## 3. Results

### 3.1. Hydrogenolysis of glycerol over Cu/Al<sub>2</sub>O<sub>3</sub>

Table 1 shows the reaction results of glycerol hydrogenolysis over two commercial Cu/Al<sub>2</sub>O<sub>3</sub>, T317 and N242, at different reaction temperatures. 20 wt% glycerol aqueous solution was fed into the reactor with an H<sub>2</sub> flow of 60 cm<sup>3</sup> min<sup>-1</sup>. At a low temperature of 190 °C over the catalysts, HA and 1,2-PDO were the main products, and the conversion of glycerol increased with increasing the reaction temperature. In the reactions of glycerol over T317, the selectivity to HA and 1,2-PDO decreased with increasing the reaction temperature, whereas the selectivity to 1-PO and propylene increased. Since 1-PO can be readily converted to form propylene by dehydration, the total selectivity to 1-PO and propylene is also summarized in Table 1. The total selectivity to 1-PO and propylene increased from 0 to 50.4% over T317 when the reaction temperature increased from 190 to 250 °C. However, in the reactions of glycerol over N242, HA and 1,2-PDO were still the main products even at 250 °C, and the total selectivity to 1-PO and propylene was only 1.3%. Acetone, PA, propionic acid, methanol, acetaldehyde, ethanol, ethylene glycol (EG), ethylene, propane, and CO<sub>2</sub> were also detected in the reactions, and the selectivity to the main by-products is summarized in Table 1. Scheme 1 also depicts a probable reaction route

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