

## Vapor-phase Dehydration of Glycerol into Hydroxyacetone over Silver Catalyst

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Silica-supported silver exhibited high catalytic activity in the dehydration of glycerol: glycerol was dehydrated into hydroxyacetone with the selectivity higher than 86% at 91% conversion over Ag/SiO<sub>2</sub> in H<sub>2</sub> flow at 240 °C. Silver metal provides an active site and showed stable catalytic activity for the glycerol dehydration in H<sub>2</sub> atmosphere, while the dehydration activity decreased in N<sub>2</sub> atmosphere. The hydrogenation of hydroxyacetone into 1,2-propanediol and the decomposition to ethylene glycol did not proceed over silver.

Catalytic conversion of carbon-neutral biomass to produce valuable chemicals is expected to reduce damage to the environment.<sup>1,2</sup> This is one of the answers to the problem of global warming. Renewable biomass fuels, such as biodiesel fuel that is fatty acid methyl esters, are produced from vegetable oil i.e., triglyceride. In the manufacture of biodiesel, glycerol is produced as a by-product, and the supply of biodiesel is increasing year by year. Glycerol is one of such promising biomass resources. Recently, research papers on the reaction of glycerol have increased drastically, and a large amount of research has been introduced in recent reviews,<sup>3,4</sup> as we also introduced in a previous paper.<sup>5</sup> In the vapor-phase dehydration of glycerol, glycerol can be dehydrated into acrolein over acidic catalysts<sup>3,6</sup> and is also dehydrated into hydroxyacetone (1-hydroxy-2-propanone) often called acetol, hereafter abbreviated as HA, in an inert atmosphere over supported copper<sup>7–9</sup> and sodium-doped base<sup>10</sup> catalysts.

In the liquid-phase reaction glycerol under compressed hydrogen conditions, pioneering work using Ru catalyst has been reported by Montassier et al.,<sup>11</sup> and numerous research papers have been reported since 2004.<sup>4</sup> In the liquid phase, side reactions reduce the selectivity to 1,2- and 1,3-propanediols along with the formation of various by-products such as propanol, propanoic acid, lactic acid, acetaldehyde, and ethylene glycol. In the vapor phase, however, copper metal works as a catalyst in the formation of 1,2-propanediol with selectivity higher than 90 mol % from glycerol.<sup>5,12–15</sup> In the catalytic conversion of glycerol into 1,2-propanediol, the developed processes can control the thermodynamic equilibrium of the second-step hydrogenation of HA.<sup>5</sup>

It is known that copper catalyzes the dehydrogenation of 1,2-diols.<sup>16</sup> However, it should be noticed that copper metal works as an effective catalyst for the dehydration of triol i.e., glycerol.<sup>7–9,17,18</sup> SiO<sub>2</sub>-supported copper catalyst shows 98.8% glycerol conversion with HA selectivity of 84.6% under the conditions of 220 °C, weight hourly space velocity of 0.08 h<sup>–1</sup>, and ambient N<sub>2</sub> pressure with 5% H<sub>2</sub>.<sup>17</sup> Raney Cu is also active in the vapor-phase dehydration of glycerol into HA.<sup>14</sup> We preliminarily found that silver metal catalyzed the dehydration of glycerol to produce HA in H<sub>2</sub> flow (Figure 1). In this paper, we report that HA is produced from glycerol with high selectivity over supported silver catalysts in H<sub>2</sub> flow. We also compare the catalytic activity of Group 11 elements in the reaction of glycerol.

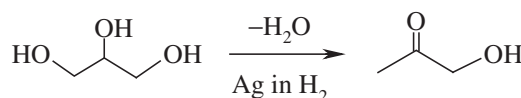


Figure 1. Dehydration of glycerol into hydroxyacetone (HA).

Table 1. Synthesis of HA over metal catalysts of Group 11<sup>a</sup>

| Catalyst<br>(metal content/wt %)               | Conversion <sup>b</sup><br>/mol % | Selectivity/mol % <sup>b</sup> |        |      |
|------------------------------------------------|-----------------------------------|--------------------------------|--------|------|
|                                                |                                   | HA                             | 12-PDO | EG   |
| Au/Al <sub>2</sub> O <sub>3</sub> (5)          | 13.7                              | 57.0                           | 3.9    | 2.5  |
| Au/SiO <sub>2</sub> (5)                        | 1.5                               | 26.3                           | 0      | 0    |
| Ag/SiO <sub>2</sub> (10)                       | 46.2                              | 91.1                           | 3.4    | 1.6  |
| Ag/Al <sub>2</sub> O <sub>3</sub> (10)         | 84.7                              | 59.8                           | 9.1    | 2.4  |
| Ag/ZrO <sub>2</sub> (10)                       | 37.1                              | 77.3                           | 9.7    | 3.1  |
| Ag/CeO <sub>2</sub> (10)                       | 10.2                              | 64.7                           | 0.6    | 6.3  |
| Ag/TiO <sub>2</sub> (10)                       | 12.4                              | 64.1                           | 0      | 3.4  |
| Ag powder <sup>c</sup> (100)                   | 30.8 <sup>d</sup>                 | 84.6                           | 4.0    | 0    |
| Cu/SiO <sub>2</sub> (10)                       | 33.0                              | 66.8                           | 1.7    | 14.1 |
| Cu/Al <sub>2</sub> O <sub>3</sub> <sup>c</sup> | 84.9                              | 44.5                           | 32.9   | 10.9 |

<sup>a</sup>Reaction temperature, 240 °C; carrier gas, H<sub>2</sub>, 210 cm<sup>3</sup> min<sup>–1</sup>; catalyst weight, 0.5 g. <sup>b</sup>Average conversion in the initial 5 h; 12-PDO: average selectivity to 1,2-propanediol; EG: ethylene glycol. <sup>c</sup>Commercially available sample. <sup>d</sup>Catalyst weight, 4.0 g.

Details of experimental procedures of catalytic reaction are described in the Supporting Information.<sup>19</sup> Procedures are briefly explained as follows: all the supported metal catalysts were prepared by incipient wetness impregnation using a solution with a prescribed amount of metal nitrate or chloroauric acid dissolved in distilled water. The catalyst sample was calcined at 500 °C for 3 h. Hereafter, unless otherwise specified, the Ag/SiO<sub>2</sub> catalyst is silver supported on a silica (CARIACT Q-10, 310 m<sup>2</sup> g<sup>–1</sup>), which was supplied by Fuji Silycia Chemical Ltd.

The catalytic reaction of glycerol was performed in a fixed-bed down-flow glass reactor at atmospheric pressure and temperatures between 200 and 300 °C. After the temperature of catalyst bed had been maintained at 200 °C in H<sub>2</sub> flow for 1 h, an aqueous solution of glycerol at 30 wt % was fed into the reactor at a feed rate of 1.8 cm<sup>3</sup> h<sup>–1</sup>, which corresponds to 5.9 mmol of glycerol per hour, in either H<sub>2</sub> or N<sub>2</sub> flow. The liquid products recovered at –78 °C every hour were analyzed on a gas chromatograph connected to a hydrogen flame ionization detector (FID-GC, Shimadzu GC-8A) using a 60-m capillary column of TC-WAX (GL Science).

In our preliminary screening of metal catalysts, gold, cobalt, and platinum were tested on several supports (Table S1).<sup>19</sup> Pt/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> decomposed the C–C bond of glycerol to produce ethylene glycol. Among the tested samples, Au/Al<sub>2</sub>O<sub>3</sub> was found to be selective to HA whereas the conversion of glycerol was low (Table 1). Ag/SiO<sub>2</sub> showed the highest

**Table 2.** Synthesis of HA over Ag on silica supports<sup>a</sup>

| Support<br>(Ag/wt %) | SA <sup>b</sup><br>/m <sup>2</sup> g <sup>-1</sup> | Conversion <sup>c</sup><br>/mol % | Selectivity/mol % <sup>c</sup> |        |     |
|----------------------|----------------------------------------------------|-----------------------------------|--------------------------------|--------|-----|
|                      |                                                    |                                   | HA                             | 12-PDO | EG  |
| Q-10 (5)             | 257                                                | 9.9                               | 83.3                           | 0      | 0   |
| Q-10 (10)            | 245                                                | 46.2                              | 91.1                           | 3.4    | 1.6 |
| Q-10 (20)            | 180                                                | 82.3                              | 83.1                           | 10.3   | 1.9 |
| Q-10 (30)            | 125                                                | 39.3                              | 90.9                           | 3.1    | 1.6 |
| Q-10 (50)            | 9.6                                                | 8.6                               | 71.6                           | 0      | 0.6 |
| Q-3 (10)             | 218                                                | 34.2                              | 86.3                           | 6.4    | 1.4 |
| Q-6 (10)             | 261                                                | 43.0                              | 86.5                           | 4.9    | 2.2 |
| Q-15 (10)            | 153                                                | 48.8                              | 88.5                           | 2.9    | 1.0 |

<sup>a</sup>Reaction temperature, 240 °C; carrier gas, H<sub>2</sub>, 210 cm<sup>3</sup> min<sup>-1</sup>; catalyst weight, 0.5 g. <sup>b</sup>SA: specific surface area. <sup>c</sup>Average conversion in the initial 5 h. 12-PDO: 1,2-propanediol; EG: ethylene glycol.

selectivity to HA, and the selectivity depends on support materials: the other supports such as Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> decreased the selectivity. Even silver powder with the specific surface area lower than 1 m<sup>2</sup> g<sup>-1</sup> showed a sufficient HA selectivity higher than 80%. Therefore, silver metal surface provides active sites for the vapor-phase dehydration of glycerol to HA. The catalytic activity of Ag/SiO<sub>2</sub> was gradually decreased with time on stream in H<sub>2</sub> flow, as shown in detail in the Supporting Information (Figure S1<sup>19</sup>). The deactivation is probably caused by carbon deposition, as discussed below.

Effect of calcination temperature was examined between 400 and 700 °C (Table S2, Figures S2 and S3).<sup>19</sup> Ag in the samples heated at 500 °C was reduced and formed Ag metals, whereas Ag in the sample heated at 400 °C was Ag<sub>2</sub>O. After reduction in H<sub>2</sub> at 240 °C, Ag<sub>2</sub>O in all the samples was reduced to Ag metal. The size of Ag on 20 wt % Ag/SiO<sub>2</sub> was estimated to be 28 nm by an FWHM of the XRD peak at  $2\theta = 37.9^\circ$ , which agrees with the size observed in the TEM photograph (Figure S4<sup>19</sup>).

Table 2 shows effect of Ag content in Ag/SiO<sub>2</sub> catalysts on the synthesis of HA. The HA selectivity exceeded 90% at Ag content of 10 wt %. The conversion is strongly dependent on Ag content: the maximum conversion was attained at Ag content of 20 wt %. Table 2 also shows the catalytic performance of silver supported on different silicas. The number in the name of silica indicates mesopore size in nm;<sup>6</sup> i.e., Q-10 has mesopores with mean pore diameter of 10 nm. The glycerol conversion seems to be dependent on pore structures: silica with large pore and small specific surface area would increase the conversion. Degradation behavior seems to depend on mesopore size of support: small pore-size catalyst such as Q-3 was readily deactivated (Figure S5<sup>19</sup>). A similar deactivation has been observed in the dehydration of glycerol: a catalyst with a small pore support was seriously deactivated by coke formation.<sup>6</sup>

At different concentrations of aqueous glycerol solution, there was no effect of water content on the catalytic performance of Ag/SiO<sub>2</sub>: both the glycerol conversion and the selectivity to HA become similar to those at high glycerol concentrations of 90 wt % (Table S3<sup>19</sup>).

We have previously reported that copper supported on alumina shows the dehydration ability to produce HA in an N<sub>2</sub> atmosphere.<sup>8</sup> In H<sub>2</sub> flow, the Cu/Al<sub>2</sub>O<sub>3</sub> has hydrogenation ability to produce 1,2-propanediol.<sup>5</sup> However, copper supported on silica was not selective to HA because it is capable of C–C bond scission (Table 1). Among the tested catalysts, Ag/SiO<sub>2</sub> was the

**Table 3.** Effect of carrier gas on the synthesis of HA over 10 wt % Ag/SiO<sub>2</sub> catalyst at 240 °C<sup>a</sup>

| Gas, Flow rate<br>/cm <sup>3</sup> min <sup>-1</sup> | Conversion <sup>b</sup><br>/mol % | Selectivity/mol % <sup>b</sup> |        |     |
|------------------------------------------------------|-----------------------------------|--------------------------------|--------|-----|
|                                                      |                                   | HA                             | 12-PDO | EG  |
| N <sub>2</sub> , 210                                 | 7.4                               | 62.3                           | 0      | 0   |
| H <sub>2</sub> , 5 + N <sub>2</sub> , 55             | 50.4                              | 85.6                           | 0.1    | 0   |
| H <sub>2</sub> , 30 + N <sub>2</sub> , 30            | 78.9                              | 89.7                           | 0      | 3.1 |
| H <sub>2</sub> , 30                                  | 90.5                              | 86.7                           | 4.3    | 2.4 |
| H <sub>2</sub> , 60                                  | 91.5                              | 86.0                           | 4.4    | 2.3 |
| H <sub>2</sub> , 120                                 | 94.7                              | 83.1                           | 7.8    | 2.5 |
| H <sub>2</sub> , 210                                 | 96.9                              | 80.8                           | 10.6   | 2.6 |
| H <sub>2</sub> , 360                                 | 86.9                              | 80.6                           | 11.1   | 2.9 |

<sup>a</sup>Catalyst weight, 1.0 g. <sup>b</sup>Average conversion and selectivity in the initial 5 h.

most selective to produce HA in H<sub>2</sub> flow because of its low hydrogenation ability (Table S4<sup>19</sup>). Table 3 shows effect of carrier gas on the conversion of glycerol over Ag/SiO<sub>2</sub>. In N<sub>2</sub> flow, Ag/SiO<sub>2</sub> was not active for the dehydration of glycerol into HA. Addition of H<sub>2</sub> into the N<sub>2</sub> flow drastically increases the glycerol conversion as well as the HA selectivity. It was confirmed that carbon deposition was inhibited during the reaction in H<sub>2</sub> using thermogravimetric analysis of the samples used in the reaction (Figures S6 and S7<sup>19</sup>).

The vapor-phase reaction of glycerol was performed over silver metal catalysts at ambient H<sub>2</sub> pressure. Glycerol was efficiently dehydrated into HA over Ag/SiO<sub>2</sub> catalyst. Glycerol was dehydrated into HA with the selectivity higher than 86% at 91% conversion over Ag/SiO<sub>2</sub> in H<sub>2</sub> flow at 240 °C. It should be noted that metallic silver catalyzes the dehydration of glycerol into HA and that the further hydrogenation to 1,2-propanediol was suppressed over the Ag/SiO<sub>2</sub> even in H<sub>2</sub> flow.

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