

Glycerol conversion in the aqueous solution under hydrogen over Ru/C + an ion-exchange resin and its reaction mechanism

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Abstract

Of the various noble metals (Ru/C, Rh/C, Pt/C, and Pd/C) and acid catalysts [an ion-exchange resin (Amberlyst), H₂SO₄(aq), and HCl(aq)], the combination of Ru/C with Amberlyst is effective in the dehydration + hydrogenation (i.e., hydrogenolysis) of glycerol under mild reaction conditions (393 K, 8.0 MPa). The dehydration of glycerol to acetol is catalyzed by the acid catalysts. The subsequent hydrogenation of acetol on the metal catalysts gives 1,2-propanediol. The activity of the metal catalyst + Amberlyst in glycerol hydrogenolysis can be related to that of acetol hydrogenation over the metal catalysts. Regarding acid catalysts, H₂SO₄(aq) shows lower glycerol dehydration activity than Amberlyst, and HCl(aq) strongly decreases the activity of acetol hydrogenation on Ru/C. In addition, the OH group on Ru/C can also catalyze the dehydration of glycerol to 3-hydroxypropionaldehyde, which can then be converted to 1,3-propanediol through subsequent hydrogenation and other degradation products.

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1. Introduction

Much attention has been given to the catalytic conversion of renewable feedstocks and chemicals. Such conversion to hydrogen can contribute to the use of renewable energy sources [1–4], and such conversion to petrochemicals can facilitate the replacement of petroleum by renewable resources [5,6]. Recently, it has been proposed that commodity chemicals used to produce pharmaceuticals, agricultural adjuvants, plastics, and transportation fuel that are now derived from fossil resources might be producible in future biorefineries from renewable resources, such as plant-derived sugar and other compounds [7]. Glycerol is a building block that might serve as an important biorefinery feedstock [7]. In addition, it is a byproduct in the production of biodiesel by transesterification of vegetable oils [8]. One method of interest is the conversion of glycerol to 1,2-propanediol and 1,3-propanediol, which are usually produced from petroleum derivatives [9]. Several routes

to propanediol can be traced from renewable feedstocks; the most common route is conversion of sugar or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst to produce propanediol and other lower polyols [10]. These routes suggest that propanediol can be a target compound produced from renewable feedstocks; it has been reported that propanediol can be produced through the catalytic conversion of polyols [11] and glycerol. Using copper and zinc catalysts along with a sulfided Ru catalyst, the reaction of glycerol has been carried out at 15 MPa and 513–543 K [12,13]. Investigations on Raney Cu [14,15], Cu/C [16], and Cu–Pt and Cu–Ru bimetallic catalysts [17] at 1.0–4.0 MPa and 493–513 K have also been reported. Using catalysts containing Co, Cu, Mn, Mo, and an inorganic polyacid, the reaction conditions were 25 MPa and 523 K [18]; using homogeneous catalysts containing W and group VIII transition metals, the reaction conditions were 32 MPa and 473 K [19]. In addition, dehydroxylation in an aqueous solution of polyols catalyzed by Ru homogeneous complexes has been reported [20], and Schlaf et al. reported dehydroxylation of glycerol in sulfolane catalyzed by homogeneous complexes of ruthenium under rather mild conditions (~5 MPa, 383 K); however, that activity was low [21]. Hydro-

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gen pressures of around 6–10 MPa and reaction temperatures of 453–513 K have been applied to supported metal catalysts [22–25]. Recently, the reaction of glycerol was conducted at 1.4 MPa and 473 K [10].

Based on these various reports, using milder reaction conditions—especially reduced reaction temperatures—appears to be difficult. Our group recently reported that the addition of solid acid catalysts to Ru/C enhanced conversion and selectivity in glycerol hydrogenolysis. Our results suggest that the conversion of glycerol to propanediols proceeds by the combination of dehydration over acid catalysts with subsequent hydrogenation over metal catalysts, as discussed in detail later. In this article, this dehydration + hydrogenation reaction is called hydrogenolysis. Among various solid acid catalysts, including zeolites, sulfated zirconia, tungstic acid, and an ion-exchange resin, the combination of Ru/C with Amberlyst (ion-exchange resin) exhibited the highest activity. In particular, this combination system catalyzed hydrogenolysis under milder reaction conditions (393 K, 4 MPa H₂) than those for the catalysts reported above [26]. In addition, the degradation of glycerol occurred as a side reaction in the glycerol hydrogenolysis.

This article focuses on the reaction scheme of glycerol hydrogenolysis and degradation. We discuss the formation route of hydrogenolysis and degradation products based on the catalytic performance in the reaction of products and expected intermediates.

2. Experimental

2.1. Catalyst

Active carbon-supported noble-metal catalysts (Ru/C, Pt/C, Rh/C, and Pd/C) were purchased from Wako; the loading of noble metals on all catalysts was 5 wt%. Table 1 lists the BET surface areas and metal particle sizes of the catalysts. All catalysts were in powdered form, with granule size of <100 mesh. They were used without further pretreatment. The cation-exchange resin Amberlyst 15 (4.7 eq/kg-resin dried; particle size, 0.4–1.2 mm; highest operating temperature, 393 K; MP Biomedicals), consisting of highly cross-linked styrene–divinyl benzene copolymer beads functionalized with sulfonic groups, was used as the solid acid catalyst. H₂SO₄(aq) and HCl(aq) were used as homogeneous acid catalysts, and NaCl(aq) and Na₂SO₄(aq) were used as references.

Table 1
Properties of active carbon supported noble metal catalysts

Catalyst	Surface area (m ² /g)	Metal particle size (nm)
Ru/C	485	3.2 ^a
Rh/C	557	17.1 ^b
Pt/C	478	11.5 ^b
Pd/C	348	13.8 ^b

^a Calculated from the measurement of CO adsorption [27].

^b Determined by X-ray diffraction method using Scherrer equation [28].

2.2. Activity test

The reaction of glycerol hydrogenolysis was carried out in a 70-mL stainless steel autoclave, using a 20-mL aqueous solution of glycerol. The standard reaction was conducted under the following conditions: 393 K reaction temperature, 8.0 MPa initial hydrogen pressure, 10 h reaction time, 20 wt% glycerol aqueous solution, 150 mg of supported metal catalysts, and 300 mg of Amberlyst. Reaction conditions were changed to investigate the dependence of the conditions. Details of the reaction conditions are described for each result. In addition, to elucidate the reaction mechanism of glycerol hydrogenolysis and degradation, we used 1,3-propanediol, 1,2-propanediol, ethylene glycol, 1-hydroxypropan-2-one(acetol), propanal, 1-propanol, 2-propanol, ethanol, and methanol as a reactant. The concentration of these reactants of the aqueous solution was 2 wt%.

In all experiments, the aqueous solution of the reactant, the catalyst powder, and the spinner were put into the autoclave, after which the reactor was purged with H₂ (99.99%; Takachiho). After purging, the reactor was heated to the reaction temperature, and the H₂ pressure was increased to 8.0 MPa in standard experiments. The temperature was monitored using a thermocouple inserted into the autoclave and connected to the thermocontroller. The reaction consumed hydrogen, and the total pressure decreased; however, the decreased hydrogen pressure was at most 1/10 of the initial pressure. After the reaction, the gas-phase products were collected in a gasbag, and the liquid-phase products were separated from the used catalyst through filtration. These products were analyzed by gas chromatography (GC), using a GL Sciences model GC-353 gas chromatograph equipped with a flame ionization detector. A TC-WAX capillary column (diameter, 0.25 mm; length, 20 m) was used for separation, and the column temperature was 493 K. Products were also identified by gas chromatography–mass spectroscopy using a Shimadzu model GCMS-QP5050 instrument with a Stab-wax column.

Conversion of the reactants in all reaction tests was calculated based on the following equation:

$$\text{Conversion of reactant (\%)} = \frac{\text{sum of C-based mol of all products}}{\text{sum of C-based mol of reactant and all products}} \times 100.$$

Although conversion of reactant is usually defined as (reactant before – reactant afterward)/(reactant before), in the present case, we must determine the conversion and the selectivity even when the conversion level is very low. Considering the error bar of the analysis procedure, we applied the foregoing calculation method. Note that the conversions calculated by our method and those calculate by the method based on the mass balance closely agree when the conversion is above about 5%.

Selectivity of the products in all reaction tests was also calculated based on the following equation, considering that the degradation byproducts were always formed:

$$\text{Selectivity (\%)} = \frac{\text{C-based mol of the product}}{\text{sum of C-based mol of all products}} \times 100.$$

Determining the precise formation route of each degradation product is difficult; therefore, we simply assume that the degradation products are formed directly from glycerol and other reactants in terms of carbon number in each molecule. For example, when one glycerol is converted to one ethylene glycol and one methane, the selectivities of ethylene glycol and methane are calculated as 66.7 and 33.3%, respectively. Here it is interpreted that two-thirds glycerol molecule is converted to one ethylene glycol molecule, and at the same time, one-third glycerol molecule is converted to one methane molecule. The yield is calculated from conversion (%) \times selectivity (%) / 100.

2.3. Characterization

The surface area of the supported metal catalysts was measured using the BET method (N₂ adsorption) with a Gemini apparatus (Micromeritics). The metal particle sizes of the carbon-supported noble-metal catalysts were determined using X-ray diffraction (XRD) spectra recorded in a Philips X'pert diffractometer with the Scherrer equation for Rh/C, Pd/C, and Pt/C. For Ru/C, the particle size was estimated from CO adsorption measurements performed at room temperature, because no peaks assigned to Ru metal particles were observed in the XRD pattern. The gas pressure at the adsorption equilibrium was about 1.1 kPa, the sample weight was about 0.2 g, and the dead volume of the apparatus was about 60 cm³. Characterization results of the fresh metal catalysts are listed in Table 1.

Transmission electron microscopy (TEM) images were obtained for particle size determination using a JEOL model JEM 2010 instrument operating at 200 kV. After reduction with H₂, the samples were stored under vacuum until measurements were made. Supersonic waves dispersed the samples in 2-propanol, after which the samples were placed on Cu grids under air atmosphere.

The thermal stability of the ion-exchange resin was evaluated using the temperature-programmed desorption (TPD) method in a fixed-bed reactor. Ion-exchange resin (50 mg) was used without pretreatment. The sample was heated from room temperature to 523 K at a rate of 5 K/min. Subsequently, the

sample temperature was kept constant at 523 K for 2 h. The carrier gas was N₂ (flow rate, 10 mL/min). The only desorbed sulfur-containing product was SO₂. Desorbed SO₂ in the effluent gas was analyzed by GC using a Shimadzu model GC-14B equipped with a flame photometric detector and a separation column (β, β' -ODPN).

3. Results and discussion

3.1. Effect of supported noble metal catalysts on glycerol hydrogenolysis

Table 2 shows results of the activity test over M/C and M/C + Amberlyst catalysts (M = Pt, Rh, Pd, and Ru) in the reaction of glycerol. For Pt/C and Pd/C, the conversions were low, and the promoting effect of Amberlyst addition was slight. In contrast, the activity of Rh/C was comparable to that of Ru/C, and the hydrogenolysis selectivity of Rh/C was much higher. A higher selectivity to 1,3-propanediol over Rh/C + H₂WO₄ has been reported [22]. However, the promoting effect of adding Amberlyst was not significant. As reported previously [10], a possible reaction intermediate of glycerol hydrogenolysis is acetol, which is formed by the dehydration reaction of glycerol and can be catalyzed by the acidic function of Amberlyst. In our experiments, acetol was observed over Ru/C + Amberlyst under standard reaction conditions, although the acetol yield was determined to be as low as 0.01%. Therefore, it is not described in the tables and figures. Consequently, glycerol hydrogenolysis is inferred to proceed via acetol. We tested the activity of noble metal catalysts for the hydrogenation of acetol; the reaction formula:

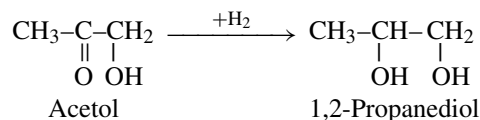


Fig. 1 shows results of acetol hydrogenation, in which acetol was hydrogenated selectively to 1,2-propanediol for all catalysts. No degradation reaction of acetol was observed. The conversion reached almost 100% when 75 mg Ru/C catalyst was

Table 2
Results of glycerol reaction over noble metal catalysts and noble metal + acid catalysts at 393 K^a

Catalysts	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^b				
				1,2-PD	1,3-PD	1-PO	2-PO	Others
Ru/C	3.5	2.0	1.5	26.4	4.9	26.7	0.3	41.7
Rh/C	1.9	1.8	<0.1	62.8	6.8	19.3	7.0	4.1
Pt/C	<0.3	0.2	<0.1	27.7	0.0	23.5	24.2	24.6
Pd/C	<0.2	<0.1	<0.1	30.7	0.0	11.3	18.3	39.7
Ru/C + Amberlyst	12.9	9.7	3.2	55.4	4.9	14.1	0.9	24.7
Rh/C + Amberlyst	3.0	2.9	<0.1	32.7	9.0	40.4	14.9	3.0
Pt/C + Amberlyst	<0.3	0.2	<0.1	27.1	0.0	21.5	35.0	16.4
Pd/C + Amberlyst	<0.2	<0.1	<0.1	26.6	0.0	15.8	30.3	27.3
Ru/C + H ₂ SO ₄ (aq)	5.1	4.1	1.0	56.3	4.0	13.1	7.1	19.5
Ru/C + HCl(aq)	0.9	0.6	0.3	34.0	0.0	21.6	7.8	36.6

^a Reaction conditions: 20 mass% glycerol aqueous solution 20 ml, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg metal catalyst (+300 mg Amberlyst). The amount of acid catalysts was adjusted on the basis of the amount of H⁺ (1.4 mmol). PD = propanediol, PO = propanol.

^b C-based selectivity.

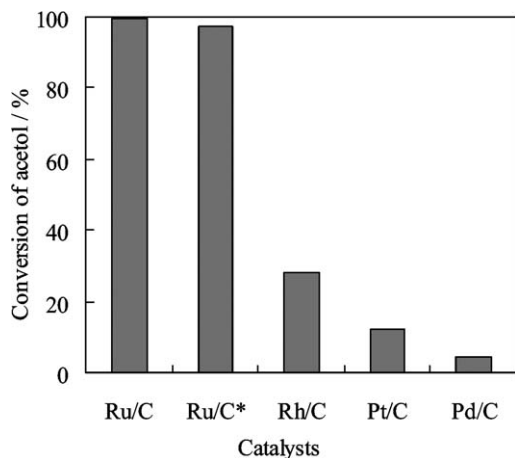


Fig. 1. Results of acetol hydrogenation over noble metal catalysts. Reaction conditions: 20 ml 2 wt% acetol aqueous solution, 373 K reaction temperature, 8.0 MPa initial H₂ pressure, 10 h reaction time, catalyst 75 mg, Ru/C*: 5 mg.

used. Therefore, the result with 5 mg Ru/C is also shown. The 5-mg Ru/C catalyst sample exhibited higher activity than the 75-mg samples of the other catalysts. The activity per catalyst weight of Ru/C is calculated to be at least 60 times higher than that of Rh/C. It is noteworthy that Ru/C is an active and selective catalyst for hydrogenation of acetol to 1,2-propanediol. This tendency of hydrogenation activity (Ru/C >>> Rh/C > Pt/C > Pd/C) can be strongly related to the promoting effect of adding Amberlyst in glycerol hydrogenolysis.

We also compared the performance of Amberlyst and conventional homogeneous acid catalysts H₂SO₄(aq) and HCl(aq). Table 2 gives the results of glycerol reactions over Ru/C + homogeneous acid catalysts. It is clear that the promoting effect of Amberlyst is much higher than that of H₂SO₄(aq), and that the addition of HCl(aq) strongly suppresses the glycerol reaction on Ru/C. Fig. 2 shows the results of acetol hydrogenation. The presence of H₂SO₄(aq) did not affect the hydrogenation of acetol over Ru/C; however, the presence of HCl(aq) significantly decreased the activity of Ru/C. Comparing the addition of HCl(aq) and NaCl(aq) suggests that the Cl⁻ ions can be adsorbed on the Ru surface and can be a poison for the hydrogenation catalyst. In contrast, Ru/C + H₂SO₄(aq) exhibited lower glycerol conversion than Ru/C + Amberlyst, possibly due to the lower dehydration activity of H₂SO₄(aq) compared with Amberlyst. This tendency can be related to previous studies in which Amberlyst exhibited higher activity per acid amount than H₂SO₄(aq) in the *N*-alkylacrylamide from acrylonitrile and alcohol [29] and the esterification of acetic acid and 1-butanol [30].

Montassier et al. have proposed that 1,2-propanediol is formed in glycerol hydrogenolysis via glyceraldehyde on Ru [31] and Cu [14] catalysts. However, in our case, dehydrogenation products such as glyceraldehyde were below the detection limit in the activity test of glycerol hydrogenolysis in the presence and the absence of hydrogen, indicating that Ru/C shows no dehydrogenation activity at 393 K, a much lower temperature than that used in the previous report [31].

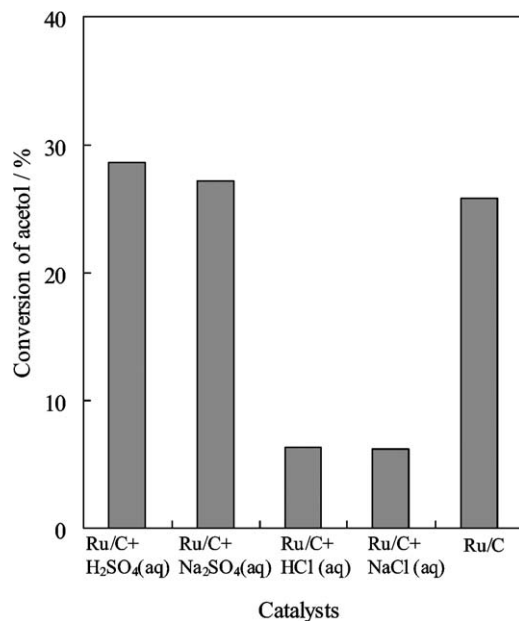


Fig. 2. Additive effect of homogeneous acid catalysts or their salts to Ru/C on the acetol hydrogenation. Reaction conditions: 20 ml 2 wt% acetol aqueous solution, 373 K reaction temperature, 8.0 MPa initial H₂ pressure, 1 h reaction time, Ru/C 2.5 mg. The amount of acid catalysts was adjusted on the basis of the amount of H⁺ (1.4 mmol).

3.2. Catalytic performance of Ru/C + Amberlyst and Ru/C in hydrogenolysis of glycerol

The combination of Ru/C + Amberlyst has proven very effective in glycerol hydrogenolysis. In this section we focus on this combination's catalytic performance. Table 3 indicates the reaction temperature dependence of the glycerol reaction over Ru/C + Amberlyst and Ru/C. Glycerol conversion reached a maximum at 413 K. The low conversion at high temperature is likely caused by the deactivation of Amberlyst, because it was higher than the highest operating temperature (393 K). We analyzed the gaseous products in the pyrolysis of the resin using TPD to elucidate what happens beyond the highest operating temperature. Fig. 3 shows the temperature-programmed pyrolysis profile of the Amberlyst. All sulfur-containing products but SO₂ were below the detection limit. Formation of SO₂ started above 393 K, and desorption reached a maximum at about 500 K. The total amount of this SO₂ desorption was 4.7 mol/kg, in agreement with the ion-exchange capacity of Amberlyst (4.7 eq/kg). This agreement indicates that the amount of acid decreased by the thermal decomposition of the sulfonic acid group above 393 K. This can explain the temperature-dependence behavior over Ru/C + Amberlyst. In addition, Ru/C + Amberlyst gave higher glycerol conversion than Ru/C at the low temperature of 393 K (Table 3), on the other hand, Ru/C + Amberlyst had a much lower conversion than Ru/C at 473 K. This behavior can be explained by poisoning of the sulfur-containing compounds formed by Amberlyst decomposition. After the reaction, the formation of SO₂ with a small amount of H₂S was observed. The amount of sulfur compounds detected in the solution and gases represented only

Table 3
Reaction temperature dependence of glycerol reaction over Ru/C + Amberlyst and Ru/C at 393 K^a

Reaction temperature (K)	Catalysts	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^b							
					1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
393	Ru/C + Amberlyst	12.9	9.7	3.2	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9
413		40.7	26.5	14.2	43.1	1.0	18.2	2.9	9.5	13.7	1.6	10.0
433		29.5	21.6	8.0	64.8	1.2	5.4	1.6	14.1	3.9	0.8	8.2
453		15.0	9.2	5.8	53.6	1.6	5.4	1.0	21.4	4.2	1.6	11.2
473		6.5	6.3	0.3	74.1	1.5	19.9	0.6	1.9	0.8	0.0	1.3
393	Ru/C	3.5	2.0	1.5	26.4	4.9	26.7	0.3	22.0	5.8	2.3	11.6
473		29.1	8.7	20.4	29.4	0.0	0.2	0.5	40.0	0.9	4.7	24.4

^a Reaction conditions: 20 mass% glycerol aqueous solution 20 ml, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg Ru/C catalyst (+300 mg Amberlyst). PD = propanediol, PO = propanol, EG = ethylene glycol.

^b C-based selectivity.

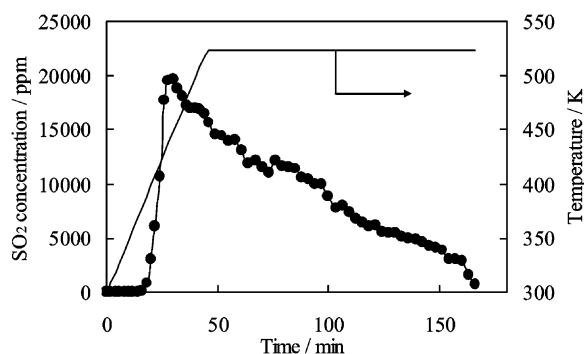


Fig. 3. Temperature-programmed desorption profile of the Amberlyst. Sample weight 10 mg, heating rate 5 K/min. SO₂ was detected by FPD.

0.6% of the total sulfur amount in the Amberlyst catalyst after 10 h at 413 K, compared with 8.1% at 433 K.

Table 4 shows the effect of the amount of catalyst on the glycerol reaction over Ru/C + Amberlyst. As shown in part (a) of the table, the yields of the hydrogenolysis products (es-

pecially 1,2-propanediol and 1-propanol) were markedly enhanced by increasing the amount of Amberlyst. In contrast, the yields of degradation products were not significantly influenced by the Amberlyst content. These results indicate that adding Amberlyst to Ru/C promoted the glycerol hydrogenolysis reaction. Part (b) of Table 4 shows the effect of Ru/C content. Without Ru/C catalyst, almost no reaction proceeded, implying that Amberlyst by itself cannot catalyze hydrogenolysis and the degradation reaction. As discussed above, Amberlyst can catalyze only the dehydration reaction to acetol, the yield of which is very low in aqueous solution, as mentioned earlier. The presence of Ru/C enhanced product yield; the conversion of glycerol was almost proportional to the amount of Ru/C in the range of 0–150 mg. In contrast, when 300 mg Ru/C was used, the yield of the degradation products increased markedly, and that of the hydrogenolysis products decreased. These results indicate that the ratio of Ru/C to Amberlyst must be optimized to ensure high selectivity of hydrogenolysis reactions; too much Ru/C promotes degradation reactions. This suggests that Ru/C

Table 4
Effect of catalyst amount on the glycerol reaction over Ru/C + Amberlyst^a

(a) Amount of Amberlyst												
Amount of Amberlyst (mg)	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^b								
				1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄	
25	4.8	2.4	2.4	26.9	4.0	18.8	0.6	16.7	11.9	9.2	11.9	
37.5	5.3	2.8	2.5	33.9	5.2	10.9	2.7	26.2	5.4	4.4	11.4	
75	6.4	3.7	2.6	43.0	5.6	9.2	1.0	24.2	3.2	0.2	13.5	
150	7.6	5.0	2.6	50.7	5.5	9.1	0.4	19.3	3.5	0.2	11.2	
225	9.6	6.5	3.1	52.5	5.6	9.2	0.4	18.7	2.8	0.2	10.6	
300	12.9	9.7	3.2	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9	

(b) Amount of Ru/C												
Amount of Ru/C (mg)	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^b								
				1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄	
0 ^c	<0.1	<0.1	<0.1	–	–	–	–	–	–	–	–	
75	6.2	4.1	2.2	53.4	2.2	9.0	0.7	21.5	1.7	0.2	11.4	
150	12.9	9.7	3.2	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9	
300	14.9	5.9	9.0	33.8	1.0	4.2	0.5	40.2	4.9	0.8	14.6	

^a Reaction conditions: 20 ml 20 wt% glycerol aqueous solution, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, for part (a) 150 mg Ru/C catalyst + Amberlyst, for part (b) Ru/C catalyst + 300 mg Amberlyst. PD = propanediol, PO = propanol, EG = ethylene glycol.

^b C-based selectivity.

^c Selectivities are not listed because the conversion level is too low to determine the product selectivity.

Table 5
Effect of the catalyst recycled use in the glycerol reaction over Ru/C + Amberlyst^a

Recycle times	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^b							
				1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
1	12.9	9.7	3.2	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9
2	12.1	10.1	2.0	67.1	4.8	10.6	1.1	9.1	1.8	0.3	5.2
3	12.6	11.3	1.3	77.4	3.5	8.3	0.6	5.3	1.5	0.1	3.3
4	11.9	11.1	0.8	76.0	4.1	11.9	1.3	3.2	1.3	0.1	2.1
5	12.0	11.1	0.9	78.3	3.2	10.6	0.7	3.3	1.5	0.1	2.3

^a Reaction conditions: 20 ml 20 wt% glycerol aqueous solution, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, 150 mg Ru/C catalyst + 300 mg Amberlyst. PD = propanediol, PO = propanol, EG = ethylene glycol.

^b C-based selectivity.

can catalyze the degradation reaction as well as the hydrogenation of acetol.

The tests of the glycerol reaction were repeated five times to evaluate the catalyst life and deactivation behavior. After each experiment, the used catalyst was separated by filtration. The catalyst was dried at 383 K for 1 h and used again for the next reaction test. The recovery ratio of the used catalyst was about 98–99%, and the catalyst loss was negligible. The results show that the conversion of glycerol remained almost constant (Table 5). With repetition, the selectivity of degradation products decreased and that of hydrogenolysis products slightly increased. Table 4 shows that the reaction behavior is very sensitive to the amounts of both Ru/C and Amberlyst, demonstrating that both Ru/C and Amberlyst are rather stable at this reaction temperature.

Fig. 4 shows a TEM image of the reduced fresh Ru/C catalyst. The average particle size of Ru is determined to be about 2.5 ± 0.3 nm. Based on the relationship, $D = 1.32/d$, between particle size (d , nm) and (D , %) [27], the dispersion is calculated as 53%, almost in agreement with the metal dispersion estimated from CO adsorption. In addition, the TEM image of Ru/C used in the glycerol reaction shows that the metal particle size of Ru is almost equal to that of the reduced Ru/C catalyst before the activity test. This equivalence indicates that high dispersion was maintained during the reaction. Therefore, it is inferred that the slight change in selectivity for the repeated reaction is attributable not to the aggregation of Ru, but rather to a change in the surface state of Ru metal particles.

Table 6 shows the effect of initial hydrogen pressure on the glycerol reaction over Ru/C + Amberlyst. Glycerol conversion increased gradually with increasing hydrogen pressure. At higher hydrogen pressures, hydrogenolysis selectivity was also

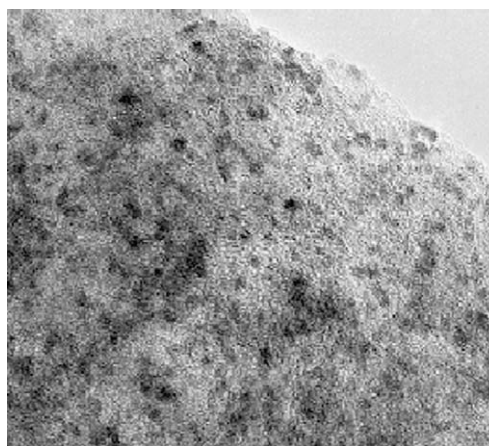


Fig. 4. TEM image of Ru/C. Sample was reduced in the solution of glycerol at 393 K for 1 h.

higher. A similar tendency has been reported over a copper-chromite catalyst [10] and Cu/C [16]. This dependence of selectivity on H₂ pressure has been explained by the increased amount of metallic Cu species and decreased amount of Cu (I) hydroxide species [16]. This report suggests that the surface state of Ru can influence selectivity, as mentioned in the discussion of the results of catalyst characterization.

Table 7 shows the effect of glycerol concentration on the glycerol reaction over Ru/C + Amberlyst and Ru/C. In both cases, higher conversion was obtained at lower glycerol concentrations. The formation rate of hydrogenolysis products over Ru/C was maximal when a 10% aqueous solution of glycerol was used [Table 7(a)]; in contrast, that over Ru/C + Amberlyst was maximal with a 40% glycerol solution [Table 7(b)]. A similar tendency was also observed for a copper-chromite cata-

Table 6
Effect of initial hydrogen pressure on the glycerol reaction over Ru/C + Amberlyst^a

Initial hydrogen pressure (MPa)	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Selectivity of each product (%) ^b							
				1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
1.0	5.3	3.3	2.1	51.8	0.5	6.4	2.8	16.5	9.2	1.5	11.3
2.0	7.2	4.5	2.7	51.2	2.1	9.1	0.3	17.4	6.6	0.2	13.1
4.0	9.8	6.4	3.4	50.4	2.1	12.5	0.8	17.5	7.3	0.7	8.7
8.0	12.9	9.7	3.2	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9

^a Reaction conditions: 20 ml 20 wt% glycerol aqueous solution, 393 K reaction temperature, 150 mg Ru/C catalyst + 300 mg Amberlyst. PD = propanediol, PO = propanol, EG = ethylene glycol.

^b C-based selectivity.

Table 7
Dependence of glycerol concentration on glycerol hydrogenolysis over Ru/C and Ru/C + Amberlyst^a

Glycerol concentration (%)	Catalysts	Conversion (%)	Total yield of hydrogenolysis products (%)	Total yield of degradation products (%)	Formation rate of hydrogenolysis products	Selectivity of each product (%) ^b							
						1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
2	Ru/C	20.8	12.0	8.8	0.5 ^c	12.7	0.4	39.1	5.6	7.6	20.6	1.6	12.4
5		14.3	10.6	3.7	1.2 ^c	29.0	1.1	41.9	2.2	8.8	8.3	0.9	7.7
10		7.9	5.8	2.1	1.3 ^c	35.3	2.6	34.6	1.3	12.4	5.1	0.4	8.4
20		3.5	2.0	1.5	0.9 ^c	26.4	4.9	26.7	0.3	22.0	5.8	2.3	11.6
40		1.7	0.9	0.8	0.8 ^c	18.4	6.2	26.3	0.2	25.5	7.1	0.5	15.7
60		0.8	0.3	0.5	0.4 ^c	20.1	9.4	6.9	0.1	40.1	2.2	0.3	20.9
2	Ru/C + Amberlyst	38.8	23.6	15.2	1.0 ^d	28.8	0.8	28.9	2.4	7.4	18.7	1.9	11.2
5		25.0	18.7	6.3	2.0 ^d	44.5	1.6	24.6	4.3	10.4	6.3	0.5	7.9
10		17.7	13.6	4.1	3.0 ^d	42.6	2.2	30.9	1.0	9.3	6.2	0.4	7.4
20		12.9	9.7	3.2	4.2 ^d	55.4	4.9	14.1	0.9	12.9	3.6	0.3	7.9
40		7.0	4.9	2.1	4.3 ^d	54.7	4.9	10.5	0.5	16.7	2.1	0.2	10.5
60		1.4	1.0	0.4	1.3 ^d	58.9	4.3	8.0	0.4	15.1	3.8	0.5	9.0

^a Reaction conditions: 20 ml glycerol aqueous solution, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, 10 h reaction time, 150 mg Ru/C catalyst (+300 mg Amberlyst). PD = propanediol, PO = propanol, EG = ethylene glycol.

^b C-based selectivity.

^c mmol/150 mg Ru/C.

^d mmol/(150 mg Ru/C + 300 mg Amberlyst).

Table 8
Results of the reactions of various compounds^a

(a) Over Ru/C under H ₂									
Reactant	Conversion (%)	Selectivity of each product (%) ^b							
		1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
Glycerol	20.8	12.7	0.4	39.1	5.6	7.6	20.6	1.6	12.4
1,2-PD	6.3	–	0.0	25.1	37.1	0.0	25.2	0.0	12.6
1,3-PD	75.1	0.0	–	25.3	0.7	0.0	49.3	0.1	24.6
EG	11.2	–	–	–	–	–	66.6	24.9	8.5
Propanal	99.6	0.0	0.0	97.8	1.7	0.0	0.3	0.0	0.2
Acetol	99.8	99.3	0.0	0.2	0.1	0.0	0.2	0.0	0.1

(b) Over Ru/C + Amberlyst under H₂

Reactant	Conversion (%)	Selectivity of each product (%) ^b							
		1,2-PD	1,3-PD	1-PO	2-PO	EG	C ₂ H ₅ OH	CH ₃ OH	CH ₄
Glycerol	38.8	28.8	0.8	28.9	2.4	7.4	18.7	1.9	11.2
1,2-PD	6.3	–	0.0	28.2	30.0	0.0	27.8	0.0	13.9
1,3-PD	77.7	0.0	–	31.0	1.8	0.0	44.8	0.0	22.4
EG	13.4	–	–	–	–	–	67.7	21.5	10.9
Propanal	99.9	0.0	0.0	98.5	1.2	0.0	0.2	0.0	0.1
Acetol	99.9	99.0	0.0	0.2	0.3	0.0	0.3	0.0	0.1

^a Reaction conditions: 2 mass% aqueous solution of reactant 20 ml, 393 K reaction temperature, 8.0 MPa initial H₂ pressure, 10 h reaction time, for part (a) catalyst Ru/C 150 mg, for part (b) catalyst Ru/C 150 mg + Amberlyst 300 mg.

^b C-based selectivity.

lyst [10]. Another important point is that the maximum hydrogenolysis rate was obtained over Ru/C + Amberlyst at a higher concentration than over Ru/C. The reaction order is higher on Ru/C + Amberlyst than on Ru/C, due to the reaction order of glycerol over Ru/C or Amberlyst.

3.3. Reaction mechanism of hydrogenolysis and degradation over Ru/C + Amberlyst and Ru/C

The foregoing results indicate that the combination of Ru/C + Amberlyst is effective for glycerol hydrogenolysis in

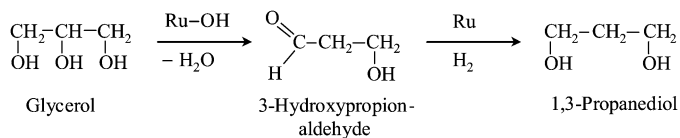
terms of activity and selectivity. We carried out activity tests of the products over Ru/C + Amberlyst and Ru/C under similar conditions as used for glycerol to elucidate the reaction routes of the products. We used 2 wt% aqueous solutions of each compound. Although the results are not listed in Table 8, in the reactions of methanol, ethanol, 1-propanol, and 2-propanol, conversion was almost zero over Ru/C and Ru/C + Amberlyst. Therefore, these compounds and methane are considered final products in the reaction of glycerol. Table 8 gives results for the reactions of glycerol, 1,2-propanediol, 1,3-propanediol, and

ethylene glycol. As mentioned above, glycerol conversion was much higher on Ru/C + Amberlyst than on Ru/C. In contrast, Amberlyst had only a small additive effect in the reactions of 1,2-propanediol, 1,3-propanediol, and ethylene glycol, indicating that the reactions of these three compounds were catalyzed by Ru/C. Comparing the conversion levels reveals a reactivity order of 1,3-propanediol > ethylene glycol > 1,2-propanediol. A high reactivity of 1,3-propanediol is related to a low selectivity of 1,3-propanediol formation in the glycerol reaction.

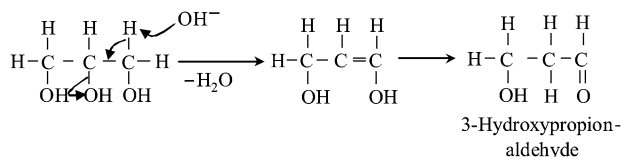
In addition, the formation of 1-propanol and 2-propanol was observed on both Ru/C + Amberlyst and Ru/C in the glycerol reaction. It is characteristic that the selectivity of 1-propanol was much higher than that of 2-propanol. The similar tendency in these selectivities can be observed in the reaction of 1,3-propanediol. On the other hand, in the reaction of 1,2-propanediol, the selectivity of 1-propanol was comparable to that of 2-propanol, and the tendency is different. These results indicate that 1-propanol and 2-propanol can be formed mainly via 1,3-propanediol in glycerol hydrogenolysis. This behavior can be supported by the different reactivities of 1,2-propanediol and 1,3-propanediol. Assuming that all 1-propanol and 2-propanol is formed via 1,3-propanediol, it is possible to estimate the ratio of 1,2-propanediol and 1,3-propanediol as primary products in glycerol hydrogenolysis. On Ru/C + Amberlyst, the ratio of 1,2-propanediol to 1,3-propanediol can be estimated as about 1:1; in contrast, on Ru/C, this ratio was calculated to be 1:4. The yield of 1,2-propanediol on Ru/C + Amberlyst was 11.2%, much higher than that on Ru/C (2.6%) estimated from the results in Table 8. This tendency can be explained by the formation of 1,2-propanediol by dehydration over Amberlyst and subsequent hydrogenation over Ru/C. In contrast, the yield of 1,3-propanediol + 1-propanol + 2-propanol on Ru/C + Amberlyst was 12.4%, comparable to that on Ru/C (9.4%). This tendency indicates that 1,3-propanediol is formed over Ru/C.

Tyrlik et al. have proposed that OH species on Ru catalyze glucose dehydration [32]. Based on this proposal, 1,3-propanediol can be formed from dehydration of glycerol to 3-hy-

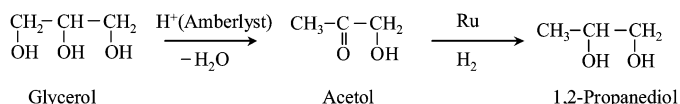
droxypropionaldehyde and subsequent hydrogenation over Ru/C,



The role of OH species on Ru is thought to be important because Ru/C is much more active than other noble metal catalysts in glycerol hydrogenolysis (Table 2). Another important point is that Ru species can catalyze dehydration to 3-hydroxypropionaldehyde, although two dehydration routes can be traced to 3-hydroxypropionaldehyde and acetol. When this OH species attacks H linked to terminal carbons, 3-hydroxypropionaldehyde is produced, which can explain the dehydration selectivity. However, the reason why OH species do not attack H linked to center carbons remains unclear:



Another product of glycerol dehydration is acetol, the subsequent hydrogenation of which can give 1,2-propanediol. It is significant that the acidity of Amberlyst catalyzes this dehydration reaction, as discussed above,



In the case of the Amberlyst, the active species is a proton. Acetol is formed when the proton attacks OH linked to terminal carbons:

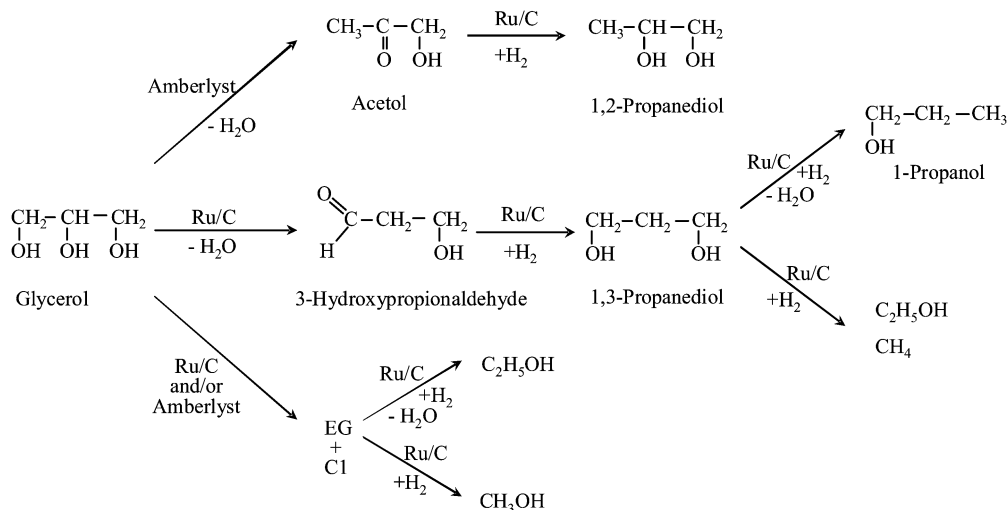
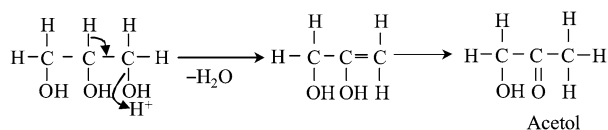


Fig. 5. Reaction scheme of glycerol hydrogenolysis and degradation reactions.

In both cases, the active species tends to attack the species linked to the terminal carbon in glycerol; this can commonly occur in the two expected reaction routes. This similarity might be related to the molecular structure of glycerol in water, for example, steric hindrance of H and OH linked to central carbon. We currently have no experimental or theoretical evidence to support this conjecture, however.

In addition, hydrogenation of acetol can proceed easily on Ru/C catalyst (Fig. 1; Table 4). Regarding 3-hydroxypropionaldehyde, we used propanal as a model compound to evaluate the hydrogenation activity of the C=O bond of this compound, because the compound is not commercially available. The Ru/C catalyst also exhibited a high activity in propanal hydrogenation to 1-propanol (Table 8). A proposed reaction scheme for glycerol hydrogenolysis is shown in Fig. 5.

Next, we considered the route of degradation products. In the case of the reaction of glycerol, ethylene glycol was obtained. However, it was not detected in the reactions of 1,2-propanediol and 1,3-propanediol at all, suggesting that ethylene glycol is formed directly from glycerol, although the selectivity was not so high. Furthermore, the conversion of ethylene glycol was rather low in the reaction of ethylene glycol (Table 8), which can explain the fact that ethylene glycol was observed in the reaction of glycerol. Ethanol and methane can be formed from the degradation reaction of 1,2-propanediol and 1,3-propanediol; in addition, ethanol also can be formed during hydrogenolysis of ethylene glycol. It is noteworthy that methanol is formed only in the degradation reaction of ethylene glycol, and methanol is formed via ethylene glycol in the reaction of glycerol. Fig. 5 shows the reaction scheme including glycerol degradation. In this reaction scheme, Ru–OH can affect the reaction rate to 1,3-propanediol and the degradation products on the basis of the results given in Table 4(b). In particular, the amount of Ru–OH species can decrease under higher H₂ partial pressure conditions (Table 6). Results of the H₂ pressure dependence of glycerol hydrogenolysis show that degradation products decrease with increasing H₂ pressure, perhaps because of the decrease of Ru–OH species under higher H₂ pressure. In addition, the selectivity change during the recycled use of catalysts can also be investigated according to the decrease of Ru–OH species.

4. Conclusion

The combination of Ru/C + Amberlyst is effective for glycerol hydrogenolysis under mild reaction conditions (393 K) compared to Rh/C, Pt/C, and Pd/C as metal catalysts and HCl(aq) and H₂SO₄(aq) as acid catalysts. The good performance of Ru/C + Amberlyst in glycerol hydrogenolysis may be due to the high activity of glycerol dehydration to acetol over Amberlyst and the high hydrogenation activity of acetol to 1,2-propanediol over Ru/C. The degradation of glycerol proceeded as a side reaction in glycerol hydrogenolysis,

and Ru/C can catalyze the degradation reaction. Ru/C catalyst can play an important role in the dehydration of glycerol to 3-hydroxypropionaldehyde, which can be converted to 1,3-propanediol through subsequent hydrogenation and other degradation products. In particular, the contribution of Ru–OH species is suggested in the dehydration of glycerol.

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