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Selective transformation of glucose into propylene glycol on Ru/C catalysts combined with ZnO under low hydrogen pressures

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Abstract[1]

Recently, biomass resources have garnered significant attention as sustainable and renewable raw materials for the production of chemicals. Propylene glycol (PG) is a valuable chemical product that can be synthesized from biomass. Herein, the selective transformation of glucose into PG was investigated on a carbon-supported 5 wt% Ru catalyst (5%-Ru/C) combined with solid acid-base catalysts under low hydrogen pressures. The reaction conditions, namely the amount of ZnO, temperature, and hydrogen pressure, were also evaluated. At a hydrogen pressure of 0.4 MPa, a full conversion of glucose and 38% yield of PG were obtained using the ZnO + Ru/C system at 453 K for 20 h, while the yield of PG on Ru/C alone was only 9.3% under the same conditions. Studies on the reaction mechanism indicated that the transformation of glucose into PG consisted of the isomerization of glucose to fructose, retro-aldol reaction of fructose to triose (dihydroxyacetone and glyceraldehyde), dehydration of glyceraldehyde to pyruvaldehyde, and successive hydrogenation of pyruvaldehyde to PG via hydroxyacetone. The ZnO catalyst promoted both the isomerization and retro-aldol reaction steps, and the Ru catalyst promoted the hydrogenation steps. The retro-aldol reaction, which included the cleavage of C3-C4 bond in glucose, enabled the selective transformation of glucose into PG under low hydrogen pressures. These

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[1] **Abbreviations:** Ru/C, carbon-supported Ru catalyst; EG, ethylene glycol; PG, propylene glycol; HA, hydroxyacetone; LA, lactic acid; DHA, dihydroxyacetone; GAL, glyceraldehyde; PAL, pyruvaldehyde; Fru, fructose; Sor, sorbitol; Man, mannitol.

findings provide novel insights into the efficient synthesis of PG from glucose, which could be achieved by combining and optimizing the retro-aldol and hydrogenation steps.

Keywords: Propylene glycol, Retro-aldol reaction, Hydrogenation, Ruthenium catalyst, Zinc oxide

1. Introduction

Energy and resource concerns have become major issues in today's modern society. Considering the depletion of fossil resources, developing and ensuring suitable oil substitutes and carbon resources are of paramount importance. Recently, biomass resources, particularly unused biomass such as agricultural residues and forest offcuts, as well as crops such as sugarcane, corn, and cassava have garnered significant attention as sustainable and renewable raw materials for the production of chemicals. New catalytic procedures have been vigorously explored worldwide in an attempt to convert biomass into valuable chemicals [1-7].

Environmentally friendly catalytic systems used in the production of bio-based chemicals are critical in the development of a recycling-oriented society. For instance, polyols such as ethylene glycol (EG) and propylene glycol (PG) are important chemical products that can be synthesized from biomass. The conversion of sugars such as cellulose and glucose as sustainable biomass resources into various polyols using noble metal or transition metal catalysts has been reported.

For example, Fukuoka et al. were successful in synthesizing hexitol (sorbitol and mannitol) via the hydrogenolysis of cellulose using Pt/γ-Al_2O_3 [8], Ru/AC [9], and Ni/C [10]. They obtained a maximum sugar alcohol yield of 67% using 70 wt% Ni/C under a hydrogen pressure of 5.1 MPa. Furthermore, Zhang et al. transformed cellulose into EG in high yields in the presence of a series of tungsten-based catalysts [11-17]. By conducting the hydrogenolysis of cellulose in the presence of Ni5-W25/SBA-15 under a hydrogen pressure of 6 MPa at 518 K for 30 min, EG was successfully obtained in a maximum yield of 75% [13]. Most recently, Zhang et al. reported the direct conversion of cellulose to both EG and PG in 63.7% yield using a versatile Ni-La(III) catalyst at 518 K, 5 MPa H_2, and 150 min [18]. The yield of PG yield was around a third of that of EG, and the authors proposed that the reaction pathway occurred via sorbitol for PG formation. Xu et al. reported the selective conversion of cellulose into polyols using a combination of sulfonic acid functionalized mesoporous silica and Ru/C. Almost 70% yield of polyols was obtained at 503 K, 6 MPa H_2, and 40 min, with approx. 50% yield of EG as the major product [19]. They proposed that the reaction pathway occurred via glycerol for PG formation. Moreover, Liu et al. demonstrated the selective conversion of cellulose to polyols (hexitols, glycerol, PG, EG, etc.) over bimetallic Pt-SnO_x/Al_2O_3 catalysts. Sn/Pt ratios over 1.5 led to the preferential conversion to C_2 and especially C_3

products (e.g., hydroxyacetone) over hexitols. When the Sn/Pt ratio was 3.8, 25.2% yield of hydroxyacetone was obtained at 473 K, 6 MPa H_2, and 30 min [20].

However, there are only a few reports which focus on selective PG synthesis from glucose or cellulose. PG is an alcohol with a wide range of applications. It is used as an unsaturated polyester resin, an antifreeze, a plasticizer lubricant, a humectant, and a solvent; in 2012, its worldwide annual production volume was at least 2 million tons [21-23]. The current industrial production of PG is based on the hydration of propylene oxide. Recently, the demand for a bio-based synthesis of PG has increased, and the synthesis of PG from glycerol, obtained as a side product of biomass diesel, has been reported [24-26]. Glucose ($C_6H_{12}O_6$) is the most abundant natural hexose, and the direct synthesis of PG from glucose is extremely useful.

For example, Mu et al. reported the synthesis of glycols directly from cellulose or glucose using 20% Ni/ZnO [27] and 2Ni･3Cu･5ZnO [28]. PG was obtained in 25.5% yield from glucose using 20% Ni/ZnO at a hydrogen pressure of 6 MPa at 518 K over 2 h. Liang et al. [29, 30] synthesized polyols by the direct hydrogenolysis of cellulose or glucose in the presence of Cu-Cr catalysts. PG was obtained in 52.8% yield [30] from glucose via a reaction conducted under a hydrogen pressure of 6 MPa at 413 K for 2 h and at 493 K for 5 h using a Cu-Cr catalyst combined with $Ca(OH)_2$. However, in the absence of a basic compound such as $Ca(OH)_2$, the yield of PG was as small as 5.4%. Zhang et al. demonstrated that a 4% Ni-20% W_2C catalyst yielded 38.5% of PG from Jerusalem Artichoke Tuber fructose-based biomass, at 518 K, 6 MPa H_2, and 80 min [31]. Recently, Xia et al. reported that Pt nanoparticles supported on carbon nanotubes (CNTs) converted cellulose to polyols at 513 K, 2 MPa H_2, and 2 h, resulting in 34.3% yield of EG and 37.1% yield of PG [32].

Based on the aforementioned reports, the primary issues encountered in the synthesis of PG from glucose include low yields (around 25%), a high hydrogen pressure (>5 MPa), and the requirement of a homogeneous system and an alkali catalyst to achieve high yields. Consequently, developing an efficient catalytic system for the synthesis of PG under mild conditions represents a challenge for establishing eco-friendly chemical processes.

Accordingly, we investigated the highly selective transformation of glucose to PG at low hydrogen pressures. We screened a variety of catalysts, both solid acid-base catalysts and noble metal catalysts, and the effects of reaction conditions such as the amount of catalyst, reaction temperature, and hydrogen pressure were evaluated. Under the optimized conditions, we obtained 38.1% yield of PG from glucose at a hydrogen pressure of 0.4 MPa. We also discuss the mechanistic pathway of the formation of PG from glucose.

2. Experimental section

2.1 Materials

All materials, except ZSM-5 and Al_2O_3, were obtained from commercial suppliers and were used as received without any pretreatment or purification; noble metal catalysts (5 wt% Ru/C, Rh/C, Pd/C, and Pt/C) were obtained from N. E. ChemCat Corporation (Tokyo, Japan); ZnO as well as other metal oxides, glucose, fructose, dihydroxyacetone, glyceraldehyde, pyruvaldehyde, hydroxyacetone, propylene glycol, sorbitol, mannitol, glycerol, lactic acid (LA), were all obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan); calibration standard gases were obtained from GL Sciences Inc. (Tokyo, Japan). ZSM-5 (JRC-Z5-90H) and Al_2O_3 (JRC-ALO-8) were obtained from the Catalysis Society of Japan.

2.2 Catalyst characterization

The textural and acid-base properties of ZnO and 5% Ru/C are listed in Table S1. ZnO does not exhibit porosity and contains both acid sites and base sites; 5% Ru/C has a high surface area (803 m^2/g) and small particles of Ru metal (1.6 nm).

2.3 Catalytic reaction

Catalytic experiments were carried out in a 50 mL stainless steel (SUS316) autoclave (Taiatsu, TSV-1) or a 100 mL Hastelloy (C-22) autoclave (OM Lab-Tech Co. Ltd., MMJ-100) with an inserted glass vessel. In a typical run using the 50 mL autoclave, 180 mg of glucose (1 mmol), 82 mg of ZnO, 30 mg of 5%-Ru/C catalyst, and 20 mL of water were charged in the autoclave. Afterwards, the reactor was purged with nitrogen 3 times to exclude air, pressurized with 0.4 MPa of hydrogen in addition to 0.5 MPa of nitrogen, and heated to the reaction temperature, which was kept constant for the duration of the intended reaction time with stirring at 600-720 rpm. In this study, a hydrogen pressure of 0.4 MPa was equivalent to approximately 4 moles of hydrogen (the theoretical amount in the transformation of glucose to PG; $C_6H_{12}O_6 + 4H_2 \rightarrow 2C_3H_8O_2 + 2H_2O$). The temperature was monitored using a thermocouple inserted in the autoclave. Approximately 30 min was required to reach the desired temperature.

"Reaction time" indicates the time between reaching the intended temperature and the beginning of the cooling treatment. Approximately 1 h was required to cool the reaction vessel. For the catalyst reuse studies, the solid phase composed of the catalysts (ZnO and Ru/C) was collected by filtration and washed with water several times. The recovered catalysts were used directly in the next experiment without pretreatment.

2.4 Analytical methods

After each reaction, the liquid products were separated by centrifugation, decantation, and filtration, and were then analyzed using high-performance liquid chromatography (Waters, 600 system; Shimadzu, Prominence) equipped with a refractive index detector. The columns used in this work included a Bio-Rad Aminex HPX-87H column (ø7.8×300 mm, mobile phase: 5 mmol L^{-1} formic acid aqueous solution, 0.7 mL min^{-1}, 313 K) and a Bio-Rad Aminex HPX-87P column (ø7.8×300 mm, mobile phase: water, 1.0 mL min^{-1}, 358 K). The products were identified using standard substances and were quantified by the external standard method using an aqueous solution of each product at a known concentration. The total amount of organic carbon dissolved in water was determined by a total organic carbon analyzer (Shimadzu, TOC-$L_{CSH/CSN}$).

The gas products (e.g., methane, ethane, carbon dioxide etc.) were collected in a Tedlar® gas sampling bag and were analyzed using a gas chromatograph (Shimadzu GC-8A) equipped with silica gel, and molecular sieve 5A columns, and a thermal conductivity detector.

The yields of the products (mol%/C) were calculated based on carbon:

$$\text{Yield [mol\%/C]} = \frac{number\ of\ C\ atoms\ in\ product}{number\ of\ C\ atoms\ in\ substrate} \times \frac{number\ of\ moles\ of\ product}{initial\ number\ of\ moles\ of\ substrate} \times 100$$

3. Results and discussion

3.1 Screening of catalysts

In the preliminary experiments, we screened various metal oxides as additives for the transformation of glucose to PG on Ru/C catalysts (Table 1). As shown in Table 1, the addition of different metal oxides led to a diverse distribution of reaction products. The addition of ZnO, Fe_3O_4, La_2O_3, and CeO_2 resulted in a high PG yield. The addition of Y_2O_3, Sm_2O_3, and MgO resulted in the formation of LA as a side product. The addition of WO_3 induced the selective formation of EG, in a similar way as that previously demonstrated in the literature [33]. The addition of SnO_2 and Nb_2O_5 selectively resulted in hexitols (sorbitol and mannitol) as the main products. The addition of Al_2O_3, TiO_2, and HZSM-5 (zeolite) led to a large amount of gaseous products. Thus, ZnO was the most effective additive that gave the highest PG yield in the transformation of glucose to PG. Subsequently, some noble metal catalysts (Ru/C, Rh/C, Pd/C, and Pt/C) combined with ZnO were tested (Table 2). With Ru/C, 38.1% was the maximum yield obtained; with all other noble metals, the yield of PG was about 30%. Based on these results, the ZnO + Ru/C system was selected for subsequent studies since this system resulted in the highest PG yield from glucose.

3.2 Effects of reaction conditions

Fig. 1 shows the results of the study regarding the amount of ZnO in the ZnO + Ru/C system. When Ru/C was used without the addition of ZnO, the yield of PG was 9.3%. Furthermore, the reaction resulted in a variety of reaction products including hexitols (sorbitol and mannitol), and a large amount of gaseous components (methane, ethane, propane, butane) that were formed by the successive hydrogenolysis of glucose via hexitols, glycols, and alcohols [6]. In contrast, the PG yield improved significantly upon addition of ZnO, and was accompanied by a small amount of minor products such as hydroxyacetone (HA) and LA. Furthermore, the addition of ZnO drastically restricted the formation of hexitols and gaseous products. The PG yield was maximized when the added quantity of ZnO was about 40–80 mg. When ≥160 mg of ZnO was used, the PG yield slightly decreased in parallel with the increase in the yield of side products (HA, LA). On the other hand, the selective formation of LA was observed without the formation of PG when ZnO was used without Ru/C (Table 1, Entry 16).

The effects of temperature on the transformation of glucose into PG using the ZnO + Ru/C system are depicted in Fig. 2. Hexitols were the major product obtained at 413 K. In a separate experiment, we found that the hydrogenolysis of glucose into hexitols by Ru/C was the predominant reaction using the ZnO + Ru/C system at 413 K (See Table S2, Entries 6-11), which means that the reduction of glucose by Ru/C was faster than the retro-aldol reaction by ZnO. As the reaction temperature increased, the production of hexitols decreased, while the yield of PG increased. However, when the temperature was ≥473 K, the yield of PG decreased slightly and the amount of gaseous products increased. The effects of hydrogen pressure on the transformation of glucose into PG using the ZnO + Ru/C system are also depicted in Fig. 2. When the reaction was carried out with increasing hydrogen pressures from 0.4 MPa to 0.8 MPa, significant differences in the yield of PG were not observed. Thus, moderate conditions such as 453 K and 0.4 MPa were optimal.

In previous reports regarding the synthesis of PG from glucose [27-31], the reactions were carried out under hydrogen pressures of ≥5 MPa at ≥453 K in most cases. However, the efficient and high yielded synthesis of PG is possible at lower temperatures and pressures using the ZnO + Ru/C system, which will be very useful in regard to industrial production.

3.3 Reaction mechanism

When glucose was treated under hydrogen with Ru/C alone, a variety of reaction products were formed owing to the hydrogenolysis of random cleavage of C-C, and C-O bonds and hydrogenation, whereas the use of ZnO + Ru/C resulted in the selective formation of PG. On the other hand, when glucose was treated with ZnO alone, the formation of LA was predominant. Herein, we aim to propose a reaction pathway to explain the selective transformation of glucose to PG by the ZnO + Ru/C under mild conditions.

As can be seen from Scheme 1, two routes can be considered in the synthesis of PG from glucose, based on review of the literature [27-32]. Route A involves the synthesis of PG from glucose by the hydrogenolysis of hexitols (sorbitol or mannitol). In the synthesis of glycols directly from glucose or cellulose using 20% Ni/ZnO [27], Mu et al. proposed a hexitol route, Route A, in which glucose is rapidly converted into sorbitol and subsequently into glycols via hydrogenolysis. However, in this route, a number of various side products such as C1-C6 polyols and alkanes are produced due to the random cleavage of C-C and C-O bonds and hydrogenation [6]. Route B consists of the isomerization of glucose to fructose, retro-aldol reaction of fructose to glyceraldehyde (GAL) and dihydroxyacetone (DHA), dehydration of GAL to pyruvaldehyde (PAL), hydrogenation of PAL to PG via hydroxyacetone (HA). It is well known that fructose is converted to DHA and GAL by the retro-aldol reaction, and that PAL is derived by the dehydration of GAL [34, 35]. A similar route was proposed by Liang et al., who used a Cu-Cr catalyst with a basic catalyst [30], Chambon et al. who used Pt/AlW [34], and Deng et al. who used Ni-SnO_x/Al_2O_3 [35] and Pt-SnO_x/Al_2O_3 [20]. Thus, the reaction pathway using the ZnO + Ru/C system was scrutinized.

3.3.1 Effect of time

Fig. 3 shows the changes in the reaction with time over the ZnO + Ru/C catalytic system. In the initial period of the reaction (reaction time 0 indicates just after raising the temperature), fructose was formed in 35.6% yield. Then, the formation of hydroxyacetone (HA) began and increased to 36.6% after 2 h, while the yield of fructose decreased with time. After 2 h, the formation of PG began with a yield of 29.6% after 4 h and 38.6% after 12 h. This indicated that fructose and HA were the intermediates in the formation of PG, and hydrogenation from HA to PG was the rate-determining step. The separate experimental results provide a clear indication that ZnO is a very effective isomerization catalyst (See Table S1, Entries 5-7).

3.3.2 Studies on the intermediates

The reaction intermediates in Routes A and B are as follows: sorbitol and mannitol in Route A; fructose (Fru), dihydroxyacetone (DHA), glyceraldehyde (GAL), pyruvaldehyde (PAL), and hydroxyacetone (HA) in Route B. These intermediates were investigated as starting materials in the hydrogenation reaction over the ZnO + Ru/C system, as shown in Fig. 4.

When sorbitol and mannitol were used as starting materials, low yields of PG were obtained (10.8% and 8.8%, respectively), while the production of HA was not observed at all. Then, when the intermediates of Route B were used as the raw materials, HA and PG were predominantly obtained after 4 h and the PG yields increased concurrently with the decrease in the HA yields after 20 h. The increase in the PG yield was approximately consistent with the decrease in the HA yield. These results indicate that Route B is the dominant pathway in our ZnO + Ru/C system.

Based on these results, the proposed reaction route for the formation of PG from glucose using ZnO and Ru/C under low hydrogen pressures is shown in Scheme 2. It consists of the isomerization of glucose to fructose, formation of triose by the retro-aldol reaction of fructose, and their dehydration to form PAL. PG is produced by the hydrogenation of PAL by Ru/C via HA. Numerous studies have evaluated the formation of triose by the retro-aldol reaction in LA production [36-50]. In such examples, the reaction proceeds with Lewis acidic or basic catalysts that function in water. ZnO appears to play this role in our catalytic system. In fact, when ZnO alone was used for the transformation of glucose, fructose was firstly formed, followed by the formation of LA in the separate experiments (See Table S2, Entries 6-8.). The cleavage of the C3-C4 bond of fructose occurs due to the retro-aldol reaction by ZnO, which does not require any hydrogen pressure. Moreover, the hydrogenation of the intermediates (PAL and HA) to PG proceeds under low hydrogen pressures over Ru/C, whereas the hydrogenolysis of hexitols to PG hardly occurs. Therefore, glucose was transformed into PG at a low hydrogen pressure using this catalytic system.

Zhang et al. reported that a Ni-La_2O_3 catalyst exhibits a dual reaction mechanism: a major route involving the selective cracking of sugars into C_2 molecules, that is EG, and a minor route involving the hydrogenolysis of sugar alcohols [18]. In this case, La species catalyze the C2-C3 bond cleavage of the C_6 sugar, resulting in the formation of a C_2 molecule (glycolaldehyde) and C_4 molecule (erythrose), which are cracked into two molecules of C_2 molecules (glycolaldehyde). That is why EG is selectively formed. On the other hand, our ZnO+Ru/C system also has a dual route: a major route involving the selective cracking of sugars into C_3 molecules, that is PG, (Route B) and a minor route involving the hydrogenolysis of sugar alcohols (Route A). In our case, Zn species catalyze C3-C4 bond cleavage of C_6 sugars, resulting in the formation of two C_3 molecules (glyceraldehyde, and dihydroxyacetone) followed by the formation of PG. That is why PG is selectively formed. Thus, the essential differences between a Ni-La_2O_3 catalyst and a ZnO + Ru/C system are the roles of the catalysis in the selective C-C bond cleavage (retro-aldol reaction) of sugars.

3.4 Reusability

The reusability of the ZnO + Ru/C system was examined in reuse experiments, and the results are shown in Fig. 5. In the recycling reaction (Reuse 1, 2), the yield of PG slightly decreased from 38.1% obtained using a fresh system to 31.6% in reuse 2; the formation of hexitols and gasification also increased in reuse 2. However, the yield of PG was maintained at ≥30%. This may be because the inhibition of the formation of hexitols and gasification by ZnO was ineffective in the reactions in which the catalyst was reused. We also measured metal leaching by XRF (X-ray Fluorescence) as well as the particle size of Ru in the reuse experiments (Table S3). The dissolved zinc species were detected at a concentration of 30-50 ppm throughout all reuse experiments. Those results indicated that the dissolved zinc species might be involved in the reaction. Even if that is the case, ZnO could be reused to release soluble zinc species in situ for the reaction so that the ZnO + Ru/C system could be reusable. On the other hand, Ru metal species seemed to be mostly unchanged; leaching was not observed and only a small increase in particle size was observed. Further investigations regarding the active species and deactivation mechanism are needed.

4. Conclusions

In conclusion, using a combination of an acid-base catalyst (to catalyze the retro-aldol reaction) and a hydrogenation catalyst, it was possible to selectively convert glucose into PG (yield 38.1%) via decomposition into triose and hydrogenation under moderate conditions (453 K, 0.4 MPa). Furthermore, an important feature of this reaction system is that ZnO not only acts as the catalyst for the retro-aldol reaction, but also inhibits excessive hydrogenolysis by Ru/C and thus leads to an increase in the yield of PG.

The reaction route was elucidated by studying changes in the reaction over time, and evaluating different intermediates as starting materials. Specifically, the isomerization of glucose to fructose, formation of triose (DHA and GAL) from fructose by retro-aldol reaction by ZnO, formation of PAL by their dehydration, and subsequent hydrogenation of PAL leads to the formation of PG via HA over Ru/C. The retro-aldol reaction that included the C3-C4 bond cleavage of fructose did not require any hydrogen pressure, and the hydrogenation of the intermediates (PAL and HA) into PG proceeded under low hydrogen pressures. Therefore, the transformation of glucose to PG at a low hydrogen pressure was achieved. This catalyst system provides some insight into the efficient synthesis of PG from glucose, which can be achieved by combining and optimizing the retro-aldol reaction and hydrogenation steps.

However, a drawback of this method is that the catalyst system is composed of a physical mixture of two catalysts. Designing a catalyst on which the retro-aldol reaction and hydrogenation may occur on the same solid surface might increase the rate of the multistep reaction more efficiently. Supporting noble metals (hydrogenation catalyst) on the solid acid-base catalyst may improve the catalyst system. To further increase the yield of PG in the future by increasing the selectivity of the retro-aldol reaction route, precise control of the properties of the acid-base catalyst (quantity, strength, and quality), control of the hydrogenation catalyst in the formation of hexitols by the hydrogenolysis of glucose and consecutive gasification, and a balance between the rates of the retro-aldol and hydrogenation reactions are required. Such studies are ongoing in our laboratory.

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References

[1] M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 114 (2014) 1827-1870.

[2] J.L. Song, H.L. Fan, J. Ma, B.X. Han, Green Chem. 15 (2013) 2619-2635.

[3] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538-1558.

[4] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502.

[5] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew. Chem. Int. Ed. 46 (2007) 7164-7183.

[6] A.M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. Int. Ed. 51 (2012) 2564-2601.

[7] H. Kobayashi, T. Komanoya, S.K. Guha, K. Hara, A. Fukuoka, Appl. Catal. A: Gen. 409 (2011) 13-20.

[8] A. Fukuoka, P.L. Dhepe, Angew. Chem. Int. Ed. 45 (2006) 5161-5163.

[9] T. Komanoya, H. Kobayashi, K. Hara, W.-J. Chun, A. Fukuoka, ChemCatChem 6 (2014) 230-236.

[10] H. Kobayashi, Y. Hosaka, K. Hara, B. Feng, Y. Hirosaki, A. Fukuoka, Green Chem. 16 (2014) 637-644.

[11] G. Zhao, M. Zheng, J. Zhang, A. Wang, T. Zhang, Ind. Eng. Chem. Res. 52 (2013) 9566-9572.

[12] A. Wang, T. Zhang, Acc. Chem. Res. 46 (2013) 1377-1386.

[13] M.-Y. Zheng, A.-Q. Wang, N. Ji, J.-F. Pang, X.-D. Wang, T. Zhang, ChemSusChem 3 (2010) 63-66.

[14] G. Zhao, M. Zheng, A. Wang, T. Zhang, Chin. J. Catal. 31 (2010) 928-932.

[15] Y. Zhang, A. Wang, T. Zhang, Chem. Commun. 46 (2010) 862-864.

[16] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, Y. Shu, A.L. Stottlemyer, J.G. Chen, Catal. Today 147 (2009) 77-85.

[17] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Angew. Chem. Int. Ed. 47 (2008) 8510-8513.

[18] R. Sun, T. Wang, M. Zheng, W. Deng, J. Pang, A. Wang, X. Wang, T. Zhang, ACS Catal. 5 (2015) 874-883.

[19] Z. Wu, S. Ge, C. Ren, M. Zhang, A. Yip, C. Xu, Green Chem. 14 (2012) 3336-3343.

[20] T. Deng, H. Liu, Green Chem. 15 (2013) 116-124.

[21] H. Finch, ICIS Chem. Bus. 283 (2013) 38.

[22] L. Landress, H. Finch, ICIS Chem. Bus. 282 (2012) 46.

[23] J. Chan, E. Burridge, ICIS Chem. Bus. 281 (2012) 43.

[24] S. Wang, K. Yin, Y. Zhang, H. Liu, ACS Catal. 3 (2013) 2112-2121.

[25] R.V. Sharma, P. Kumar, A.K. Dalai, Appl. Catal. A: Gen. 477 (2014) 147-156.

[26] S. Wang, H. Liu, Catal. Lett. 117 (2007) 62-67.

[27] X. Wang, L. Meng, F. Wu, Y. Jiang, L. Wang, X. Mu, Green Chem. 14 (2012) 758-765.

[28] X.C. Wang, F. Wu, S.X. Yao, Y.J. Jiang, J. Guan, X.D. Mui, Chem. Lett. 41 (2012) 476-478.

[29] Z. Xiao, S. Jin, M. Pang, C. Liang, Green Chem. 15 (2013) 891-895.

[30] Z.H. Xiao, S.H. Jin, G.Y. Sha, C.T. Williams, C.H. Liang, Ind. Eng. Chem. Res. 53 (2014) 8735-8743.

[31] L. Zhou, A. Wang, C. Li, M. Zheng, T. Zhang, ChemSusChem 5 (2012) 932-938.

[32] L. Yang, X. Yan, Q. Wang, Q. Wang, H. Xia, Carbohydrate Res. 404 (2015) 87-92.

[33] Y. Liu, C. Luo, H.C. Liu, Angew. Chem. Int. Ed. 51 (2012) 3249-3253.

[34] F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem, ChemSusChem 6 (2013) 500-507.

[35] T.Y. Deng, H.C. Liu, J. Mol. Catal. A Chem. 388 (2014) 66-73.

[36] X.Y. Yan, F.M. Jin, K. Tohji, A. Kishita, H. Enomoto, AlChE J. 56 (2010) 2727-2733.

[37] F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem, Appl. Catal. B Environ. 105 (2011) 171-181.

[38] Z. Liu, W. Li, C.Y. Pan, P. Chen, H. Lou, X.M. Zheng, Catal. Commun. 15 (2011) 82-87.

[39] A. Onda, T. Ochi, K. Kajiyoshi, K. Yanagisawa, Catal. Commun. 9 (2008) 1050-1053.

[40] W. Zeng, D.-g. Cheng, F. Chen, X. Zhan, Catal. Lett. 133 (2009) 221-226.

[41] J.B. dos Santos, F.L. da Silva, F. Altino, T.D. Moreira, M.R. Meneghetti, S.M.P. Meneghetti, Catal. Sci. Technol. 3 (2013) 673-678.

[42] C. Sanchez, I. Egues, A. Garcia, R. Llano-Ponte, J. Labidi, Chem. Eng. J. 181 (2012) 655-660.

[43] D. Esposito, M. Antonietti, ChemSusChem 6 (2013) 989-992.

[44] F.-F. Wang, C.-L. Liu, W.-S. Dong, Green Chem. 15 (2013) 2091-2095.

[45] L.Z. Kong, G.M. Li, H. Wang, W.Z. He, F. Ling, J. Chem. Technol. Biotechnol. 83 (2008) 383-388.

[46] X.Y. Yan, F.M. Jin, K. Tohji, T. Moriya, H. Enomoto, J. Mater. Sci. 42 (2007) 9995-9999.

[47] M. Bicker, S. Endres, L. Ott, H. Vogel, J. Mol. Catal. A Chem. 239 (2005) 151-157.

[48] Y.L. Wang, W.P. Deng, B.J. Wang, Q.H. Zhang, X.Y. Wan, Z.C. Tang, Y. Wang, C. Zhu, Z.X. Cao, G.C. Wang, H.L. Wan, Nat. Commun. 4 (2013) DOI: 10.1038/ncomms3141.
[49] M.S. Holm, S. Saravanamurugan, E. Taarning, Science 328 (2010) 602-605.
[50] C.B. Rasrendra, I.G.B.N. Makertihartha, S. Adisasmito, H.J. Heeres, Top. Catal. 53 (2010) 1241-1247.

Table 1. Transformation of glucose on Ru/C combined with various acid/base catalysts.
Conditions: glucose, 180 mg; catalyst, 82 mg; 5%-Ru/C, 30 mg; water, 20 mL; 453 K; 20 h; H_2, 0.4 MPa.

Entry	Catalyst	Liquid product yields[a]/ mol-C%							TOC yield[b] / mol-C%	Gaseous product yield[a]/ mol-C%	Carbon balance[c] / mol-C%
		PG	HA	LA	Glycerol	EG	Hexitols	Diols			
1	ZnO	38.1	2.9	1.6	0	5.1	3.4	11.9	83.2	3.3	86.5
2	Fe_3O_4	31.2	4.1	1.7	0	2.6	3.4	11.1	82.1	4.0	86.1
3	La_2O_3	29.7	2.8	4.7	0	1.5	5.8	5.1	72.5	12.2	84.7
4	CeO_2	29.5	2.3	1.0	2.2	3.8	8.4	6.8	68.1	11.3	79.4
5	Yb_2O_3	24.3	2.0	2.3	0	1.5	14.6	6.5	71.7	7.0	78.7
6	Y_2O_3	17.0	2.0	5.7	0	1.5	8.8	3.5	62.2	11.2	73.4
7	Sm_2O_3	16.3	2.4	7.3	0.0	1.8	5.1	3.1	66.5	9.1	75.6
8	MgO	15.8	3.2	10.5	0	1.3	0.6	1.2	72.5	6.7	79.2
9	WO_3	12.8	1.7	0	1.9	20.9	8.6	8.6	66.5	12.0	78.5
10	SnO_2	11.6	1.9	0	3.8	3.6	20.8	3.3	70.6	16.4	87.0
11	Nb_2O_5	4.9	3.3	0	0	1.0	24.6	6.5	69.3	8.9	78.2
12	Al_2O_3	3.3	0.7	0	3.5	0.8	9.2	2.0	41.3	33.1	77.4
13	TiO_2	1.7	2.6	0.8	1.8	0.4	5.4	2.1	41.6	33.0	74.6
14	HZSM-5	1.3	0	0	3.2	0.8	5.7	0.3	29.9	35.4	65.3
15	none	9.3	0	0	0	0	16.7	2.4	59.9	26.8	86.7
16	ZnO alone	0.0	4.6	26.4	0	0	0	0	72.5	8.9	81.4

PG, propylene glycol; EG, ethylene glycol; HA, hydroxyacetone; LA, lactic acid; Hexitols: sorbitol and mannitol; Diols: 1,2-butanediol and 1,2-hexanediol; Gaseous products: methane, ethane, propane, butane, carbon monoxide, and carbon dioxide. Max error: ±2%.

[a] Liquid and gaseous product yields were determined by HPLC and GC analysis, respectively.

[b] TOC yields indicate the total organic carbon yield of the liquid products determined by TOC analysis.
[c] Carbon balance was determined by adding TOC and gaseous product yields.

Table 2. Transformation of glucose to propylene glycol on various carbon-supported noble metal catalysts combined with ZnO.

Conditions: glucose, 180 mg; ZnO, 82 mg; 5%-metal/C, 30 mg; water, 20 mL; 453 K; 20 h; H_2, 0.4 MPa.

Catalyst	Product Yield/ mol-C%						
	PG	HA	LA	Glycerol	Hexitols	Others	Gas
Ru/C	38.1	2.9	1.6	0	3.4	17.0	3.3
Rh/C	31.4	4.2	1.9	0	2.5	7.4	5.4
Pd/C	31.4	2.0	2.9	2.0	2	4.8	1.8
Pt/C	30.5	2.9	0	2.4	1.4	11.1	1.6

PG, propylene glycol; HA, hydroxyacetone; LA, lactic acid; Hexitols: sorbitol and mannitol; Others: ethylene glycol, 1,2-butanediol, and 1,2-hexanediol; Gas: methane, ethane, propane, butane, carbon monoxide, and carbon dioxide.

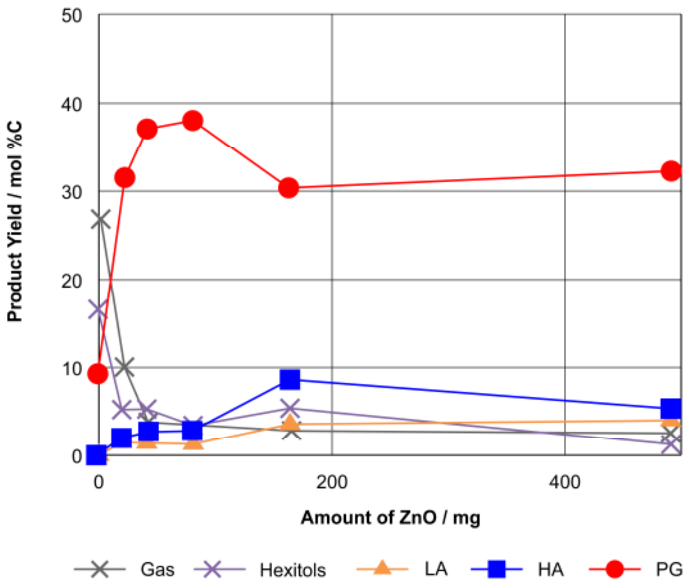


Fig. 1. Effect of amount of ZnO on the transformation of glucose into propylene glycol on ZnO + Ru/C system.

Conditions: glucose, 180 mg; 5%-Ru/C, 30 mg; water, 20 mL; H_2, 0.4 MPa; 453 K.

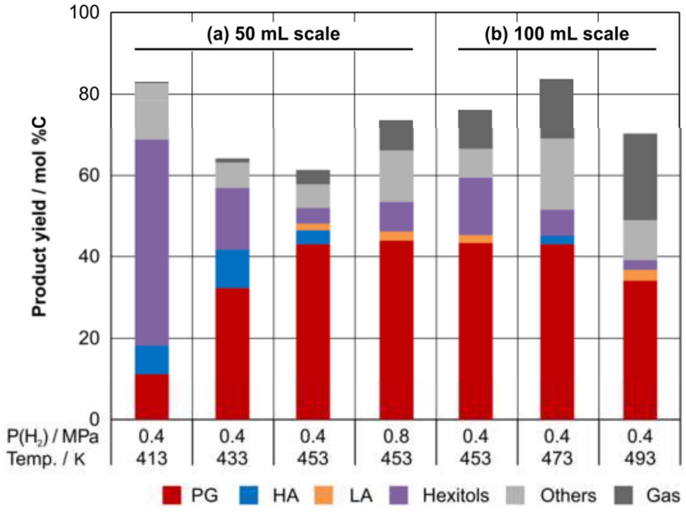


Fig. 2. Effect of reaction conditions on the transformation of glucose into propylene glycol on ZnO + Ru/C system.

Conditions: (a) glucose, 180 mg; ZnO, 82 mg; 5%-Ru/C, 30 mg; water, 20 mL; 20 h; (b) glucose, 360 mg; ZnO, 164 mg; 5%-Ru/C, 60 mg; water, 40 mL; 8 h.

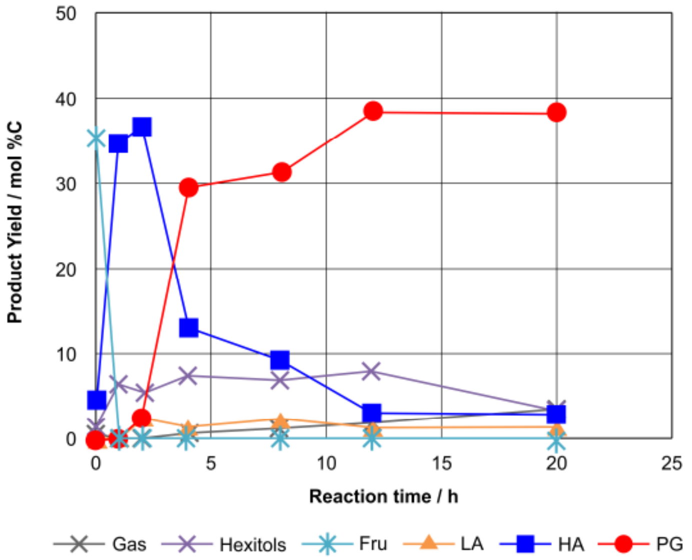


Fig. 3. Effect of time in the transformation of glucose into propylene glycol on ZnO + Ru/C system.

Conditions: glucose, 180 mg; ZnO, 82 mg; 5%-Ru/C, 30 mg; water, 20 mL; H_2, 0.4 MPa; 453 K.

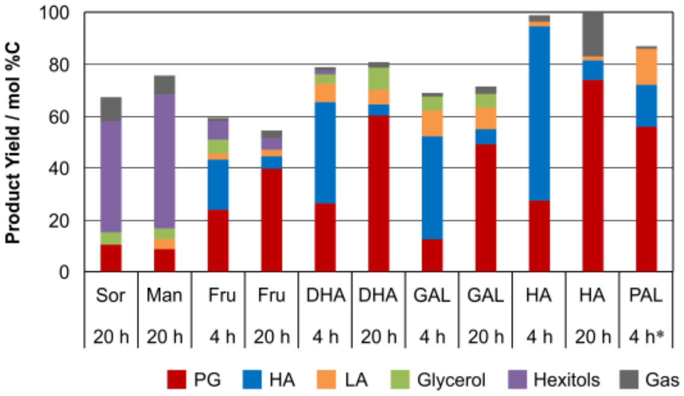


Fig. 4. Transformation of various substrates into propylene glycol on ZnO + Ru/C system.

Conditions: substrates equivalent to 6 mmol of carbon; water, 20 mL; ZnO, 82 mg; 5%-Ru/C, 30 mg; H_2, 0.4 MPa; 453 K. * double scale, substrate fed at reaction temp.

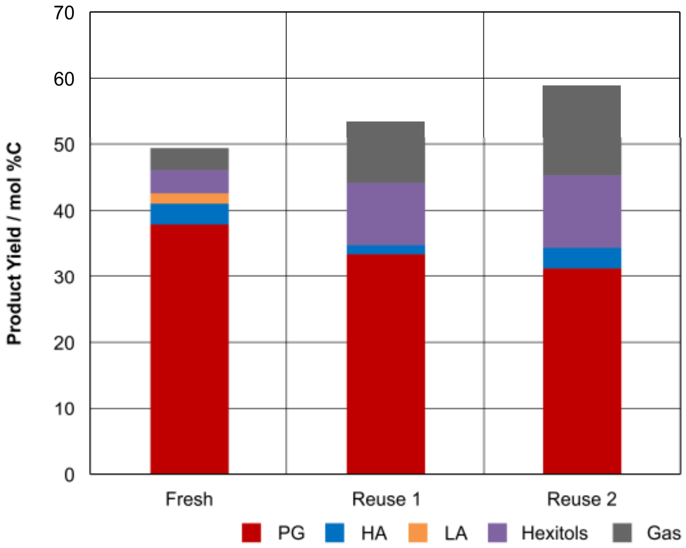
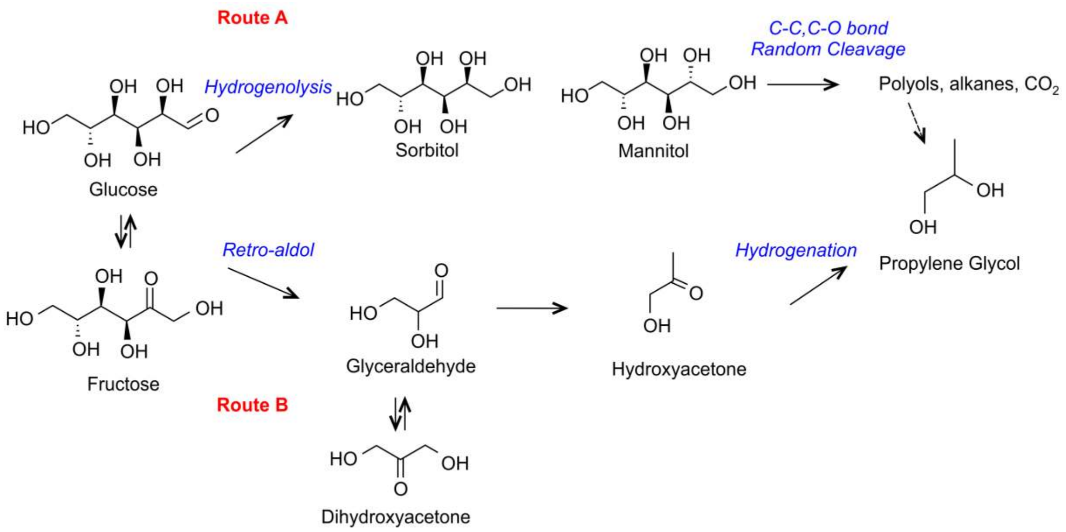


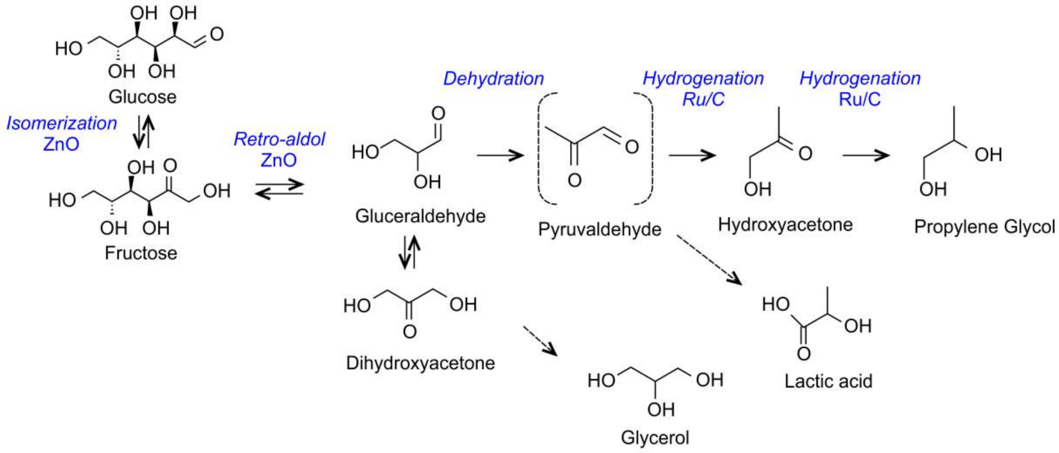
Fig. 5. Reuse of ZnO + Ru/C catalyst system.

Conditions: glucose, 180 mg; ZnO, 82 mg; 5%-Ru/C, 30 mg; water, 20 mL; 453 K; 20 h.

Note: 40 ppm of Zn was observed in the solution after the reaction with fresh catalysts for 20 h.



Scheme 1. Possible routes for the transformation of glucose into propylene glycol.



Scheme 2. Proposed reaction pathway for the transformation of glucose into propylene glycol on Ru/C combined with ZnO.

Supplementary material:

Experimental

N_2 adsorption–desorption isotherms were measured at 77 K using a BELSORP-mini instrument (MicrotracBEL Corp., Japan) after degassing at 393 K to remove physically adsorbed impurities for 8 h under vacuum. The BET surface area, BJH, and MP pore size distribution were calculated according to the desorption branch of the isotherms.

The Ru metal particle sizes were obtained using a JEM-2100F (JEOL, Japan) Field Emission Electron Microscope (FE-TEM).

NH_3-TPD and CO_2–TPD measurements were carried out using TPD-1-ATw equipment (MicrotracBEL Corp., Japan). Prior to the adsorption of probe molecules, the catalyst (0.10 g) was pretreated in He at 773 K for 1 h to remove moisture and other adsorbed gases. After cooling to 373 K, the catalyst was saturated with 0.5 vol% NH_3/He or 0.5 vol% CO_2/He for 30 min and then purged with He to remove excess adsorbed gas (NH_3 or CO_2) for 30 min. Subsequently, the sample was heated to 1073 K at a ramp rate of 10 K/min and the NH_3 or CO_2 desorption was detected by a quadrupole mass spectrometer. The total amounts of desorbed NH_3 and CO_2 on ZnO are listed in Table S1.

Table S1. Textural and acid-base properties of the catalysts.

Catalyst	Surface area[a] (m^2/g)	Mesopore volume[b] (cm^3/g)	Micropore volume[c] (cm^3/g)	Particle size of Ru[d] (nm)	Amount of acid site[e] (μ mol/g)	Amount of base site[f] (μ mol/g)
ZnO	3.5	0.014	-	-	6.6	14
5% Ru/C	803	0.54	0.31	1.6	-	-

a: BET surface area determined from N_2 adsorption.

b: Mesopore volume determined by BJH method for 1.3 nm−100 nm.

c: Micropore volume determined by MP method for 0.42 nm−2 nm.

d: Particle size of Ru determined by TEM images (average of thirty particles).

e: The total amount of desorbed NH_3 determined by TPD measurements.

f: The total amount of desorbed CO_2 determined by TPD measurements.

Table S2. Transformation of various substrates on ZnO and/or Ru/C.

Entry	Substrate	Catalyst	Temp (K)	Time (h)	Conversion (%)	Product yield/ mol-C%										
						PG	HA	LA	Glycerol	EG	Hexitols	Sorbitol	Mannitol	Diols	Gas	er products
1[a]	Glyceraldehyde	ZnO	453	4	100	0	7.1	29.4	0	0	0			3.8	3.9	AcA(3.8)
2[a]	Glyceraldehyde	ZnO	453	20	100	0	5.3	30.5	0	0	0			0	4.3	AcA(3.9)
3[a]	Glyceraldehyde	none	453	4	100	0	0	6.2	0	0	0			4.9	4.0	AcA(4.9)
4[a]	Glyceraldehyde	none	453	20	100	0	0	6.7	0	0	0			5.0	3.9	AcA(5.0)
5[a]	Glucose	ZnO	453	0	51.5	0	0	3.4	0	0	0			0	0.2	), GA(3.8)
6[a]	Glucose	ZnO	413	0	n.a.	0	0	0	0	0	0			0		Fru(11.8)
7[a]	Glucose	ZnO	413	4	58.9	0	0	2.9	0	0	0			0	0.3	Fru(34.8)
8[a]	Glucose	ZnO	413	20	100	0	5.5	29.6	0	0	0			0		AcA(3.0), HMF(2.5)
9[a]	Glucose	Ru/C	413	0	57.7	0	0	0	0	0	56.2	54.9	1.3	0	0.1	
10[a]	Glucose	Ru/C	413	4	100	0	0	0	0	0	68.7	52.7	16.0	0	3.0	
11[a]	Glucose	Ru/C	413	20	100	0	0	0	2.5	0	24.8	9.8	15.0	0	18.2	
12[a]	Glucose	ZnO + Ru/C	453 468	1 3	100	19.3	18.5	0	0	3.0	10.5	10.5	0	11.0	1.2	
13[a]	Glucose	ZnO + Ru/C	453 493	1 3	100	29.7	5.5	1.6	0	3.8	10.0	9.1	0.9	11.0	3.5	GA(0.9)
14[a]	Cellulose 50 mL	ZnO + Ru/C	453	20	n.a.	3.1	0.8	1.0	0.5		0	0.2		3.2	18.9	
15[b]	Cellulose 100 mL	ZnO + Ru/C	513	4	100	10.9	4.5	1.9	1.1	4.9	5.8	3.3	2.5	4.9	21.7	

PG, propylene glycol; EG, ethylene glycol; HA, hydroxyacetone; LA, lactic acid; Hexitols: sorbitol and mannitol; Diols: 1,2-butanediol and 1,2-hexanediol; Gas: methane, ethane, propane, butane, carbon monoxide, and carbon dioxide; AcA, acetic acid; Fru, fructose; GA, glycolic acid; HMF, 5-hydroxymethylfurfural.

Conditions: (a) substrates equivalent to 6 mmol of carbon; water, 20 mL; ZnO, 82 mg; 5%-Ru/C, 30 mg; H_2, 0.4 MPa; (b) substrates equivalent to 12 mmol of carbon; water, 40 mL; ZnO, 164 mg; 5%-Ru/C, 60 mg H_2, 0.8 MPa

Table S3. Leaching of Zn and Ru and particle size of Ru in the reuse experiments.

	Zn concentration in liquid phase[a] (ppm)	Ru concentration in liquid phase[a] (ppm)	Zn recovery[b] (wt%)	Particle size of Ru (nm)
Fresh	30	0	99.1	1.6
Reuse 1	45	0	97.7	2.2
Reuse 2	50	0	96.2	2.3

a: Zn or Ru concentration in liquid phase was determined by XRF.

b: Zinc recovery was calculated by the following formula:

[1-(sum of weight of Zinc in all the reuse reaction solution / weight of Zinc put in the reactor in first run)] × 100%.