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ARTICLE TYPE

Highly Efficient Conversion of Biomass-derived Glycolide to Ethylene Glycol over CuO in Water

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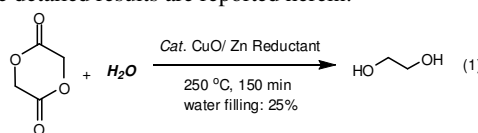
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The efficient conversion of biomass-derived glycolide into ethylene glycol over CuO in water was investigated. The reaction of glycolide was carried out with 25 mmol Zn and 6 mmol CuO with 25% water filling at 250 °C for 150 min, which yielded the desired ethylene glycol at 94% yield.

Ethylene glycol (EG) is an important intermediate chemical and solvent that has been widely used in antifreeze, liquid detergents, biodegradable polyester fibers, cosmetic products, pharmaceuticals, explosives, and plasticisers, among other products and often as a protecting group for carbonyl groups in organic synthesis.¹ Because of its industrial importance, the synthesis of ethylene glycol is of considerable interest. The current conventional process involves industrial production from petroleum-derived ethylene via hydration of the intermediate ethylene oxide.² However, over-consumption of fossil fuels and their limited supply has necessitated a reduction in our dependence on petroleum oil and the development of renewable and green energy sources.³ Over the past several decades, biomass as a source for producing high value-added chemicals has attracted much attention due to its excellent properties: it is abundant, renewable, and produces less pollution, among other advantages.⁴ The conversion of biomass-derived carbohydrates into 1,2-diols is currently receiving increasing attention.⁵

The hydrogenation of esters to alcohols is an important reaction in organic chemistry.⁶ However, the reaction of ester groups, which have a less electrophilic carbonyl group, is still a great challenge of both academic and practical importance, especially for cyclic di-esters.⁷ To date, very few studies have reported this transformation. Glycolides-important biomass-derived compounds, can be obtained from biomass sources such as sugar cane, sugarbeet, and immature grape juice.⁸ Recently, Milstein *et al.* reported the hydrogenation of biomass-derived glycolide to the corresponding ethylene glycol by well-defined electron rich bipyridine-based PNN [2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl) pyridine] Ru (II) pincer complexes under mild conditions.⁹ However, these reactions still have considerable drawbacks, including the use of high-pressure gaseous hydrogen (10-50 atm), which is not easy to obtain at a reduced energy cost; organic solvents (THF or 1,4-dioxane); expensive prepared catalysts (PNN-Ru); and longer reaction times (12-48 h). Therefore, the development of a suitable reaction process for the production of ethylene glycol from glycolide is highly desirable.

Previously, we and other groups reported a series of experiments investigating the conversion of CO₂¹⁰ and biomass¹¹ into value-added chemicals in high-temperature water. In this process, water acts not only as an excellent environmentally benign reaction medium but also as a source of hydrogen generated by the reduction of cheap metal reductants.¹² Recently, some research groups have also reported that ZnO can be cycled to Zn through a ZnO/Zn redox process using solar energy.¹³ On the basis of these findings, we reasoned that glycolide might produce ethylene glycol in a similar manner. The results obtained showed that the hypothesis proved feasible, and the reaction of glycolide proceeded effectively in the presence of CuO to give the desired ethylene glycol in high yield with high selectivity (Eq. 1). The detailed results are reported herein.



Initially, we carried out an experiment to investigate the effectiveness of metal or metal oxides in the synthesis of ethylene glycol from glycolide in the presence of 6 mmol Cu and 20 mmol Zn at 250 °C for 150 min in water (water filling: 25%). The reaction proceeded efficiently and produced the desired ethylene glycol at a 23% yield, as determined by GC-FID and GC-MS (entry 4). The solid residual remaining after the reaction was analysed by XRD (see Supporting Information, Fig. SI-1-SI-3), which showed that Cu was still present in the solid samples, while Zn was oxidised to ZnO. In this case, Zn acts as a reductant, and Cu acts as a catalyst for the conversion of glycolide. Next, we screened various catalysts to determine the most suitable one. The results are summarised in Table 1. The reaction did not give the desired ethylene glycol at all in the absence of both reductant and catalyst or in the presence of the catalyst only (entries 1 and 3). The reaction in the presence of 20 mmol Zn, without the addition of any catalyst, gave the desired ethylene glycol at a 9% yield (entry 2), indicating the importance of the combined use of both reductant and catalyst. Among the various catalysts we investigated (entries 5-13), Cu₂O and CuO improved the transformation efficiency and afforded ethylene glycol at a good yield with no glycolide recovery observed by thin layer chromatography (TLC) (entries 12 and 13); CuO gave much better results. A low yield was observed with the catalysts Fe₂O₃, Fe₃O₄, and Ni₂O₃ (entries 7, 8 and 9), which no reaction

occurred when the catalysts Fe, Co, TiO₂, or ZrO₂ were used (entries 5, 6, 10 and 11).

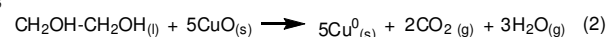
Table 1. Effect of catalysts on the yields of ethylene glycol.^a

Entry	Reductant	Catalyst	Yield (%) ^b
1	-	-	0
2	Zn	-	9
3	-	Cu	0
4	Zn	Cu	23
5	Zn	Fe	0
6	Zn	Co	0
7	Zn	Fe ₂ O ₃	14
8	Zn	Fe ₃ O ₄	10
9	Zn	Ni ₂ O ₃	10
10	Zn	TiO ₂	0
11	Zn	ZrO ₂	0
12	Zn	CuO	45
13	Zn	Cu ₂ O	37

^a Reaction conditions: glycolide: 0.5 mmol; Zn: 20 mmol; catalyst: 6 mmol; water filling: 25%; time: 150 min; temp: 250 °C. ^b The yield is calculated as the percentage of ethylene glycol to the initial glycolide on the carbon base.

The residual solid sample remaining after reaction in the presence of CuO and Zn was analysed by XRD. It can be seen that Cu and ZnO existed in solid samples in Fig. SI-3. Unexpectedly, the Cu was observed in the solid sample instead of CuO. From this result, we reasoned that CuO as a catalyst might be reduced completely to Cu by *in situ*-formed hydrogen via the oxidation of Zn in high-temperature water.¹⁴ We measured the Cu ion concentration in the solution by ICP and found only a small amount of Cu ions (<1 ppm) in the liquid sample. This result suggested that Cu was most likely present in the solid residual. Thus, we performed the experiment under the same reaction conditions without the addition of glycolide to investigate the role of *in situ*-formed hydrogen. The results suggested that our hypothesis was completely realistic. CuO was reduced completely to Cu by *in situ*-formed hydrogen, and Cu and ZnO were found in the solid samples by XRD analysis after reaction.

Next, we investigated the effect of the amount of CuO on the yield of ethylene glycol. The reaction was conducted in the presence of 20 mmol Zn with 25% water filling at 250 °C for 150 min and 3 to 12 mmol CuO, the results are shown in Fig. SI-4. The yield of ethylene glycol increased significantly at first as the amount of CuO increased from 0 to 6 mmol, and the best yield of 45% ethylene glycol was achieved at 6 mmol CuO. The yield decreased as the amount of CuO was further increased. This may be because more CuO would lead to more cracking products such as acetic acid, CO₂ and H₂O (Eq. 2), which might result in a decrease in glycolide selectivity.¹⁵



Finally, a carbon balance was conducted. The results showed that the conversion of glycolide for liquid products was approximately 98%. The main product observed for this transformation was ethylene glycol, with a yield of 45%, other products included acetic acid, which had a 5% yield, and unknown compounds, CO₂ was the gas product observed in the transformation.

Experiments were performed using the various active metals, such as Zn, Al, Fe, Mn, and Mg, to search for a suitable reductant for the conversion of glycolide to ethylene glycol. Fig. 1(a) shows the effect of different reductants on the yields of ethylene glycol. Among the various metals tested, Zn was highly effective in the conversion of glycolide and gave the best yield of ethylene glycol (45%) compared to Al, Mg, Mn, and Fe. Thus, Zn was chosen for the following experiments.

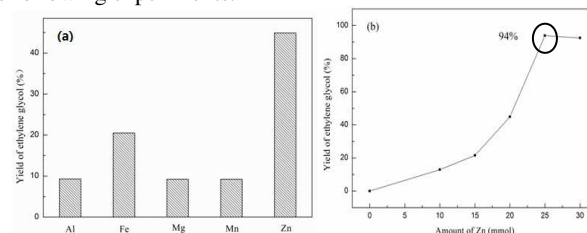


Fig. 1. (a) Effect of reductants (glycolide: 0.5 mmol; Metal: 20 mmol; CuO: 6 mmol; water filling: 25%; time: 150 min; temp: 250 °C). (b) Effect of the amount of Zn (glycolide: 0.5 mmol; CuO: 6 mmol; time: 150 min; temp: 250 °C; water filling: 25%).

Fig. 1(b) shows the effect of the amount of Zn on the yield of ethylene glycol, using concentrations from 0 to 30 mmol. No ethylene glycol was observed without the addition of Zn. The yields of ethylene glycol improved gradually as the amount of Zn was increased from 0 to 15 mmol, then remarkably increased from 15 to 25 mmol. The yield of ethylene glycol decreased somewhat when the amount of Zn exceeded 25 mmol. The results indicated that the improvement in hydrogen production with an increased amount of Zn in high temperature water is in favourable for the conversion of glycolide to ethylene glycol. The optimal amount of Zn was 25 mmol, yielding ethylene glycol at a maximum value of 94%.

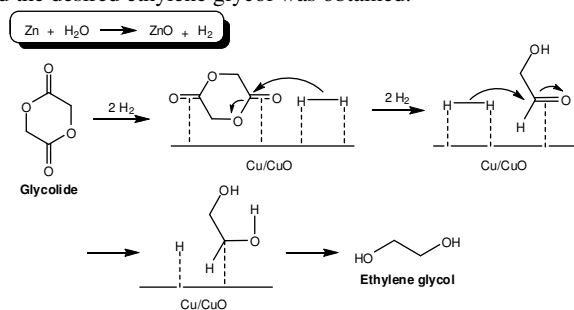
The effect of water filling on the yield of ethylene glycol from glycolide was investigated at different water filling values from 15% to 45% with the addition of 6 mmol CuO and 25 mmol Zn at 250 °C for 150 min. The results are shown in Fig. SI-5. First, the ethylene glycol yield increased slightly when the water filling was changed from 15% to 20%. The yield of ethylene glycol significantly increased as the water filling increased from 15% to 25% and then decreased after 25%. The optimum water filling was 25% obtaining the highest yield of 94% ethylene glycol from glycolide. The decrease in conversion of glycolide at a higher water filling is most likely due to a decreased concentration of the initial starting materials when water filling increased.

The effect of different temperatures from 100 to 250 °C on the yields of ethylene glycol was examined. The results are shown in Fig. SI-6 (A). The reaction did not take place at 100 °C, and no ethylene glycol was observed. This finding indicated that a lower reaction temperature was completely ineffective in the conversion of glycolide. The yield of ethylene glycol improved gradually as the reaction temperature was increased gradually from 100 °C to 200 °C, and then remarkably increased as the temperature increased from 200 to 250 °C. The maximum value of 94% ethylene glycol was obtained at 250 °C. However, the temperature was limited to 250 °C due to the maximum tolerated temperature of the Teflon material.

Experiments were performed by changing the reaction time from 100 to 300 min at 250 °C to examine the effect of reaction

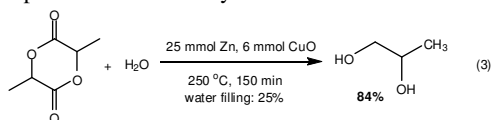
time on the yield of ethylene glycol. Fig. SI-6 (B) indicates that the yield increased drastically with increasing reaction time for the first 150 min, the maximum yield was obtained at 150 min, with a value of 94%. However, the yield of ethylene glycol decreased as the time was further increased. The decreasing yield of ethylene glycol after 150 min can be attributed to the decomposition of produced ethylene glycol. To confirm this assumption, the reaction of ethylene glycol was performed in the presence of 6 mmol Cu and 25 mmol ZnO with 25% water filling at 250 °C for 300 min. The GC-FID results indicated that the initial concentration of ethylene glycol 120 mmol/L was decomposed and decreased to 52 mmol/L, XRD analysis also showed that Cu and ZnO had not changed and were still present in the solid residual. These results suggest that a long reaction time has an influence on the yield of ethylene glycol obtained in the reaction in the presence of Cu and ZnO.¹⁵

Based on previous reports⁸ and the findings in this work, the pathway for the conversion of glycolide to ethylene glycol over CuO in high temperature water (HTW) was proposed in Scheme 1. First, hydrogen was formed via the oxidation of Zn in high temperature water.¹⁶ The *in situ*-formed hydrogen was adsorbed on the surface of Cu/CuO though the formation of hydrogen bonds between hydrogen and Cu/CuO. Additionally, glycolide was adsorbed on the surface of Cu/CuO by the combination of Cu/CuO with carbonylic C and O atoms.¹⁷ When the hydrogen reacted with glycolide molecules, an intermediate 2-hydroxyacetaldehyde was obtained. Next, both the intermediate 2-hydroxyacetaldehyde and the hydrogen formed were adsorbed on the surface of Cu/CuO, first, H was added to C=O and an intermediate linked by an α -bond was formed, then the intermediate acquired one more H from the surface of Cu/CuO and the desired ethylene glycol was obtained.



Scheme 1. Proposed mechanism for the formation of ethylene glycol.

Following the success in developing the conversion of glycolide to ethylene glycol in high temperature water, we next examined the scope of the reaction with respect to DL-lactide, and the results are shown in Eq. 3. The reaction of DL-lactide was carried out in the presence of 25 mmol Zn and 6 mmol Cu with 25% water filling at 250 °C for 150 min and gave the desired 1,2-propanediol at an 84% yield.



In summary, we first developed a highly efficient conversion for the synthesis of ethylene glycol from biomass-derived glycolide over CuO in high temperature water. With optimized conditions in hand, the maximum value of 94% ethylene glycol

was achieved in the presence of 25 mmol Zn and 6 mmol CuO with 25% water filling at 250 °C for 150 min. The conversion of DL-lactide also produced 1,2-propanediol at 84% yield under optimal reaction conditions. This study provided a significant process for the conversion of biomass-derived cyclic di-esters to 1,2-diols with high selectivity and high yield. Further research is underway to develop efficient methods for the conversion of biomass-derived compounds to value-added chemicals in water.

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