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Supporting Information

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

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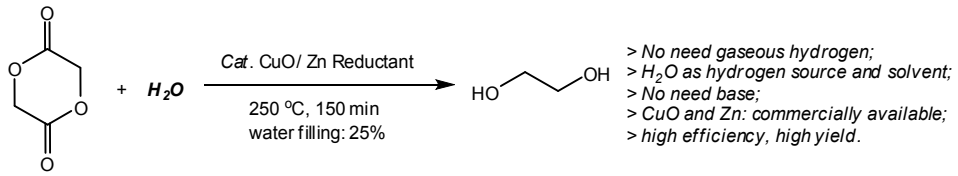

Contents of Supporting Information

(6 Pages)

1. General Information: Glycolide (≥ 99%，Sigma-Aldrich) was used as reagent and ethylene glycol (≥ 99.5%, GC) was purchased from TCI for the qualitative analysis of the products in the liquid samples. As preliminary tests, various active metals including Zn, Mg, Fe, Al, Mn (AR, Sinopharm Chemical Reagent Co., Ltd) were used as reductants in powder form, metal oxide including Fe_3O_4, Fe_2O_3, Ni_2O_3, TiO_2, ZrO_2, Cu_2O and CuO (150-200 mesh, i.e. 0.074-0.1 mm) (AR, Sinopharm Chemical Reagent Co., Ltd) were used as catalysts in powder form.

2. Product analysis: After reaction, the liquid samples were analyzed with a GC-FID (Shimadzu GC-2010) equipped with an DB-FFAP capillary column with dimensions of 30 m × 250 μm × 0.25 μm for the quantification of ethylene glycol. The liquid samples' analyses were confirmed by GC-MS (Aglient GC7890A-MS5975C) equipped with an HP Innowax polyethylene glycol capillary column with dimensions of 30 m × 250 μm × 0.25 μm. Thin layer chromatography (TLC) was performed on aluminum-precoated plates of silica gel 60 with an HSGF254 indicator and visualized under UV light or developed by immersion in the solution of 0.6 % $KmnO_4$ and 6 % K_2CO_3 in water. The solid samples were characterized by X-ray diffraction (XRD) (Shimadzu XRD-6100) to determine the composition and phase purity.

The yield of ethylene glycol is defined as the carbon mole ratio of produced ethylene glycol to the initial glycolide as follows below. The yields were obtained from experiments over three times and relative error was less than 5%.

$$Yield,\ mmol\ \% = \frac{C\ in\ ethylene\ glycols,\ mmol}{C\ in\ the\ initial\ glycolide,\ mmol}\ \text{x}\ 100\ \%$$

3. General Procedure for the Synthesis of ethylene glycol from glycolide: Experiments were conducted in a Teflon-lined stainless steel batch reactor with an inner volume of 30 mL. The typical procedure for the synthesis of ethylene glycol from glycolide was as follows. First, glycolide (0.058 g, 0.5 mmol), Zn (1.63 g, 25 mmol), CuO (0.48 g, 6 mmol) and ultrapure water (7.5 mL) were loaded into reactor. Next, nitrogen was charged into reactor in order to exclude the effect of air and then the reactor was sealed and placed into an oven that had been preheated to the desired temperature. After 150 min, the reactor was removed from the oven and cooled to room temperature with an electric fan. The reaction time was defined as the time when the reactor's

temperature was up to 250 °C. Water filling was defined as the ratio of the volume of the ultrapure water (7.5 mL) put into the reactor to the inner volume (30 mL) of the reactor. Final, after cooling off, liquid sample was collected and filtered with 0.45 μm Syringe Filter, the highest yield of ethylene glycol (94%) was obtained. Solid sample was collected and washed with deionized water and ethanol several times to remove impurities and dried in the oven at 50 °C for 24 h.

4. General Procedure for the Synthesis of 1,2-propanediol from DL-lactide: Experiments were conducted in a Teflon-lined stainless steel batch reactor with an inner volume of 30 mL. The typical procedure for the synthesis of ethylene glycol from glycolide was as follows. First, DL-lactide (0.072 g, 0.5 mmol), Zn (1.63 g, 25 mmol), CuO (0.48 g, 6 mmol) and ultrapure water (7.5 mL) were loaded into reactor. Next, nitrogen was charged into reactor in order to exclude the effect of air and then the reactor was sealed and placed into an oven that had been preheated to the desired temperature. After 150 min, the reactor was removed from the oven and cooled to room temperature with an electric fan. The reaction time was defined as the time when the reactor's temperature was up to 250 °C. Water filling was defined as the ratio of the volume of the ultrapure water (7.5 mL) put into the reactor to the inner volume (30 mL) of the reactor. Final, after cooling off, liquid sample was collected and filtered with 0.45 μm Syringe Filter, the highest yield of 1,2-propanediol (84%) was obtained. Solid sample was collected and washed with deionized water and ethanol several times to remove impurities and dried in the oven at 50 °C for 24 h.

5. GC-MS chart of ethylene glycol

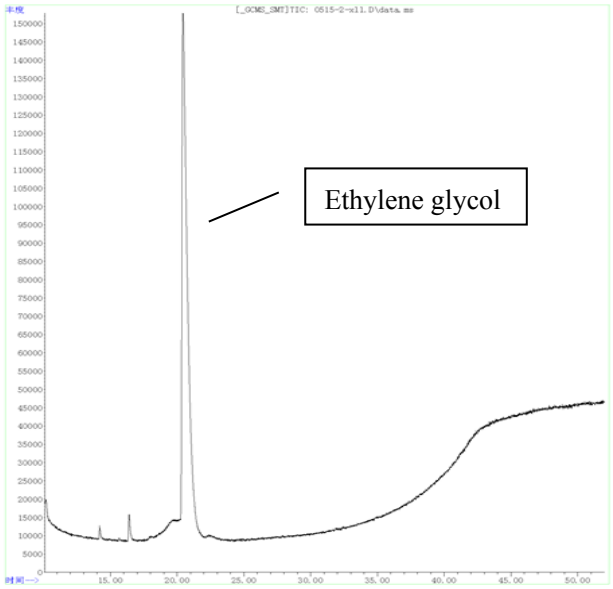

Fig. SI-1. GC/MS chart of ethylene glycol

GC-FID chart of ethylene glycol

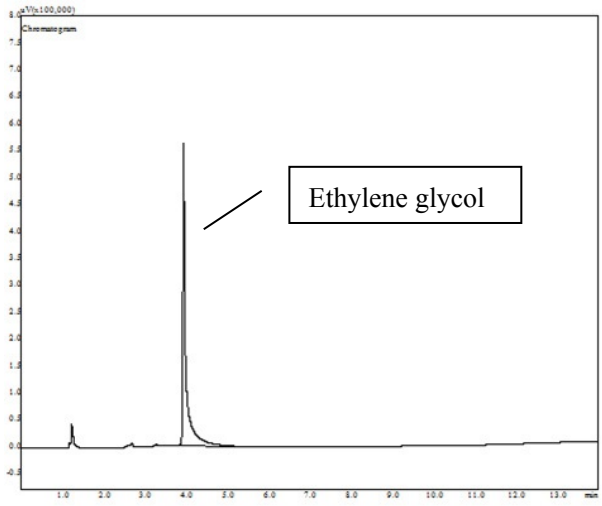

Fig. SI-2. GC-FID chart of ethylene glycol

6. XRD analysis

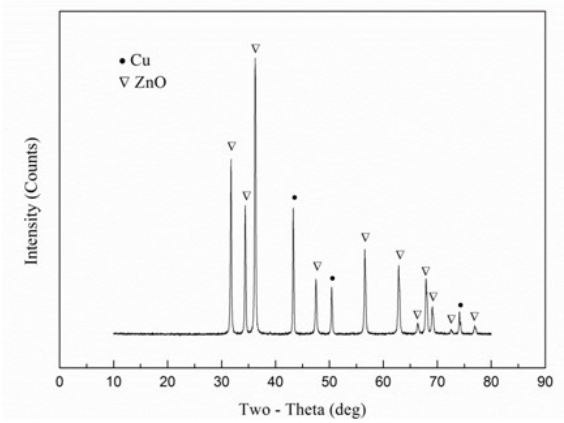

Fig. SI-3. XRD patterns of solid samples after reaction (glycolide: 0.5 mmol; Zn: 20 mmol; Cu (or CuO): 6 mmol; water filling: 25%; time: 150 min; temp: 250 ^{o}C).

7. Complementary reaction optimization data

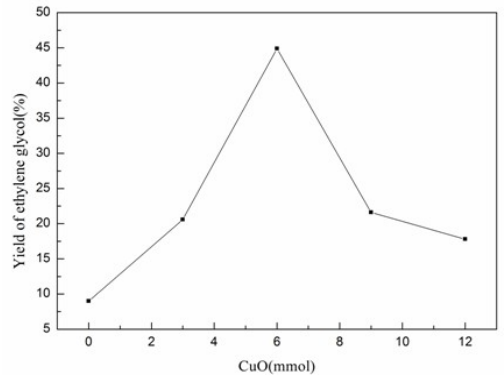

Fig. SI-4. Effect of the amount of CuO on the yields of ethylene glycol (glycolide: 0.5 mmol; Zn: 20 mmol; temp: 250 ^{o}C; time: 150 min; water filling: 25%).

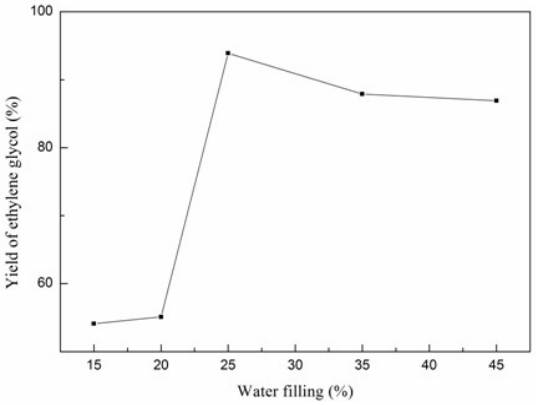

Fig. SI-5. Effect of water filling on the yields of ethylene glycol (glycolide: 0.5 mmol; Zn: 25 mmol; CuO: 6 mmol; time: 150 min; temp: 250 ^{o}C).

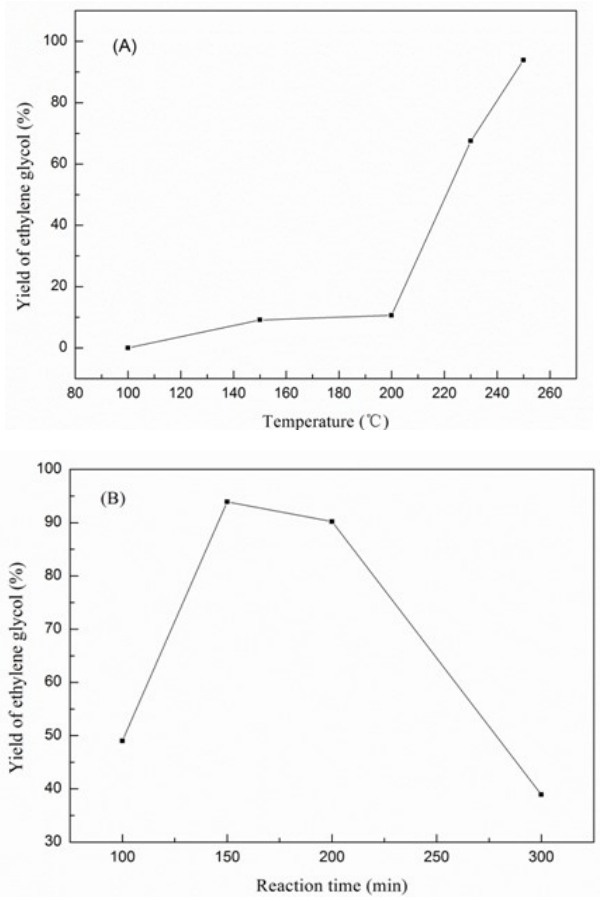

Fig. SI-6. Effect of reaction temperature and reaction time on the yields of ethylene glycol ((A) glycolide: 0.5 mmol; Zn: 25 mmol; CuO: 6 mmol; time: 150 min; water filling: 25%; (B) glycolide: 0.5 mmol; Zn: 25 mmol; CuO: 6 mmol; temp: 250 ^{o}C; water filling: 25%).