



Heterogeneous Cu₂O-mediated ethylene glycol production from dimethyl oxalate

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ABSTRACT

An efficient process for the conversion of dimethyl oxalate into ethylene glycol with high selectivity and high yield over Cu₂O was investigated. In situ formed Cu as a true catalytically active species showed a good catalytic performance for DMO conversion to produce EG in 95% yield.

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1. Introduction

Ethylene glycol (EG), as an important intermediate chemical and solvent, has often been found as antifreeze, lubricant, plasticizer, and surfactant, which own an important status in chemical industry [1,2]. Due to its application value and the increasing industrial demand, the development of the efficient methods for the synthesis of EG is attracting great interest. Currently, the industrial synthetic methods of EG are mainly the oxidation of petroleum-derived ethylene [3,4]. However, over-dependence on fossil fuels still has drawbacks. In view of problems, to develop a research towards more economical and efficient synthetic methods of EG is necessary.

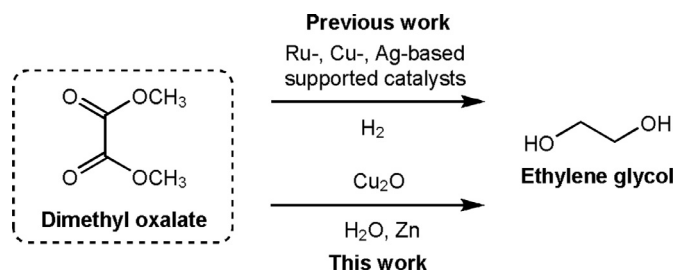
In recent years, the hydrogenation of biomass-derived DMO to EG had been receiving increasing attention [5]. However, DMO with a less electrophilic carbonyl group is a stable compound and the reaction to produce EG is still a great challenge (Scheme 1). Since the 1970s, some interesting results in the hydrogenation of DMO to EG had been reported using ruthenium-based homogeneous catalysts, such as H₄Ru₄(CO)₈(PBU₃)₄ [6,7] and Ru(acac)₃ [8]. In 2010, Dai et al. first reported a facile and efficient one pot route for the gas-phase selective hydrogenation of DMO to EG over the

Ag/SiO₂ catalyst [9,10]. Recently, the supported copper-based catalysts, such as Cu/HMS [11], CuB/HMS [12], Cu/SiO₂ [13], Cu-Cr₂O₃ [14] and Cu/ZnO/Al₂O₃ [15], have been reported to exhibit a high catalytic activity for the hydrogenation of DMO to EG, and good conversion of DMO and selectivity to EG were obtained in the transformation. However, although these methods had proven to be extremely efficient in the hydrogenation of DMO to EG, most of them still have their numerous limitations, for instance, the use of high-pressure gaseous hydrogen, organic solvents, expensive prepared catalysts, and longer reaction times, etc. In addition, the use of Ru-based catalysts can form byproducts and separated difficultly products from catalysts, and the toxicity of Cr-containing Cu-based catalysts is harmful to humans and can cause a severe environmental pollution. Therefore, the development of an efficient synthetic process is highly desirable in the conversion of DMO to EG.

The development of economical hydrogen sources for the conversion of DMO to EG is essential. Previously, our studies [16–21] reported some interesting results in high temperature water. In this process, water acts not only as environmentally benign reaction medium but also as a source of hydrogen, which could be advantageous to avoid the use of gaseous hydrogen. For example, we reported an efficient method for the production of EG from glycolide in high yield over CuO in water [18]. Furthermore, ZnO can be cycled to Zn through a ZnO/Zn redox process using solar energy [22–24]. Inspired by the findings above, we herein present a new strategy for the conversion of DMO to EG over heterogeneous Cu₂O in high temperature water (Scheme 1).

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Scheme 1. Formation of EG from DMO.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Dimethyl oxalate (Aladdin Chemical, > 98%) was used as the initial reactant. EG (TCI Scientific Ltd, > 98%) and some compounds in the reactions such as ethanol and methanol (J&K Chemical, > 98%) were used as test materials. Zn power (AR) was obtained from Aladdin Chemical Reagent Co. Ltd. Cu_2O power (under 200-mesh in size) and other metals were obtained from Sinopharm Chemical Reagent Co. Ltd, China.

2.1.2. Experimental procedure

All reactions were performed in a Teflon reactor, whose internal volume is 30 mL covered by a metal reaction kettle. The experiment procedure is as follows. Firstly, the 7.5 mL water mixture of test materials with 0.5 mmol DMO, 25 mmol Zn, and 5 mmol CuO were loaded into the reactor. Then the reactor was put into a drying oven at a desired temperature. The reaction time was defined as the duration the reactor was kept in the oven. Water filling was defined as the ratio of the volume of the solution to the internal volume (30 mL) of the reactor. After a desired reaction time, the reactor was quickly moved out from the drying oven to cool down. Finally, after cooling off, the liquid samples were collected and filtered with $0.45 \mu\text{m}$ filter membrane for GC-MS and HPLC analysis. Solid samples were washed with deionized water and ethanol several times and dried in air for XRD analysis.

2.1.3. Analysis methods

After the reactions, the qualitative analysis results of liquid samples were based on the GC-MS analysis (Agilent 7890A). And the quantitative estimation of EG and byproducts was based on average values obtained from the HPLC analysis (Agilent 1260 serials, VIS detector) of three samples. Details on the conditions of

GC-MS/FID and HPLC analyses are available elsewhere [25]. The EG yield is defined as the percentage of EG to initial DMO on the mole basis, calculated as following equation:

$$Y (\%) = \frac{\text{Mole of product}}{\text{Initial mole of DMO}} \times 100$$

3. Results and discussion

Initially, a tentative experiment was conducted to investigate whether hydrogenation of DMO could produce EG in the presence of CuO using 2.8 MPa H_2 with 25% water filling at 250°C for 2 h. However, no desired EG was obtained, indicating that the use of gaseous hydrogen was not effective for the conversion of DMO in high temperature water. Thus, we focused our study on the use of in situ formed hydrogen for the synthesis of EG from DMO.

3.1. Metals or metal oxides screening

The effect of metals or metal oxides was investigated whether DMO could be converted into EG in the presence of CuO and Zn with 25% water filling at 250°C for 2 h. As a result, the HPLC chromatograms and GC-MS spectrum of the liquid samples showed that the desired EG appeared, and EG was the main product with little amounts of ethanol [26] and methanol as shown in Fig. 1(a) and (b).

The effect of metals or metal oxides, such as Cu, Fe, Ni, CuO , and Cu_2O on the yield of EG was tested. The results showed in Table 1 that the desired EG was obtained in 22%, 28%, 62% and 70% yields over Ni, Co, CuO , and Cu_2O , respectively (entries 6–9). Among them, Cu_2O exhibited a high catalytic performance for the conversion of DMO and the corresponding EG yield of 70% was obtained (entry 9). However, no desired EG was obtained when the other metals or metal oxides, such as Fe, Cu, Cr, Al_2O_3 , and Fe_2O_3 were used (entries 4, 5, 10–14). In addition, no desired EG was obtained in the absence of metals or metal oxides and/or reductant in the transformation (entries 1–3), which indicated that the importance of the combined use of both reductant and metals or metal oxides was fairly crucial to this reaction.

To investigate the role of the metals or metal oxides in the conversion of DMO into EG, the XRD patterns of the solid residue after the reaction showed that Zn was oxidized to ZnO , and Co and Ni still existed. This indicated that Zn acted as a reductant and Co and Ni as catalysts (Figure SI-1b and SI-1c). Unexpectedly, Cu was observed in the solid residue instead of Cu_2O when Cu_2O was used, and the most likely reason is that Cu_2O was reduced completely to Cu by in situ formed hydrogen via the oxidation of Zn in high-temperature water (Figure SI-1a) [15]. To confirm this hypothesis,

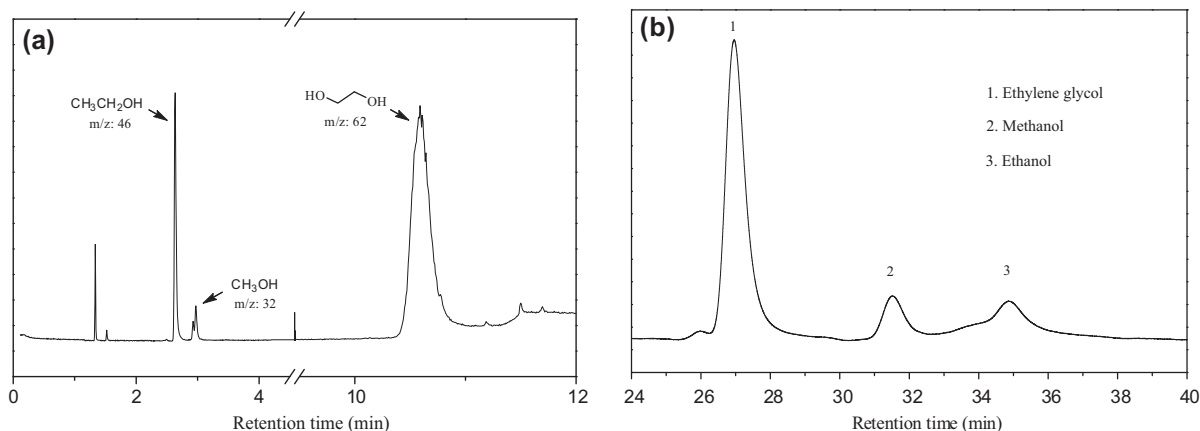


Fig. 1. (a) GC-MS spectrum of liquid samples after the reaction, (b) HPLC chromatograms of liquid samples after the reaction.

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