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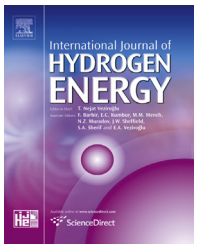

Hydrothermal conversion of ethylene carbonate to ethylene glycol

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ABSTRACT

A novel process for the conversion of ethylene carbonate (EC) to ethylene glycol (EG) in high temperature water was investigated. As a result, even there is no external catalyst and additive, the reaction of EC proceeded well and provided the desired EG in 99% yield with 25% water filling at 250 °C for 2 h. Moreover, only CO_2 as by-product was observed in the process. High temperature water exhibits an unique merits and plays an catalytic role for EC conversion. From viewpoint of practice, this work provides a simple, environmentally benign, catalyst/additive-free process for the production of ethylene glycol from ethylene carbonate.

Introduction

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 plasticizers, etc, 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].

Ethylene carbonate (EC) as an important compound can be obtained via the insertion of CO_2 to ethylene oxide, the lots of synthetic methods has been reported in the literature [3,4]. As a general rule, conversion of EC into EG is a feasible and commercial method. To date, many studies have been developed for this transformation [5–9]. The most frequently used methods for the production of EG are catalytic hydrolysis of EC and catalytic hydrogenation of EC in organic solvent. Recently, Ding et al. reported the highly efficient homogeneous catalytic

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hydrogenation of EC to produce simultaneous the corresponding EG and methanol in the presence of a (PNP)Ru^{II} pincer complexes as the catalysts under relatively mild conditions (THF, 140 °C, 50 atm H_2), and high yields of EG and methanol were obtained in the process [9]. However, these methods still face challenges in academic and industry, including the use of high-pressure gaseous hydrogen, which is difficult to store and sometimes dangerous; or expensive synthesized catalysts; or organic solvents; or longer reaction time. Therefore, development of efficient process for the production of EG from EC is still highly desired.

Recently, hydrothermal treatment in the conversion of CO_2 into high value-added chemicals has attracted much attention and gradually becomes a novel way of utilizing CO_2 because of its unique merits (dielectric constant, density and caloric capacity, etc.) [10–13]. Previously, our group reported some interesting results in the conversion of CO_2 into value-added chemicals in high-temperature water [14–16]. In this process, water is not only environmentally benign reaction medium but also the most abundant hydrogen resource by the reduction of cheap metal reductants [17]. More recently, we also reported new results in efficient synthesis of diols from biomass-derived compounds over CuO in high yield with high selectivity in high temperature water [18,19]. On the basis of these findings, it occurs to us that EC may produce EG in similar manners.

Herein, we present a highly efficient hydrothermal conversion of EC to EG without the addition of any catalysts and additives. The reaction of EC proceeded well to give the desired EG in high yield along with CO_2 as a by-product. (Scheme 1). The role of high temperature water for the transformation is also discussed.

Experimental

Experimental materials

EC (>99%) as the initial reactant was purchased from J&K. EG (≥99%, chromatographic grade, J&K Scientific Ltd.) was used for quantitative analysis. Zn (200 mesh, Aladdin) was used as the reductant. Pd/C, MnO_2, $CuFe_2O_4$, TiO_2, ZrO_2, Co, Cu, Ni, Sn, Mo, Cr (200 mesh, Sinopharm Chemical Reagent Co., Ltd) were also used in the experiment.

Experimental procedure

All experiments were carried out in a Tefion-lined stainless steel batch reactor with an internal volume of 30 mL. 10 g/L EC was used in all experiments. The typical procedure for the synthesis of EG was as follows. First, EC, ultrapure water and catalyst were loaded into reactor. Then, nitrogen was charged into reactor in order to exclude the effect of air and then the sealed reactor was put into an drying oven, it will take about 20 min to be preheated to the desired temperature. After a desired reaction time, the reactor was quickly moved from the drying oven to cool down. Liquid sample was collected and then filtered with 0.45 μm Syringe Filter. 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. The schematic of the reactor system was shown in Figure SI-1.

Substrates 0.85 mmol, methyl and ethyl substituted ethylene carbonates, was used. The procedure is similar with the synthesis of EG from EC.

Product analysis

After the reaction was quenched, solution samples were collected and filtered for GC-MS analysis (Aglient GC7890A-MS5975C) equipped with an INNOVAX polyethylene glycol capillary column with dimensions of 30 m × 250 μm × 0.25 μm, and GC-FID. Details on the conditions of GC-MS/FID analyses are available elsewhere [20]. The total residual organic carbon concentration in liquid samples was also measured with a TOC analyzer (Shimadzu TOC-V). The gas product was detected by thermal conductivity detector (GCMS-QP2010, Shimadzu). 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. Solid samples were collected and analyzed by X-ray diffractometer (Shimadzu XRD-6100) to determine the composition and phase purity.

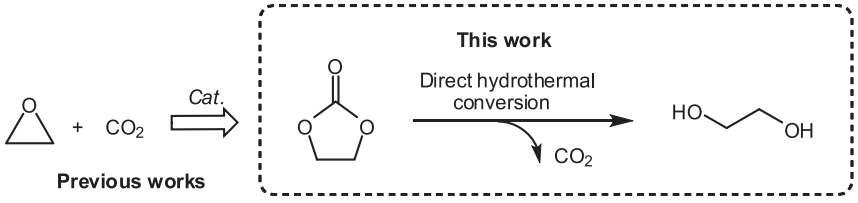
The yield of EG is calculated as the following equation.

$$\text{The yield } (\%) = \frac{\text{the amount of EG obtained}}{\text{the amount of EG in theory}} \times 100\%$$

Results and discussion

EC conversion with and without catalysts

As is known to all, hydrogenation of carbonyl compound is an important reaction to produce alcohol. In our previous studies, *in situ*-formed hydrogen by the oxidation of Zn in water is effective for the conversion of carbonyl compound. Therefore, we screened initially various metal or metal oxides as catalysts to investigate the feasibility of converting EC to EG



Scheme 1 – Process for the formation of EG.