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Catalytic conversion of ethyl lactate to 1,2-propanediol over CuO☆

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ABSTRACT

An efficient conversion of biomass-derived ethyl lactate to 1,2-propanediol (1,2-PDO) over CuO was investigated. Among the catalysts we tested, CuO, Cu_2O and Co showed excellent catalytic activity for the conversion of ethyl lactate to 1,2-PDO in water, and CuO was more active and gave the best result. The 1,2-PDO yield of 93.6% was achieved when Zn acted as a reductant. The results indicated that *in situ* formed hydrogen by the oxidation of Zn in water is more effective than gaseous hydrogen, which failed to produce the 1,2-PDO from ethyl lactate. From a practical point of view, the present method may provide a useful route for the production of 1,2-PDO from ethyl lactate.

1. Introduction

Over the past several decades, consumption of fossil fuels and their limited supply have necessitated a reduction in our dependence on petroleum oil. Biomass as a source for producing high value-added chemicals has attracted much attention due to its excellent properties, such as abundant, renewable, and less pollution. A number of efficient methods in the conversion of biomass to chemicals including various alcohols [1], hydroxymethylfurfural [2] and dimethylfuran [3,4] had been reported.

1,2-propanediol (1,2-PDO), a bulk commodity chemical that is mainly used for the production of unsaturated polyester resins [5] and as an antifreeze and de-icing agent and in pharmaceuticals, cosmetics, and foods [6], is industrially produced by the hydration of propylene oxide derived from petrochemical resource [7]. With reducing fossil fuel reserves, the development of renewable and green synthetic methods for the 1,2-PDO production is necessary [8,9]. Recently, the hydrogenation of biomass-derived ethyl lactate to 1,2-PDO using gaseous hydrogen over transition metal catalysts has attracted much interest, which provides an environmental benign alternative to the petroleum-based process for the 1,2-PDO production [10–14]. Ethyl lactate can be easily obtained on a large amount ($120000\ t \cdot a^{-1}$) by the fermentation of renewable sources such as agricultural crops and biomass streams. Several groups had disclosed that Ru-based catalysts were effective in significantly increasing the activity and selectivity for the conversion of ethyl lactate to 1,2-PDO due to their excellent intrinsic activities. The examples include: RuB/TiO_2 [11], RuB/-Al_2O_3 and RuB/SBA-15 [12], and Ru/SiO_2 [14]. Li *et al.* reported vapor-phase hydrogenolysis of ethyl lactate to 1,2-PDO over Co/SiO_2 and Cu/SiO_2, and the 1,2-PDO selectivity was in excess of 98% at 90.2% ethyl lactate conversion [13]. However, these methods suffer from several drawbacks, such as the use of high-pressure gaseous hydrogen which is not easy to obtain at a reduced energy cost; organic solvents; the use of prepared catalysts, such as Ru-based catalysts supported on some additives (boron, tin or iron, *etc.*) increased the cost of the preparation and separation process; formation of by-products and longer reaction times. Thus, the development of a cleanly and economically synthetic approach of 1,2-PDO from ethyl lactate is of great importance.

One of the major challenges in the conversion of ethyl lactate to 1,2-PDO is the development of economical hydrogen sources. The previous works showed that the hydrothermal process had a promising potential for environmental benign conversion of biomass into useful chemicals [15–18]. Water is not only the most abundant hydrogen resource in the process, but also a greener solvent. Recently, we reported an efficient process for the formation of ethylene glycol from glycolide over CuO in water, and a high yield of 94% was achieved [19]. It occurs to us that the conversion of ethyl lactate to 1,2-PDO may be implemented in a similar manner. Herein, we present a highly efficient conversion of ethyl lactate to 1,2-PDO in the presence of CuO in high temperature water (Fig. 1).

2. Experimental

2.1. Experimental materials

Ethyl lactate (>97%) as the initial reactant was purchased from TCI. 1,2-PDO (≥99.8%, chromatographic grade, J&K Scientific Ltd.) was used

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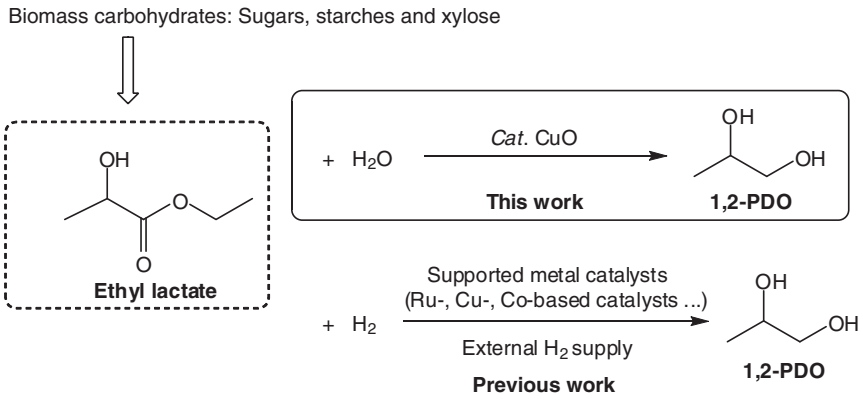

Fig. 1. Previous and current process for the formation of 1,2-PDO.

for quantitative analysis. Zn [200 mesh (0.075 mm), Aladdin] was used as the reductant. Ni, Fe, Al, Mn, Mg, CuO, Al_2O_3, CuO, Cu_2O, Fe_2O_3 and Fe_3O_4 [200 mesh (0.075 mm), Sinopharm Chemical Reagent Co., Ltd.] were also used in the experiment.

2.2. Experimental procedure

All experiments were carried out in a Teflon-lined stainless steel batch reactor with an internal volume of 30 ml. 0.47 mmol ethyl lactate was used in all experiments. The typical procedure for the synthesis of 1,2-PDO was as follows. First, desired ethyl lactate, reductant, catalyst and ultrapure water were loaded into the reactor. Then, nitrogen was charged into the reactor in order to exclude the effect of air and then the sealed reactor was put into a 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 filtered with a 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 Fig. 2.

2.3. Product analysis

After the reaction was quenched, solution samples were collected and filtered for GC–MS analysis (Agilent GC7890A–MS5975C) equipped with an HP INNOWax polyethylene glycol capillary column with dimensions of 30 m × 250 μm × 0.25 μm, and HPLC analysis (Agilent 1260 serials, Vis detector). Details on the conditions of HPLC and GC–MS 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 a thermal conductivity detector (TCD, Agilent Technologies). 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 an X-ray diffractometer (Shimadzu XRD-6100) to determine the composition and phase purity.

The yield of 1,2-PDO is calculated as the following equation:

$$\text{The yield} = \frac{\text{the amount of 1,2-PDO obtained}}{\text{the amount of 1,2-PDO in theory}} \times 100\%.$$

3. Results and Discussion

3.1. Catalyst screening

First of all, a series of experiments were carried out to investigate the feasibility of ethyl lactate to 1,2-PDO in the presence of 5 mmol Co and 26 mmol Zn with 17% water filling at 250 °C for 150 min. The GC–MS image of the liquid product after the reaction clearly showed that the desired 1,2-PDO was observed (Fig. 3). The yield of 37.6% was achieved

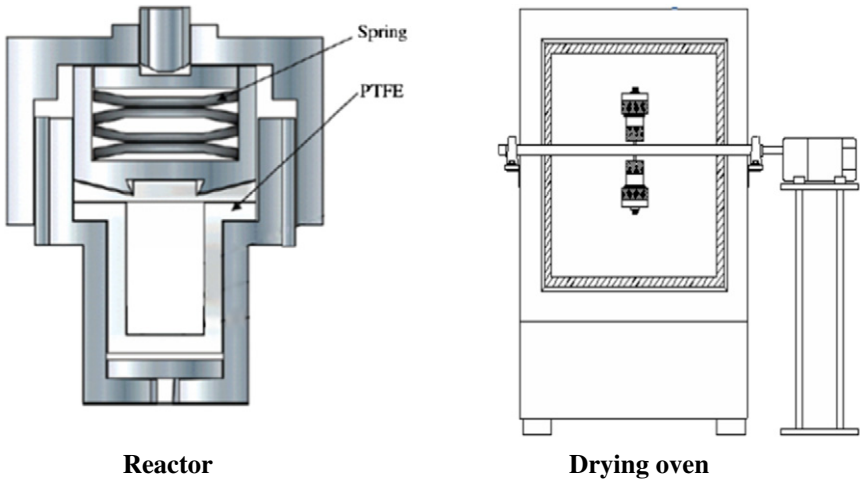

Fig. 2. Schematic of batch reactor system.