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A novel approach for 1,2-propylene glycol production from biomass-derived lactic acid

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A B S T R A C T

A novel and efficient process for the production of 1,2-propylene glycol with high productivity and high selectivity from biomass-derived lactic acid over CuO was investigated. As a result, CuO exhibited a high catalytic activity while Zn acted as a reductant for the conversion of lactic acid to 1,2-propylene glycol. Among the various reaction parameters, such as catalysts, reductants, temperature, water filling and reaction time we investigated, a 93% yield of 1,2-propylene glycol in the presence of 0.83 mmol lactic acid, 5 mmol CuO and 30 mmol Zn with 35% water filling at 250 °C for 2 h was achieved. In addition, a carbon balance at optimum reaction conditions by TOC indicated that approximately 99% lactic acid was converted into liquid products in the transformation. In situ formed hydrogen by the oxidation of Zn in water is effective for the transformation compared to added gases hydrogen. The proposed mechanism for the conversion of lactic acid to 1,2-propylene glycol over CuO is also discussed.

1. Introduction

The development and utilization of renewable and clean biomass resource have attracted much attention because of the energy shortages and environmental pollution, caused by the over-consumption of non-renewable fossil fuel. As an abundant, renewable, low-cost, and less pollution resource, biomass resource has its own advantages in comparison with fossil resource. Previous researches showed that the application of biomass as the raw material for the production of chemical stocks has a promising future to replace the petroleum-derived materials [1–4].

1,2-Propylene glycol, an important multi-purpose chemical that has an extensive use as anti-freeze agent, chemical application, consumer products and foods [5,6], is industrially produced by the hydration of propylene oxide that derived from petroleum-derived propylene or by the hydroperoxide process [7]. Due to its industrial application value, the synthesis of 1,2-propylene glycol is attracting interest in recent years, 1,2-propylene glycol and other polyols can be effectively obtained from cellulose and chitin derived sugars [8,9]. Lactic acid as an important biomass-derived compound, which has high reactivity because of the connection of hydroxyl and carboxyl groups, can be obtained by the fermentation of agricultural crops and biomass waste [10–12], the catalytic hydrogenation of lactic acid into 1,2-propylene glycol is becoming a feasible and commercial method to use the renewable biomass energy (Eq. (1)). For example, in the 1930s, Adkins et al. reported the conversion of neat ethyl lactate into 1,2-propylene glycol over Raney Ni in exceeding 80% yield at very high hydrogen pressures (>25 MPa) [13,14]. Broadbent et al. performed the catalytic hydrogenation of free lactic acid into 1,2-propylene glycol in 84% yield over unsupported rhenium black at 27 MPa hydrogen pressure [15]. Dumesic et al. converted lactic acid into 1,2-propylene glycol in 88% yield over a silica-supported copper catalyst with a lower 0.10 MPa hydrogen pressure [16]. Miller et al. reported the catalytic hydrogenation of lactic acid into 1,2-propylene glycol in 90% yield over ruthenium supported on activated carbon at 14 MPa hydrogen pressure [17]. More recently, Baeck et al. reported a novel method for the synthesis of 1,2-propylene glycol from lactic acid over ruthenium catalyst at hydrogen pressure 50 bar and gave middle yields [18,19]. However, these methods still face academic and industrial challenges, such as use of high pressure gases hydrogen, expensive synthesized catalysts and longer reaction time. Thus, the development of an efficient process for the production of 1,2-propylene glycol from lactic acid is highly desired.

Recently, hydrothermal treatment in the conversion of biomass into high value-added chemicals has caught much attention and gradually becomes a novel way of utilizing the renewable energy because of its unique merits (dielectric constant, density, caloric

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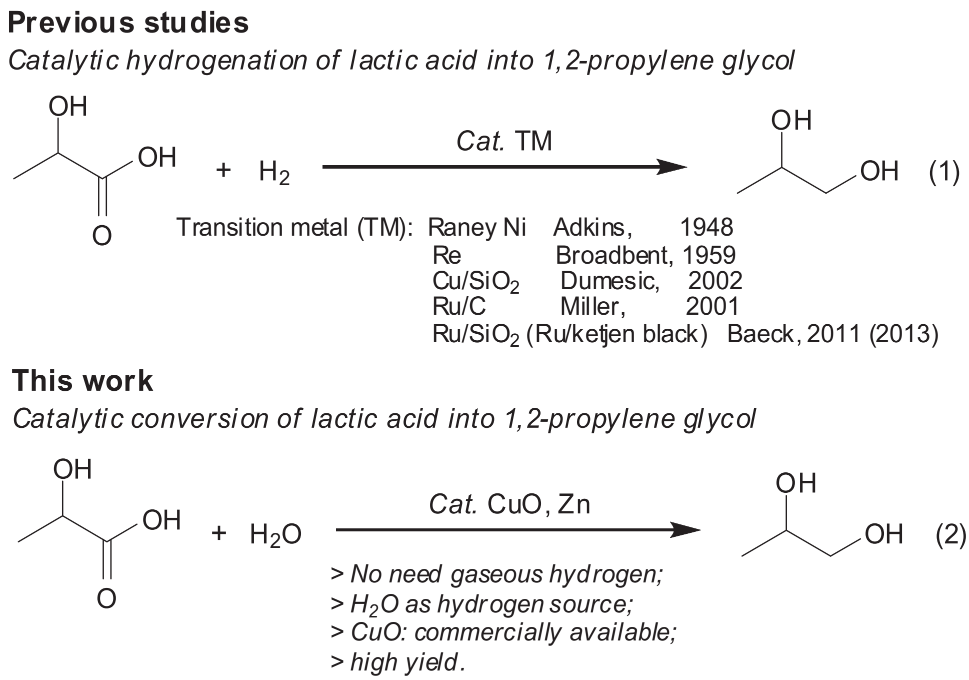

Scheme 1. Previous studies and our concept of lactic acid conversion.

capacity, etc.) [20–26]. Previously, our researches found that CO_2 could be reduced to formic acid and/or methanol by in situ formed hydrogen by the oxidation of Zn in water [27,28]. More recently, we reported that a highly efficient synthesis of ethylene glycol from biomass-derived glycolide over CuO in high yield with high selectivity [29]. Inspired by the findings above, this led us to an idea that 1,2-propylene glycol could be synthesized catalytically from lactic acid in high temperature water (Eq. (2)). The purpose of this study was to present an efficient method for the production of 1,2-propylene glycol from lactic acid with high selectivity and productivity (Scheme 1).

2. Materials and methods

2.1. General information

Lactic acid (DL, ~90%T) was obtained from Sigma–Aldrich Chemical Reagent Co., Ltd. Zn powder (AR) was obtained from Aladdin Chemical Reagent Co. Ltd. CuO powder (200-mesh, 99.7%), other metals and metal oxides were obtained from Sinopharm Chemical Reagent Co. Ltd., China. The standard reagents 1,2-propylene glycol (J&K Chemical, >99.8%), Hydroxyacetone (Alfa Aesar, >95%), acetic acid (Sigma–Aldrich, >99.7%), propionic acid (Sigma–Aldrich, >99.7%) and lactic acid (Alfa Aesar, 1.0 N Standardized lactic acid solution) were used in the qualitative analysis of liquid example.

2.2. Product analysis

The qualitative analysis of obtained liquid samples was based on the results of GC–MS (Agilent 7890 system, equipped with 5985C inert MSD with triple-axis detector) while the quantitative analysis of 1,2-propylene glycol and byproducts was conducted by HPLC (Agilent 1200 system, equipped with VW and RI detectors). The solution was also tested by ICP to measure the ion concentration. Solid sample was dried in an oven at 60 °C for 24 h after filtered cleaning with distilled water. Then the precipitate was analyzed by XRD (Bruker D8 Advance X-Ray Diffractometer, equipped with Cu Kα radiation: λ = 1.5406 Å, scanning rate: 0.02° s^{-1}, 2θ ranges: 10–80°).

The lactic acid conversion ($LA_{Conv.}$), product i yield (Y_i) and selectivity to product i (S_i) were calculated using following equations. The yield was obtained from three replicate experiments, and the relative error was less than 5%.

$$LA_{Conv.}(\%) = \left(1 - \frac{\text{mole of lactic acid at particular time}}{\text{initial mole of lactic acid}}\right) \times 100 \quad (1)$$

$$Y_i(\%) = \left(\frac{\text{mole of product } i}{\text{initial mole of lactic acid}}\right) \times 100 \quad (2)$$

$$S_i(\%) = \left(\frac{\text{mole of product } i}{\text{mole of all products formed}}\right) \times 100 \quad (3)$$

2.3. Experimental procedure for the synthesis of 1,2-propylene glycol from lactic acid

All reactions were performed in a batch Teflon reactor whose inner volume is 30 mL. The procedure was as follows. Firstly, the desired concentration of lactic acid solution was prepared according to water filling. Then, the desired catalysts and reductants were loaded into the reactor. The reactor was put into the preheated oven for 20 min for temperature rising to the desired temperature. Afterward, the reactor was moved from the oven and cooled with an electric fan. The reaction time was defined as the time when the reactor's temperature was up to 250 °C. The water filling was defined as the ratio of volume of the lactic acid solution put into the reactor and inner volume of the reactor. Finally, after cooling off, liquid sample was collected and 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.

3. Results and discussion

The reactions of lactic acid to 1,2-propylene glycol were carried out to investigate the optimum conditions. Some parameters, such as the activity of catalysts, catalyst loading, reductant,