



Synthesis of high-value organic acids from sugars promoted by hydrothermally loaded Cu oxide species on magnesia



Hemant Choudhary, Shun Nishimura, Kohki Ebitani*

School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

ARTICLE INFO

Article history:

Received 14 February 2014
Received in revised form 11 April 2014
Accepted 6 May 2014
Available online 13 May 2014

Keywords:

Sugars
Lactic acid
Formic acid
Copper oxide catalysis
Alkaline hydrothermal synthesis

ABSTRACT

Design of a suitable catalyst for the conversion of inedible-biomass, a renewable resource, into high-value chemicals is an immense and important area of research in an era of energy crisis. This paper demonstrates batch conversion of sugars into lactic acid (LA) and formic acid (FA) employing a supported copper catalyst. A magnesia-supported copper catalyst was synthesized by a hydrothermal methodology using CTAB as the capping agent (denoted as CuCTAB/MgO). We found that the CuCTAB/MgO not only dramatically boosted the yields of LA and FA from sugars but also decreased the energy demand of the process by decreasing the reaction temperature from 523 K to 393 K. The high yields of LA (70%) in the presence of NaOH and of FA (65%) in the presence of H₂O₂ were achieved from glucose at 393 K in water using a CuCTAB/MgO catalyst, which could be recycled without any significant loss of activity. The copper catalyst was also found to exhibit excellent activity for the transformation of other sugars. The catalyst was characterized using PXRD, H₂-TPR, N₂ adsorption–desorption, and other analytical techniques to investigate the active Cu species and propose a plausible mechanistic pathway to LA.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

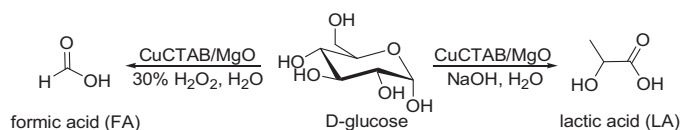
The demanding consumption of non-renewable fossil fuels has increased CO₂ concentrations in the environment. Depleting resources and increasing environmental concerns are inspiring researchers to develop renewable sources for a sustainable and stable future. The potential to use biomass as a substitute for the conventional petroleum feedstock has been known and realized in the past few years [1,2]. In principle, the uses of biomass could be more diverse than for crude oil; however, realization of this is challenging. Currently, both academic and industrial professionals are striving to convert cellulosic or lignocellulosic biomass into commodity chemicals at higher efficiencies. A variety of chemicals, such as 5-hydroxymethyl-2-furaldehyde [3], 2-furaldehyde [3], 2,5-dimethylfuran [4], 2,5-diformylfuran [5], succinic acid [6], levulinic acid [7], fatty acids and alcohols [8], and lactic acid (LA) [9], can be produced from biomass by engineering suitable catalysts and reaction conditions. Among these commodity chemicals, LA has attracted the most attention, and the direct conversion of sugars

into LA is highly desired. Formic acid (FA) is another organic acid of high interest to the researchers of this era, who are trying to harvest it in higher yields from renewable feedstock. LA is used extensively in detergents, antibacterial agents, cosmetics, food additives, and biodegradable plastics, whereas FA is used as a potential hydrogen donor and reserve [10,11]. The increasing global demand for high-value and high-energy chemicals emphasizes the importance of research on cellulosic biomass transformation.

The fermentation of sugars is the key process among potential candidates for syntheses of LA [12] and FA [13]. The industrial synthesis of LA is dominated by the fermentation method because of the increasing market demand for *bio*-LA [14]. The hydrolysis of methyl formate is currently the state of the art for FA, constituting approximately 49% of the total production capacity [15]. The fermentation processes are, however, expensive due to product purification, strict control of reaction conditions, and restricted large-scale operations. Water at higher temperatures has a unique property that eases the reaction pathway to such an extent that the use of a catalyst is not necessary. Inspired by this, many researchers have successfully converted carbohydrates into chemicals, mainly LA and formic acid (FA), with or without additives, as discussed later. The employment of extreme conditions of high temperatures and pressures to produce LA and FA in moderate yields opens up new areas of research to decrease energy demand for such severe processes. Moreover, the hydrothermal conditions at higher temperatures often decrease the selectivity, and thus a variety of

Abbreviations: LA, lactic acid; FA, formic acid; GlycAld, glyceraldehyde; GlycA, glyceric acid; DHA, dihydroxyacetone; PAL, pyruvaldehyde; AA, acetic acid; GlcoA, glycolic acid.

* Corresponding author. Tel.: +81 761 51 1610; fax: +81 761 51 1149.
E-mail address: ebitani@jaist.ac.jp (K. Ebitani).



Scheme 1. Glucose conversions into LA and FA.

products are obtained, such as 5-hydroxymethyl-2-furaldehyde, organic acids, and char [16]. Herein, we have focused on the development of process technologies for the selective conversion of sugars to LA and FA under less extreme conditions using a catalyst.

Previous studies have reported the synthesis of LA from biomass under alkaline hydrothermal conditions or with acidic catalysts [9], producing LA in low to moderate yields. Although LA has long been known as an alkaline degradation product of sugars [17], extensive research regarding the improvement of the yields has occurred in recent years. Enomoto and others studied glycoaldehyde and glucose as substrates to synthesize LA in lower yields at higher temperatures [18]. As an improvement, they also reported that the use of sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)₂) could produce LA with 27% yield (from glucose) for shorter reaction times at 573 K [19]. Most reports in the literature focused on NaOH or Ca(OH)₂ for the alkaline hydrolysis of biomass. These results encouraged Esposito and Antonietti to investigate the effects of other bases; an impressive LA yield of 53% with homogeneous barium hydroxide (Ba(OH)₂) at 493 K for a longer reaction time was reported [20]. In contrast with the studies of LA production from biomass, very little has been reported regarding the direct formation of FA from biomass. Gao et al. successfully produced FA with 22% yield from pretreated cellulose at 483 K for 30 h [21]. A high yield of 75% FA was produced by Jin et al. at 523 K using 120% H₂O₂ from glucose [22]. Other studies report the formation of FA in trace amounts as a side product during LA synthesis.

The major disadvantage of the previous studies is that the operations occur at high temperatures (493–623 K) or yield low to moderate amounts of the desired organic acids. This disadvantage kindles the need for the development of a suitable catalyst or process for decreasing the energy demand involved in the alkaline hydrolysis of carbohydrates. Many researchers have focused on the role of earlier transition metals for improving the LA yields under alkaline hydrothermal conditions [23–25]. Onda et al. introduced calcined hydrotalcite as a heterogeneous base catalyst to obtain 20% LA yield from glucose [23]. Zhang et al. reported a 42% increase in the yields of LA from cellulose using Zn and Ni as co-catalysts [24]. In another recent study, the use of copper oxide in alkaline hydrothermal conversion was explored, improving the yields from 37–42% to 59% at 573 K [26]. The copper clusters synthesized under hydrothermal conditions were reported to exhibit superior activity for oxidation reaction compared with previous studies [27]. These achievements inspired us to synthesize hydrothermally loaded copper catalysts for high yields of organic acids via alkaline hydrolysis of saccharides.

In this study, we demonstrated the promotional effect of a hydrothermally loaded copper oxide species on magnesia using a capping agent (cetyltrimethylammonium bromide; CTAB) as an effective heterogeneous catalyst for the batch conversions of biomass-derived sugar into LA or FA in high yields under less extreme conditions (Scheme 1). In addition, the copper catalyst was found to be reusable with a simple reactivation by calcination, which is an advantage over the non-recyclable conventional methodologies involved for LA and/or FA synthesis from sugars. Moreover, in addition to glucose, other sugars including mono and disaccharides were also successfully converted into LA and FA using the supported copper catalyst. A plausible reaction pathway to LA

is proposed based on the characterization results, which identify the active Cu species.

2. Experimental

2.1. Chemicals

D(+)-glucose, starch (soluble), lactose monohydrate, sucrose, D(+)-raffinose pentahydrate, cetyltrimethylammonium bromide (CTAB), formic acid (FA), DL-glyceraldehyde, copper(I) oxide (Cu₂O), copper nitrate hexahydrate (Cu(NO₃)₂·6H₂O), and 30% hydrogen peroxide (H₂O₂) were purchased from Wako Pure Chemical Industries, Ltd. D(–)-fructose, D(+)-xylose, D(+)-cellobiose, acetic acid, magnesium oxide (MgO), sulfuric acid (H₂SO₄), and sodium hydroxide (NaOH) were procured from Kanto Chemical Co., Inc. Tokyo Chemical Industry Co. Ltd. supplied D(+)-galactose and glycolic acid, whereas DL-glyceric acid (GlycA) was bought from Nacalai Tesque Inc. L(+)-Lactic acid (LA) and pyruvaldehyde (PAL) were obtained from Sigma–Aldrich Co. LLC. Merck KGaA provided dihydroxyacetone (DHA) and microcrystalline cellulose. Strem Chemicals Inc. was the source for high purity (99.999%) copper(II) oxide (CuO).

2.2. Catalyst preparation

CTAB capped copper supported on magnesia (CuCTAB/MgO) was synthesized using a hydrothermal method described by Sarkar et al. with some modifications [27b]. CTAB, a cationic surfactant, was selected as the capping agent and dissolved in deionized water. In a typical synthesis methodology, MgO was dispersed in deionized water, and then an aqueous solution of Cu(NO₃)₂·6H₂O containing the requisite amount of copper was added dropwise into the solution under vigorous stirring. To this mixture, an aqueous solution of CTAB was added and vigorously stirred for 3 h. The obtained mixture was sealed in a 100 mL Teflon lined autoclave, heated to 453 K in an oven at a heating rate of 6 K min^{–1}, and maintained at the same temperature for 24 h. The oven was allowed to cool slowly to room temperature. The obtained solid was washed with deionized water until the pH of the filtrate became neutral; this was followed by washing with ethanol and then drying *in vacuo* overnight at room temperature. The dried materials were further calcined at 383, 573, 773, 973 or 1173 K with a ramp-rate of 10 K min^{–1} for 6 h in air. Various copper-loaded magnesia catalysts were denoted as xCuCTAB/MgO, where the x is the Cu content in mmol per gram of catalyst (mmol g^{–1}) in theory.

2.3. Catalytic testing

All experiments to test the catalytic activity were performed in a 50 mL Teflon lined autoclave. The catalytic activity was evaluated for conversion of glucose into LA or FA in aqueous media. In a general reaction procedure, glucose (or sugar) was dissolved in 5 mL deionized water. The catalyst was added to the solution, followed by the addition of NaOH solution or 30% H₂O₂ solution. The autoclave was sealed, purged with Ar (0.4 MPa), and mounted on a preheated oil bath at 373–413 K. The mixture was allowed to react for various time intervals with continuous magnetic stirring. After the reaction, a portion of the resultant solution was diluted 20 times with deionized water (or 10 mM H₂SO₄ for the samples containing alkali), and the catalyst was filtered off using a Millex®-LG 0.20 μm filter. The obtained filtrate was analyzed by high performance liquid chromatography (HPLC, WATERS 600) using an Aminex HPX-87H column (Bio-Rad Laboratories Inc.) attached to a refractive index detector. Aqueous 10 mM H₂SO₄ (as the mobile phase) was run through the column (maintained at 323 K) at a flow rate of 0.5 mL min^{–1}. The conversion and yield(s) were determined

Download English Version:

<https://daneshyari.com/en/article/45615>

Download Persian Version:

<https://daneshyari.com/article/45615>

[Daneshyari.com](https://daneshyari.com)