Production of carboxylic acids from glucose with metal oxides under hydrothermal conditions

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Abstract Production of low molecular weight carboxylic acids from glucose with the addition of metal oxides under hydrothermal conditions was investigated. The results showed that CuO, as an oxidant can significantly promote the production of lactic acid, and can also promote the production of acetic acid and formic acid. Fe₃O₄ can also enhance lactic acid production as a catalyst. The highest yields of 37.1, 9.4, and 4.9 % for lactic acid, acetic acid, and formic acid were achieved, respectively, which occurred at 300 °C for 60 s with CuO 1.5 mmol, NaOH 2.5 M, and water filling 35 %.

Keywords Glucose \cdot Carboxylic acids \cdot Metal oxides \cdot CuO \cdot Hydrothermal reactions

Introduction

Biomass is commonly recognized as one of the most important renewable resources. Biomass is cleaner compared with mineral energy because it does not increase the concentration of CO_2 in the atmosphere. In recent years, much attention has been paid to developing efficient processes for the conversion of biomass into fuel and

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useful chemicals [1-3]. Among these processes, hydrothermal treatment is one of the most promising ways of utilizing biomass because of its unique advantages [4], such as fast reaction and green solvent. Therefore, hydrothermal conversion of biomass to chemicals has become a major topic of research [5, 6].

Carboxylic acids such as lactic acid, acetic acid, and formic acid are very important organic chemicals. For example: (1) lactic acid is used as a raw material for the preparation of biodegradable lactic acid polymers with limited environmental impact [7-9]; (2) acetic acid can be used for producing calcium-magnesium acetate, which is known as an environmentally friendly deicer [10-12]; and (3)formic acid can be utilized as a concrete cure accelerator and its Na or Ca salt has been proposed as an environmental-friendly road deicer [13]. In addition, recent research has demonstrated that formic acid has the potential importance to produce power fuel cells for electricity generation and automobiles [14]. Due to the potential importance of lactic, acetic, and formic acids, many methods for converting biomass into these acids have been developed [15-17]. However, H2O2 or O2 have previously generally been used as oxidants for converting carbohydrate biomass into carboxylic acids, which was relatively costly and corrosive [18, 19]. On the other hand, metal oxides are also oxidants, such as Cu smelt from CuO mines in which CuO is an oxidant and CO from fossil works is reductant, but they are rarely used in biomass conversion,. Therefore, it is hypothesized that metal oxides could act as oxidants in carboxylic acid production from biomass and be reduced to metal at the same time. Thus, the development of new methods for converting biomass into carboxylic acids would improve the process for producing acids and metal smelt at the same time. Our group have found that metal oxides are able to be reduced to metal by using biomass in hydrothermal reactions [20, 21], which is a much greener process compared with traditional metal production with its high energy consumption and high pollution. Therefore, the purpose of this paper is to investigate the effect of metal oxides on carboxylic acids under hydrothermal reactions to improve carboxylic acids production and simultaneously reduce metal oxides to metal.

Experimental

Experimental materials and procedure

All reagents used in this study were of analytical grade (≥ 99 %). Glucose, as a model compound of carbohydrate biomass, was used in all experiments. Fe₃O₄, Fe₂O₃, Al₂O₃, ZnO, TiO₂, CuO (150–200 mesh, i.e. 0.074–0.1 mm) and sodium hydroxide were obtained from Sinopharm Chemical Reagent (China).

All experiments were carried out in a batch reactor made of SUS 316, which is constructed of a piece of stainless steel 316 tubing (3/8 inch/9.5 mm diameter, 1 mm wall thickness and 120 mm length) with an internal volume of 5.7 mL. The schematic drawings of the experimental set-up can be found elsewhere [19]. The reaction time is shorter than the apparent reaction time because the time required to raise the temperature of the reaction medium from room temperature to 300 °C was

approximately 15 s. The desired amounts of glucose, metal oxides and deionized water were put in the batch reactor and 0.035 g glucose was used in all experiments. Sequentially, the reactor was placed horizontally in a salt bath that had been preheated to the desired temperature. In the salt bath, the reactor was shaken horizontally to enhance the mixture. After the desired reaction time, the reactor was transferred from the salt bath and immediately placed in a cold water bath to quench the reaction. The reaction time was defined as the time the reactor was kept in the salt bath. The loading, shaking, and cooling procedures were all done with a mechanical arm to ensure accuracy. At 300 °C, the density of water is about 0.7, and thus the pressure during reactions is its saturated vapor pressure, e.g., about 8 MPa when water filling is less than 70 %.

Analytical methods

After the reaction, the liquid samples were collected and analyzed by Capillary Electrophoresis (CE, P/ACE MDQ; Beckman Coulter) and High Performance Liquid Chromatography (HPLC, Agilent 1200LC). Formic acid, acetic acid, and lactic acid were quantified by CE with sodium chromate and octadecy trimethyl ammonium bromide (OTAB) as background electrolyte (pH 8.1) at 214 nm. The temperature of the capillary cassette was 25 °C and the sample injection was performed in the hydrodynamic mode by applying a 0.5 p.s.i. pressure for 5 s. The flowing solution used in HPLC was 2 mM HClO₄ with a flowing rate of 1 mL/min.

Products in solid phase were also collected and determined by X-ray Diffraction (XRD; Bruker D8 Advance X-ray Diffractometer, equipped with Cu K α radiation) to determine the composition and phase purity.

The yield of carboxylic acids is defined as the percentage of lactic acid, formic acid, or acetic acid to the initial glucose on the carbon base, as follows. The yields were obtained from experiments over three times and relative error was less than 5 %.

Yield, wt% =
$$\frac{\text{C in carboxylic acids, g}}{\text{C in the initial glucose, g}} \times 100 \%$$

Results and discussion

The effect of various metal oxides on yields of carboxylic acids

In our previous researches, it was found that lactic acid, acetic acid, and formic acid were the main products from glucose under hydrothermal conditions. Initially, the effect of various metal oxides on the yields of lactic acid, formic acid, and acetic acid was investigated. The reactions were carried out with 2.5 M NaOH at 300 °C for 60 s in the presence of 1.5 mmol metal oxides and 2 mL H₂O (water filling 35 %). The results are summarized in Table 1. The results showed that yields of three acids in the presence of CuO were enhanced compared to that without CuO although the increasing of formic acid, and 4.9 % for formic acid, in the presence of CuO (Entries 1 and 2). The use of Fe₃O₄ also proved to be effective for the

conversion of glucose into these acids (Entry 3). However, the other metal oxides such as Fe_2O_3 , Al_2O_3 , ZnO and TiO₂ did not give a significant increase in yields of these acids compared to that with the addition of CuO and Fe_3O_4 .

The role of CuO and other metal oxides on the production of carboxylic acids from glucose under hydrothermal reaction conditions was investigated by analyzing XRD of the solid residue after the reactions. From Fig. 1a, it can be seen that CuO was converted into Cu₂O and Cu, which suggests that CuO acts as an oxidant in improving conversion of glucose into carboxylic acids under hydrothermal conditions. The yields of carboxylic acids increased with the increase of yields of Cu and Cu₂O from CuO under hydrothermal conditions. Further, Cu ions concentration in the solution was measured by ICP. The results showed that few of the Cu ions (<1 ppm) in all liquid samples were identified, which suggests that Cu probably existed in the solid product. The XRD patterns of the residue obtained for Fe₃O₄ and other metal oxides from the hydrothermal reactions are also given in Figs. 1b and 2. There was no change in metal valence. It is indicated that Fe₃O₄ acts as a catalyst rather than as an oxidant in the conversion of glucose.

Considering that CuO or Fe_3O_4 are effective in improving the yields of carboxylic acids from glucose under hydrothermal conditions, in which CuO acts as an oxidant and Fe_3O_4 acts as a catalyst, we investigated the effect of the addition of both CuO and Fe_3O_4 on glucose conversion, to test if there is the synergetic effect between CuO and Fe_3O_4 for improving the yield of these acids. However, the yields of carboxylic acids were not improved compared to those in the presence of only CuO or only Fe_3O_4 (see Table 1, Entry 8).

Effect of the amount of CuO and Fe₃O₄ on yields of carboxylic acids

To study the effect of the amount of CuO or Fe_3O_4 on hydrothermal conversion of glucose into carboxylic acids, we treated glucose with NaOH 2.5 M at 300 °C for 60 s with various amounts of CuO or Fe_3O_4 . It can be seen from Fig. 3a that CuO has a great influence on the improvement of the yields of carboxylic acids from glucose, and the yields of carboxylic acids increased as the CuO amount increased. Furthermore, CuO has a greater effect on lactic acid and acetic acid yields than on formic acid yield. Similarly, it can be seen from Fig. 3b that the amount of Fe_3O_4 also has an obvious improvement effect on lactic acid production, but the improvement of the production of acetic acid and formic acid was not obvious.

As mentioned above, CuO or Fe_3O_4 can improve the conversion of glucose to carboxylic acids, and CuO is more significant for the promotion of carboxylic acids formation compared with Fe_3O_4 . Therefore, CuO was selected to investigate the effect of various parameters on yields of carboxylic acids.

Effect of various parameters on yields of carboxylic acids in the presence of CuO

Effect of alkali concentration on yields of carboxylic acids

Experiments were carried out by varying the NaOH concentration from 0 to 3 M at 300 °C for 60 s to examine the effect of alkali concentration. As shown in Fig. 4,

Entry	Additives	Lactic acid (%)	Acetic acid (%)	Formic acid (%)
1	None	31.1	2.6	2.2
2	CuO	37.1	9.4	4.9
3	Fe ₃ O ₄	35.0	3.7	3.0
4	Fe ₂ O3	26.4	2.6	2.1
5	Al_2O_3	17.1	6.1	2.7
6	ZnO	25.3	3.6	2.2
7	TiO ₂	24.3	4.3	2.5
8	$CuO + Fe_3O_4$	36.6	9.0	4.6

Table 1 Effect of metal oxides on yields of carboxylic acids from glucose

Temp 300 °C, time 60 s, metal oxides 1.5 mmol, NaOH 2.5 M



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Fig. 2 XRD patterns of solid residual after the reaction with the addition of metal oxides (temp 300 °C, time 60 s, metal oxides 1.5 mmol, NaOH 2.5 M)

Fig. 3 Effect of CuO and Fe_3O_4 amount on the yields of carboxylic acids (temp 300 °C, time 60 s, NaOH 2.5 M). a Effect of CuO. b Effect of Fe₃O₄

the yields of lactic acid and acetic acid increased as the concentration of NaOH increased from 0 to 2.5 M, particularly for lactic acid. And 2.5 M for the optimum NaOH concentration reached a maximum value of 37.1 % for lactic acid and 9.4 % for acetic acid. When the concentration of NaOH further increased to 3 M, lactic acid and acetic acid yield clearly decreased.

Effects of reaction time and temperature on yields of carboxylic acids

Figure 5 shows the effect of reaction time on the yields of carboxylic acids at 300 °C with 2.5 M NaOH and 1.5 mmol CuO. The yield of lactic acid increased greatly from 30 to 60 s and reached a maximum value of 37.1 % for 60 s and decreased with further increasing the reaction time from 60 to 150 s. The yield of acetic acid increased from 30 to 60 s and reached a value of 9.4 % for 60 s. However, the yield of acetic acid showed no significant change with further increasing the reaction time from 60 to 150 s. The yield of obviously change. After 60 s, the acetic acid yield kept almost the same, while lactic acid yield obviously decreased. This may be because the degradation rate of acetic acid is much faster than that of lactic acid.

Experiments were carried out for 60 s by varying the temperature from 260 to 320 °C to examine the effect of reaction temperature on yields of three carboxylic acids. As shown in Fig. 6, the yield of lactic acid increased as the temperature increased from 260 to 300 °C. The reaction temperature to achieve the highest yield of lactic acid was 300 °C, and then the yields decreased when the temperature increased from 300 to 320 °C. However, the reaction temperature had no obvious effect on the yields of acetic acid and formic acid. It is known that the constant ionization (k_w) of high temperature water is a maximum at near 300 °C at saturated vapor pressure, and under these conditions the k_w is approximately 1,000 times larger than that of water at normal temperature and pressure [22]. The highest yields of lactic acid obtained at 300 °C may be related to the fact that the maximum ion product (k_w) of high temperature water occurs at about 300 °C. The yields decreased when the temperature was at 320 °C. This may also be because the higher temperature leads to the further decomposition of the formed carboxylic acids.

Effect of water filling on yields of carboxylic acids

Figure 7 shows the effect of water filling on the yields of three carboxylic acids. It is obvious that the yield of lactic acid increased as the water filling increased from 25 to 35 % and then decreased, while the yields of acetic acid and formic acid changed little as water filling varied from 25 to 40 %. The optimum water filling was 35 % to achieve the maximum value of 37.1 % for lactic acid.

Finally, a carbon balance was conducted. As a result, the conversion of glucose for liquid products was about 90 %. The main products for this transformation were three detected acids including formic, acetic, and lactic acids, and the total yields of the three acids were 51.4 %, with other products possibly being other acids and unknown compounds. Gas products in this transformation were H_2 and CH_4 , while the conversion of initial carbon should be less than 10 %.



Reaction temperature (°C)



Fig. 5 Effect of reaction time on yields of carboxylic acids (temp 300 °C, CuO 1.5 mmol, NaOH 2.5 M)

Fig. 6 Effect of reaction temperature on yields of carboxylic acids (time 60 s, CuO 1.5 mmol, NaOH 2.5 M)



Fig. 8 Proposed mechanism for the conversion of glucose into carboxylic acids over CuO

Proposed mechanism for the production of carboxylic acids from glucose with CuO

Based on our previous research [21] and findings in this study, a plausible mechanism is given in Fig. 8 to explain the effect of CuO in improving the yields of

carboxylic acids. Initially, glucose probably involves a glucose alkoxide transition in alkaline conditions due to its weak acidity, and then Cu^{2+} coordinates formed by reacting CuO with NaOH with the two oxygen atom of adjacent hydroxyl group to form intermediate 1. This intermediate 1 could be in equilibrium with the intermediate 2. Nucleophilic attack of the OH⁻ on hydrogen atoms of the hydroxyl group takes place easily because electron density decreases by coordination with Cu^{2+} . Subsequently, the proposed retro-aldolization and the double bond rule of the respective enediols formed from the Lobry de Bruyn Alberda van Ekenstein (LBAE) [23] transformation of D-glucose via coordination with Cu^{2+} occurs, along with the formation of glyceraldehyde (adoses of three carbon atoms) and reduction elimination of Cu²⁺ to Cu. Glyceraldehyde produces lactic acids via the formation of pyruvaldehyde through the elimination of water and a benzilic acid rearrangement. Next, lactic acid is further oxidized to produce acetic acid and formic acid along with the reduction of Cu²⁺ to Cu. As mentioned before, the yield of formic acid is lower. This is probably because formic acid is easily decomposed under hydrothermal reaction conditions at 300 °C [24].

Conclusions

The production of carboxylic acids from glucose under hydrothermal conditions with the addition of metal oxides has been developed. It has been found that the yields of lactic acid and acetic acid were enhanced in the presence of CuO. In addition, Fe_3O_4 also enhanced lactic acid production. CuO acts as an oxidant while Fe_3O_4 acts as a catalyst in improving conversion of glucose into carboxylic acids. The highest yield of carboxylic acids with the addition of CuO was lactic acid up to 37.1 %, acetic acid to 9.4 %, and formic acid to 4.9 % at 300 °C for 60 s with CuO 1.5 mmol and NaOH 2.5 M. The present results have considerable significance for developing green processes for the production of carboxylic acids from biomass.

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