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Formation of Formic Acid from Glucose with Simultaneous Conversion of Ag_2O to Ag under Mild Hydrothermal Conditions

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ABSTRACT: Formation of formic acid from renewable biomass resources is of great interest since formic acid is a widely used platform chemical and has recently been regarded as an important liquid hydrogen carrier. Herein, a novel approach is reported for the conversion of glucose, the constituent carbohydrate from the cellulose fraction of biomass, to formic acid under mild hydrothermal conditions with simultaneous reduction of Ag_2O to Ag. Results showed that glucose was selectively converted to formic acid with an optimum yield of 40.7% and glycolic acid with a yield of 6.1% with 53.2% glucose converting to carbon dioxide (CO_2) immediately at a mild reaction temperature of 135 °C for 30 min. In addition, Ag_2O was used as a solid oxidant for glucose oxidation, which avoids the use of traditionally dangerous liquid oxidant H_2O_2. Furthermore, complete conversion of Ag_2O to Ag can be achieved. This study not only developed a new method for value-added chemical production from renewable biomass but also explored an alternative low-carbon and energy-saving route for silver extraction and recovery.
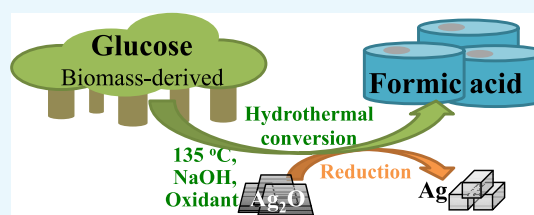
1. INTRODUCTION

Formic acid (FA) is an important chemical that is widely used in chemical, textile, leather, pharmaceutical, rubber, and other industries.[1,2] Currently, FA is considered as one of the promising hydrogen storage materials due to a number of inherent advantages. Because of its low toxicity, high hydrogen storage capacity, and availability from renewable resources, FA has recently attracted significant attention for its potential applications as a chemical hydrogen storage medium.[3–9] Some promising methods were reported for the conversion of renewable biomass or carbon dioxide (CO_2) into FA, such as acid hydrolysis of biomass, wet oxidation of biomass, catalytic oxidation of biomass, homogeneous or heterogeneous catalysis of CO_2, hydrothermal conversion of CO_2, and photo/electrochemical reduction of CO_2.[10–15] Particularly, the hydrothermal reaction is often used for biomass conversion since high-temperature water has unique properties as a reaction medium such as low dielectric constant, few and weak hydrogen bonds, and high isothermal compressibility.[16–23] Jin's group first presented the hydrothermal conversion of carbohydrates into FA with a H_2O_2 oxidant at 250 °C in 60 s. In the absence of alkali, the highest yield of FA was about 24%, while it could achieve 75% with the alkali in the reaction.[16] Wasserschied's group reported that a total FA yield of 60% could be achieved from glucose catalyzed by $H_8PV_5Mo_7O_{40}$ within an 8 h reaction time at 90 °C and a 30 bar O_2 atmosphere.[24] Albert's group continued to study the switchable catalytic system of glucose into FA and lactic acid (LA). Under the reaction in parallel at 160 °C within 1 h using a $H_6PV_3Mo_9O_{40}$ catalyst, 42% yield of FA could be achieved

under the O_2 atmosphere and 40% yield of LA was obtained under the N_2 atmosphere.[25] Moreover, Moret's group has demonstrated the production of FA from direct reduction of CO_2 gas by H_2 using a homogeneous $[RuCl_2(PTA)_4]$ complex in an acidic aqueous solution.[26] Jin's group also reported the hydrothermal reduction of CO_2 into FA using metallic manganese,[27] H_2S,[28] and microalgae,[29] respectively. However, in reported conversion routes of biomass into FA, H_2O_2 or O_2 was generally used as an oxidant and thus led to high energy costs due to the compressing gas or potential insecurity hazards.[30] On the other hand, the poor selectivity of FA, high reaction temperature, and expensive and tedious preparations of noble-metal catalysts make these methods inappropriate for the synthesis of FA.[31] For example, CuO was used in biomass conversion as a solid oxidant but only acetic acid was acquirable.[32]

Recently, the cost of silver production increases rapidly with decreasing natural silver resources, but silver has a huge demand for photographs, radiographs, electronics, photonics, catalysts, jewelry, silverware, dental materials, medicines, and disinfectants in wastewater treatment.[33,34] Therefore, the market demand urgently requires the recovery of silver from
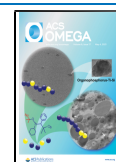
silver-containing wastes through new cost-effective and environmentally friendly technologies.[35] Many researchers studied the methods to recycle silver by chemical reduction, chemical replacement, and ion exchange.[36−38] However, these methods were short of economy and environmental friend-liness due to the use of expensive resins or high energy input. Herein, we propose a new method for selective conversion of glucose into FA with easily separated byproduct glycolic acid using Ag_2O as a solid oxidant and simultaneous transformation of Ag_2O into Ag under mild hydrothermal conditions. The results show that glucose was selectively converted into FA with an optimum yield of 40.7% and glycolic acid yield of 6.1% with 53.2% glucose converting to CO_2 immediately at a mild reaction temperature of 135 °C for 30 min. The proposed method is not only a promising way for the conversion of biomass into value-added chemicals but also an effective and green route for silver extraction.

2. RESULTS AND DISCUSSION

2.1. Characteristics of Ag_2O/Ag with Hydrothermal Conversion of Glucose to Formic Acid. A series of experiments with glucose and Ag_2O as reactants were carried out under mild hydrothermal conditions to investigate whether glucose could be selectively converted to FA. As shown in Figure 1, only lactic acid was detected from the liquid sample
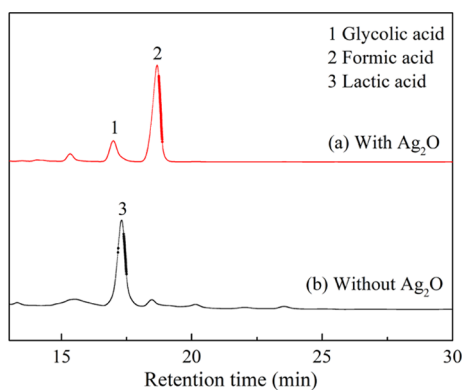

Figure 1. HPLC chromatography of liquid samples after reactions (a) with and (b) without 10 mmol Ag_2O (1 mmol glucose, 1 mol/L NaOH with 6.25 mL, 180 °C, 2 h).

by high-performance liquid chromatography (HPLC) analysis when glucose was reacted without Ag_2O under the basic hydrothermal condition. However, when Ag_2O was added, the production of FA was clearly increased and the formation of glycolic acid was also detected. The previous study has revealed that a relatively high yield of lactic acid can be obtained from the hydrothermal conversion of glucose under alkaline conditions.[12] Notably, as shown in Figure 1, the amount of lactic acid in the presence of Ag_2O was much less than that without Ag_2O, which suggested that glucose was selectively converted into FA by reacting with Ag_2O under mild hydrothermal conditions.

To investigate the reduction of Ag_2O, solid samples were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. Figure 2 shows the XRD patterns of the Ag_2O before the reaction and solid products after the reaction. No Ag peak appeared in the solid sample before reaction (Figure 2a). However, four diffraction peaks were observed at 38.20, 44.40, 64.60, and 77.60°, respectively, which
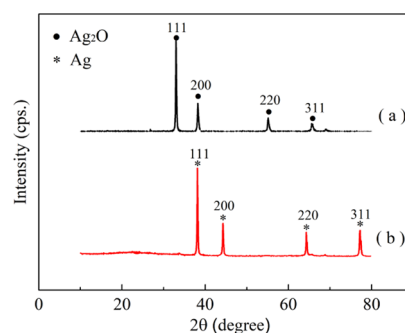

Figure 2. XRD patterns of (a) Ag_2O before the reaction and (b) solid products after the reaction at 135 °C for 2 h (1 mmol glucose, 4 mmol Ag_2O, 1 mol/L NaOH).

were indexed as the (111), (200), (220), and (311) orientations of cubic Ag (Figure 2b). These results indicated that Ag_2O was converted into Ag after the reaction. Furthermore, the SEM image shows that the obtained Ag particle has a diameter of 0.1−0.3 μm (Figure 3).
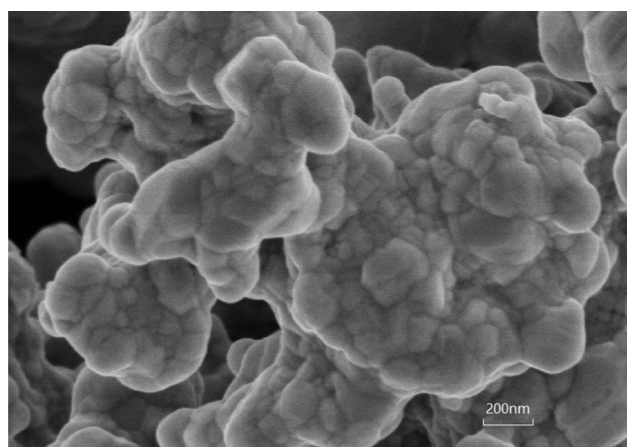

Figure 3. SEM image of silver obtained after the reaction (4 mmol Ag_2O, 1 mmol glucose, 135 °C, 2 h, 1 mol/L NaOH with 6.25 mL).

2.2. Investigating the Influences of Reaction Conditions on Yields of Formic Acid. Next, the relationship between reaction conditions and yields of FA from glucose was further investigated. Above all, the influence of reaction temperature was examined by varying the temperature from 105 to 210 °C. As shown in Figure 4a, FA was identified as the major product. When the temperature was increased from 105 to 135 °C, the yield of FA increased from 22.9 to 29.1%. However, a further increase of the temperature led to a slight decrease in the FA yield. For the production of glycolic acid, a similar trend was observed. However, when the temperature was increased to 210 °C, lactic acid was detected at the cost of the yields of glycolic acid and FA. The change in the product yield and selectivity suggested that the temperature could affect the cleavage patterns of glucose and alter the reaction pathway. Furthermore, there was no glucose detected in the liquid phase after the reaction at all tested temperatures, which showed that glucose was completely decomposed. Figure 4b shows the influence of reaction time on yields of different products and conversion of glucose in the hydrothermal oxidation of glucose to FA. In the first 30 min, the yield of FA dramatically increased to 29.7%; however, a slow decrease in the FA yield
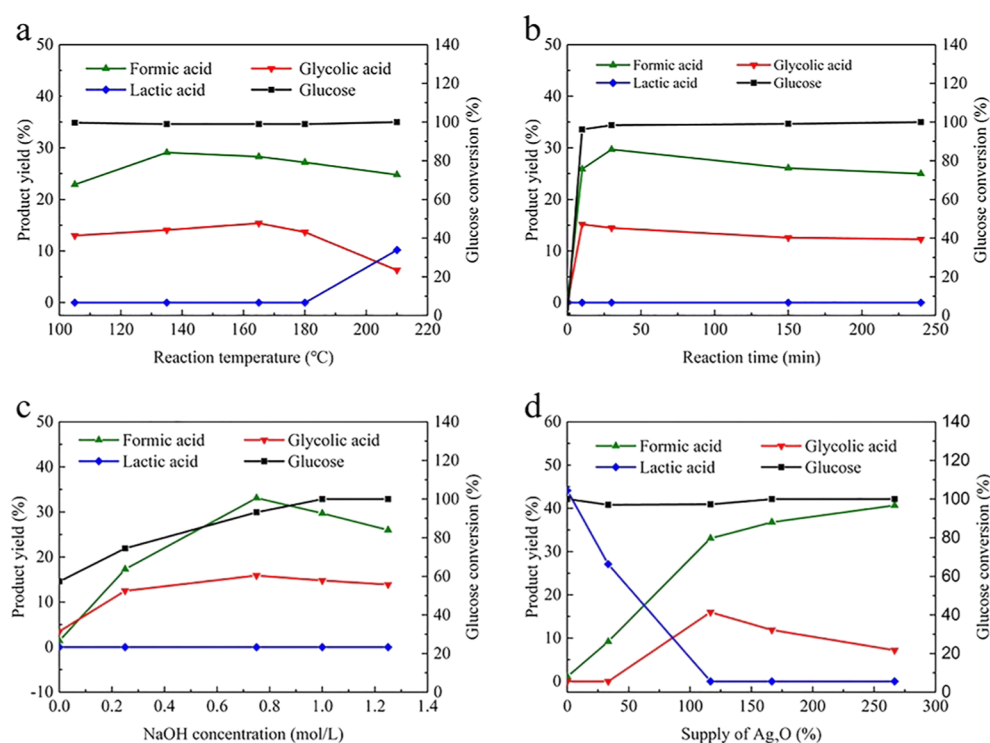
Figure 4. Effect of (a) reaction temperature (7 mmol Ag_2O, 1 mol/L NaOH with 6.25 mL, 120 min), (b) reaction time (7 mmol Ag_2O, 1 mol/L NaOH with 6.25 mL, 135 °C), (c) NaOH concentration (7 mmol Ag_2O, 135 °C, 30 min, 6.25 mL NaOH solution), and (d) amount of Ag_2O (0.75 mol/L NaOH 6.25 mL, 135 °C, 30 min) on yields of different products and conversion of glucose in hydrothermal oxidation of glucose to formic acid (1 mmol glucose was used for all cases).

was observed when the reaction time prolonged to 240 min. Similar trends were observed for the glycolic acid yield. The decrease in the yields of FA and glycolic acid with a long reaction time is probably caused by the decomposition of the formed products under hydrothermal conditions.

The influence of the concentration of NaOH on the oxidation of glucose was also investigated. A sharp increase in glucose conversion was noted from 57.4% to 100% when NaOH concentration increased from 0 to 1 M (Figure 4c). This is probably because the NaOH solution with higher concentration accelerated glucose conversion, which has been studied in detail in previous research.[18] The yield of FA was less than 2% in the absence of NaOH. However, FA yield ascended simultaneously with increasing NaOH concentration and reached 34% at 0.75 M NaOH. The previous research has demonstrated that a certain amount of alkali could convert the FA to formate, which is more stable than FA under hydrothermal conditions.[39] Thus, the addition of alkali could prevent the produced FA from being decomposed that resulted in a higher yield. However, further increasing the NaOH concentration exceeding 0.75 M got a decrease in the FA yield, which is probably because the reaction pathway of glucose conversion was negatively affected by additional NaOH.

The effect of the Ag_2O amount was examined (Figure 4d). The yield of FA first quickly increased from 1.1 to 33.1% when the Ag_2O addition increased from 0 to 116.7% relative to glucose. At the same time, a glycolic acid yield of 15% was gained. While then FA yield slowly ascended to 40.7% when the Ag_2O supply was further increased to 266.7%, the glycolic acid yield was descended to 6.1%. In addition, lactic acid with a yield of 44.0% without any formation of FA was observed in the absence of the oxidant. This result was similar to other

literature studies, in which glucose was dominantly isomerized into fructose and then cleaved into lactic acid via retro-aldol condensation under alkaline conditions.[18,30] The above results indicated that the Ag_2O oxidant was advantageous for the oxidation of glucose to FA, and increasing the amount of Ag_2O had a positive effect on the FA yield.

All products were calculated by mass balance, and the results for the sample before and after the reaction are shown in Table 1. It is clear that all Ag_2O and glucose were completely converted, while there is no undesired product in this reaction and 53.2% glucose was oxidized to CO_2.
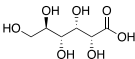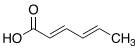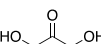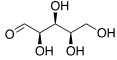
Table 1. Mass Balance and Total Organic Carbon (TOC) Content of the Sample before (S1) and after (S2) the Reaction[a]

entry	Ag/Ag_2O (g)	TOC (mg)	glucose (mg)	formic acid (mg)	lactic acid (mg)	CO_2 (mg)
S1	0/0.324	14.40	36	0	0	0
S2	0.301/0	6.74	0	22.08	6.21	27.15

[a]S2 was separated by filtration.

2.3. Investigating the Oxidation Pathways of Glucose to Formic Acid. Oxidation pathways of glucose to FA were then investigated. Based on the previous research, glucose was probably first oxidized to gluconic acid under basic hydrothermal conditions, which was further converted to FA through a series of reactions.[18] Thus, gluconic acid was first chosen as the starting material instead of glucose for hydrothermal FA production. Results revealed that gluconic acid was completely converted with a FA yield of 34.4% (Table 2, Entry 1), which is close to that obtained from glucose directly. This result indicates that gluconic acid was a crucial intermediate for FA

Table 2. Oxidation of Different Model Compounds with Ag$_2$O under Hydrothermal Conditions[a]

Entry	Substrate	Conversion (%)	Formic acid (%)	Acetic acid (%)	Lactic acid (%)	Glycolic acid (%)
1	Gluconic acid	100	34.4	0	0	2.4
2	Sodium oxalic	0	0	0	0	0
3	Glycolic acid	0	0	0	0	100
4	Acetic acid	0	0	100	0	0
5	Lactic acid	3.3	0	0	96.7	0
6	Methanol	100	0	0	0	0
7	Sorbitol	100	0	0	0	0
8	Glycolaldehyde (dimer)	100	24.1	0	0	16.5
9	Pyruvaldehyde	100	3.2	21.4	53.6	0
10	Glyceraldehyde	100	1.1	0	2.2	2.8
11	1,3-dihydroxyacetone	100	24.7	7.1	14.6	47.4
12	Xylose	100	30.9	0.4	0	7.5

[a]Reaction conditions: 0.5 mmol substrate, 0.75 mol/L NaOH, 100% Ag$_2$O, 135 °C, 30 min.

Scheme 1. Proposed Reaction Pathway of the Oxidation of Glucose into Formic Acid
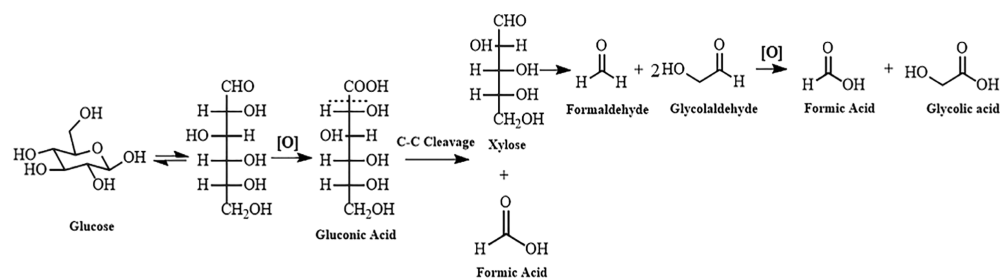
generation. Other organic acids, such as oxalic acid, glycolic acid, acetic acid, and lactic acid, could be hardly converted under such hydrothermal conditions (Table 2, Entries 2−5), which inferred that these organic acids were unlikely the intermediates for FA production. Meanwhile, methanol and sorbitol were completely converted but without any production of FA (Table 2, Entries 6 and 7), which suggested that these alcohols were unlikely the intermediates for FA production, although they were more reactive than organic acids under hydrothermal conditions.

Aldehyde/ketone species such as glycolaldehyde, pyruvaldehyde, glyceraldehyde, and 1,3-dihydroxyacetone displayed high reaction activity under hydrothermal conditions, and they all had 100% conversion (Table 2, Entries 8−11). Glycolaldehyde afforded FA and glycolic acid as the major products with yields of 24.1 and 16.5%, respectively, which indicated that glycolaldehyde was likely an intermediate for FA generation. FA yields obtained with pyruvaldehyde and glyceraldehyde were 3.2 and 1.1%, respectively. Especially, the major products of pyruvaldehyde were lactic acid and acetic acid with yields of

53.6 and 21.4%, respectively. Hence, these two aldehydes were unlikely the key intermediates for FA production. When 1,3-dihydroxyacetone was engaged as the substrate, glycolic acid was identified as the major product with FA, lactic acid, and acetic acid as side products. Thus, 1,3-dihydroxyacetone was unlikely the key intermediates for FA production. Furthermore, xylose was tested and displayed high activity to produce FA (Table 2, Entry 12), which indicated that xylose might be a key intermediate for FA production.

Based on the tested results, Scheme 1 shows the proposed reaction pathway for glucose conversion into FA with the oxidation of Ag_2O under mild hydrothermal conditions. Glucose first transforms into its open-chain form and the aldehyde group is oxidized by Ag_2O and then gives the gluconic acid. Subsequently, FA and xylose are formed by the breakage of the C1−C2 bond of gluconic acid. Finally, xylose transforms into formaldehyde and glycolaldehyde, which are further oxidized into FA and glycolic acid, respectively.

3. CONCLUSIONS

We developed a new method of one-step conversion of glucose into FA with simultaneous reduction of Ag_2O to Ag under mild hydrothermal conditions. At optimum reaction conditions, a 40.7% yield of FA, 6.1% yield of glycolic acid from glucose, and 100% conversion of Ag_2O to Ag were obtained. This study not only developed a new way for value-added chemical production from renewable biomass resources but also proposed an alternative low-carbon and energy-saving route for silver extraction and recovery.

4. MATERIAL AND METHODS

4.1. Materials. In this research, glucose (99.9%), formic acid (98%), glycolic acid (98%), methanol (99.5%), and xylose (99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (96%), acetic acid (99.5%), and lactic acid (85%) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Gluconic acid (49−53 wt % in water) was purchased from Sun Chemical Technology (Shanghai) Co., Ltd. Sorbitol (98%) was purchased from Innochem (Beijing) Technology Co., Ltd. Glycolaldehyde dimer was offered by Aladdin Reagent Company. Sodium oxalate (99.8%) and pyruvaldehyde (40% w/w aq. solution) were purchased from Shanghai Titan Scientific Co., Ltd. Glyceraldehyde (85%) was obtained from Bide Pharmatech Ltd. 1,3-Dihydroxyacetone (98%) was provided by J&K Scientific Ltd. Ag_2O (99.7%, Macklin Biochemical Co., Ltd.) was chosen as the model compound of Ag(I) in the basic solution because Ag(I) ion could form AgOH and then generate Ag_2O at a high pH (pH > 11). The stoichiometric demand for complete oxidation of glucose to FA was defined as a 100% Ag_2O supply according to eq 1.

$$C_6H_{12}O_6 + 6Ag_2O \rightarrow 6HCOOH + 12Ag \tag{1}$$

4.2. Conversion of Glucose. The conversion of glucose was conducted in a Teflon-lined stainless steel batch reactor with an inner volume of 25 mL. In a typical procedure, the desired amounts of glucose and Ag_2O and 6.25 mL of NaOH solution were first loaded into the reactor. Then, the reactor was sealed and put into an isothermal oven preheated to 135 °C for 30 min. After the desired reaction time, the reactor was taken out from the oven and cooled to room temperature.

4.3. Analytical Methods. After the reaction, liquid samples were filtered through a 0.22 μm membrane filter and analyzed by an Agilent 1200 high-performance liquid chromatograph (HPLC), which was equipped with two KC-811 columns, a differential refractometer detector, and a tunable ultraviolet/visible absorbance detector. A 2 mmol/L $HClO_4$ aqueous solution with a flow rate of 1.0 ml/min was used as the mobile phase of HPLC. Solid samples were washed with deionized water and then dried in a vacuum oven at 40 °C for 6 h. X-ray diffraction (XRD) patterns of the solid samples were collected by a Shimadzu 6100 X-ray diffractometer equipped with Cu Kα radiation at a scan rate of 2°/min wit 2θ ranging from 10 to 80°. Total organic carbon (TOC) residuals of samples were measured by an Analytik Jena AG multi 3100 Liquid TOC instrument.

The conversion X and yield Y of products were defined based on the following equations

$$X = \frac{\text{moles of carbon in feedstock consumed}}{\text{moles of carbon in feedstock input}} \times 100\%$$

$$Y = \frac{\text{moles of carbon in product molecule}}{\text{moles of carbon in feedstock input}} \times 100\%$$

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