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Hydrothermal conversion of glucose into lactic acid with sodium silicate as a base catalyst

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ABSTRACT

In this paper, the hydrothermal conversion of glucose to lactic acid (LA) using sodium silicate (Na_2SiO_3) as a mild base catalyst was investigated. The results showed that Na_2SiO_3 was effective catalyst for the conversion of glucose. The highest LA yield of about 30% was obtained from glucose with a lower concentration of Na_2SiO_3 at 300 °C for 60 s. It was also found that the use of Na_2SiO_3 led to a much less corrosion and a higher LA yield than that with NaOH at the same pH value. This process provides an environmentally friendly and highly effective method toward the synthesis of useful LA from glucose.

1. Introduction

The restricted availability of fossil resources urges human beings to identify possibilities for the use of renewable and environmentally friendly resources as an alternative [1]. Biomass, as the most abundant green renewable resource, has been considered as a potential feedstock to dwindle fossil fuel consumption. Carbohydrates with relatively high purity, accounting for 75 wt.% of plant biomass, can be harvested from a wide variety of crops. Considerable studies have been performed to investigate the conversion of various carbohydrates into high value-added chemicals. Among these useful chemicals, LA has particularly gained much attentions due to its wide applications in the food, cosmetics and pharmaceutical industries, especially in the synthesis of biodegradable LA polymers with limited environmental impact and other commodity chemicals, such as ethyl lactate (a green organic solvent) or 1,2-propanediol [2–4].

Hydrothermal reactions have received an increasing attention in the conversion of biomass into useful chemicals for the reason that water serves as a reaction medium with unique properties at high temperature and high pressure [5–7]. Many investigations [8,9] have demonstrated that carbohydrate biomass can be easily degraded into oligomers and glucose under hydrothermal conditions, and thus hydrothermal process can be directly available to the conversion of cellulose and lignocelluloses. Recently, several researches [10,11] have reported that carbohydrate biomass can be converted into LA through hydrothermal reactions and alkali plays a significant role in this process. Our group has also conducted many works involving the production of LA from carbohydrate under hydrothermal conditions, the highest 27% yield of LA from glucose was obtained in the presence of NaOH [12]. However, strong alkali catalysts such as NaOH, KOH are generally applied, which results in the serious corrosion of the reactors. Thus, the development of mild catalysts to solve the corrosion problem is strongly desired. Salami et al. [13] have demonstrated that Na_2SiO_3 can play an important role to improve the corrosion resistance of micro arc oxidation coated magnesium alloy AZ31. Moreover, Na_2SiO_3 is low-cost, easily available, highly active, and it is also an effective base catalyst in biodiesel production [14–16]. Hence, Na_2SiO_3 should have high potential for converting carbohydrate biomass into LA.

The purpose of present study is to study the possibility and effectivity of Na_2SiO_3 as a base catalyst for promoting the conversion of glucose into LA under hydrothermal conditions along with less reactor corrosion and decent catalytic activity.

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2. Materials and methods

2.1. Materials

Glucose (≥99.9%, Sinopharm Chemical Reagent Co., Ltd) was used as reagent and LA (1.0 N) was purchased from Alfa Aesar for the qualitative analysis of the products in the liquid samples. As preliminary tests, various additives including Na_2SiO_3 (19.3–22.8 wt.% of Na_2O), MnO_2 (≥97.5%), TiO_2 (≥98.0%), $NaHCO_3$ (≥99.5%), $Al(OH)_3$ (≥97.0%), NaOH (≥96.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout the study.

2.2. Experimental procedure

Experiments were conducted using a series of batch SUS 316 tubing reactors [9.525 mm (3/8 in.) outer diameter, 1 mm wall thickness, and 120 mm length] with end fittings, providing an inner volume of 5.7 mL. The schematic drawing can be found elsewhere [17,18]. The experimental procedure was conducted as follows. The desired amounts of glucose, Na_2SiO_3, and deionized water were added to the reactor chamber. The reactor was then sealed and put into a salt bath that had been preheated to the desired temperature. In the salt bath, the reactor was vibrated and agitated during the reaction. After the preset reaction time, the reactor was removed from the salt bath and then placed into a cold water bath to quench the reaction. After cooling to room temperature, the reaction liquid sample was collected and filtered through a 0.22 μm syringe for analysis. The working pressure is saturated vapor pressure of water at 300 °C (8.58 MPa), because the density of water at 300 °C is about 0.7, and a less 70% of water filling was used in this study.

2.3. Analysis

The LA yield was defined as the percentage of LA to initial glucose on a carbon basis as follows:

$$\text{Yield,}\quad \text{mmol\%} = \frac{\text{C in LA, mmol}}{\text{C in the glucose, mmol}} \times 100\% \qquad (1)$$

The water filling was defined as the ratio of the volume of the water put into the reactor to the inner volume of the reactor.

Liquid samples were filtered and then analyzed by high performance liquid chromatography (HPLC), total organic carbon (TOC), inductive coupled plasma emission spectrometer (ICP) and gas chromatography/mass spectroscopy (GC/MS). HPLC analysis was performed on KC-811 columns (SHODEX) with an Agilent Technologies 1200 system, which was equipped with a tunable ultraviolet/visible (UV/vis) absorbance detector adjusted to 210 nm and a differential refractometer detector. The system used a 2 mmol/L $HClO_4$ solution as the mobile phase at a flow rate of 1.0 mL/min. TOC was analyzed using a Shimadzu TOC 5000A. The concentrations of various metals in the effluent were monitored by ICP. The Agilent 7890 GC/MS system, which was equipped with a 5985 C inert mass selective detector (MSD) and a triple-axis detector, was used to investigate other possible chemicals in liquid samples.

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. Surface morphologies of the tested specimens were examined by a scanning electron microscope (SEM) with the model of Sirion 200. The components of total salt and the variation of metals in the oxide films were identified by an INCA X-Act energy dispersive spectrum (EDS). The oxide crystal structures were analyzed using the X-ray diffraction (XRD) instrument. XRD analyses were performed on a Bruker D8 Advance X-ray diffractometer. The step scan covered angles of 10–80° (2θ) at a rate of 2°/s.

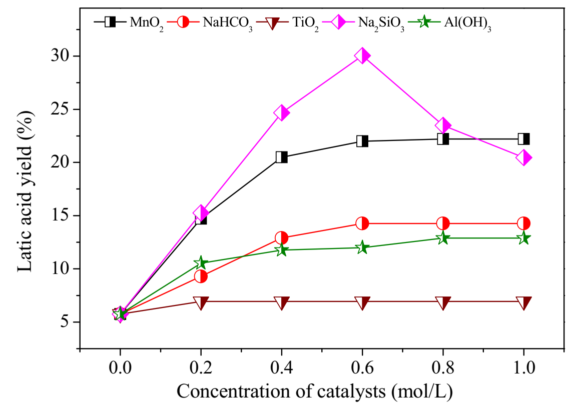


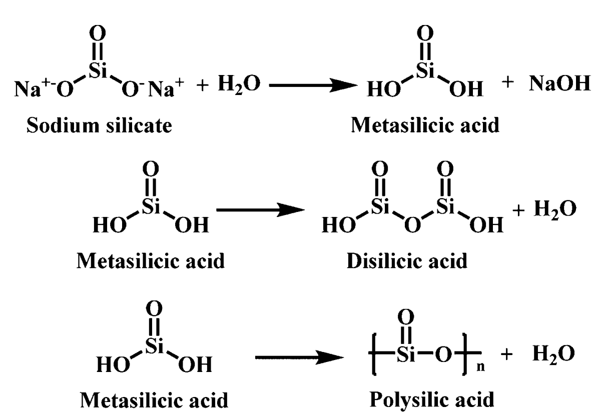
Fig. 1. Effect of different catalysts on yield of LA (0.1 mol/L glucose, 35% water filling, 300 °C, 60 s).

3. Results and discussion

3.1. Catalyst screening

Initially, various catalysts such as bases and metal oxides were screened in order to enhance the yield of LA with less reactor corrosion. According to our previous study, 300 °C and 60 s are better reaction conditions for the production of LA from glucose as a model compound of biomass. Thus, Na_2SiO_3, MnO_2, TiO_2, $NaHCO_3$, and $Al(OH)_3$ were chosen as the catalyst in the conversion of glucose at 300 °C for 60 s. As shown in Fig. 1, among the catalysts investigated, Na_2SiO_3 showed better performance, affording LA with rapidly increased yield. Because a good LA yield was also obtained in the presence of MnO_2, we performed the reaction for a higher yield of LA through increasing the amount of MnO_2 from 1 mol/L to 2 mol/L. As a result, the highest LA yield remained 22%. The use of TiO_2, $NaHCO_3$, and $Al(OH)_3$ afforded the LA yield of less than 15%. Therefore, Na_2SiO_3 as the catalyst was used for the conversion of glucose into LA under hydrothermal process and explored the best reaction conditions.

Fig. 1 shows that the LA yield firstly increased with the initial concentration of Na_2SiO_3, and then decreased and the highest LA yield (30%) was obtained with 0.6 mol/L Na_2SiO_3. As the increase in Na_2SiO_3 concentration would lead to a higher concentration of OH^- which can be released by the hydrolysis of Na_2SiO_3 as shown Scheme 1, the yield of LA displayed increasing tendency initially. However, pH remained 13.5 when Na_2SiO_3 increased to 0.6 mol/L. Then, the LA yield decreased with the increase in Na_2SiO_3 concentration. Therefore, the increase in Na_2SiO_3 concentration did not



Scheme 1. Hydrolysis and condensation of Na_2SiO_3 for the generation of colloidal silica particles.