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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.

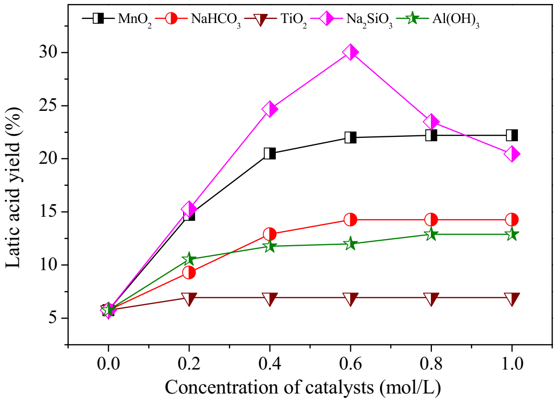


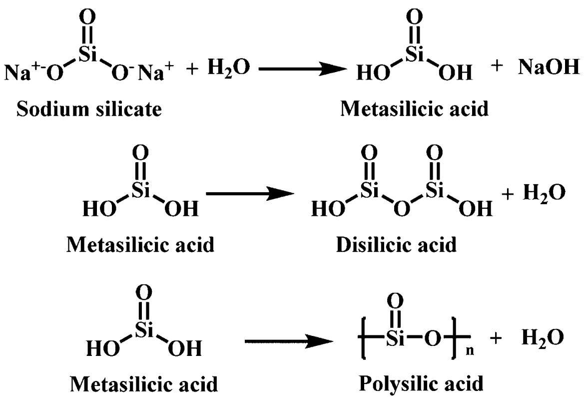
Fig. 1. Effect of different catalysts on yield of LA (0.1 mol/L glucose, 35% water filling, 300 °C, 60 s).

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.

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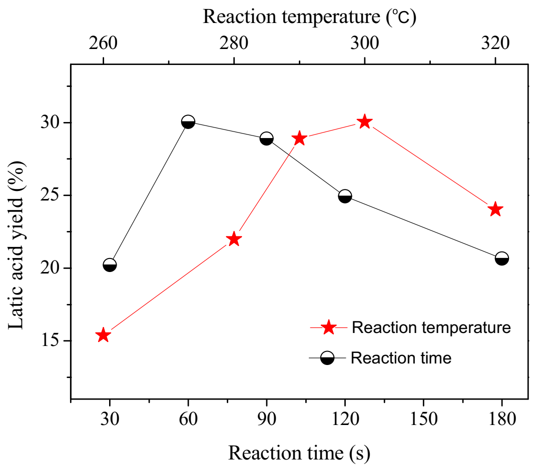


Fig. 2. Effect of reaction time and temperature on LA yield (For reaction temperature: 0.1 mol/L glucose, 0.6 mol/L Na_2SiO_3, 35% water filling, 60 s; For reaction time: 0.1 mol/L glucose, 0.6 mol/L Na_2SiO_3, 35% water filling, 300 °C).

effectively change the OH^-concentration when Na_2SiO_3 concentration was over 0.6 mol/L.

3.2. Optimization of reaction conditions for high yield of LA with Na_2SiO_3

Subsequently, effects of other reaction conditions on the yield of LA with Na_2SiO_3 were studied. As illustrated in Fig. 2, the LA yield increased remarkably with raising the temperature and reached a maximum value at 300 °C, then decreased from 300 °C to 320 °C. It is possibly that the significant change occurs due to water properties such as ion product at 280–300 °C, in addition to the increase in reaction rate caused by the increase in temperatures. However, the decreased LA yield at 320 °C may be attributed to the decomposition of LA at higher temperatures. This observation was consistent with our previous reports [19].

The reaction time also had a significant effect on the yield of LA. The experiments were conducted by changing the reaction time from 30 s to 180 s at 300 °C with 0.6 mol/L Na_2SiO_3. As shown in Fig. 2, the yield increased drastically with increasing the reaction time at the first 60 s, however, the yield of LA decreased after 60 s. In general, the decomposition of LA to acetic acid and formic acid at hydrothermal conditions may occur at a longer reaction time [20], but it can be seen that LA formation was likely faster than LA decomposition during the first 60 s. Hence, 60 s was chosen in further investigations.

The pressure of the reaction system usually has a strong influence on the product yield, so the experiments were conducted by varying water filling to investigate the effect of the pressure on the LA yield. As shown in Fig. 3, the yield of LA at a fixed amount of glucose increased slightly when the water filling increased from 20% to 35% and then gradually decreased. It is likely that the initial concentration of glucose decreased with the increase in water. Then the experiments were conducted by changing water filling at a fixed initial concentration of glucose, and similar results were shown in Fig. 3. Therefore, the effect of the initial concentration of glucose on the LA yield is not obvious, while the pressure of the reactor system is the one of the main effect factors. The suitable pressure is beneficial to form the LA, but too higher pressure lead to the decomposition of LA.

3.3. Other intermediate products and reaction pathways

Fig. 4 shows the HPLC chromatograms of the samples obtained after the reaction of glucose with and without Na_2SiO_3. For two

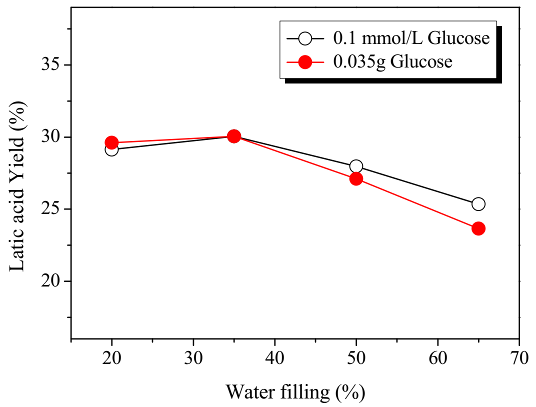


Fig. 3. Effect of water filling on yield of LA (0.6 mol/L Na_2SiO_3, 300 °C, 60 s).

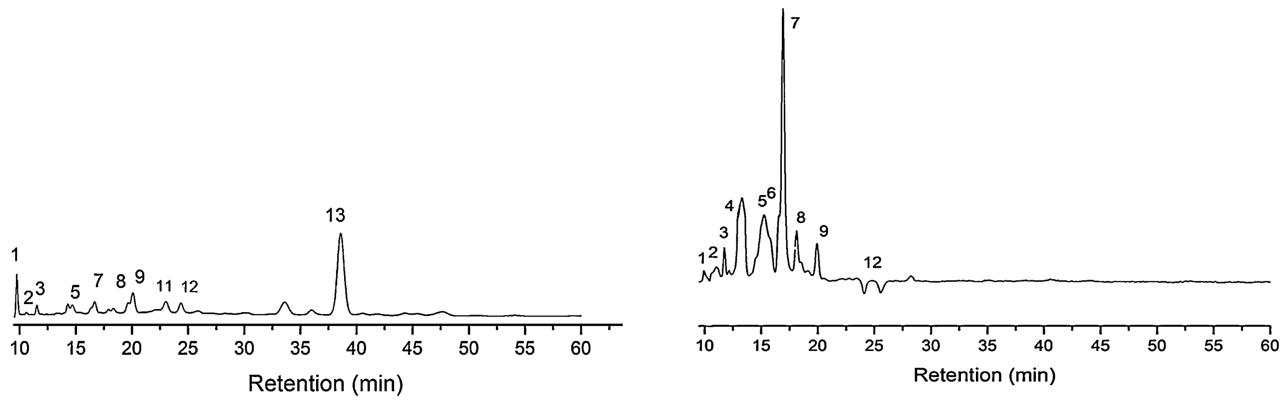
chromatograms with and without Na_2SiO_3, many peaks of low molecular weight carboxylic acids appeared, such as oxalic acid, maleic acid, pyruvate acid and so on. However, the peaks of low molecular weight carboxylic acids with Na_2SiO_3 were larger than those without Na_2SiO_3. Also, in the presence of Na_2SiO_3, the peak of LA was the highest in all low molecular weight carboxylic acids and peaks of higher molecular weight carboxylic acid almost disappeared.

On the basis of above discussion and results, the proposed reaction pathway of the formation of LA from glucose can be illustrated in Fig. 5. Firstly, Na_2SiO_3 may be hydrolyzed to produce OH^- and then hydrothermal conversion glucose into LA under alkali condition. For the alkaline conversion of glucose into LA, glucose firstly isomerizes to fructose, and then fructose is further decomposed to glyceraldehyde under the hydrothermal conditions. Finally, glyceraldehyde converts to LA via the formation of pyruvaldehyde, accompanied with the decomposition of LA to acetic acid and formic acid. The detail mechanism is in the process.

3.4. The reactor corrosion characterization

Although our previous studies have shown that NaOH is an efficient alkali catalyst for hydrothermal conversion of carbohydrate into LA, serious corrosion of the reactor was observed. For this reason, Na_2SiO_3 was chosen to decrease the corrosion. To evaluate the corrosion degree of the reactor with Na_2SiO_3, the reactor corrosion tests with NaOH or Na_2SiO_3 and without any catalyst were compared. Fig. 6 presents the high magnification (×80,000) SEM images of surfaces of SUS 316 after the reaction with NaOH or Na_2SiO_3 and without any catalyst. Significant variation in the morphologies of the oxide films was observed with different alkaline catalyst. As shown in Fig. 6, rod-like and platelet-like oxide crystals grew on the surface of SUS 316 with NaOH, which indicates the severest corrosion. However, crystals on the surface of SUS 316 with Na_2SiO_3 obviously reduced, suggesting that the corrosion became weak. Meanwhile, these results are corresponding to the energy dispersive spectrum (EDS) of the surface of reactor after the reaction. As shown in Fig. 7, the mass percentages of iron, chromium, nickel, manganese and O on the surfaces were no significant difference among the tests with Na_2SiO_3 and without any catalyst, compared to that before the reaction. However, in the presence of NaOH, oxygen dominated at the surfaces of metal alloys and the intensities of iron, chromium, nickel and manganese decreased significantly, further suggesting that NaOH lead to more severe corrosion of the reactor than Na_2SiO_3.

The average concentrations of Fe, Cr, Ni and Mn in the solution samples after reactions were also monitored by ICP as shown



(a) 0 mol/L Na_2SiO_3 (b) 0.6 mol/L Na_2SiO_3

Fig. 4. HPLC chromatographs of the liquid sample of hydrothermal reaction of glucose (1. oxalic acid, 2. maleic acid, 3. pyruvate acid, 4. malonic acid, 5. succinic acid, 6. glycolic acid, 7. lactic acid, 8. formic acid, 9. acetic acid, 10. levulinic acid, 11. crylic acid, 12. propionic acid, and 13. 5-(hydroxymethyl)-2-furaldehyde).

$$\equiv Si{-}O{-}Na + H_2O \rightarrow \equiv Si{-}O{-}H + NaOH$$

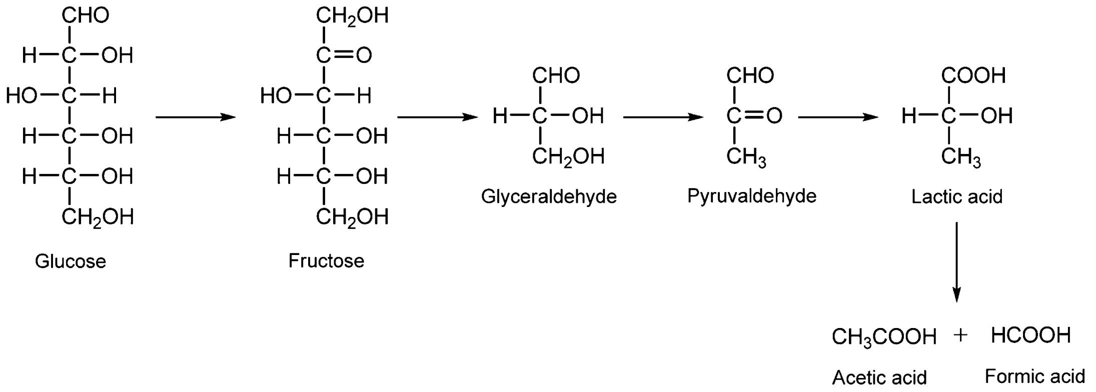


Fig. 5. Proposed pathways of conversion of glucose to lactic acid in subcritical water.

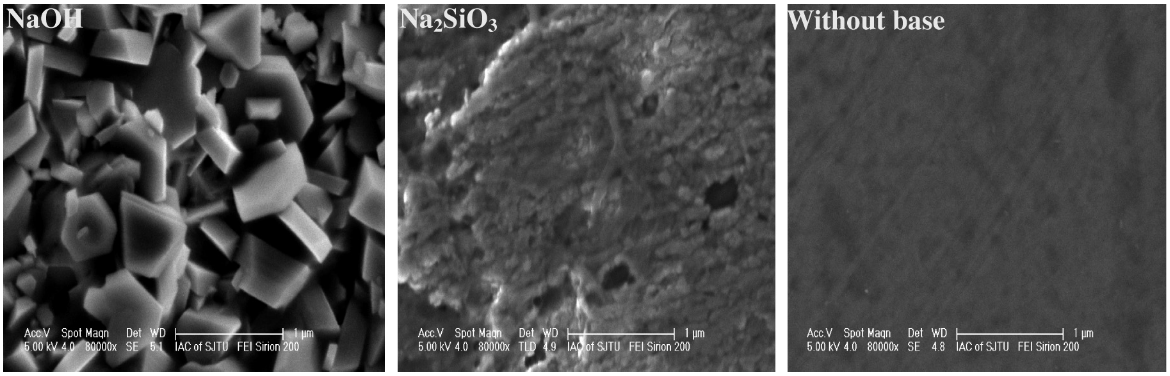


Fig. 6. SEM images of surfaces of SUS 316 after hydrothermal process.

in Fig. 8. Compared to that with NaOH, the sample with Na_2SiO_3 showed much lower metal concentrations, which was equal to that without any catalyst, indicating that Na_2SiO_3 is a milder catalyst than NaOH. The results of ICP analysis are in accord with those of SEM and EDS analysis, confirming less corrosion and dealloying in stainless steel SUS 316 with Na_2SiO_3 than that with NaOH.

For the less corrosion to reactor with Na_2SiO_3, as mentioned in Scheme 1, the polymerization of Na_2SiO_3 might occur by hydrolysis and condensation of Na_2SiO_3 under the hydrothermal conditions, and then form the small silica clusters and larger colloidal silica particles. It is most likely that these colloidal silica particles aggregate on the surface of the reactor and prevent the further corrosion to the reactor.

Finally, the experiments with cellulose were conducted at 300 °C for 90 s with 0.6 mol/L Na_2SiO_3, LA yield reached to 29%, which was almost the same as that with glucose.

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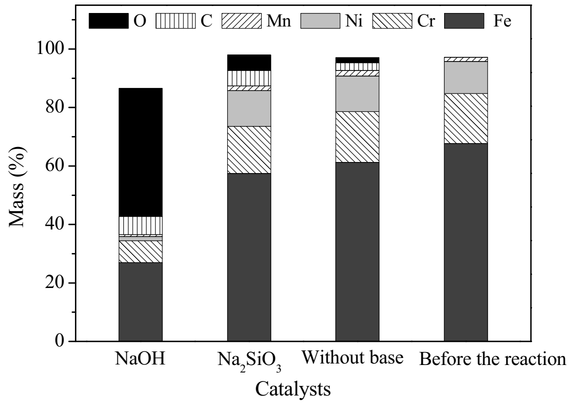

Fig. 7. Surface composition of cross-section of the SUS316 reactor after the reaction with NaOH, Na_2SiO_3, without base, and before the reaction.

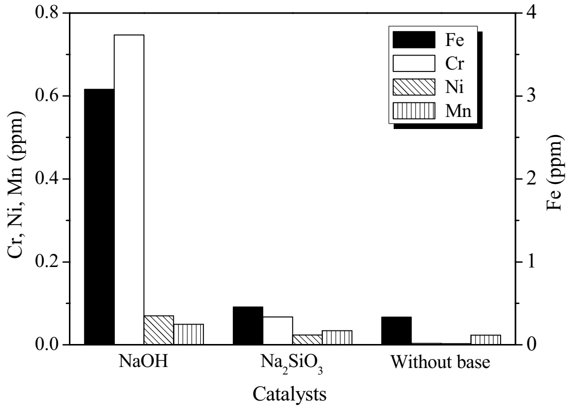

Fig. 8. Concentrations of metals in liquid sample after the reaction with NaOH, Na_2SiO_3 and without base.

4. Conclusions

We have developed a mild base catalyst of Na_2SiO_3 for highly efficient conversion of glucose into LA under hydrothermal conditions. Among the catalysts tested, such as Na_2SiO_3, MnO_2, TiO_2, $NaHCO_3$, and $Al(OH)_3$, the use of Na_2SiO_3 gave the best result for the conversion of glucose. The maximum value of 30% LA from glucose was achieved with a lower concentration of 0.6 mol/L Na_2SiO_3 at 300 °C for 60 s. 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.

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