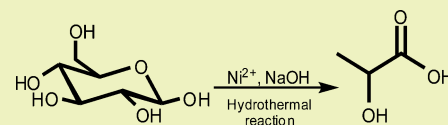


Selective Conversion of Glucose into Lactic Acid with Transition Metal Ions in Diluted Aqueous NaOH Solution

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ABSTRACT: An efficient process for the selective conversion of glucose to lactic acid with transition metal ions in diluted aqueous NaOH solution under alkaline hydrothermal conditions was investigated. As a result, Ni²⁺ was found to be efficient in the production of lactic acid from glucose and decreased simultaneously the NaOH concentration. The highest yield of 25% for lactic acid was achieved with 0.01 M Ni²⁺, 0.01 M NaOH, and 35% water filling at 300 °C for 1 min. In addition, our results suggest that the role of Ni²⁺ acts as not only as a catalyst but also as an oxidant for the conversion of glucose into lactic acid and differs from CuO as an oxidant in the conversion of cellulose or glucose into carboxylic acids in previous works. Also, the NaOH concentration in this process is remarkably reduced and gives almost the same yield compared to 2.5 M NaOH as reported previously. The mechanistic studies for lactic acid formation from glucose showed that the glyceraldehyde might act as an intermediate with Ni²⁺ under alkaline hydrothermal conditions.



KEYWORDS: Glucose, Lactic acid, Transition metal ions, NaOH, Hydrothermal reactions

INTRODUCTION

The problems of energy shortage and global warming have become more and more a threat to social development. Decreasing dependence on petroleum resources and developing clean and sustainable energy are very important tasks for our future.^{1,2} Biomass, which is the most abundant, clean, and renewable resource, has been the research topic for conversion and utilization of fuels and chemicals.^{3–7} Lactic acid is a very important organic chemical, which is commonly used as a raw material for the preparation of biodegradable plastics. Due to the potential importance and demand for industrial applications, the development of efficient and greener processes for the production of lactic acid from biomass, such as fermentation of glucose, has attracted much attention in recent years.^{8–14} Among these processes, hydrothermal treatment is the most attractive route for the transformation of glucose to lactic acid because of the unique properties of high-temperature water,^{15–22} such as fast reactions and being a green solvent. The advantages of hydrothermal process is to avoid predrying of feedstocks and carbonization during the conversion reaction of biomass.²³ But this process still remained a great challenge, either from a practical or an economic point of view.

Previously, our group reported on the efficient production of lactic acid from carbohydrates, including glycerin, starch, glucose, and cellulose, with NaOH as the alkaline catalyst^{24–26} or with CuO as the oxidant and NaOH^{27–29} under hydrothermal conditions. However, many factors still remained unsatisfactory. For example, in these processes, the improvement of lactic acid yields are strongly dependent on high concentration OH[−] (2.5 M). As we all know, high concentration NaOH has a high corrosiveness for the reactor

and a high cost for industrialization. Therefore, to satisfy the demand for practical application, the exploration of efficient methods for a decrease in NaOH concentration has great significance and is highly desirable. Recently, Vogel et al. reported a new process for selective lactic acid production from glucose and fructose by adding small quantities of Zn (II) as a catalyst in subcritical water.³⁰ Wang et al. reported the synthesis of lactic acid from cellulose by lead (II) ions or vanadyl cations in water.^{31,32} Tagaya et al. also reported on the influence of ZnCl₂ on 1,2-propylene glycol conversion in near critical water ($T = 360$ °C).³³ Encouraged by these findings, it is hypothesized that transition metal ions could improve lactic acid production from glucose and also decrease the NaOH concentration at the same time. Therefore, the purpose of this study is to investigate lactic acid production from glucose and the decrease the concentration of NaOH simultaneously with transition metal ions under hydrothermal conditions (Scheme 1).

MATERIALS AND METHODS

Experimental Materials and Procedure. All reagents used in this study were analytical reagents ($\geq 99\%$). Glucose, as a model compound of carbohydrate biomass, was used in all experiments. NiCl₂, FeCl₂, FeCl₃, MgCl₂, CdCl₂, CuCl₂, ZnCl₂, SnCl₂, CoCl₂, sodium hydroxide, and glucose were obtained from Sinopharm Chemical Reagent (China).

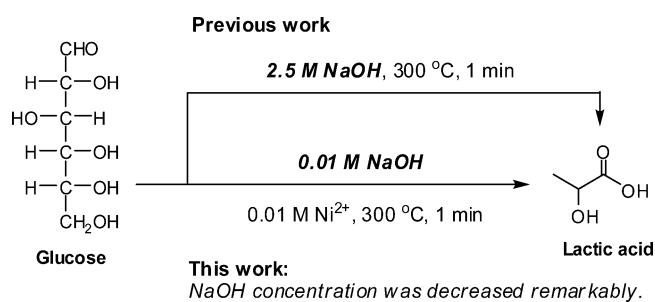
All experiments were conducted in a batch reactor made of SUS316, which is constructed of a piece of stainless steel 316 tubing (3/8 in.

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Scheme 1. Previous Work and Our Concept for Lactic Acid Production from Glucose



diameter, 1 mm wall thickness, and 120 mm length) with an internal volume of 5.7 mL. The schematic drawings of the experimental setup can be found elsewhere.³⁴ 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 (0.035 g), NiCl₂ (2.6 mg), NaOH (0.8 mg), and deionized water (2 mL) were put in the batch reactor. Sequentially, the reactor was placed horizontally in a salt bath that had been preheated to the desired temperature (300 °C). After 1 min, the reactor was transferred from the salt bath and immediately placed in a cold water bath to quench the reaction. The liquid samples were analyzed by HPLC. The loading, shaking, and cooling procedures were all done with a mechanic arm to ensure accuracy.

Analytical Methods. After the reaction, the liquid samples were collected and analyzed by high performance liquid chromatography (HPLC, Agilent 1200LC). Formic, acetic, and lactic acid were quantified by HPLC. The flowing solution used in HPLC was 2 mM HClO₄ with a flowing rate of 1 mL/min. Carbon balance was conducted by total organic carbon (TOC, Shimadzu, V-CPN).

Solid samples 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. Transition metal ions concentration in the solution was measured by inductively coupled plasma (ICP, PerkinElmer, Optima 2100DV).

The yields of organic acids were calculated based on the following formulas. The yields were obtained from experiments over three times, and relative error was less than 5%.

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

RESULTS AND DISCUSSION

Transition Metal Ions Screening. In our previous studies, it was found that lactic acid, acetic acid, and formic acid were main products from glucose under alkaline hydrothermal conditions. First, the effect of various transition metal ions on lactic acid production from glucose was screened. The results are summarized in Figure 1. The reaction was carried out in the absence of both NaOH and transition metal ions with 35% water filling at 250 °C for 2 min, which obtained only a 2% yield of lactic acid. The reaction gave lactic acid at a 3% yield in the presence of NaOH only. Various transition metal ions such as Fe³⁺, Ni²⁺, Zn²⁺, and Co²⁺ in the absence of NaOH were examined; all of them improved the transformation efficiency and gave a significant increase in the yield of lactic acid. Ni²⁺ gave a much better yield (13%) compared to Fe³⁺, Zn²⁺, and Co²⁺. From these experiments, it is very clear that transition metal ions can promote efficient lactic acid production from glucose. Thus, Ni²⁺ was selected for the following optimization.

Effect of Ni²⁺ Concentration on Lactic Acid Production with and without NaOH. To investigate the effect of the

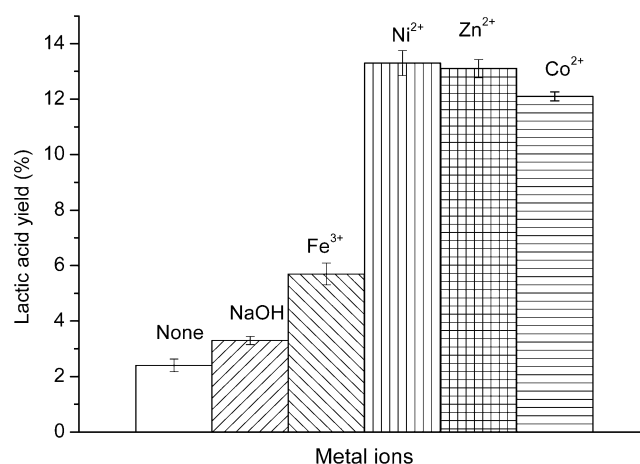


Figure 1. Effect of transition metal ions on lactic acid production. Reaction conditions: glucose, 0.035 g; 0.1 M transition metal ions; 0.1 M NaOH; 250 °C; 2 min).

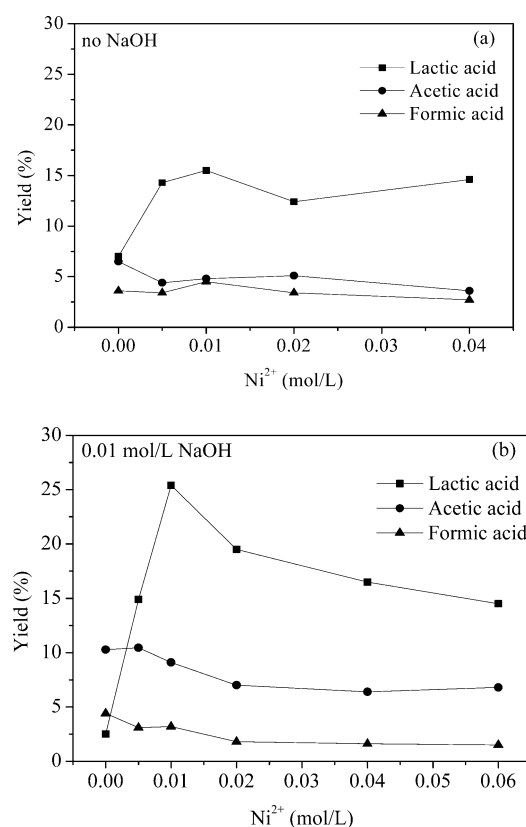


Figure 2. Effect of concentration of Ni²⁺ on lactic acid production. Reaction conditions: glucose, 0.035 g; 300 °C; 1 min).

Table 1. Effect of Ni²⁺ and NaOH on Lactic Acid Production

run	NaOH (mol/L)	Ni ²⁺ (mol/L)	lactic acid (%)	acetic acid (%)	formic acid (%)
1	0.01	0	3	10	4
2	0	0.01	16	5	5
3	0.005	0.01	23	6	3
4	0.01	0.01	25	9	3
5	0.02	0.01	24	6	1
6	0.01	0.04	22	8	2

Reaction conditions: 300 °C; 1 min.

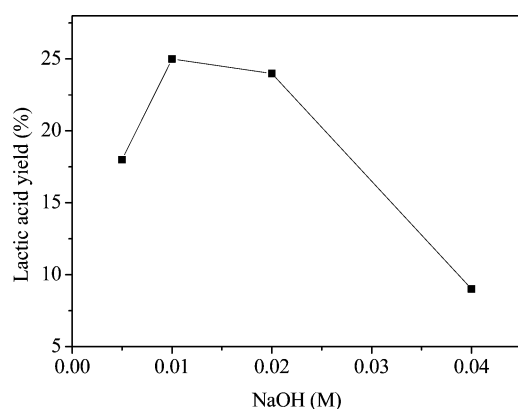


Figure 3. Effect of NaOH concentration on lactic acid production. Reaction conditions: 0.005–0.04 M Ni^{2+} ; 300 °C; 1 min).

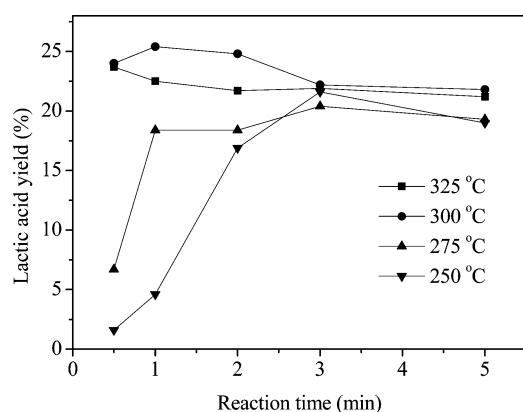


Figure 4. Effect of temperature and time on lactic acid production. Reaction conditions: 0.01 M Ni^{2+} ; 0.01 M NaOH).

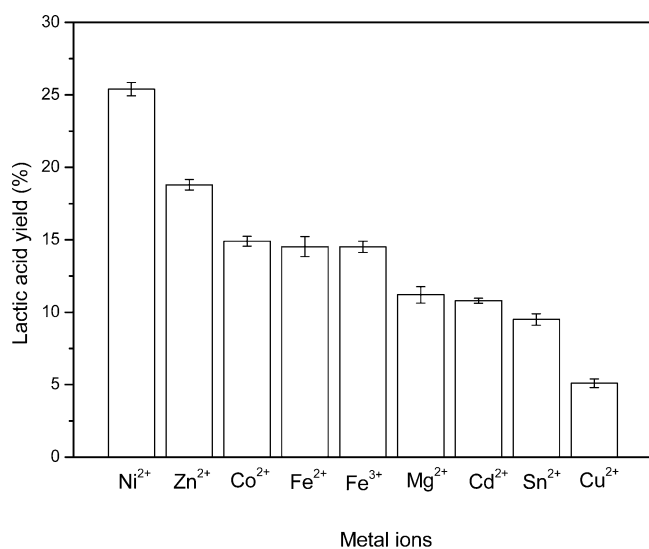


Figure 5. Effect of various transition metal ions on lactic acid production under optimized conditions. Reaction conditions: 0.01 M transition metal ions; 0.01 M NaOH; 300 °C; 1 min).

concentration of Ni^{2+} on the hydrothermal conversion of glucose into lactic acid, we carried out the reaction of glucose without NaOH at 300 °C for 1 min with the concentration of Ni^{2+} from 0 to 0.04 M. As shown in Figure 2a, the yield of 7% of lactic acid was obtained without the addition of Ni^{2+} . The yield of lactic acid increased as the concentration of Ni^{2+}

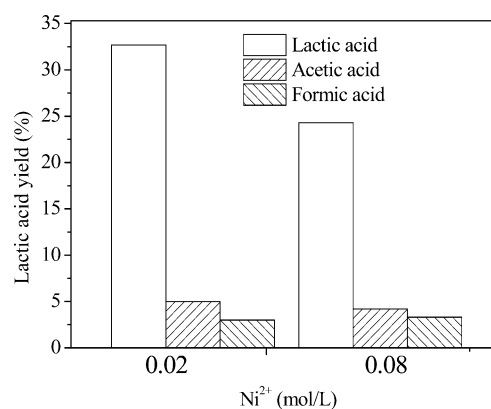


Figure 6. Effect of transition metal ions on lactic acid production. Reaction conditions: 2.5 M NaOH; 300 °C; 1 min.

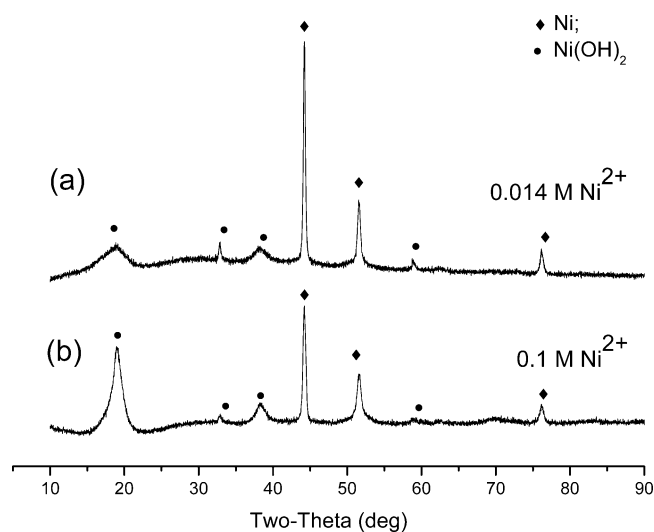


Figure 7. XRD patterns of solid samples after reaction: (a) Ni, 56.61%; $\text{Ni}(\text{OH})_2$, 43.39%. Reaction conditions: 0.014 M Ni^{2+} ; 2.5 M NaOH; 300 °C; 1 min. (b) Ni, 45.01%; $\text{Ni}(\text{OH})_2$, 54.99%. Reaction conditions: 0.1 M Ni^{2+} ; 2.5 M NaOH; 300 °C; 1 min).

increased, and a maximum value of 16% was obtained when the concentration of Ni^{2+} further increased to 0.01 M. The profile became irregular when the concentration of Ni^{2+} exceeded 0.01 M. In addition, the yield of acetic acid decreased gradually with further increasing the concentration of Ni^{2+} from 0 to 0.04 M. The yield of formic acid increased from 0 to 0.01 M, reached a maximum value of 4% at 0.01 M Ni^{2+} , and decreased with further increasing the concentration of Ni^{2+} from 0.01 to 0.04 M. However, the concentration of Ni^{2+} causes little impact on the acetic acid and formic acid yields in contrast to the lactic acid yield.

Similarly, in Figure 2b, when 0.01 M NaOH was used, the yield of 3% of lactic acid was obtained without the addition of Ni^{2+} . The yield of lactic acid increased as the concentration of Ni^{2+} increased, and a maximum value of 25% was obtained when the concentration of Ni^{2+} further increased to 0.01 M. The yield of lactic acid decreased when the concentration of Ni^{2+} exceeded 0.01 M, but the yields of acetic acid and formic acid decreased with further increasing the concentration of Ni^{2+} from 0 to 0.02 M and almost remained unchanged when the concentration of Ni^{2+} exceeded 0.02 M.

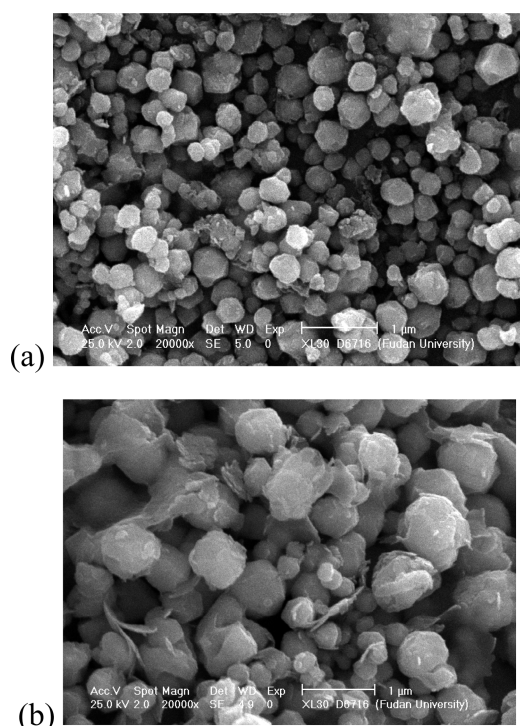


Figure 8. SEM images of Ni after the reaction. Reaction conditions: (a) 0.014 M Ni²⁺; 2.5 M NaOH; 300 °C; 1 min and (b) 0.1 M Ni²⁺; 2.5 M NaOH; 300 °C; 1 min).

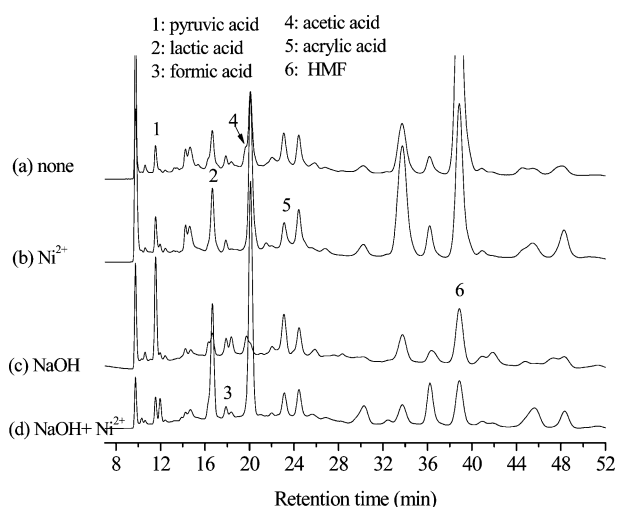


Figure 9. Chromatogram obtained by HPLC of the liquid sample after hydrothermal conditions. Reaction conditions: 0.01 M Ni²⁺; 0.01 M NaOH; 300 °C; 1 min).

Experiments were conducted by varying the NaOH concentration from 0 to 0.04 M with the Ni²⁺ concentration from 0 to 0.04 M at 300 °C for 1 min to investigate the effect of NaOH concentration. As summarized in Table 1 and Figure 3, the reaction in the absence of either Ni²⁺ or NaOH led to a low yield of lactic acid (entries 1 and 2). The use of Ni²⁺ afforded a much better yield. The yield of lactic acid increased significantly at first in the presence of Ni²⁺ as the concentration of NaOH increased from 0.005 to 0.02 M (entries 3–5). A total of 0.01 M for the optimum concentration of both NaOH and Ni²⁺ reached a maximum value of 25% for lactic acid, 9% for acetic acid, and 3% for formic acid (entry 4). The yield of lactic acid

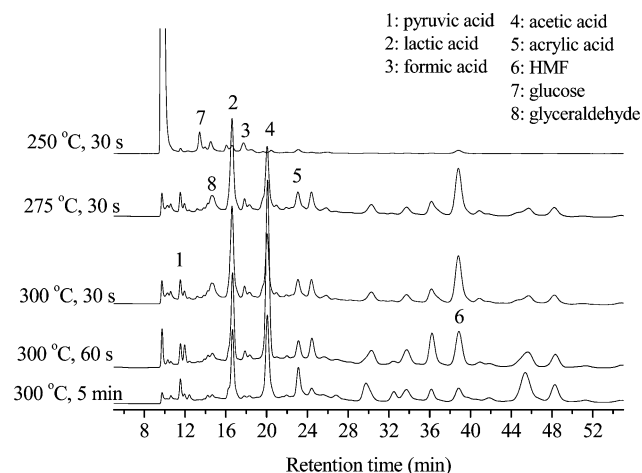


Figure 10. Chromatogram obtained by HPLC of the liquid sample after hydrothermal conditions. Reaction conditions: 0.01 M Ni²⁺; 0.01 M NaOH).

decreased a little when the concentration of Ni²⁺ exceeded 0.01 M, even increasing the concentration of NaOH, and 22% of lactic acids was obtained (entry 6). The decrease in lactic acid yield with the addition of high concentration NaOH might be due to decomposition of lactic acid.

Effects of Reaction Temperature and Time on Lactic Acid Production. Figure 4 shows that reaction temperature has a significant effect on lactic acid production in this transformation. The reaction of glucose was performed by varying temperatures from 250 to 325 °C with 0.01 M NaOH and 0.01 M Ni²⁺ at different times from 0.5 to 5 min. At 250 °C, the yield of lactic acid increased greatly from 0.5 to 3 min to reach to a maximum value of 22% for 3 min, and it subsequently decreased with further increasing the reaction time from 3 to 5 min. At 275 °C, the yield of lactic acid increased significantly at first from 0.5 to 1 min. The yield after 1 min had not changed obviously, and a maximum value of 21% was achieved for 3 min. When temperature was further increased to 300 °C, the yield of lactic acid increased from 0.5 to 1 min to reach to the best yield of 25% for 1 min and decreased from 1 to 5 min, which indicated that a higher temperature is beneficial to lactic acid production from glucose than a lower temperature. In addition, it is known that the constant ionization (k_w) of high temperature water is the maximum at near 300 °C at saturated vapor pressure.³⁵ The highest yield 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. However, the yield of lactic acid further decreased with increasing reaction time from 1 to 5 min at 325 °C. The decreasing yield in conversion of glucose at a higher temperature may be attributed to further decomposition of formed lactic acid.

Reproducibility of Various Transition Metal Ions on Lactic Acid Production under Optimum Conditions. After optimization of reaction conditions, we carried out the experiments to examine the reproducibility of various transition metal ions on lactic acid production with 0.01 M Ni²⁺ and 0.01 M NaOH at 300 °C for 1 min, and the results are summarized in Figure 5. Among various transition metal ions we tested, such as Ni²⁺, Zn²⁺, Co²⁺, Fe²⁺, Fe³⁺, Mg²⁺, Cd²⁺, Sn²⁺, and Cu²⁺, Ni²⁺ afforded the much better result than other transition metal ions, which is similar to no optimum original result as shown in

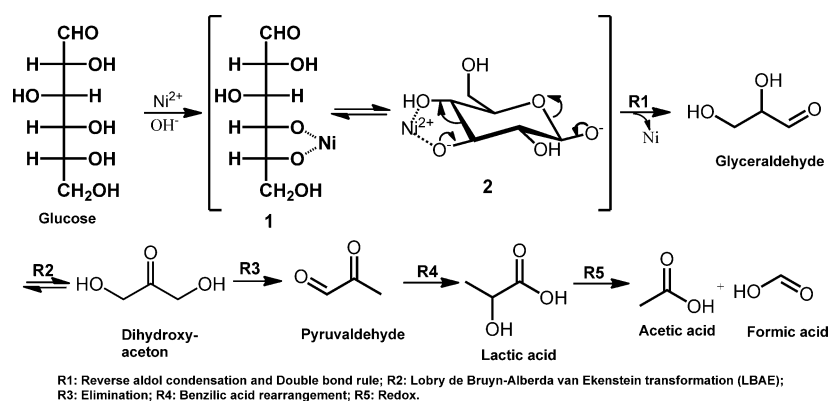


Figure 11. Proposed pathway for lactic acid production from glucose over Ni^{2+} .

Figure 1. Ni^{2+} can promote efficiently lactic acid production with lower concentrations of 0.01 M NaOH and afforded the highest yield of 25%. Expectedly, Zn^{2+} reported by H. Vogel et al. was also effective in the transformation under alkaline hydrothermal conditions.³⁰

Finally, a carbon balance was conducted. The result showed that the conversion of glucose to liquid products was about 89%. The total yields of the main products, such as lactic, acetic, and formic acid, were 37%; other products might be smaller amounts of other acids (such as acrylic acid, pyruvic acid) and HMF and unknown compounds. The main gas products were H_2 and CH_4 , and the conversion of initial carbon should be less 11%.

Mechanism Studies for Lactic Acid Production from Glucose. First, we investigated the effect of the different Ni^{2+} concentrations on lactic acid production. In Figure 6, comparison of the yields of three acids using 0.02 M Ni^{2+} with 0.08 M Ni^{2+} , indicates clearly that low concentration Ni^{2+} gave better results. In addition, we investigated the solid residues after the reaction by XRD analysis. It is shown in Figure 7 that Ni^{2+} existed as Ni and $\text{Ni}(\text{OH})_2$, which suggests that Ni^{2+} acts not only as a catalyst but also as an oxidant in improving conversion of glucose into lactic acid under hydrothermal conditions. XRD quantitative analyses of the solid samples after the reaction were examined. A total of 56.61% for Ni and 43.39% for $\text{Ni}(\text{OH})_2$, with the addition of 0.014 M Ni^{2+} , and 45.01% for Ni and 54.99% for $\text{Ni}(\text{OH})_2$, with the addition of 0.1 M Ni^{2+} , were obtained. This might explain why low concentration Ni^{2+} would provide high transformation efficiency compared to that of high concentration Ni^{2+} .

The SEM images of the two types of solid residue after the reaction are shown in Figure 8. As indicated in Figure 8a, the reduced Ni powder from 0.014 M Ni^{2+} has spherical shapes and disordered surface morphology with particle sizes of approximately 200 nm. The Ni powder exhibits similar shapes when 0.1 M Ni^{2+} was used, but the particle sizes are approximately 500 nm as shown in Figure 8b. From Figure 8, the reduced Ni powder from 0.014 M Ni^{2+} has much smaller particle sizes than those of Ni powder from 0.1 M Ni^{2+} .

Next, we expanded our study to investigate the peak changes of compounds on the transformation of glucose under hydrothermal conditions. Products obtained from glucose were identified by HPLC analysis as shown in Figures 9 and 10. In Figure 9b, it is shown that the peaks for these organic acids were clearly increased in the presence of Ni^{2+} compared to the absence of Ni^{2+} . The peaks of organic acids were weak in

Figure 9c when low concentration of NaOH only was used. The solution after the reaction was quite cloudy; this may be because glucose was carbonized during the reaction, which might result in a decrease in glucose selectivity. Comparison of the spectra of Figure 9d with those of Figure 9a–c, indicates clearly that the peaks for these organic acids were increased after mixing Ni^{2+} and NaOH. The solution after the reaction was very clear, and no precipitate was given. From the HPLC experiments, it is clear that combined Ni^{2+} with NaOH has a significant influence on the reaction progress.

From Figure 10, it should be noted that spectral changes on reaction progress depended on temperature. At 250 °C for 0.5 min, the peak of glucose still remained, while smaller peaks of organic acids were detected. At 275 °C, the peak of glyceraldehyde was also observed besides organic acids. Increasing from 250 to 300 °C, the rate of reaction is very fast with an increase in temperature. The detected signals of glucose became smaller gradually and then completely disappeared at 300 °C. Glyceraldehyde further decreased clearly from 275 to 300 °C as time goes up to 5 min, whereas the organic acids increased. Therefore, it was thought that the glyceraldehyde acted as an intermediate for the formation of lactic acid during the reaction.

A plausible mechanism for lactic acid production from glucose with Ni^{2+} is given in Figure 11. Initially, glucose probably involves a glucose alkoxide transition in alkaline conditions due to its weak acidity and then coordinates with Ni^{2+} with the two oxygen atoms of the adjacent hydroxyl group to form intermediate 1.³⁶ Intermediate 1 could be in equilibrium with intermediate 2. The nucleophilic attack of OH^- on the hydrogen atom of the hydroxyl group takes place easily because electron density decreases by coordination with Ni^{2+} . Subsequent the proposed retro-aldolization and the double bond rule of the respective enediols formed from the Lobry de Bruyn Alberda van Ekenstein (LBAE)³⁷ transformation of D-glucose via coordination with Ni^{2+} occurs, along with the formation of glyceraldehyde (three carbon atoms) and reduction of part of Ni^{2+} to Ni. Glyceraldehyde produces lactic acid 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.³⁸

CONCLUSIONS

We have disclosed an efficient process for the production of lactic acid from glucose with the addition of transition metal ions under alkaline hydrothermal conditions. The results

showed that transition metal ions were effective in the production of lactic acid from glucose and simultaneously decreased NaOH concentration. Among the transition metal ions tested, Ni²⁺ acts not only as a catalyst but also as an oxidant and was more effective in the present transformation. The highest yields of 25% for lactic acid were obtained with 0.01 M Ni²⁺ and 0.01 M NaOH and 35% water filling at 300 °C for 1 min. The presence of Ni²⁺ afforded almost the same yield of lactic acid with a NaOH concentration lower than that of 2.5 M NaOH reported previously. Mechanistic studies showed that the glyceraldehyde might act as an intermediate for the formation of lactic acid during the reaction. The present work shows great significance for practical applications of the production of lactic acid from glucose and also provides a potential and economical utilization of various small amounts of transition metal ions in a mine's waste water.

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Notes

The authors declare no competing financial interest.

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