

One-pot Conversion of Cellulose to Lactic Acid Catalyzed by Metal Ion Gd^{3+} and A Detailed Analysis on the Product Distribution

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Abstract

The Lewis acid salt was used as a catalyst to study the reaction of cellulose conversion to lactic acid in a pure water system. The catalytic system can effectively inhibit the dehydration of fructose and promote the isomerization of glucose and the reverse aldol reaction of fructose. The catalytic performance of different metal salts was investigated and it was found that gadolinium nitrate was more effective as a catalyst. The effects of reaction temperature, time, catalyst loading, N_2 content and solid-liquid ratio on the yield of lactic acid were analyzed by plotting. The results show that in the 30 mL system, the maximum lactic acid yield was 56.6% when the reaction temperature was 240°C, the reaction time was 30 minutes, the catalyst was 0.135 mmol, the N_2 pressure was 2 MPa, and the solid-liquid ratio was 1: 300 (w/v).

Keywords

Lewis acid salt; Cellulose; Lactic acid; Isomerization; Reverse aldol reaction; Catalyst.

1. INTRODUCTION

Lactic acid (LA) is one of the high-potential and versatile chemicals that can be converted to a wide range of platform chemicals. LA has abundant applications in pharmaceutical, food, cosmetics industries and environmentally benign solvents. The global LA market needs to be 1220.0 kt in 2016, with an annual growth rate of 16.2%. It is expected that this demand will reach 1960.1kt by 2025 and the global market profits will reach \$9.8 billion (Regiane A D O et al., 2018).

At present, the main methods of LA production include conventional biotechnological process and petroleum-based chemical process. The biotechnological route is an anaerobic fermentation of glucose and sucrose using microorganisms, which is still suffering from low production rate and the pH control of fermentation liquid is complicated. Another route is the petroleum-based chemical process that using highly toxic cyanide as a starting material, possessing a high risk to environment. Hence, developing an efficient catalytic reaction system for selective production of LA is strongly needed. In addition, increasing research have been focused on the preparation of LA by catalytic conversion of cheap and widely available raw materials, such as cellulose and lignocellulose. Cellulose is the most widely distributed polysaccharide in nature. It is also the most abundant component in lignocellulose, accounting for about 30-50% of the dry weight bases. Under the hydrothermal condition, cellulose can be hydrolyzed to form glucose, and further converted into a wide range of platform chemicals.

Due to the challenges remain in selective cleavage of C-C or C-O bonds in cellulose and hexoses under mild reaction conditions to obtain target chemicals, a large amount of studies for catalytic production of LA by both homogeneous and heterogeneous catalysts has been

investigated. Compared to heterogeneous catalyst, homogeneous catalysts have been under intensive investigation due to the mass transfer merit and providing of deeper mechanism insights. Deng et al reported that the combination of Al(III)-Sn(II) at 463K promoted complete conversion of cellulose and provided a LA yield of 65% (Deng W P et al., 2018). Whereas, many studies have shown that metal ions such as Ni (II), Zn (II), Al (III) have obvious effects on the conversion of cellulose, but the LA yields were still not satisfactory. Thus, it is highly attractive to develop efficient catalytic system that is effective and benign to environment for the production of LA from cellulose or lignocellulosic sources.

Herein, we reported a novel metal ion Gd^{3+} (Gadolinium) as a prospective catalyst for the selective hydrothermal conversion of cellulose to LA with a high yield. In a pure water aqueous solution without base, 100% cellulose conversion and a LA yield of 56.6% were achieved within 30 mins at 240°C. In addition, the catalytic mechanism was proposed based on a detail study of the reaction intermediates in this process.

2. MATERIALS AND METHODS

2.1. Materials

The chemical reagents used in this study, such as L-(+) - lactic acid ($P \geq 98.0\%$, AR), microcrystalline cellulose ($\varphi \leq 25\mu m$), $Gd(NO_3)_3 \cdot 6H_2O$ ($P \geq 99.0\%$, AR) were all purchased from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China).

2.2. Catalytic Reaction

All catalytic reactions were performed in a 100 mL high temperature and high-pressure batch reactor, which equipped with a stainless-steel pressure vessel and a heating jacket. Reaction substrates were mixed with deionized water and catalysts in different ratios. After sealed, nitrogen was injected into the reactor and raised to the specific pressure, then the reactor was heated to the specific temperature and kept for certain time under stirring. After the reaction, the reactor was quickly quenched in an iced water bath and then the hydrolysate mixture was filtrated. The remaining solid was dried and quantified to determine the conversion of the substrate by the differential weight analysis method.

Raw material conversion rate(%)

$$= \left[1 - \frac{\text{the weight of unconverted raw material(g)}}{\text{the weight of raw material(g)}} \right] \times 100\%$$

2.3. Analytical Methods

The high-performance liquid chromatography (HPLC) used in this study was equipped with an Aminex HPX-87H column (Bio-Rad Laboratories, Hercules, CA). The mobile phase employed 0.5 mM sulfuric acid solution at a flow rate of 0.5 mL/min. The column temperature was set to 65°C, and the detector temperature was hold at 30°C. The concentrations of LA and other organic acids were quantitatively analyzed based on UV absorbance at 210 nm by comparing to the corresponding standard curves. The calculation methods of different indices were defined as below:

$$\text{Yield of product } i(\%) = \frac{\text{moles of carbon in product } i}{\text{moles of carbon in cellulose}} \times 100\%$$

3. RESULTS AND DISCUSSION

3.1. Catalytic Behavior of Different Metal Ions on the Conversion of Cellulose to LA

The catalytic activities of a variety of metal ions for LA formation were surveyed by using cellulose as the reaction substrate. Metal ions, comparatively easily accessible, cheap, and low toxic, were selected from three different groups which were main group metal ions, transition metal ions and rare earth metal ions. Most of the metal ions tested shown significant catalytic effects on cellulose degradation as the cellulose conversion rates were all higher than 80%, and the yields of organic acids such as LA and levulinic acid increased significantly. However, it was also evident that the catalytic pathway of different metal ions was comparatively different. Sn^{4+} , Al^{3+} , and Cr^{3+} showed a comparatively low cellulose conversion and tended to dehydrate fructose to 5-hydroxymethylfurfural (5-HMF) and levulinic acid. On the other hand, Sn^{2+} , Pb^{2+} , Er^{3+} , Gd^{3+} and Tb^{3+} could almost promote the complete conversion of cellulose during the reaction, and selectively formed LA as the main product of the reaction with yields higher than 50%. Among these five metal ions, Gd^{3+} was firstly reported as catalyst for this reaction, and also exhibited a slight advantage of the LA yield over other catalysts. In addition, the three rare earth metal ions evaluated here showed higher selectivities for the preparation of LA from cellulose. This may be due to their ability to maintain high Lewis acidity in aqueous solution and to promote the reaction to the direction of LA formation. Considering the novelty of employing Gd^{3+} as reaction catalyst and the high concentration of LA and LA formation pathway related intermediate products in the reaction solution, we selected $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the catalyst in this research.

3.2. Study on the Mechanisms of Cellulose Degradation Catalyzed by Gd^{3+}

During the above experiment, diversified carbon-based compounds, such as 5-HMF, levulinic acid and LA, had been detected in the reaction medium. Due to the diversity of the degradation products, it was presumed that the reaction of cellulose in this catalytic system involves many complex reaction processes. By analyzing the experimental results and referring to the relevant literature, we speculated that the degradation of cellulose may be involved in two different directions (Scheme 1 below). Under high temperature conditions (above 200°C), water would generate more hydroxide ions that can promote acid-catalyzed reactions (Wang F F et al., 2013). Gd^{3+} may interact with these hydroxide ions, becoming the driving force for the degradation of cellulose into small molecules, such as glucose or glucose oligomers. Glucose could be reversed to fructose due to the action of Lewis acid (Qian X H., 2012). We believed that $\text{Gd}(\text{NO}_3)_3$ would be partially hydrolyzed in water and complexed with water molecules to form $[\text{Gd}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ with octahedral structure, glucose was adsorbed on Gd^{3+} (Lewis acid center) in the structure, so that C1-O and C2-O replace two water molecules on Gd^{3+} to form $[\text{Gd}(\text{C}_6\text{H}_{12}\text{O}_6)(\text{H}_2\text{O})_3\text{OH}]^{2+}$. Finally, the process of isomerization of glucose to fructose was completed through the transfer of hydrogen atoms on C1 and C2 and the coordination of the cation center with the oxygen atom as indicated by Scheme 2. From then on, the process of fructose conversion bifurcated two paths. On one hand, fructose removed 3 molecules of water under the catalysis of Bronsted acid to form 5-HMF, and then continued to be degraded to form levulinic acid and formic acid. On the other hand, fructose underwent reverse aldol condensation reaction under the catalysis of Lewis acid to produce glyceraldehyde. There are few studies on the catalytic mechanism of fructose reverse aldol condensation, and many researchers believe that this process occurs between the α and β carbon atoms adjacent to the carbonyl group (Wattanapaphawong P et al., 2017). The carbonyl group on the sugar molecule and the hydroxyl groups on adjacent carbons coordinate with Gd^{3+} (Lewis acid center) as scheme 3. The hydrogen and hydroxide radicals in the water attack the α and β carbon atoms, respectively, which weakens the C-C bond, and then

breaks to reverse hydroxyl aldehyde reaction. Glyceraldehyde is easily affected by Lewis acid and reversibly converted to dihydroxyacetone.

Appropriate Bronsted acidity on the catalyst could promote the dehydration of the two to form pyruvaldehyde, which was rehydrated and rearranged to produce the target product LA. The intermediate product glyceraldehyde and the target product LA were easily oxidized by the residual air in the reaction apparatus, and then generated by-products such as glycolic acid and acetic acid. The isomerization of glucose, the reaction of the furaldehyde of the fructose, and the dehydration of glyceraldehyde and dihydroxyacetone are all regulated by the Lewis acidity of the catalytic system. Therefore, it was very important to optimize the reaction parameters to promote the selective conversion of cellulose to LA.

3.3. Impacts of Reaction Condition on Cellulose Catalytic Degradation

The dependence of cellulose conversion and product distribution on reaction temperature for the catalytic degradation of cellulose was investigated as the results shown in Fig. 2. When the temperature was lower than 210°C, it might be difficult for the free hydroxide ions in the aqueous solution to completely destroy the cellulose structure in a short time, so the cellulose conversion rate was less than 80%. As a result, the yields of the degradation products were also low, probably mainly formed low DP oligosaccharides. With the increasing of temperature, the yield of LA increased rapidly until reaching a maximum of 53.4% at 240°C. In the meanwhile, the degradation by-products, such as acetic acid and formic acid, involved in the pathway of cellulose degradation to LA increased slightly. The results showed that the reaction temperature not only affected the reverse reaction of fructose to LA, but also facilitated the hydrogen atom transfer and oxygen atom coordination between glucose and Lewis acid to realize the efficient isomerization between glucose and fructose. On the other hand, high temperature was conducive to the oxidation reaction. During the process from 200°C to 250°C, the yield of acetic acid was gradually increasing, which was mainly caused by the intensification of the LA conversion process. Considering these factors, reaction temperature of 240°C was chosen for subsequent studies.

The impacts of reaction duration were evaluated at the reaction temperature of 240°C as implied on Fig. 3. Compared to Fig. 2, it was obvious that the reaction temperature had a dominate effect on the cellulose conversion rate. The cellulose conversion rates were close to 100% under 240°C, no matter of the reaction durations. When the reaction time was less than 30 minutes, the yield of LA showed an upward trend and reached a maximum of 53.4%. At the same time, the yield of levulinic acid and formic acid reached the maximum. The yield of LA and other organic acids kept stable within the reaction duration of 30 to 50 minutes, and the degradation product distribution was comparable. However, when the reaction time exceeded 50 min, the yield of each intermediate product decreased which was mainly reflected by the reduction of the content of LA, acetic acid and levulinic acid. However, the content of acetic acid increased slightly after 60 minutes, which may be the result of LA being partially oxidized while being degraded. After 1 hour reaction, 5-HMF and levulinic acid could hardly be detected in the reaction medium. It was concluded that long reaction duration under high temperature was not conducive to the formation of target products, and the harsh reaction condition could lead to more humins formed during the reaction.

The influences of catalyst loading on cellulose conversion and the product distribution were also compared as shown in Fig. 4. Without the addition of catalyst, the cellulose conversion was only 60.9%, and the degradation product formed mainly were 5-HMF, glycolic acid, and acetol. The conversion of cellulose and formation of LA were significantly enhanced by the addition of Gd³⁺, indicating that Gd³⁺ could effectively help free hydroxide to destroy the cellulose structure and promote the subsequent process. When 0.045mmol catalyst was added, the yield of LA increased from 5.4% to 45.2%, while the 5-HMF yield decreased from 7.7% to 3.3%. It

was found that in the presence of Gd^{3+} , fructose was mainly converted along the reverse aldol pathway. Increasing the catalyst loading, the generation of 5-HMF decreased, and the amount of levulinic acid and formic acid increased, indicating that the catalyst loading affected the degradation of 5-HMF toward downstream products to a certain extent. When the catalyst loading increased to 0.135mmol, the yield of LA reached 56.6%. However, when the catalyst loading reached 0.180mmol, the yield of LA decreased slightly and acetic acid was detected in the reaction solution. It was speculated that the increased nitrate ions would generate more oxygen at high temperature, which would make LA more easily oxidized to acetic acid.

As shown in Fig. 5, the correlation between solid to liquid ratio and the cellulose conversion and product distribution was studied. It could be concluded that the solid to liquid ratio had little impact on the catalytic degradation of cellulose compared to the indices discussed above. Only when the solid loading increased to 1% (mass-volume ratio), the LA yield noticeably decreased to 40.4%, which might be related to the increase of viscosity of the solution that limited the contacts between catalyst and reaction substrates. At the same time, it was observed that the yield of acetic acid gradually decreased. When the solvent volume reached 30 mL acetic acid was hardly detected and the yield of levulinic acid was also the lowest, in the meanwhile the LA yield reached a maximum of 56.6%. The volume of the reaction solution was changed, but the presence of 5-HMF was not detected, indicating that the solvent content had little effect on the presence of 5-HMF.

4. CONCLUSION

In this paper, cellulose was catalyzed by metal ion Gd^{3+} in aqueous phase, 56.6% of LA yield and complete cellulose conversion were obtained. By comparing the degradation of cellulose and distribution of degradation product, it was concluded that Gd^{3+} promoted the reaction pathway towards the formation of LA instead of 5-HMF. The conversion of cellulose has a strong dependence on the reaction temperature, while the product distribution could be affected by different reaction conditions.

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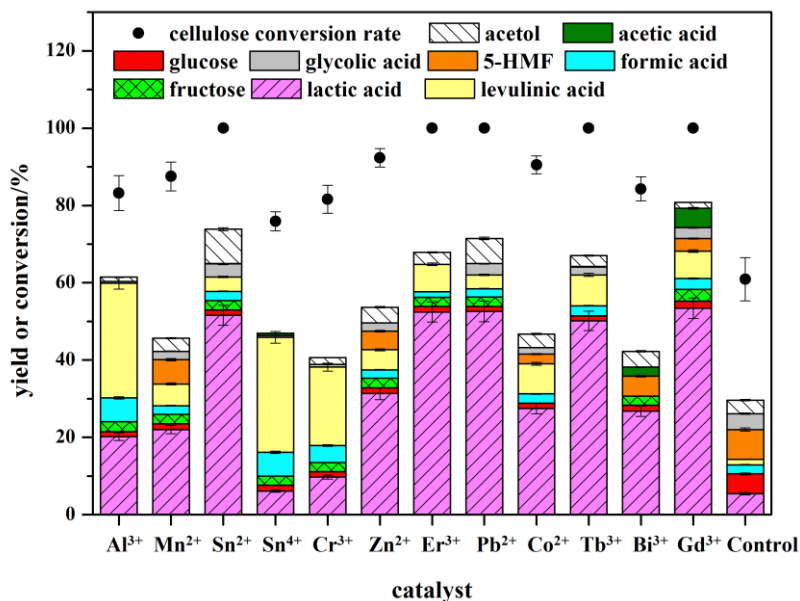


Fig 1. Catalytic effects of different metal ions on the conversion of cellulose and different degradation product yields. Reaction condition: cellulose 0.1g, water 30 mL, catalyst 0.18mmol, 240°C, 30 minutes, 2 MPa N₂.

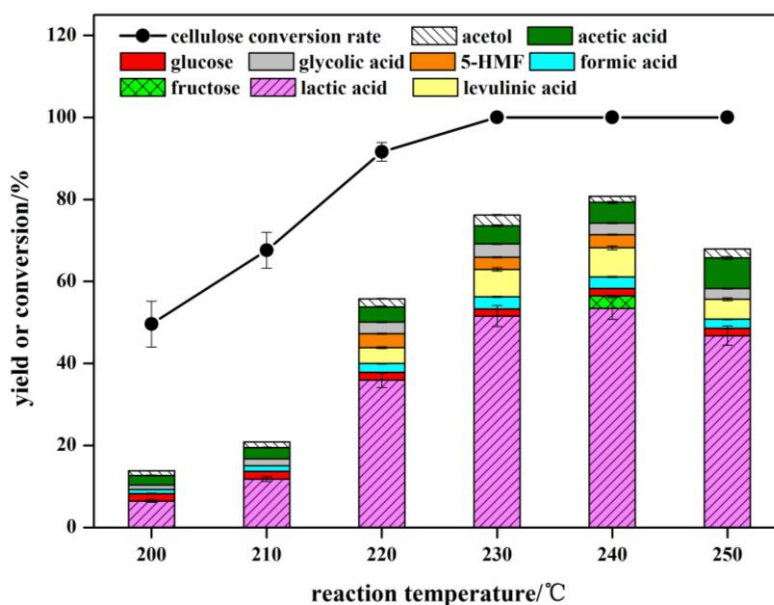


Fig 2. Impacts of reaction temperature on degradation product distribution and cellulose conversion rate. Reaction condition: cellulose 0.1g, water 30 mL, catalyst 0.18mmol, 30 minutes, 2 MPa N₂.

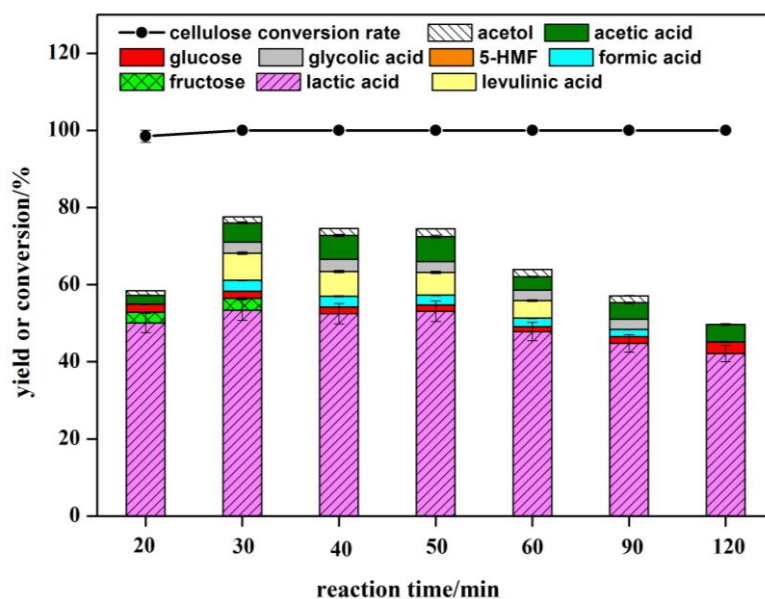


Fig 3. Impacts of reaction duration on product yields and cellulose conversion rate. Reaction condition: cellulose 0.1g, water 30 mL, catalyst 0.18mmol, 240°C, 2 MPa N₂.

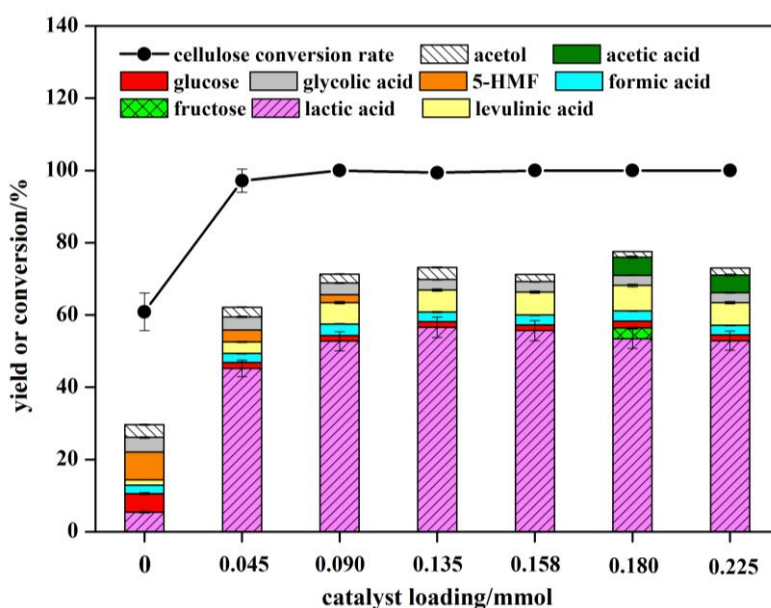


Fig 4. Impact of catalyst loading on product distribution and cellulose conversion rate. Reaction condition: cellulose 0.1g, water 30 mL, 240°C, 30 minutes, 2 MPa N₂.

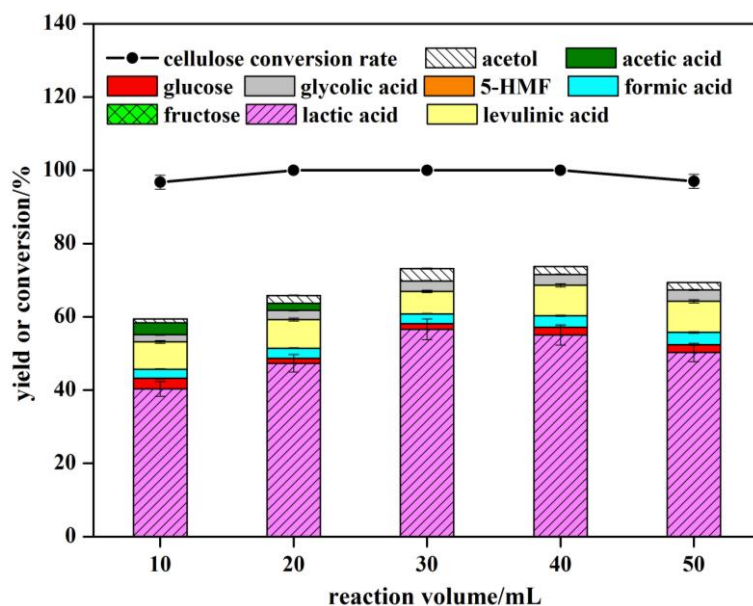
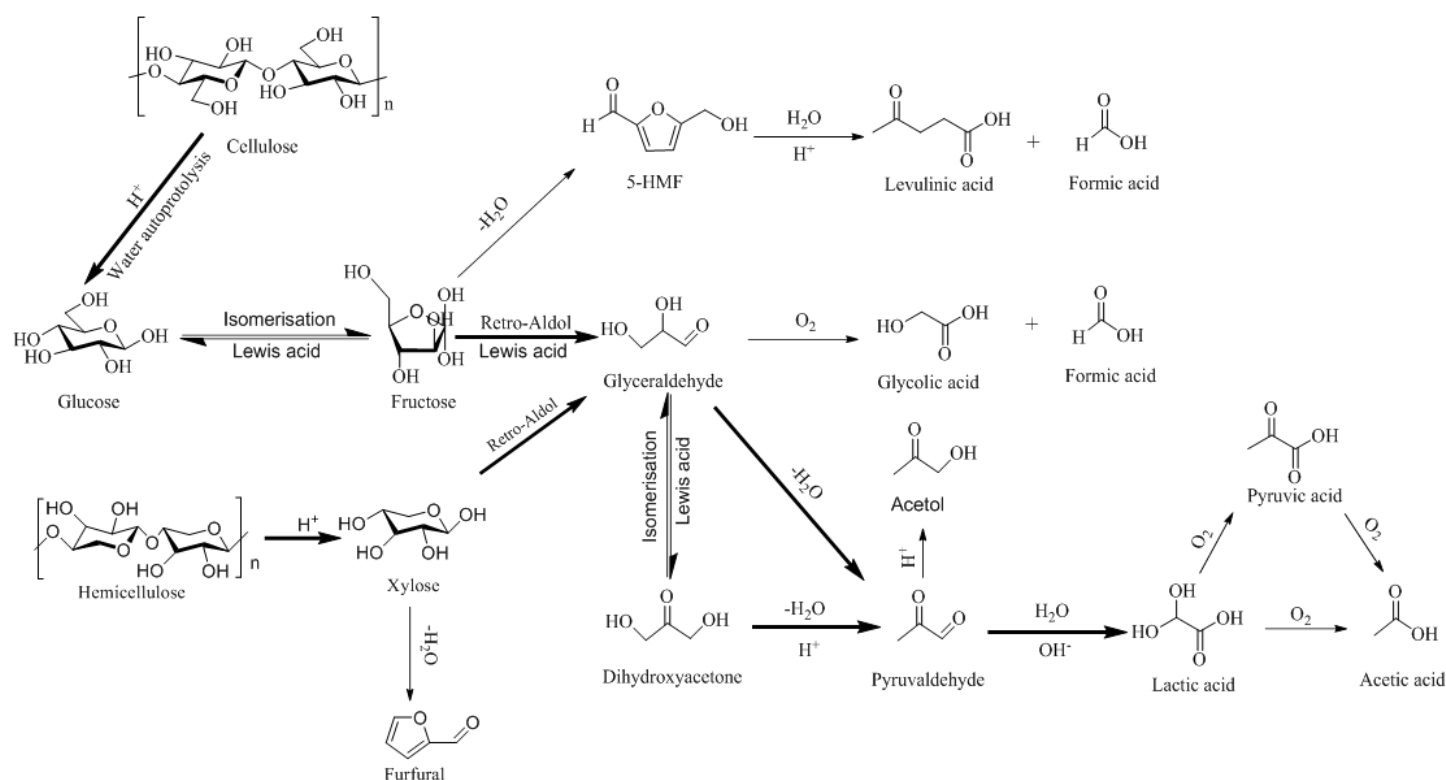
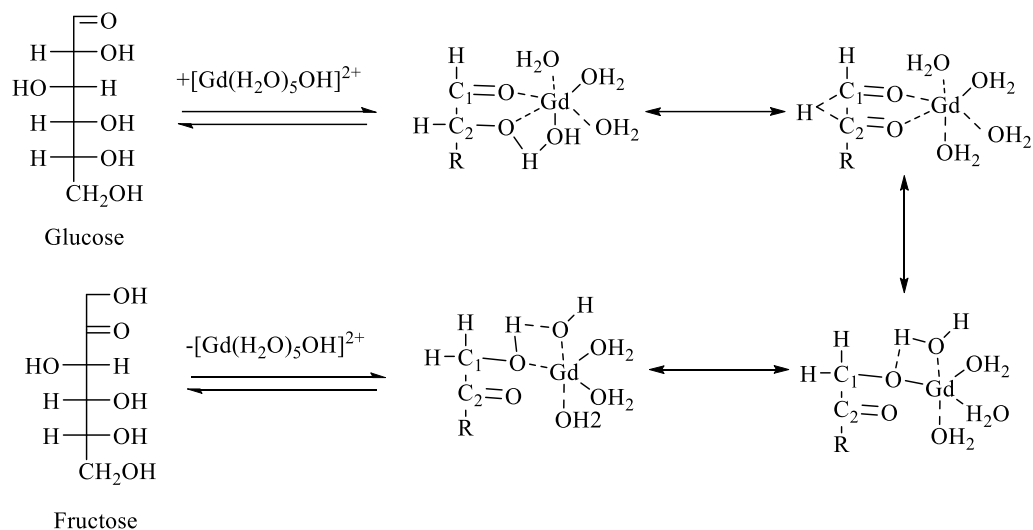


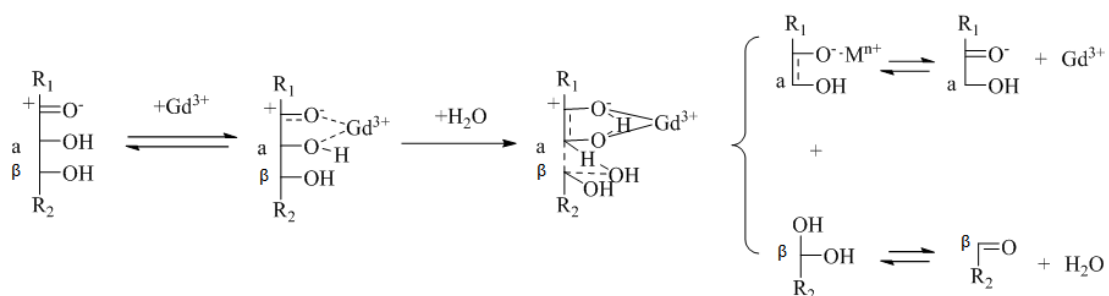
Fig 5. Effect of solvent volume on product distribution and cellulose conversion rate. Reaction condition: cellulose 0.1g, catalyst 0.135mmol, 240°C, 30 minutes, 2 MPa N₂.



Scheme 1. Proposed reaction mechanism for Gd³⁺ catalyzed reaction of cellulose and hemicellulose to prepare LA. The black thick line is the main reaction route.



Scheme 2. Gd^{3+} catalyzed isomerization mechanism of glucose to fructose.



Scheme 3. Reaction mechanism of retro-aldol condensation of fructose catalyzed by Gd^{3+} .