

# Efficient Catalytic Conversion of Glucose into Lactic Acid over Y- $\beta$ and Yb- $\beta$ Zeolites

Zheng Shen,\* Wenbo Chen, Wei Zhang, Minyan Gu, Wenjie Dong, Meng Xia, Huiping Si, and Yalei Zhang



Cite This: *ACS Omega* 2022, 7, 25200–25209



Read Online

ACCESS |



Metrics & More

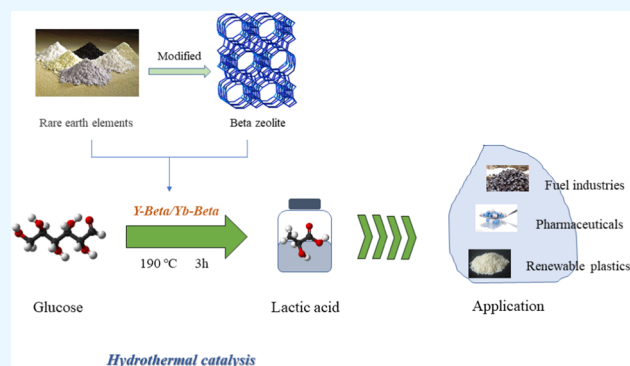


Article Recommendations



Supporting Information

**ABSTRACT:** In this work, a new type of modified  $\beta$  zeolites with rare earth elements (ree) was discovered for producing lactic acid from glucose and achieved a good catalytic effect. At first, the catalytic performances of ree- $\beta$  zeolites, ree oxides, and single-transition-metal- $\beta$  zeolites were compared, and the result showed that Y- $\beta$  and Yb- $\beta$  zeolites had the best catalytic activity under the same reaction conditions. Under the best reaction conditions, the maximum yields of lactic acid with Y- $\beta$  and Yb- $\beta$  catalysts were 45.3 and 43.6%, respectively. The acid characterization showed that Y/Yb- $\beta$  zeolites had a similar number of Lewis acid sites as Sn- $\beta$  zeolites, and they were also more than other transition-metal- $\beta$  zeolites. Thus, Y- $\beta$  and Yb- $\beta$  zeolites had a higher lactic acid yield than those catalysts. It is interesting to note that Y- $\beta$  and Yb- $\beta$  zeolites owned more Brønsted acids but produced fewer byproducts. Combining the decomposition experiment of 5-hydroxymethyl furfural, fewer byproducts were produced with Y- $\beta$  and Yb- $\beta$  zeolites because the low amount of Brønsted acid contained could hinder the decomposition of 5-hydroxymethyl furfural, thereby slowing down the side reaction.



## 1. INTRODUCTION

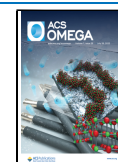
With the continuous consumption of fossil energy,<sup>1</sup> the world's resources are becoming increasingly scarce and the environment is gradually deteriorating.<sup>2,3</sup> At the same time, the development of clean and renewable energy has become more and more of concern because of the shortage of fossil energy.<sup>4,5</sup> Biomass energy is regarded as the most potential alternative energy because of its wide distribution, low price, environmental friendliness, and sustainable use.<sup>6,7</sup> Among the chemicals obtained from the biomass resources, lactic acid, as an important platform molecular compound,<sup>8,9</sup> has a wide range of uses in the chemical, pharmaceutical, and food industries.<sup>10,11</sup> Especially, it is often used as a synthetic material for biodegradable plastics.<sup>12,13</sup> The traditional methods of producing lactic acid are mainly microbial fermentation methods, and the main raw materials for microbial fermentation are starch-rich crops such as rice, corn, wheat, and potatoes. The production process of the fermentation method is complicated, and the production cycle is long.<sup>14,15</sup> Compared with the biological fermentation method of the production of lactic acid, the catalytic method has a higher large-scale production potential and higher production efficiency, and especially, it uses biomass instead of food as a substrate. Thus, the catalytic method seems to provide a more acceptable way for the preparation of lactic acid.<sup>16</sup>

According to the mixing state of the catalyst and the reaction substrate during the catalytic reaction of biomass, the catalysts can be divided into homogeneous catalysts and heterogeneous catalysts. However, the homogeneous catalyst has the disadvantages of difficult separation and inconvenient recycling.<sup>17,18</sup> Therefore, heterogeneous catalysts without the above shortcomings have attracted greater attention. The  $\beta$  molecular sieve, as a heterogeneous catalyst, was synthesized for the first time in 1967. Because of the unique pore structure and high silicon–aluminum ratio, the  $\beta$  molecular sieve has good acid resistance, thermal stability, and hydrophobicity.<sup>19</sup> It is even widely used in petroleum refining and petrochemical processes such as isomerization, hydrocracking, alkylation, dewaxing, etc. In particular, adding a small amount of  $\beta$  molecular sieve or modified  $\beta$  molecular sieve to the cracking reactions can significantly improve the hydrothermal stability, coking resistance, and abrasion resistance.<sup>20,21</sup> In addition, the  $\beta$  molecular sieve has also been found to have unique effects in the fields of biomass catalysis.<sup>22–27</sup> Therefore, it is very

Received: April 3, 2022

Accepted: June 29, 2022

Published: July 11, 2022



worthwhile to look forward to the application of the  $\beta$  molecular sieve or the modified  $\beta$  molecular sieve in biomass catalytic reactions. Taarning et al. reported in 2010 that Sn- $\beta$  zeolites prepared by the hydrothermal synthesis method catalyzed sugars to produce lactic acid or lactate in the aqueous and organic phases.<sup>28</sup> As a heterogeneous catalyst, the excellent catalytic performance and structural stability of modified  $\beta$  zeolites immediately triggered a research boom in its catalytic utilization of biomass.<sup>29–31</sup> In 2016, Dong et al. reported the chemical conversion of sugars using Zn-Sn- $\beta$  zeolites. The glucose conversion rate exceeded 99% and the lactic acid production rate reached 54% within 2 h under ambient pressure at 190 °C.<sup>32</sup>

The Sn element is the dominant element of the modified  $\beta$  zeolite catalyst commonly used for converting biomass into lactic acid. Is it possible to find a new type of metal element that can replace Sn? Rare earth elements have attracted our attention due to their excellent catalytic properties and abundant reserves in the chemical industry.<sup>33,34</sup> Currently, rare earth catalytic materials play an important role in petrochemical catalysis, vehicle exhaust catalysis, fuel cell catalysis, catalytic combustion, photocatalysis, and so on.<sup>35–37</sup> However, there is very little research in the field of lactic acid production from biomass using rare earth catalytic materials. Herein, we investigated the effects of different rare earth elements on the production of lactic acid from glucose and the various influencing factors such as reaction time, temperature, and metal loading. The result showed that ree- $\beta$  zeolites developed in this study could produce more lactic acid and fewer byproducts than those prior catalysts. Therefore, this work broke the situation that most modified  $\beta$  zeolites were dominated by Sn<sup>38,39</sup> and applied rare earth elements with excellent catalytic efficiency in the field of catalytic biomass production of lactic acid, which was of great significance for the industrial production of lactic acid.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Experimental Procedure.** D-(+)-glucose (99.5%), D-(–)-fructose (99%), ethanol ( $\geq 99.5\%$ ), indium acetate, zinc acetate, copper acetate, lanthanum acetate, cerium acetate, ytterbium acetate, yttrium acetate, lanthanum oxide, cerium oxide, yttrium oxide, and ytterbium oxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tin(II) acetate was obtained from Sigma-Aldrich. Formic acid ( $\geq 98\%$ ), acetic acid (99.8%), and levulinic acid (99%) were purchased from Wako Co., Ltd. Lactic acid (1.0 M) was purchased from Alfa Isa (China) Chemical Co., Ltd. 5-Hydroxymethyl furfural (98%) was purchased from Johnson & Johnson Technology Co., Ltd. The  $\beta$  molecular sieve was purchased from Nankai University Catalyst Factory Co., Ltd.

**2.2. Synthesis of Materials.** The catalysts were prepared following the previously published protocol.<sup>40</sup> The dealumination of  $\beta$  zeolite (deAl- $\beta$ ) was prepared as follows: 25 g of commercial  $\beta$  zeolite (Catalyst Plant of Nankai University) with a Si/Al ratio of 25 was put into 0.5 L of HNO<sub>3</sub> solution (65–68%, w/w) at 103 °C for 20 h. The deAl- $\beta$  zeolite was washed until the supernatant was neutral; then, the solid was collected and dried overnight at 100 °C.

**2.2.1. Catalyst Preparation.** Solid-state ion exchange was performed by grinding the deAl- $\beta$  and the metallic acetate for 40 min. Finally, the samples were calcined in static air at 550 °C with a ramp of 2 °C/min for 6 h.

**2.2.2. Catalyst Recycling.** The catalysts were recovered by centrifugation, washed extensively with absolute ethanol, dried at 90 °C overnight, and then roasted at 550 °C for 6 h.

**2.3. Catalytic Reactions.** The catalytic reactions were performed in a closed Teflon vessel (25 mL) in a stainless-steel autoclave. In a typical procedure, the vessel was charged with glucose, catalyst, and water (10 mL) followed by heating to the desired reaction temperature in a rotating oven (20 rpm). After hours of stirring, the autoclave was cooled, and the reaction mixture was analyzed. All of the experiments were replicated at least three times, and the mean values are reported.

**2.4. Products Analysis.** The concentrations of sugars, organic acids (i.e., lactic acid, formic acid, and levulinic acid), and 5-hydroxymethyl furfural were determined on an Agilent 1260 series HPLC equipped with an RI detector and a UV detector (210 nm) using a column (Bio-Rad HPX-87H). The mobile phase was a 5 mM H<sub>2</sub>SO<sub>4</sub> aqueous solution at a flow rate of 0.4 mL/min, and the temperatures of the column and the RI detector were set at 55 and 45 °C, respectively. The concentration of each respective component was determined based on the external standard calibration curves.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Different Catalysts on the Reaction.

Before the experiments, we checked the literature and learned the specific yields of lactic acid catalyzed from glucose by some single-transition-metal- $\beta$  zeolites,<sup>41,42</sup> and repeated the experiments. To investigate the effect of rare earth elements on the production of lactic acid from glucose, we loaded the rare earth elements (Y, Yb, Ce, and La) on  $\beta$  molecular sieves according to the above method. The catalytic performances of converting glucose into lactic acid by ree oxides, ree- $\beta$  zeolites, and single-transition-metal- $\beta$  zeolites are shown in Figure 1. During the

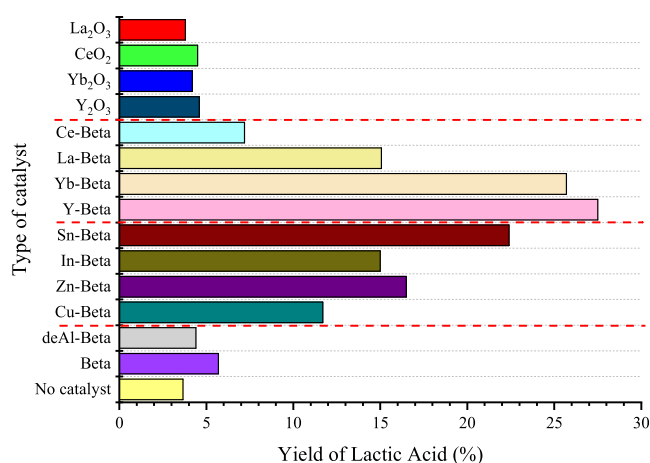


Figure 1. Yield of lactic acid from glucose over different catalysts.

catalyst preparation process, the metal loading of the catalyst was 0.42 mmol/g, and the hydrothermal reaction conditions were 190 °C, 2 h, catalyst 160 mg, glucose 225 mg, H<sub>2</sub>O 10 mL.

It could be seen in Figure 1 that the lactic acid yield of the blank experimental group was less than 4%, indicating that it was difficult to convert glucose into lactic acid under purely hydrothermal conditions without adding a catalyst. After adding  $\beta$  or deAl- $\beta$  zeolite, the lactic acid yields were 5.7 and 4.4%, respectively. Compared with the experimental group

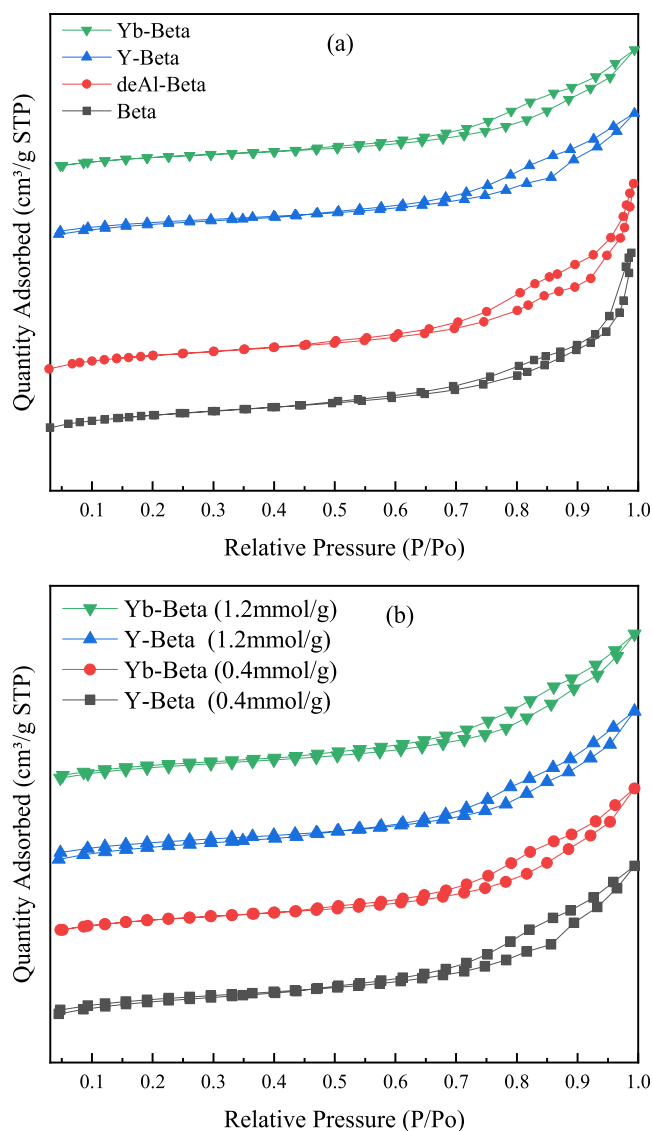
without the catalyst, the lactic acid yields did not increase significantly, showing that  $\beta$  or deAl- $\beta$  zeolite could hardly produce lactic acid from glucose. The yield of lactic acid was greatly improved when using single-transition-metal- $\beta$  zeolites as catalysts, and their catalytic capacity for producing lactic acid was as follows: Sn- $\beta$  > Zn- $\beta$  > In- $\beta$  > Cu- $\beta$ . Among them, Sn- $\beta$  zeolite showed the best catalytic effect, and the lactic acid yield reached 22.4%. As for the four rare earth element-supported catalysts, Y- $\beta$  and Yb- $\beta$  zeolites showed excellent catalytic efficiency and obtained lactic acid yields of 27.5 and 25.7%, respectively. This might be due to the unique properties of Y and Yb as heavy rare earth elements. The catalytic effects of Y- $\beta$  and Yb- $\beta$  zeolites were even better than those of Sn- $\beta$  zeolites. By the way, the catalytic effect of the rare earth oxide was very poor, and only a small amount of lactic acid (<5%) was produced. In summary, the efficiency sequence of modified  $\beta$  zeolites to catalyze glucose into lactic acid was as follows: Y- $\beta$  > Yb- $\beta$  > Sn- $\beta$  > Zn- $\beta$  > La- $\beta$  > In- $\beta$  > Cu- $\beta$  > Ce- $\beta$ . In the above work, we found that the zeolites loaded with rare earth metal Y and Yb exhibited the best performance for the formation of lactic acid from glucose, so we selected these two rare earth elements for exploration in the follow-up research.

**3.2. Catalyst Characterization.** **3.2.1. BET Characterization of Catalysts.** Figure 2a shows the nitrogen adsorption–desorption curve of different  $\beta$  zeolites. It shows fine hysteresis loops at the relative pressure of  $0.4 < P/P_0 < 0.9$  in all catalysts, which is a typical type I isotherm. This meant that micropores existed in all catalysts and the modification did not change the overall framework structure. The hysteresis loop of  $\beta$  zeolites became larger after dealumination treatment. Compared with deAl- $\beta$  zeolites, the modified Y/Yb- $\beta$  zeolites showed a smaller hysteresis loop, indicating that the metal had been successfully loaded and the channel was partially filled. In addition, it could be seen from Figure 2b that the hysteresis loop decreased with the increase of metal loading, indicating that the number of internal holes of the catalyst decreased with the increase of metal loading.

**3.2.2. XRD Characterization of Catalysts.** The structure and morphology characteristics of various catalysts and rare earth oxides were also characterized, and the XRD patterns of each catalyst are shown in Figure 3. All  $\beta$  zeolites had typical topological characteristics of BEA, with a typical diffraction peak at  $2\theta = 22.38^\circ$ , confirming that the structure of the commercial  $\beta$  zeolite was not notably destroyed during the process of dealumination and modification, and all catalysts maintained the integrity of the phase structure. As the metal (Y/Yb) loading increased, the peak width of the modified catalyst decreased at  $2\theta = 22.38^\circ$ . It was worth mentioning that hardly ree oxides were observed for the peaks that occurred at  $29.2$  and  $29.84^\circ$ , respectively, indicating that the introduced metal elements did not form a nonframework oxide structure on the surface, but might have entered the framework structure of the molecular sieve.<sup>41</sup>

**3.2.3. Acid–Base Characterization of Catalyst.** The excellent catalytic activity of the Y- $\beta$  and Yb- $\beta$  zeolites might be explained by its acid–base properties.  $\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD characterization is a more general and simpler method for determining the acid–base distribution of catalysts.<sup>32</sup> The acid and base properties of the  $\beta$ -type zeolites were examined by  $\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD characterizations in the study.

Generally speaking, according to the different desorption temperatures, acid sites can be divided into weak acid sites, medium-strong acid sites, and strong acid sites. The  $\text{NH}_3$ -TPD

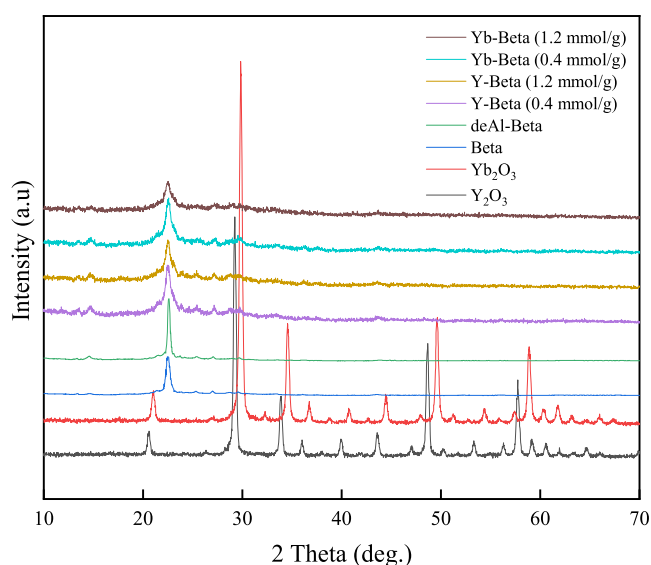


**Figure 2.** (a) Nitrogen adsorption/desorption isotherms of different catalysts. (b) Nitrogen adsorption/desorption isotherms of catalysts with different loadings.

characterization results of each catalyst are shown in Figure 4. It could be seen that deAl- $\beta$  after the dealumination had no acidic sites, while both modified catalysts showed weak acidic sites at  $100$ – $200$  °C. Y- $\beta$  exhibited certain medium acidic sites at  $300$ – $400$  °C, and Yb- $\beta$  exhibited strong acidic sites at  $400$ – $600$  °C. Table 1 lists the distribution of specific acidic sites of the catalysts. On the whole, the total number of acidic sites of the two catalysts was basically the same, which might be the reason for the similar lactic acid yields obtained under the two catalytic systems.

The distribution of acidic sites between the two catalysts is shown in Table 1. They were both mainly based on weak acid sites, and Y- $\beta$  zeolites had more weak acid sites and less medium/strong acids comparatively.

Pyridine-probed FT-IR (Py-IR) analysis could identify and quantify the Brønsted and Lewis acid sites readily. Figure 5 presents the infrared spectra of pyridine adsorbed on the catalysts at  $150$  °C. The characteristic peaks of Lewis acid sites were mainly at  $1450$  and  $1610$   $\text{cm}^{-1}$ , and the characteristic peaks of Brønsted acid sites were mainly at  $1544$  and  $1633$



**Figure 3.** X-ray diffraction patterns of various catalysts.

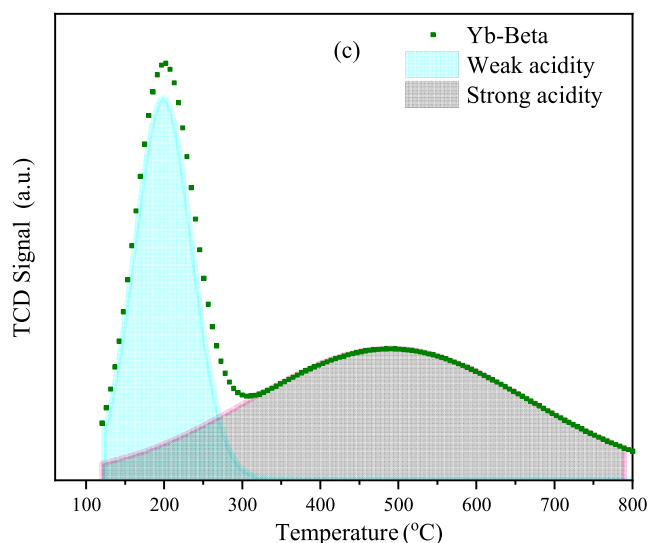
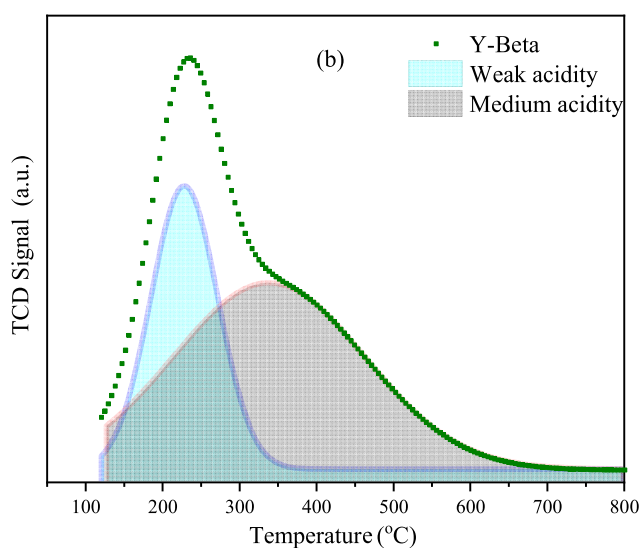
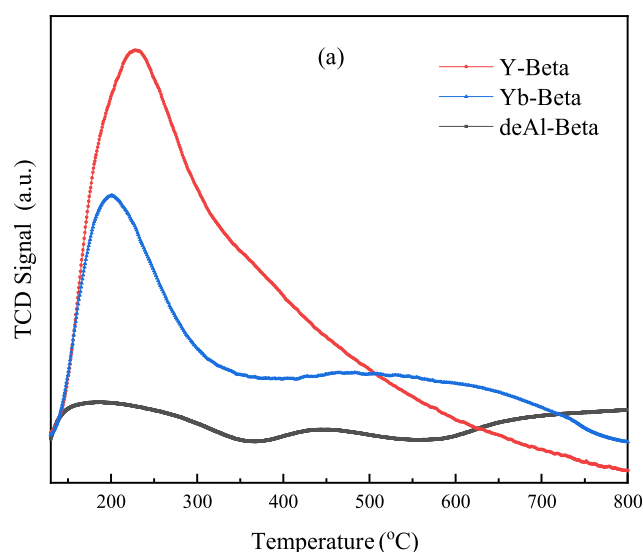
$\text{cm}^{-1}$ . It could be seen from the figure that there were two types of acidic sites at the same time in the catalysts. The content of Lewis acid also increased with the increase in metal loading, and the content of Brønsted acid did not change significantly.

The base properties of the catalysts were analyzed, as shown in Figure 6. It could be seen that the modified catalysts (Y/Yb- $\beta$  zeolites) exhibited a new strong desorption peak located at about 300 °C, associated with the moderate base sites at 300–600 °C, and the deAl- $\beta$  showed no basic sites. These phenomena confirmed the incorporation of rare metal (Y/Yb) and the resultant basicity increase.

**3.3. Effect of Metal Loading on the Reaction.** The effect of the metal contents of Y and Yb in the  $\beta$  zeolite employed in the catalytic reaction on the formation of lactic acid from glucose was also studied in this section.

ICP characterization of catalysts with different metal loadings was also carried out (as shown in Table S1). ICP analysis showed that the amount of metal was identical to the desired value, confirming that the modification method selected in this study successfully loaded the metal to  $\beta$  zeolites. As shown in Figure 7, the lactic acid yields of Y- $\beta$  and Yb- $\beta$  zeolites increased gradually with the increase in metal loading from 0.2 to 1.2 mmol/g. At a metal loading of 1.2 mmol/g, the maximum lactic acid yields of Y- $\beta$  and Yb- $\beta$  zeolites were 45.2 and 43.6%, respectively. When the metal loading continued to increase to 1.4 and 1.6 mmol/g, the lactic acid yield decreased instead. It is speculated that the decrease in lactic acid yield might be due to the congestion inside the catalysts. In addition, it could be also seen from Figure 2b that the hysteresis loop decreased with the increase in metal loading from 0.4 to 1.2 mmol/g, indicating that the number of internal holes of the catalyst decreased with the increase of metal loading. In summary, the metal loading of the catalyst selected in the subsequent experiments was 1.2 mmol/g.

**3.4. Effect of Temperature and Time on the Reaction.** To optimize the yield of lactic acid, we investigated the effects of different reaction temperatures and reaction times on the production of lactic acid from glucose under the Y- $\beta$  and Yb- $\beta$  catalytic systems (as shown in Figure 8).



**Figure 4.** (a)  $\text{NH}_3$ -TPD curves of various catalysts. (b) Acid strength distribution of Y- $\beta$ . (c) Acid strength distribution of Yb- $\beta$ .

It could be seen in Figure 8 that in the two catalytic systems of Y- $\beta$  and Yb- $\beta$  zeolites, when the reaction temperature was 130 °C, the formation of lactic acid was almost undetectable in



Table 1. Acidity of Different Catalysts

catalyst	weak acidity (%)	medium acidity (%)	strong acidity (%)	B150 (mmol·g <sup>-1</sup> )	L150 (mmol·g <sup>-1</sup> )
Y-β	61.3	38.7		0.028	0.032
Yb-β	53.4		46.6	0.025	0.030

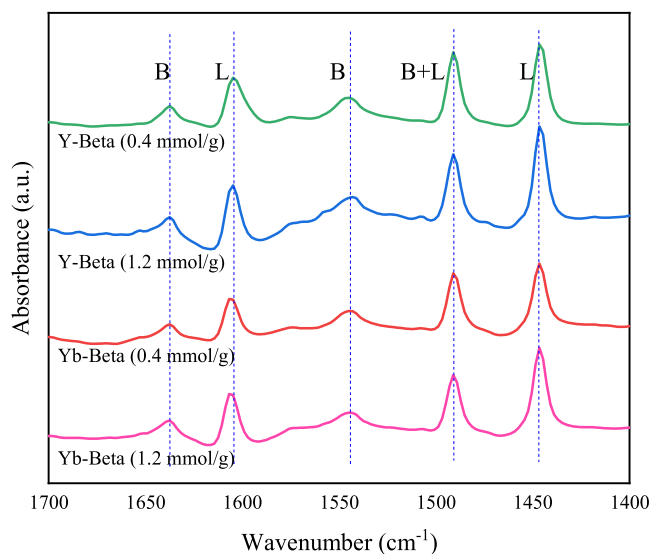
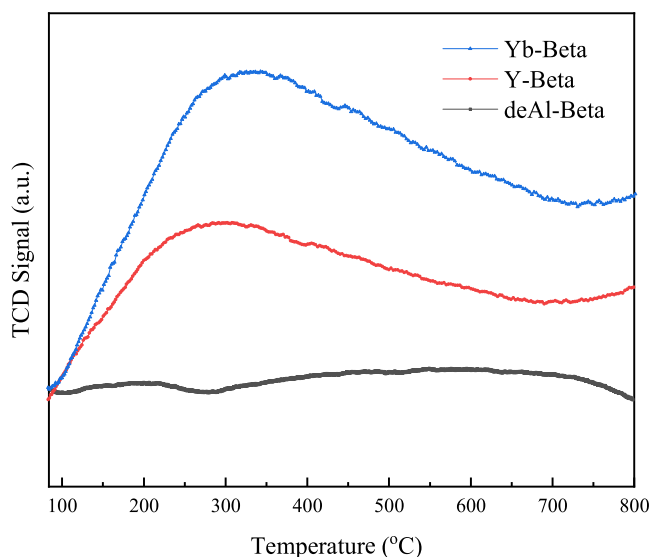
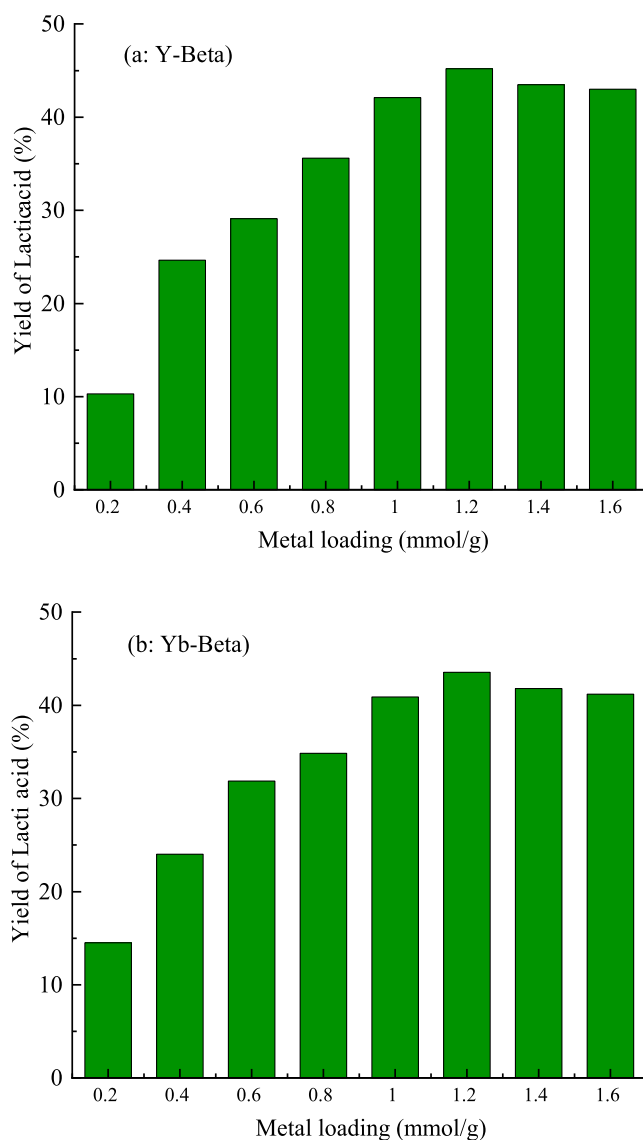


Figure 5. FT-IR spectra following the adsorption of pyridine on various catalysts.

Figure 6. CO<sub>2</sub>-TPD curves of various catalysts.

the first 2 h. After 5 h of reaction, only a small amount of lactic acid was produced, indicating that the catalytic reaction did not proceed to a high degree under this temperature condition. This might be because fructose in the intermediate reaction step generates dihydroxyacetone or glyceraldehyde through retro aldol, which required higher energy to open the C–C bond. Therefore, in general experiments, the reaction temperature involved in this step was above 140 °C.<sup>43</sup>

As the reaction temperature increased from 130 to 230 °C, the lactic acid yield and the catalytic rate obviously increased in the first 1 h. The yield of lactic acid reached the highest at 3 h when the temperatures were 190, 210, and 230 °C. As the

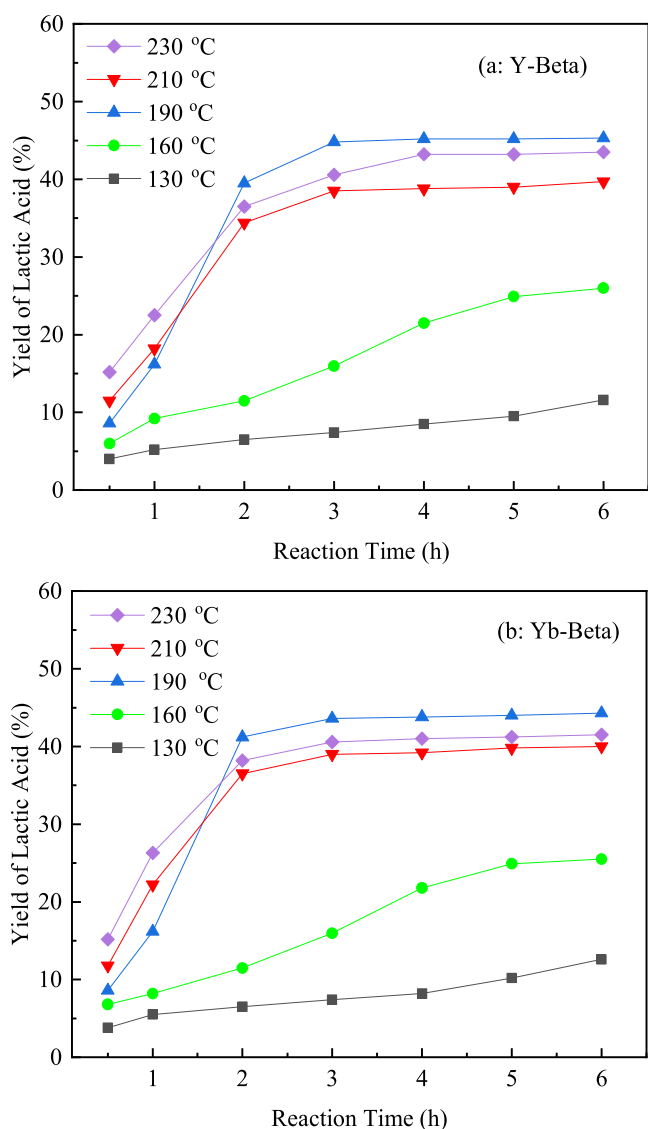
Figure 7. Effect of metal loading on the yield of lactic acid. Reaction condition: 225 mg of glucose, 160 mg of catalyst, 10 mL of H<sub>2</sub>O, 190 °C, 3 h.

temperature rose to 210 and 230 °C from 190 °C, the yield of lactic acid decreased in the end of the reaction. It has been reported that lactic acid could be converted to formic acid and acetic acid in high-temperature water.<sup>44,45</sup> Thus, the reason for this phenomenon (decreased yield of lactic acid) in the preliminary analysis might be that the decomposition rate of lactic acid is higher than the production rate at 210 and 230 °C.

When the temperature was 190 °C, with the extension of the reaction time, the glucose conversion rate gradually increased, and the maximum yield of lactic acid (45.2% for Y-β, 43.2% for Yb-β) was obtained at 3 h. Then, the lactic acid yield remained unchanged without a noticeable trend of increasing or decreasing, indicating that the produced lactic acid was relatively stable. In summary, we ensured the optimal reaction conditions for converting glucose into lactic acid as 190 °C, 3 h.

### 3.5. Catalyst Stability Research (Recycling Research).

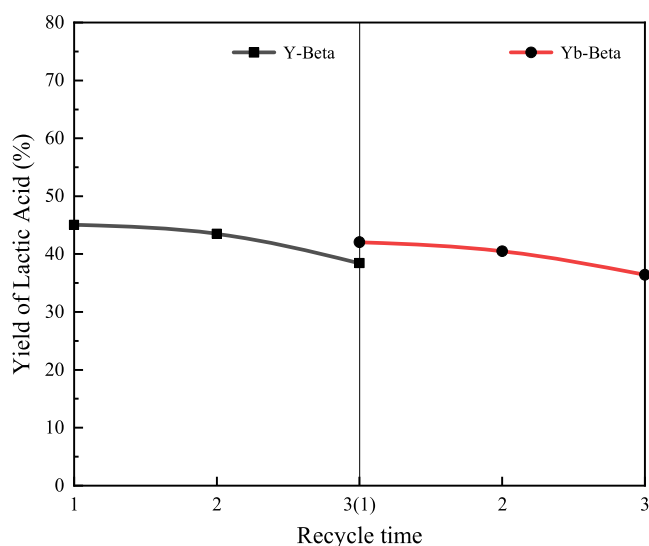
The recycling ability of the Y-β and Yb-β zeolites for the conversion of glucose was investigated, and the results are



**Figure 8.** Effect of reaction temperature and reaction time on lactic acid yield. Reaction condition: 225 mg of glucose, 160 mg of catalyst, 10 mL of H<sub>2</sub>O.

shown in Figure 9. After each reaction, the solid–liquid mixture in the reactor was taken out, centrifuged, and then washed with absolute ethanol. Then, the separated solids were dried overnight and roasted at a temperature of 550 °C for 6 h. As shown in Figure 9, the catalytic systems of Y- $\beta$  and Yb- $\beta$  zeolites achieved lactic acid yields of 45.24 and 42.05% in the first recycle reaction, respectively. Then, a decrease in the yield of lactic acid was observed within three cycles, and the leaching of metals during the reaction might be the cause.<sup>46</sup> ICP characterization was supplemented for the catalysts with three cycles of recycling (as shown in Table S2). As could be seen from the data in the table, the measured metal content in the catalyst decreased with the increase in recycling times, confirming the possibility of metal leaching in the recycling process.

However, the yields of lactic acid could still reach more than 35% after three cycles, which were still higher than those of Sn- $\beta$  zeolites and single-metal- $\beta$  zeolites. Therefore, Y- $\beta$  and Yb- $\beta$  zeolites were potential catalysts for future application in the conversion of biomass to lactic acid.

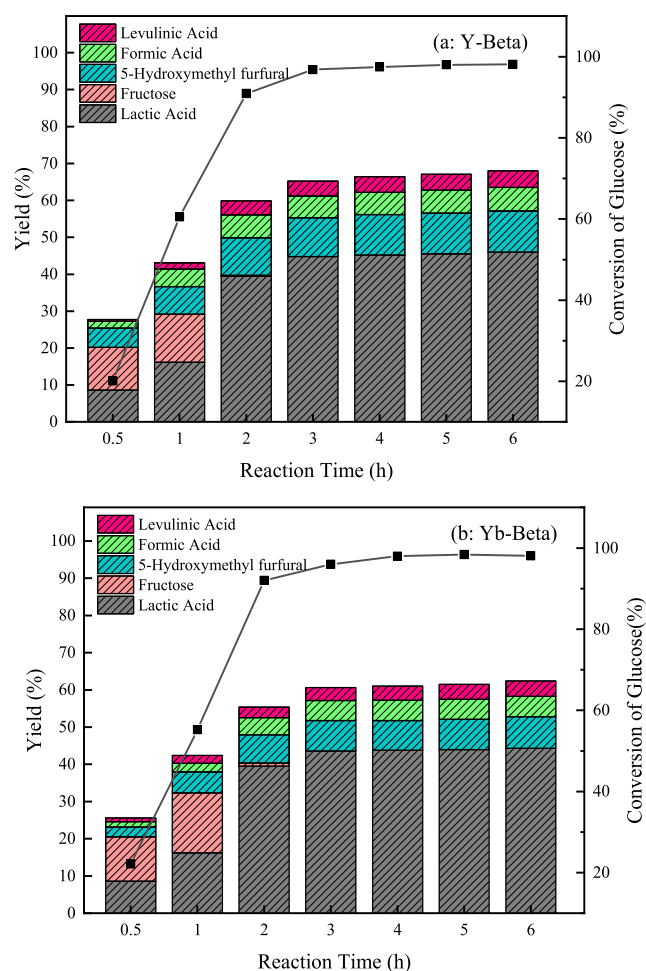


**Figure 9.** Recyclability tests of catalysts on production of lactic acid. Reaction condition: 225 mg of glucose, 160 mg of catalyst, 10 mL of H<sub>2</sub>O, 190 °C, 3 h.

**3.6. Product Analysis of the Catalytic System.** We further examined the glucose conversion and product distributions using the Y- $\beta$  and Yb- $\beta$  zeolites as a function of reaction time (Figure 10). It could be seen that the conversion processes of the products using the two catalysts were very similar. As the reaction time increased from 0.5 to 3.0 h, the conversion of glucose increased to about 95%, and the yield of lactic acid with Y- $\beta$  and Yb- $\beta$  zeolites increased from about 7 to 45.2% and 43.2%, respectively. For a longer reaction time, the yield of lactic acid did not further change.

In the early stage of the reaction, fructose was mainly produced by the isomerization of glucose. As the reaction time went by, fructose disappeared, and lactic acid began to form rapidly. Soluble byproducts such as formic acid, levulinic acid, and 5-hydroxymethyl furfural gradually increased with the time of reaction. The yield of the main byproduct (5-hydroxymethyl furfural) eventually stabilized at around 10%. According to previous reports, the current mainstream Sn- $\beta$  catalytic system could finally obtain a lactic acid yield of about 20% and a 5-hydroxymethyl furfural yield of about 15% in the reaction of catalyzing glucose into lactic acid.<sup>28,32</sup> Compared with Sn- $\beta$  zeolites, the catalysts found in this study produced more lactic acid and less 5-hydroxymethyl furfural, showing a better catalytic efficiency.

**3.7. Acidity Comparison of Catalysts.** The quantitative data of Brønsted acid and Lewis acid for different catalysts at the desorption temperature of 150 °C are shown in Table 2. It could be seen from the table that with the same metal loading, Y- $\beta$  and Yb- $\beta$  zeolites had more Lewis acid quantification than other single-transition-metal- $\beta$  zeolites except for Sn- $\beta$  zeolite. This might be the reason why Y- $\beta$  and Yb- $\beta$  zeolites could obtain higher lactic acid yields in the preliminary screening experiments. As the metal loading increased, so did the Lewis acid contents of Y- $\beta$  and Yb- $\beta$  zeolites. However, Y- $\beta$  and Yb- $\beta$  zeolites had less Lewis acid quantification than those double-metal- $\beta$  zeolites, so they produced less lactic acid than those double-metal- $\beta$  zeolites. The experimental results in this study confirmed that the lactic acid yield was directly related to the acid–base distribution of the catalyst, which was consistent with previous reports (Kong ammoniated Sn- $\beta$  to increase the



**Figure 10.** Conversion of glucose and yields of lactic acid, formic acid, levulinic acid, and 5-hydroxymethyl furfural (HMF) over the catalyst. Reaction condition: 225 mg of glucose, 160 mg of catalyst, 10 mL of H<sub>2</sub>O, 190 °C.

**Table 2.** Acidity of Different Catalysts

entry	catalyst	B150 (mmol·g <sup>-1</sup> )	L150 (mmol·g <sup>-1</sup> )	B/L
1	$\beta$	0.127	0.100	1.270
2	deAl- $\beta$	0.003	0.015	0.020
3	Pb- $\beta$ (0.4 mmol/g)	0.004	0.016	0.250
4	Cu- $\beta$ (0.4 mmol/g)	0.003	0.020	0.150
5	Zn- $\beta$ (0.4 mmol/g)	0.003	0.022	0.130
6	Sn- $\beta$ (0.4 mmol/g)	0.004	0.026	0.154
7	Y- $\beta$ (0.4 mmol/g)	0.021	0.027	0.778
8	Yb- $\beta$ (0.4 mmol/g)	0.019	0.025	0.760
9	Y- $\beta$ (1.2 mmol/g)	0.028	0.032	0.875
10	Yb- $\beta$ (1.2 mmol/g)	0.025	0.030	0.833
11	Zn-Sn- $\beta$ (0.4 mmol/g)	0.007	0.058	0.121
12	Pb-Sn- $\beta$ (0.4 mmol/g)	0.005	0.056	0.089
13	Cr-Sn- $\beta$ (0.4 mmol/g)	0.018	0.055	0.327

basicity;<sup>47</sup> Xia supported various metals on  $\beta$  to adjust the acidity and alkalinity of the catalyst<sup>40,41</sup>). Therefore, the acidic sites with appropriate strength and type played a key role in the catalytic reaction.

It could also be seen from Table 2 that Y- $\beta$  and Yb- $\beta$  zeolites had much more Brønsted acids than other single-transition-metal- $\beta$  zeolites. As is known, Brønsted acid could dehydrate

fructose to produce 5-hydroxymethyl furfural,<sup>48</sup> and the occurrence of side reactions would inevitably reduce the production of lactic acid, the target product. Thus, it is interesting that more lactic acid and less 5-hydroxymethyl furfural were produced in the catalytic systems of this study.

To find out why Y- $\beta$  and Yb- $\beta$  zeolites obtained fewer byproducts when they had more Brønsted acid sites, we carried out the 5-hydroxymethyl furfural decomposition experiment under the same hydrothermal conditions as the previous experiment, and the experimental results are shown in Table 3.

**Table 3.** Reaction Behaviors of 5-Hydroxymethyl Furfural under Water or Lactic Acid Solution<sup>a</sup>

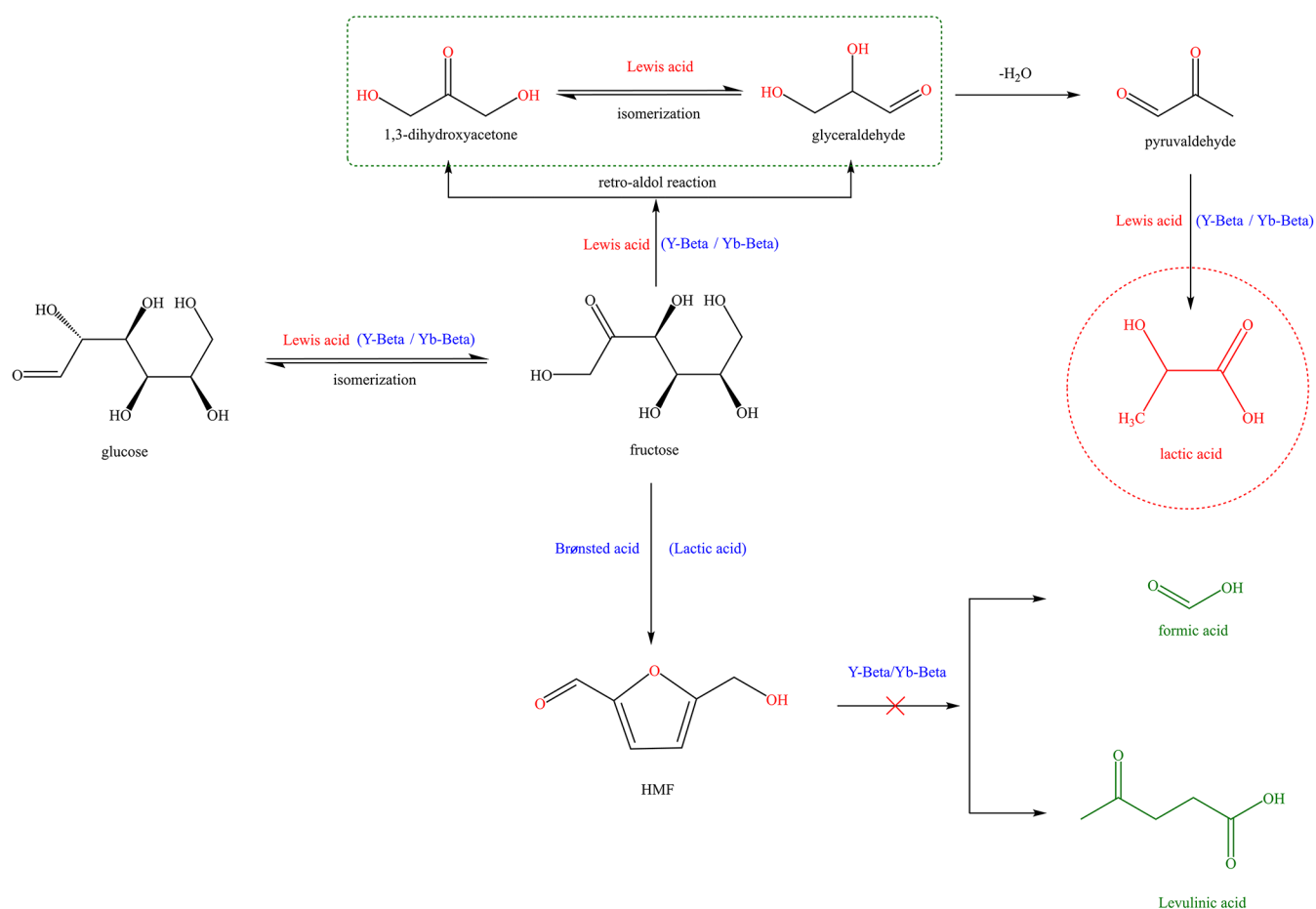
no.	catalyst	conversion (%)
1	Y- $\beta$	66
2	Yb- $\beta$	68
3	Sn- $\beta$	80
4	no catalyst	50
5	lactic acid	78

<sup>a</sup>Nos. 1–4: 50 mg of 5-hydroxymethyl furfural, 10 mL of H<sub>2</sub>O, 160 mg of catalyst, 190 °C, 3 h; No. 5: 50 mg of 5-hydroxymethyl furfural, 10 mL of lactic acid (5 mg/mL), 190 °C, 3 h.

Comparing the experimental data in Table 3, it could be seen that 5-hydroxymethyl furfural was only decomposed by 50% under the hydrothermal condition without a catalyst, and the decomposition efficiency was improved after the catalyst was added. The Y- $\beta$  and Yb- $\beta$  zeolites showed a poor decomposition effect on 5-hydroxymethyl furfural compared with Sn- $\beta$  zeolites, whose conversion rate of 5-hydroxymethyl furfural reached 80%. Therefore, in the process of catalyzing glucose to produce lactic acid, accumulation of the byproduct (5-hydroxymethyl furfural) would hinder the side reaction, resulting in more lactic acid and fewer byproducts.

The lactic acid was used as the catalyst to decompose 5-hydroxymethyl furfural (Table 3, No. 5). A conversion rate of 78% was obtained in this system, indicating that lactic acid as Brønsted acid promoted the decomposition of 5-hydroxymethyl furfural. Under the same reaction conditions, the decompositions effects of Y- $\beta$  and Yb- $\beta$  zeolites on 5-hydroxymethyl furfural were 66 and 68%, respectively, and weaker than that of the lactic acid. Compared with the Brønsted acid brought by lactic acid, Brønsted acid in Y- $\beta$  and Yb- $\beta$  zeolites had little effect on the experiment. In conclusion, we speculated that during the conversion of glucose to lactic acid, a larger amount of Brønsted acids such as lactic acid produced would promote the progress of the side reaction (dehydration of fructose to 5-hydroxymethyl furfural) and a smaller amount of Brønsted acids such as the catalysts found in the study would hinder the hydrolysis of 5-hydroxymethyl furfural. Based on the reaction pathways proposed in previous reports<sup>32,46</sup> and the reaction effect of Y/Yb- $\beta$  zeolites in this study, the reaction pathways in the conversion of glucose to lactic acid were speculated as shown in Figure 11.

In the catalytic reaction, the acidic strength and type of acid sites of the catalyst might affect the reaction steps. In this study for example, the more Lewis acids shown in Y- $\beta$  and Yb- $\beta$  zeolites promoted the main reaction to produce more lactic acid, and their unique Brønsted acidity could hinder the decomposition of 5-hydroxymethyl furfural and thus slow down the progression of side reactions.



**Figure 11.** Proposed reaction pathways in the conversion of glucose to lactic acid.

#### 4. CONCLUSIONS

This study developed a new modified  $\beta$  zeolite ( $Y-\beta$  and  $Yb-\beta$ ) for catalyzing glucose to produce lactic acid, and the effects of reaction parameters were mainly investigated. Results showed that the  $Y-\beta$  and  $Yb-\beta$  zeolites obtained the maximum lactic acid yields of 45.2 and 43.2%, respectively, under optimized conditions (metal loading 1.2 mmol/g, 190 °C, 3 h). The reusability of the two catalysts was explored, and the lactic acid yield of more than 35% was maintained after reusing three times. Compared with the  $Sn-\beta$  zeolite or other single-transition-metal- $\beta$  zeolites,  $Y-\beta$  and  $Yb-\beta$  zeolites showed more Lewis acid sites, resulting in a higher yield of lactic acid. Combining the decomposition experiment of 5-hydroxymethyl furfural with each catalyst and the unique Brønsted acidity in catalysts revealed by characterization, we speculated that a smaller amount of Brønsted acids would hinder the hydrolysis of 5-hydroxymethyl furfural, thereby slowing down the side reaction. Therefore,  $Y-\beta$  and  $Yb-\beta$  could produce more lactic acid and fewer byproducts than those prior catalysts. This study had a certain guiding significance for the industrial production of lactic acid.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02051>.

Table S1, ICP-OES characterization of catalysts with different metal loadings; and Table S2, ICP-OES characterization of catalysts with different cycles (PDF)

#### ■ AUTHOR INFORMATION

##### Corresponding Author

**Zheng Shen** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China; [orcid.org/0000-0003-3668-7820](https://orcid.org/0000-0003-3668-7820); Phone: +86 21 65985811; Email: [shenzheng@tongji.edu.cn](mailto:shenzheng@tongji.edu.cn)

##### Authors

**Wenbo Chen** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China

**Wei Zhang** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China



**Minyan Gu** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China

**Wenjie Dong** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China

**Meng Xia** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China; [orcid.org/0000-0003-0626-9601](https://orcid.org/0000-0003-0626-9601)

**Huiping Si** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China

**Yalei Zhang** – State Key Laboratory of Pollution Control and Resources Reuse, Key Laboratory of Yangtze River Water Environment of MOE, National Engineering Research Center of Protected Agriculture, Shanghai Engineering Research Center of Protected Agriculture, Tongji University, Shanghai 200092, China; Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China; [orcid.org/0000-0002-3254-8965](https://orcid.org/0000-0002-3254-8965)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.2c02051>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Plan (No. 2019YFC1906700), the National Natural Science Foundation of China (Nos. 21978224 and 21676205), and the Shanghai Science and Technology Committee (Nos. 20dz1203600 and 20232410200).

## REFERENCES

- (1) Valentine, S. V. Emerging symbiosis: Renewable energy and energy security. *Renewable Sustainable Energy Rev.* **2011**, *15*, 4572–4578.
- (2) Wang, Z. Does biomass energy consumption help to control environmental pollution? Evidence from BRICS countries. *Sci. Total Environ.* **2019**, *670*, 1075–1083.
- (3) Adewuyi, A. O.; Awodumi, O. B. Biomass energy consumption, economic growth and carbon emissions: fresh evidence from West Africa using a simultaneous equation model. *Energy* **2017**, *119*, 453–471.
- (4) Chen, C.; Pinar, M.; Stengos, T. Renewable energy consumption and economic growth nexus: Evidence from a threshold model. *Energy Policy* **2020**, *139*, No. 111295.
- (5) Khare, V.; Nema, S.; Baredar, P. Solar–wind hybrid renewable energy system: A review. *Renewable Sustainable Energy Rev.* **2016**, *58*, 23–33.

(6) Mafakheri, F.; Nasiri, F. Modeling of biomass-to-energy supply chain operations: Applications, challenges and research directions. *Energy Policy* **2014**, *67*, 116–126.

(7) Wang, Z.; Bui, Q.; Zhang, B. The relationship between biomass energy consumption and human development: Empirical evidence from BRICS countries. *Energy* **2020**, *194*, No. 116906.

(8) Fan, Y.; Zhou, C.; Zhu, X. Selective catalysis of lactic acid to produce commodity chemicals. *Catal. Rev.* **2009**, *51*, 293–324.

(9) de Oliveira, R. A.; Komesu, A.; Rossell, C. E. V.; Maciel, R. Challenges and opportunities in lactic acid bioprocess design—From economic to production aspects. *Biochem. Eng. J.* **2018**, *133*, 219–239.

(10) Yu, B.; Zeng, Y.; Jiang, X.; Wang, L.; Ma, Y. Trends in polymer-grade L-lactic acid fermentation by non-food biomass. *Chin. J. Biotechnol.* **2013**, *29*, 411–421.

(11) Gao, C.; Ma, C.; Xu, P. Progress in biotransformation of bio-based lactic acid. *Chin. J. Biotechnol.* **2013**, *29*, 1411–1420.

(12) Farrokhpayam, S. R.; Shahabi, M. A.; Sheshkal, B. N.; Gargari, R. M. The morphology, physical, and mechanical properties of poly (lactic acid)-based wood flour and pulp fiber biocomposites. *J. Indian Acad. Wood Sci.* **2021**, 1–6.

(13) De Falco, F.; Avolio, R.; Errico, M. E.; Di Pace, E.; Avella, M.; Cocca, M.; Gentile, G. Comparison of biodegradable polyesters degradation behavior in sand. *J. Hazard. Mater.* **2021**, *416*, No. 126231.

(14) Eş, L.; Khaneghah, A. M.; Barba, F. J.; Saraiva, J. A.; Sant'Ana, A. S.; Hashemi, S. M. B. Recent advancements in lactic acid production—a review. *Food Res. Int.* **2018**, *107*, 763–770.

(15) Zhao, G.; Xiong, X.; Chen, C. Application of Amylolytic Lactic Acid Bacterial in Production of L-lactic Acid by Fermentation. *China Biotechnol.* **2009**, *29*, 134–139.

(16) Jantasee, S.; Kienberger, M.; Mungma, N.; Siebenhofer, M. Potential and assessment of lactic acid production and isolation—a review. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 2885–2893.

(17) Onda, A.; Ochi, T.; Yanagisawa, K. Selective hydrolysis of cellulose into glucose over solid acid catalysts. *Green Chem.* **2008**, *10*, 1033–1037.

(18) Yan, X.; Jin, F.; Tohji, K.; Kishita, A.; Enomoto, H. Hydrothermal conversion of carbohydrate biomass to lactic acid. *AIChE J.* **2010**, *56*, 2727–2733.

(19) Lu, T.; Yan, W.; Xu, R. Chiral zeolite beta: structure, synthesis, and application. *Inorg. Chem. Front.* **2019**, *6*, 1938–1951.

(20) Nayak, Y. N.; Nayak, S.; Nadaf, Y. F.; Shetty, N. S.; Gaonkar, S. L. Zeolite Catalyzed Friedel-Crafts Reactions: A Review. *Lett. Org. Chem.* **2020**, *17*, 491–506.

(21) Dedeček, J.; Tabor, E.; Sklenak, S. Tuning the aluminum distribution in zeolites to increase their performance in acid-catalyzed reactions. *ChemSusChem* **2019**, *12*, 556–576.

(22) Innes, R. A.; Zones, S. I.; Nacamuli, G. J. Liquid Phase Alkylation Or Transalkylation Process Using Zeolite Beta. U.S. Patent US4,891,458, 1992.

(23) Halgeri, A. B.; Das, J. Novel catalytic aspects of beta zeolite for alkyl aromatics transformation. *Appl. Catal., A* **1999**, *181*, 347–354.

(24) Aho, A.; Kumar, N.; Eränen, K.; Salmi, T.; Hupa, M.; Murzin, D. Y. Catalytic pyrolysis of biomass in a fluidized bed reactor: influence of the acidity of H-beta zeolite. *Process Saf. Environ.* **2007**, *85*, 473–480.

(25) Tarach, K.; Góra-Marek, K.; Tekla, J.; Brylewska, K.; Datka, J.; Mlekodaj, K.; Makowski, W.; Igualada Lopez, M. C.; Martinez Triguero, J.; Rey, F. Catalytic cracking performance of alkaline-treated zeolite Beta in the terms of acid sites properties and their accessibility. *J. Catal.* **2014**, *312*, 46–57.

(26) Mallmann, A. Adsorption of benzene and ethylbenzene on the acidic and basic sites of beta zeolite. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 431–435.

(27) Bácia, P. S.; Silva, J. A. C.; Rodrigues, A. E. Adsorption equilibrium and kinetics of branched hexane isomers in pellets of BETA zeolite. *Microporous Mesoporous Mater.* **2005**, *79*, 145–163.

- (28) Holm, M. S.; Saravanamurugan, S.; Taarning, E. Conversion of sugars to lactic acid derivatives using heterogeneous zeolite catalysts. *Science* **2010**, *328*, 602–605.
- (29) Yue, X. Y.; Ren, H. F.; Wu, C.; Xu, J.; Li, J.; Liu, C. L.; Dong, W. S. Highly efficient conversion of glucose to methyl lactate over hierarchical bimetal-doped Beta zeolite catalysts. *J. Chem. Technol. Biotechnol.* **2021**, *96*, 2238–2248.
- (30) Hu, W.; Chi, Z.; Wan, Y.; Wang, S.; Lin, J.; Wan, S.; Wang, Y. Synergistic effect of Lewis acid and base in modified Sn- $\beta$  on the direct conversion of levoglucosan to lactic acid. *Catal. Sci. Technol.* **2020**, *10*, 2986–2993.
- (31) Luo, D.; Liu, S.; Yin, W.; Xia, S. Methyl lactate production from levoglucosan by using Sn-Beta and H-Beta catalysts. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 798–805.
- (32) Dong, W.; Shen, Z.; Peng, B.; Gu, M.; Zhou, X.; Xiang, B.; Zhang, Y. Selective chemical conversion of sugars in aqueous solutions without alkali to lactic acid over a Zn-Sn-Beta Lewis acid-base catalyst. *Sci. Rep.* **2016**, *6*, No. 26713.
- (33) Hu, J.; Xue, D. Research Progress on the Characteristics of Rare Earth Ions and Rare Earth Functional Materials. *Chin. J. Appl. Chem.* **2020**, *37*, 245.
- (34) Akah, A. Application of rare earths in fluid catalytic cracking: A review. *J. Rare Earth* **2017**, *35*, 941–956.
- (35) Giese, E. C. Biosorption as green technology for the recovery and separation of rare earth elements. *World J. Microbiol. Biotechnol.* **2020**, *36*, 1–11.
- (36) Hong, E.; Liu, L.; Bai, L.; Xia, C.; Gao, L.; Zhang, L.; Wang, B. Control synthesis, subtle surface modification of rare-earth-doped up conversion nanoparticles and their applications in cancer diagnosis and treatment. *Mater. Sci. Eng. C* **2019**, *105*, No. 110097.
- (37) Songzhe, C.; Shengming, X.; Gang, X.; Linyan, L. Application of Rare Earth Elements in Photocatalysts and the Mechanism of Action. *Rare Met. Mater. Eng.* **2006**, *35*, 505.
- (38) Mäki-Arvela, P.; Aho, A.; Murzin, D. Y. Heterogeneous catalytic synthesis of methyl lactate and lactic acid from sugars and their derivatives. *ChemSusChem* **2020**, *13*, 4833–4855.
- (39) Zhu, P.; Li, H.; Riisager, A. Sn-Beta Catalyzed Transformations of Sugars—Advances in Catalyst and Applications. *Catalysts* **2022**, *12*, 405.
- (40) Xia, M.; Dong, W.; Gu, M.; Chang, C.; Shen, Z.; Zhang, Y. Synergistic effects of bimetal in modified beta zeolite for lactic acid synthesis from biomass-derived carbohydrates. *RSC Adv.* **2018**, *8*, 8965–8975.
- (41) Xia, M.; Dong, W.; Shen, Z.; Xiao, S.; Chen, W.; Gu, M.; Zhang, Y. Efficient production of lactic acid from biomass-derived carbohydrates under synergistic effects of indium and tin in In-Sn-Beta zeolites. *Sustainable Energy Fuels* **2020**, *4*, 5327–5338.
- (42) Xia, M.; Shen, Z.; Gu, M.; Chen, W.; Dong, W.; Zhang, Y. Efficient catalytic conversion of microalgae residue solid waste into lactic acid over a Fe-Sn-Beta catalyst. *Sci. Total Environ.* **2021**, *771*, No. 144891.
- (43) Wang, Y.; Deng, W.; Wang, B.; Zhang, Q.; Wan, X.; Tang, Z.; Wang, Y.; Zhu, C.; Cao, Z.; Wan, H. Chemical synthesis of lactic acid from cellulose catalyzed by lead (II) ions in water. *Nat. Commun.* **2013**, *4*, No. 2141.
- (44) Mok, W. S. L.; Antal, M. J.; Jones, M. Formation of acrylic acid from lactic acid in supercritical water. *J. Org. Chem.* **1989**, *54*, 4596–4602.
- (45) Lira, C. T.; McCrackin, P. J. Conversion of lactic acid to acrylic acid in near-critical water. *Ind. Eng. Chem. Res.* **1993**, *32*, 2608–2613.
- (46) Kong, L.; Shen, Z.; Zhang, W.; Xia, M.; Gu, M.; Zhou, X.; Zhang, Y. Conversion of sucrose into lactic acid over functionalized Sn-beta zeolite catalyst by 3-Aminopropyltrimethoxysilane. *ACS Omega* **2018**, *3*, 17430–17438.
- (47) Shen, Z.; Kong, L.; Zhang, W.; Gu, M.; Xia, M.; Zhou, X.; Zhang, Y. Surface amino-functionalization of Sn-Beta zeolite catalyst for lactic acid production from glucose. *RSC Adv.* **2019**, *9*, 18989–18995.
- (48) Xia, M.; Shen, Z.; Xiao, S.; Peng, B. Y.; Gu, M.; Dong, W.; Zhang, Y. Synergistic effects and kinetic evidence of a transition metal-tin modified Beta zeolite on conversion of Miscanthus to lactic acid. *Appl. Catal., A* **2019**, *583*, No. 117126.