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# Efficient conversion of cellulose to lactic acid over yttrium modified siliceous Beta zeolites

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#### ABSTRACT

The selective one-pot synthesis of lactic acid (LA) from cellulose, and further the raw biomass, on heterogeneous catalysts is the key point for the development of biorefinery technology. Herein, we reported an yttrium (Y) modified siliceous Beta zeolites catalyst via two-step post-synthesis for highly efficient conversion of cellulose to LA. Under condition of 220 °C and 2 MPa N<sub>2</sub>, the cellulose could be transformed to LA with a yield of 49.2 % within 30 min, and the substrate can be extended to various raw biomass. It was demonstrated that the deal-umination and modification of Y can efficiently modulate the acidity on the surface of zeolite. The dehydration products HMF and other derivatives were suppressed, and the yield of LA was correlated in line with the acid amount, which were attributed to the increased Lewis acidity originated by Y incorporation. These results contribute to the development of the green and efficient synthesis of bio-chemicals.

#### 1. Introduction

With the wide availability and huge scale of annual yield, biomass, the only sustainable and green carbon source, possesses an immense potential to complement fossil-derived carbons [1,2]. The clean and efficient conversion of biomass to energy and chemicals, generally termed as "biorefinery technology", has become a crucial strategy of development all over the world [3,4]. As the most abundant component of biomass, cellulose can be hydrolyzed to yield glucose, which can be subsequently converted into a variety of platform chemicals such as fructose [5], sorbitol [6,7], 5-hydromethylfurfural (HMF) [8,9], levulinic acid (LeA) [10], glycol [11], LA [12,13], etc. Among these, LA has a wide range of applications in food industry, pharmaceuticals, biodegradable plastics, and green solvents, with a global market valued at approximately \$2.9 billion in 2018 and assessed around \$8 to 10 billion by 2025 [14,15].

The hydrothermal conversion of cellulose into LA involves consecutive steps of cellulose hydrolysis to glucose, glucose isomerization to fructose and fructose transformation into LA via retro-aldol pathway

[15–18]. Among them, the redro-aldol of fructose is considered to be the rate-determining step [16,19]. Furthermore, the selectivity for LA suffered from multiple side-reactions with by-products such as HMF, LeA and solid humins. Hence, specific C-C cleavage and C-O activation are essential for the efficient one-pot synthesis of LA from cellulose [17], which requires well-designed catalysis systems. Specifically, the first hydrolysis of cellulose can be driven by Brønsted acidity; while the following steps of isomerization and retro-aldol reaction are favored via catalysts with Lewis acidity and/or basicity [12]. Catalysts with acidic sites, especially various types of solid Lewis acids, have been extensively studied in recent years. For instance, Marianou et al. [15] investigated various oxides, heteropolyacids, and oxides supported heteropolyacids, and found that TSA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, with the highest Lewis to Brønsted acidity ratio, led to the highest LA selectivity (38.4 %) and yield (23.5 %), at 61.2 % cellulose conversion. Other solid catalysts with pronounced Lewis acidity, such as Zr-SBA-15 [20], NbF5-AlF3 [21], ZrO2 [22], Er/K10(S)-3 [23], Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> [24], are also employed as active catalysts to facilitate the sluggish steps.

Among all the chosen materials, Beta zeolites are one of the most

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studied and enjoy multiple inherent merits [25–30]. The three-dimensional interconnected channel structures render them large surface area and confinement effect for loading of active catalytic components and the complete reaction of intermediates. They also have abundant acidity sites on their surface, making them promising catalyst and/or multifunctional supports. Furthermore, their surface chemical properties can be adjusted by acid treatment and ion exchange with metal ions. As an example, Holm et al. [16] reported that, the H-Al-Beta zeolite with Brønsted acidity catalyzed the dehydration of the sugars, leading to HMF and other derivatives. While after modified with Ti, Sn, or Zr, the zeolites featured Lewis acidity and were active for the conversion of sugars to LA derivatives, and Sn-Beta zeolite with the strongest Lewis acidic sites exhibited the most selectivity. Besides, with hemicellulose and cellulose in its components, the raw lignocellulosic biomass, such as corn stover, can be utilized as feedstock for the production of LA [31]. A transition metal and Sn incorporated Beta zeolite was reported to directly convert raw biomass into lactic acid with a yield of 33.4 %. The strong Lewis acidity originated from transition metal and the relatively weak Lewis acidity from Sn were rationalized to serve as multifunctional active sites [32]. However, the application of Beta zeolites in the one-pot conversion of cellulose and the raw biomass to LA still suffered from low yield.

The introduction of Y species can lead to the formation of Lewis acidity in the catalysis system, and have been applied in plenty of acidcatalyzed organic transformations [33,34]. Yan et al. [35] developed a Y modified siliceous Beta zeolite catalyst via dealumination of the parent Beta zeolite and then introduction of Y species via wet impregnation. They demonstrated that the surface Brønsted acidic sites were eliminated by the dealumination, and the surface Lewis acidic sites increased in line with the incorporation of Y raised from 2% to 10 %, which accounted for the high efficiency of one-pot conversion of acetic acid to isobutene. In the field of biomass conversion, trivalent Y species was reported as a homogeneous catalyst for the direct synthesis of LA from the actual biomass. The  $[Y(OH)_2(H_2O)_2]^+$  species derived from  $Y^{3+}$ hydrolysis was responsible for the the simultaneous conversion of hemicellulose and cellulose components in rice straw to obtain a LA yield of 66.3 % [36]. While to the best of our knowledge, there has been few reports of supported Y catalysts on the conversion of cellulose or raw lignocellulose to LA yet.

Based on the above discussion, we herein reported a Beta zeolite supported Y (Y-Beta) catalyst for efficient conversion of cellulose, and further the raw biomass to LA. The catalysts were synthesized through the modified method reported by Yan et al. [35], with the incorporation of Y via a solid-state ion-exchange. The prepared catalysts were thoroughly characterized with respect to their crystal structure, morphology, porosity and acidity. The product yield was correlated with the acidity. The as-prepared Y-Beta can efficiently transform cellulose to LA, and the substrates can be extended to several raw biomass. Attempts have been made to optimize reaction conditions and investigate the reaction mechanism.

#### 2. Experimental

#### 2.1. Materials

Microcrystalline cellulose (average particle size 50 µm), D-fructose (99 %), D-(+)-glucose (99 %), D-(+)-xylose (99 %), LeA (95 %), LA (90 %), formic acid (88 %), acetol (90 %), HMF ( $\geq$ 99 %), Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.5 %) and Y<sub>2</sub>O<sub>3</sub> (99.99 %) were purchased from Aladdin. A commercial beta zeolite (Si/Al ratio of 25) was purchased from Catalyst Plant of Nankai University (Tianjin, China). Bamboo, pine and rice husk were obtained from Fujian province, China. Before reaction, they were dried at 393 K, milled, and screened into powder with the size of <60 meshes. Other reagents were all analytical grade and used without further purification.

#### 2.2. Catalyst preparation

Y-Beta zeolite catalysts were prepared through a two-step procedure, consisting of the dealumination of the Al-Beta zeolite and then introduction of Y species via solid-state ion-exchange. In a typical process, the commercial Al-Beta zeolite was stirred in a 13 mol/L nitric acid aqueous solution at 100 °C overnight to obtain dealuminated Beta (deAl-Beta). The deAl-Beta was filtered, washed thoroughly with deionized water, and dried at 110 °C overnight. Afterward, the dried deAl-Beta was ground with  $Y(NO_3)_3 \cdot 6H_2O$  in agate mortar for 0.5 h; then the mixture was dried at 110 °C overnight and calcined at 550 °C for 6 h to obtain Y-Beta. The zeolite samples after calcination were directly used as the catalysts without any reduction treatment. The final product was labeled by x%-Y-Beta, where x indicated the designated weight loading of metal in the sample.

#### 2.3. Characterization techniques

Powder X-ray diffraction (XRD) patterns were acquired with an XPert Pro MRD diffractometer equipped with a Cu-Kα source (40 kV, 40 mA). Data points were acquired by step scanning with a rate of  $5^{\circ}$ / min from  $2\theta = 5^{\circ} - 50^{\circ}$ . Nitrogen adsorption-desorption measurements were performed at -196 °C with a Micromeritics ASAP-2460 surface area analyzer. Prior to the measurements, the samples were degassed at 110 °C and 250 °C for 1.5 h and 5 h, respectively. The specific surface areas were calculated with BET equation. The micropore volume was determined by t-plot model, and the micropore size distribution was obtained by DFT method. FTIR spectra of the silanol vibration region and pyridine adsorption were obtained using a Thermo Scientific Nicolet 6700 spectrometer equipped with a liquid nitrogen-cooled MCT detector. Samples for IR spectroscopy were prepared by pressing catalyst into a 20 mm diameter pellet and placing it into a custom-built transmission cell fitted with CaF2 windows. All pellets were pretreated in dry air at 450 °C for 1 h to remove any water in the material; spectra were acquired at 150 °C. For pyridine adsorption, 2 µL of pyridine was injected for each experiment and desorbed at 150 °C, then the FTIR spectrum of pyridine was obtained. The total acid capacity was determined by ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) using the Micromeritics Autochem 2910 unit. Scanning electron microscopy (SEM) was conducted on a SU8220 electron microscope at an acceleration voltage of 5.0 kV. Transmission electron microscopes (TEM) was carried out on a JEM-2100 F electron microscope equipped with a field emission gun operating at an accelerating voltage of 200 kV. The samples were prepared by dropping ethanol dispersion of catalysts onto carbon-coated copper TEM grids (Ted Pella, Redding, CA) using pipettes and dried under ambient condition. X-ray photoelectron spectroscopic (XPS) analyses were performed on a Kratos Axis Ultra spectrometer (Kratos Analytical, UK) equipped with a monochromatized aluminum Xray source. Inductively coupled plasma (ICP) experiments were performed on a Thermo IRIS Intrepid II spectrum apparatus to determine the actual Y contents. The carbon content of cellulose and lignocellulose was measured by the Thermo Flash 2000 CHNS/O Elemental Analyzer.

#### 2.4. Catalytic experiments and product analysis

The catalytic conversion was conducted in a stainless steel autoclave (HuoTong, 50 mL) with a mechanical stirrer. Generally, a mixture of cellulose, the solid acid catalyst, and ultra-pure water were loaded into the autoclave. After the autoclave was sealed, the atmosphere in the reactor was replaced three times with N<sub>2</sub> and then 2 MPa N<sub>2</sub> was charged. The reactor was heated to the desired temperature with a heating rate of ~5 °C min<sup>-1</sup> and kept for a designed time. After the reaction, the aqueous solution was separated from the solid catalyst by filtration and cooled in an ice bath. The solid catalyst was collected and dried at 120 °C overnight.



Fig. 1. a) XRD patterns of  $Y_2O_3$ , deAl-Beta, and different Y-Beta catalysts; b) TEM images of Y-Beta with corresponding element mapping. c)  $N_2$  adsorptiondesorption isotherms and d) corresponding pore size distribution curves for various catalysts.

Products analysis were analysed by high performance liquid chromatography (HPLC) in a Shimadzu LC-10 chromatograph equipped with a refractive index detector (RID-10A, Shimadzu) and a Xtimate Sugar-H ion exclusion column ( $300 \times 7.8$  mm, 8 µm particle, YueXu), using 5 mM H<sub>2</sub>SO<sub>4</sub> as the mobile phase at a flow rate of 0.6 mL/min. The column temperature was 60 °C and the detector temperature was set to 40 °C. The concentrations of all components were determined by comparison to the standard calibration curves. The mass of unconverted cellulose was determined by deducting the mass of the initial catalyst from the total mass of the solid residue after reaction, ignoring the wastage of the catalyst. The cellulose conversion can be calculated as followed:

Cellulose conversion (%):



Fig. 2. a) FTIR spectra in the hydroxyl stretching vibration region of H-Beta, deAl-Beta and 10 % Y-Beta. b) Y 3d XPS of 10 % Y-Beta and reference Y<sub>2</sub>O<sub>3.</sub> c) NH<sub>3</sub>-TPD profiles of the catalysts. d) Py-IR spectra of the catalysts at 150 °C.

$$Conversion(\%) = \left(1 - \frac{\text{mass of the solid residue - mass of the initial catalyst}}{\text{mass of initial cellulose}}\right) \times 100\%$$

Yield of product i (C %):

$$Yield(\%) = \frac{\text{mol of carbon in target product}}{\text{mol of carbon in initial cellulose}} \times 100\%$$
(2)

For the raw biomass, only cellulose (composed of C6 units) and hemicellulose (composed of C5 units) can be converted into lactic acid, whereas lignin cannot produce lactic acid. Therefore, as commonly applied in literatures, the yield of lactic acid here was calculated based on C6 and C5 monomeric units contained in the raw biomass using the following equation [18,36,37]:

of all samples demonstrated the inherent microporous structure of the zeolite. It also indicated the presence of mesopores, which may be attributed to the interparticle voids of the random stack of the nanocrystals and/or the collapse inside the zeolite crystals after the deal-umination (Fig. 1c-d). As listed in Table S1, after modification with the Y species, the micropore surface area of the catalysts decreased from  $429 \text{ m}^2 \text{ g}^{-1}$  to  $295 \text{ m}^2 \text{ g}^{-1}$ , and the micropore pore volume decreased from 0.17 cm<sup>3</sup> g<sup>-1</sup> to  $0.12 \text{ cm}^3 \text{ g}^{-1}$ .

The FTIR spectra spectrum in the hydroxyl stretching region were given in Fig. 2a). For parent H-Beta, there were two characteristic bands centered at  $3735 \text{ cm}^{-1}$  and  $3600 \text{ cm}^{-1}$ , which were assigned to the

 $Yield(\%) = \frac{\text{moles of obtained lactic acid}}{\text{moles of C5 units in the feedstock} + 2 \times \text{moles of C6 units in feedstock}} \times 100\%$ 

#### 3. Results and discussion

Y-Beta catalysts were prepared through a two-step procedure, consisting of the dealumination of the H-Beta (deAl-Beta) and then introduction of Y species via solid-state ion-exchange. As can be seen from the XRD results (Fig. 1a), samples after dealumination and Y introduction inherited the crystalline structure of the original H-Beta, with typical diffraction lines characteristic of the BEA topology [28,38]. However, compared to the parent zeolite, the intensities of the reflections decreased with the increase of Y content, indicating the gradual loss of the crystallinity. No obvious diffraction peaks from Y2O3 crystallites (JCPDS: 76-0151) were detected, demonstrating that Y was either amorphous or highly dispersed within the zeolite matrix. The TEM images (Fig. S1) and the element mapping (Fig. 1b) of 10 % Y-Beta displayed the hierarchical pores of the support, and no obvious Y-containing aggregates, further confirming the homogeneous distribution of Y species. The SEM images of 10 % Y-Beta (Fig. S2) showed that the catalyst was composed of closely stacked zeolite nanocrystals and the particle size of the final catalyst was in range of 50–100 nm. The N<sub>2</sub> physisorption isotherms and the corresponding pore size distribution



Fig. 3. Catalytic performances of various catalysts. Reaction conditions: cellulose 0.3 g, water 30 mL, catalyst 0.1 g, 220  $^\circ$ C, 2 MPa  $N_2$ , 30 min.

isolated external Si—OH groups and the bridging hydroxyls (Si-OH-Al), respectively<sup>27</sup>. After the dealumination, the band related to Al species (Si-OH-Al) disappeared, meanwhile the band due to the isolated internal Si—OH groups intensified, and a new band at around 3540 cm<sup>-1</sup> attributed to hydrogen-bonded silanol groups occurred. With the introduction of Y species, the intensities of the bands related to the Si—OH decreased obviously, indicating the incorporation of Y with silanol groups [35].The XPS analyses were further carried out. As can be seen from Fig. 2b), in the Y 3d XPS spectra of the Y-Beta, signals of binding energy at 160.2 and 158.5 eV were corresponded to Y 3d5/2 and 3d3/2, respectively, which were obviously higher than those for bulk  $Y_2O_3$  (158.5 and 156.6 eV), demonstrating the formation of the Si-O-Y bond [35,39,40].

The NH<sub>3</sub>-TPD analyses were conducted to investigate the modification of surface acidity. As can be seen from Fig. 2c), the parent H-Beta showed a large NH<sub>3</sub> desorption peak centered at approximately 200 °C and a broad peak at 300–500 °C, corresponding to weak and strong acidic sites, respectively. After dealumination and introduction of Y, the intensities of the peaks for NH<sub>3</sub> desorbed from both weak and strong acidic sites decreased significantly compared to the parent H-Beta, revealing the disappearance of a large number of acidic sites because of removal of aluminum atoms from the framework [41]. With the increase of the Y amount, the peak areas gradually rose up, revealing an increase on total acid amount, which was specifically listed in Table S2.

To further identify the surface acidity, the pyridine adsorption IR spectroscopies were taken out. Three main classes of vibrations could be assigned: i) vibrations related to physiosorbed and/or hydrogen bonded pyridine generated by both Lewis and Brønsed acid sites  $(1490 \text{ cm}^{-1})$ ; ii) vibrations arising from coordination of pyridine to Lewis acid centers  $(1620-1600, 1455-1445 \text{ cm}^{-1})$ ; and iii) vibrations related to pyridine protonated by Brønsted acid centers (1637, 1540 cm<sup>-1</sup>) [25,42]. As can be seen from Fig. 2d), there existed vibrations attributed to both Brønsted and Lewis acid sites on the surface of parent H-Beta. After dealumination and introduction of 10 % Y, the characteristic of Brønsted acid was almost absent and only Lewis acid sites were present. These findings were consisting with the previous studies that the incorporation of Y within the zeolite could create Lewis acid sites<sup>35</sup>. Hence, the increased acid amount from NH3-TPD analysis was attributed to the Lewis acidity originated from Y loading. These results demonstrated the dealumination and modification of Y could efficiently modulate the

(3)

(1)

#### Table 1

The comparison of to LA by different catalyst systems.

Substrate	Catalyst	Temperature (°C)	Time (h)	LA yield (%)	Year	ref
glucose	In–Sn-Beta	190	2	53	2020	[43]
cellulose	ZrW	190	24	28	2019	[44]
cellulose	$Al_2(WO_4)_3$	220	3	46	2019	[24]
cellulose	TSA/SiO <sub>2</sub> - Al <sub>2</sub> O <sub>3</sub>	175	24	23.5	2019	[15]
cellulose	Y-Beta	220	0.5	49.2		This work

acidity on the surface of zeolite.

To evaluate the catalytic performance of the as-obtained catalysts, the hydrothermal conversion of cellulose to LA was conducted under conditions of 220 °C and 2 MPa N2. The cellulose can be 100 % converted with all catalysts while the carbon balance varied due to the different degree of humins and coke formation. The products distribution of the as-obtained catalysts were displayed in Fig. 3. Besides the desired product of LA, by-products including glucose, fructose, pyruvaldehyde, HMF, LeA, and formic acid were also detected. In the presence of the H-Beta, the yield of LA was low, approximately 6.3 %, while the main products were the hydrolysis product of cellulose and the further dehydration product, with glucose yield of 13.1 % and HMF of 22.7 %, together with a small amount of formic acid and LeA. The presence of LeA and formic acid indicated the further hydration of HMF. When Y was introduced into the deAl-Beta with loading from 1 % to 15 %, the LA yield was significantly improved from 19.5–51.6%, which was in line with the increased surface acidities (Fig. S3). In contrast, the yield of HMF was greatly reduced from 22.0%-5.6%. This result was pleasurably competitive to the reported systems, as compared in Table 1. The difference in the performance could be attributed to the internal variation of Brønsted and Lewis acids in the catalysts. It was accepted

that cellulose hydrolysis to glucose was catalyzed by Brønsted acid sites. Afterwards, with the aid of Lewis acidity, glucose may isomerize to fructose, which subsequently either dehydrates to HMF (Brønsted acidity) or converts into LA via retro-aldol reactions (Lewis acidity) [15, 16]. In our case, the cellulose could be depolymerized by the water autoprotolysis due to the increased ionization constant of hot water (220 °C). While for the Y-Beta, the elimination of Brønsted acid sites dramatically suppressed the dehydration of fructose to HMF and the further decomposition of HMF. The re-formation of sufficient Lewis acid sites facilitated the isomerization and retro-aldol reactions, leading to high selectivity of LA.

The optimal reaction conditions for the conversion of cellulose to LA were further investigated. It can be seen from Fig. 4 a and b that the optimal temperature and reaction time were 220 °C and 30 min, respectively. With further increasing the temperature and reaction time, the conversion of cellulose and the yield of LA remained almost stable, confirming the stability and negligible overreaction of the LA. The best catalyst dosage was determined to be 0.1 g for 0.3 g cellulose amount (Fig.4c), for the balance of the availability of active sites.

One issue associated with the practical application is the catalyst

#### Table 2

Catalytic conversion of various raw biomass feedstock. Reaction conditions: Biomass material 0.3 g, water 30 mL, catalyst 0.1 g, 240  $^\circ$ C, 2 MPa  $N_2,$  60 min.

Substrate	Element content (wt.%)		Componen	LA yield			
	С	Н	Ν	cellulose	hemicellulose	lignin	(%)
Bamboo	47.8	6.6	0.1	46.0	19.3	21.5	75.9
Pine	46.7	6.8	0.1	44.6	14.9	25.4	60.8
Rice	41.7	6.0	0.5	39.9	18.7	16.8	44.0
husk							

<sup>a</sup> Analyzed according to the procedures of the Van-Soest method [45].

<sup>b</sup> Calculated based on C6 and C5 units contained in the raw biomass.



Fig. 4. Effect of a) temperature, b) time and c) catalyst amount on the conversion of cellulose over 10 %Y-Beta.

adaptability to raw biomass feedstock. The complex structure of lignocellulosic biomass consisting of cellulose, hemicellulose and lignin restricts the efficiency of the cellulose hydrolysis reaction. The performance of the catalysts for the conversion of lignocellulosic biomass into LA was evaluated over 10 % Y-Beta at 240 °C for 60 min. To our delight, as can be seen from Table 2, satisfactory LA yields were obtained, with bamboo as high as 75.9 %, pine 60.8 %, and rice husk 44.0 % (based on the amount of C6 and C5 monosaccharide units contained in the raw biomass feedstock, with more explanations in **Catalytic experiments and product analysis**). It was also revealed that the yield of LA was affected by the composition of biomass, especially correlated with the content of cellulose and hemicellulose. The above results indicated that the Y-Beta catalyst not only had outstanding activity in converting cellulose into LA, but also performed well on lignocellulose with more complex structure.

To verify the reusability of the catalyst, three consecutive reactions were conducted with 10 %Y-Beta under the same reaction conditions after catalyst recovery (Fig. S4). Between runs, the solid catalyst was dried at 80 °C overnight and calcined at 500 °C for 2 h. After the second use of the catalyst, the cellulose could still be fully converted, but the LA vield dropped from 49.2–40.8%, while still slightly decreased to 37.3 % in the third run. The ICP analysis of the used catalyst was conducted and showed that the Y loading was reduced from 9.8 wt%to 6.3 wt% in the second run. The resulting LA yield of 40.8 % was comparable to that on fresh 5 % Y-Beta (40.1 %), indicating that the leaching of Y may be the main reason for the deactivation of the used catalyst. In order to further determine whether the dissolved Y species play the key catalytic role for cellulose conversion, the fresh 10 %Y-Beta was treated in hot compressed water at 220 °C for 0.5 h and then filtered to get the filtrate solution. The result showed that the yield of LA was only about 5% when the recovered filtrate solution was used as reaction media, comparable to that in the condition of absence of catalyst. It was indicated that the reaction was heterogeneous catalysis. The stability of the catalyst would continue to be improved in the future.

#### 4. Conclusions

Herein, we successfully synthesized a Y modified Beta zeolite catalyst for highly efficient conversion of cellulose to LA. It was confirmed that the Brønsted acidities on the parent H-Beta resulted in the formation of dehydration by-products. After dealumination and modification of Y, the Brønsted acidities were removed and the Lewis acidic sites reformed, which promoted the isomerization and retro-aldol reaction and led to the selective production of LA. Over the 10 % Y-Beta, the cellulose can be converted into LA with a yield of 49.2 % within 30 min, and the substrate can be extended to bamboo powder, pine and other raw biomass. Further attempts should be addressed to stabilize the Y species confined within the zeolite matrix in water solution and promote the recyclability of catalyst. These results possess a promise for the development of biorefinery technology.

#### CRediT authorship contribution statement

Juan Ye: Methodology, Data curation, Investigation, Software. Chenyu Chen: Software, Visualization. Ying Zheng: Resources. Dan Zhou: Resources. Yunzhen Liu: Resources. Denglong Chen: Funding acquisition. Liufang Ni: Methodology. Gang Xu: Conceptualization, Methodology, Supervision. Fanan Wang: Writing - review & editing, Project administration.

#### **Declaration of Competing Interest**

There are no conflicts to declare.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118133.

#### References

- [1] D.R. Dodds, R.A. Gross, Science 318 (2007) 1250-1251.
- [2] K. Li, Y. Sun, Chemistry 24 (2018) 18258–18270.
- [3] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502.
- [4] C. Mondelli, G. Gozaydin, N. Yan, J. Perez-Ramirez, Chem. Soc. Rev. 49 (2020) 3764–3782.
- [5] V. Choudhary, A.B. Pinar, R.F. Lobo, D.G. Vlachos, S.I. Sandler, ChemSusChem 6 (2013) 2369–2376.
- [6] Y. Liao, Q. Liu, T. Wang, J. Long, L. Ma, Q. Zhang, Green Chem. 16 (2014) 3305–3312.
- [7] N. Yan, C. Zhao, C. Luo, P.J. Dyson, H. Liu, Y. Kou, J. Am. Chem. Soc. 128 (2006) 8714–8715.
- [8] N. Shi, Q.Y. Liu, Q. Zhang, T.J. Wang, L.L. Ma, Green Chem. 15 (2013) 1967–1974.
  [9] R.J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Chem. Rev. 113 (2013) 1499–1597.
- [10] S.M. Kang, J.X. Fu, G. Zhang, Renew. Sust. Energ. Rev. 94 (2018) 340–362.
- [11] Y. Liu, C. Luo, H. Liu, Angew. Chem. Int. Ed. Engl. 51 (2012) 3249–3253.
- [12] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A. A. Lappas, Appl. Catal. A-Gen. 555 (2018) 75–87.
- [13] W. Deng, P. Wang, B. Wang, Y. Wang, L. Yan, Y. Li, Q. Zhang, Z. Cao, Y. Wang, Green Chem. 20 (2018) 735–744.
- [14] https://www.zionmarketresearch.com/sample/lactic-acidmarket).
- [15] A.A. Marianou, C.C. Michailof, D. Ipsakis, K. Triantafyllidis, A.A. Lappas, Green Chem. 21 (2019) 6161–6178.
- [16] M.S. Holm, S. Saravanamurugan, E. Taarning, Science 328 (2010) 602-605.
- [17] S. Li, W.P. Deng, Y.Y. Li, Q.H. Zhang, Y. Wang, Int. J. Energ. Mater. Chem. Propuls. 32 (2019) 138–151.
- [18] Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tang, Y. Wang, C. Zhu, Z. Cao, G. Wang, H. Wan, Nat. Commun. 4 (2013) 2141.
- [19] M. Orazov, M.E. Davis, P. Natl. Acad. Sci. U. S. A. 112 (2015) 11777-11782.
- [20] L. Yang, X. Yang, E. Tian, H. Lin, ChemSusChem 9 (2016) 36-41.
- [21] S.M. Coman, M. Verziu, A. Tirsoaga, B. Jurca, C. Teodorescu, V. Kuncser, V.
- I. Parvulescu, G. Scholz, E. Kemnitz, ACS Catal. 5 (2015) 3013–3026. [22] P. Wattanapaphawong, P. Reubroycharoen, A. Yamaguchi, RSC Adv. 7 (2017)
- 18561–18568. [23] F.-F. Wang, J. Liu, H. Li, C.-L. Liu, R.-Z. Yang, W.-S. Dong, Green Chem. 17 (2015)
- 2455-2463.
- [24] N. Shi, Q. Liu, X. He, H. Cen, R. Ju, Y. Zhang, L. Ma, Bioresour. Technol. Rep. 5 (2019) 66–73.
- [25] M. Xia, W. Dong, M. Gu, C. Chang, Z. Shen, Y. Zhang, RSC Adv. 8 (2018) 8965–8975.
- [26] J. Dijkmans, M. Dusselier, D. Gabriëls, K. Houthoofd, P.C.M.M. Magusin, S. Huang, Y. Pontikes, M. Trekels, A. Vantomme, L. Giebeler, S. Oswald, B.F. Sels, ACS Catal. 5 (2015) 928–940.
- [27] D. Yu, W. Dai, G. Wu, N. Guan, L. Li, Chinese J. Catal 40 (2019) 1375–1384.
- [28] F.-F. Wang, H.-Z. Wu, H.-F. Ren, C.-L. Liu, C.-L. Xu, W.-S. Dong, J. Porous Mater 24 (2016) 697–706.
- [29] Y.Y. Sun, L. Shi, H. Wang, G. Miao, L.Z. Kong, S.G. Li, Y.H. Sun, Sustain. Energ. Fuels 3 (2019) 1163–1171.
- [30] X. Yang, Y. Zhang, L. Zhou, B. Gao, T. Lu, Y. Su, J. Xu, Food Chem. 289 (2019) 285–291.
- [31] T. He, Z.C. Jiang, P. Wu, J. Yi, J.M. Li, C.W. Hu, Sci. Rep. 6 (2016) 38623.
- [32] M. Xia, Z. Shen, S. Xiao, B.-y. Peng, M. Gu, W. Dong, Y. Zhang, Appl. Catal. A-Gen. 583 (2019), 117126.
- [33] W. Dai, S. Zhang, Z. Yu, T. Yan, G. Wu, N. Guan, L. Li, ACS Catal. 7 (2017) 3703–3706.
- [34] T. Yan, W. Dai, G. Wu, S. Lang, M. Hunger, N. Guan, L. Li, ACS Catal. 8 (2018) 2760–2773.
- [35] T.T. Yan, L. Yang, W.L. Dai, G.J. Wu, N.J. Guan, M. Hunger, L.D. Li, ACS Catal. 9 (2019) 9726–9738.
- [36] S. Xu, Y. Wu, J. Li, et al., ACS Sustain. Chem. Eng. 8 (2020) 4244-4255.
- [37] S. Xu, J. Li, J. Li, Y. Wu, Y. Xiao, C. Hu, iScience 12 (2019) 132–140.

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- [38] P. Li, G. Liu, H. Wu, Y. Liu, J.-g. Jiang, P. Wu, J. Phys. Chem. C 115 (2011) 3663–3670.
- [39] W.L. Dai, S.S. Zhang, Z.Y. Yu, T.T. Yan, G.J. Wu, N.J. Guan, L.D. Li, ACS Catal. 7 (2017) 3703–3706.
- [40] H. Behner, J. Wecker, T. Matthée, K. Samwer, Surf. Interface Anal. 18 (1992) 685–690.
- [41] M. Maache, A. Janin, J.C. Lavalley, J.F. Joly, E. Benazzi, Zeolites 13 (1993) 419–426.
- [42] J. Pang, M. Zheng, X. Li, L. Song, R. Sun, J. Sebastian, A. Wang, J. Wang, X. Wang, T. Zhang, ChemistrySelect 2 (2017) 309–314.
- [43] M. Xia, W. Dong, Z. Shen, S. Xiao, W. Chen, M. Gu, Y. Zhang, Sustain Energ Fuels 4 (2020) 5327–5338.
- [44] V.C. Nguyen, A. Dandach, T.T.H. Vu, P. Fongarland, N. Essayem, Mol Catal. 476 (2019) 110518.
- [45] P.J. Van Soest, J.B. Robertson, B.A. Lewis, J. Dairy Sci. 74 (1991) 3583-3597.