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conversion of levoglucosan to lactic acid

ARTICLE

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Synergetic effect of Lewis acid and base in modified Sn-β on direct

DOI: 10.1039/x0xx00000x

This work presents a novel method to selectively convert levoglucosan to Lactic acid (LA), via initially adding LA as Brønsted acid together with modified Sn- β as Lewis acid. Sn- β catalysts exchanged with various cations significantly enhance the yield of LA, following the order of Sn-β< Sn-β-Na< Sn-β-K< Sn-β-Mg, Sn-β-Ca. The role of exchanged alkali ions stems from removing the remaining Brønsted acid sites in the zeolite and tuning the framework oxygen as more Lewis base sites. The exchange with alkaline earth cations such as Ca2+ and Mg2+ appears to be more effective in promoting the retro-aldol condensation, due to the synergetic effect of their stronger Lewis acid that can stabilize the oxygen atom of deprotonated alkoxide during the reaction. The LA yield from Levoglucosan can reach up to 66% on Sn-β-Ca under the optimized conditions. We also demonstrated that such a synergetic effect of alkaline-earth ion exchanged Sn-β shows great universality toward enhanced retrol-aldol condensation, which can significantly promote the yield of methyl lactate over glucose conversion in methanol solvent.

1 Introduction

Levoglucosan is a major product from fast pyrolysis of abundant lignocellulose biomass, which accounts for 23 wt% yield with sugar cane bagasse as the feed,¹ or even reaches up to 60 wt% upon using isolated cellulose.²⁻³ It provides an important platform molecule for the synthesis of a variety of value-added chemicals.⁴⁻⁸ Santhanaraj *et al.* reported a twostep method for the production of gluconic acid from a high purity solution of levoglucosan.⁵ Herein, we target its selective conversion to another important chemical, namely lactic acid (LA). LA is a valuable monomer for the production of biodegradable plastics, as well as an important building-block

chemical widely used in the food, pharmaceutical, cosmetic and chemical industries.9-11 Currently, LA is primarily produced by the fermentation of glucose, which is limited by the drawbacks such as low efficiency of biological process and a plethora of waste accompanied.¹² Hence, substantial studies have been dedicated to the catalytic thermochemical processes for LA production from different carbohydrates such as triose sugars, 13-15 monosaccharide and polysaccharide. 12, 16-¹⁷ Accordingly a variety of efficient homogeneous¹³⁻¹⁶ or heterogeneous catalysts²⁰⁻²² have been developed, among which much interest has been paid to $Sn-\beta$ catalysts due to their strong and water-tolerant solid Lewis acid properties.18-24 Moreover, modified Sn- β zeolites, such as Zn-Sn- β , Sn- β exchanged with alkali metal, and hierarchical Sn- β , have been reported to increase the selectivity of LA or its derivates.12, 25-26 The advances achieved over post-synthetic methods also enable more efficient preparation of Sn-β catalysts with higher framework-Sn content compared to the conventional hydrothermal synthesis routes.^{13, 22, 27-31} However, most of these heterogeneous practices are limited to the conversion of

these heterogeneous practices are limited to the conversion of triose or C_6 monomer sugars that have to be produced through costly chemical processes,⁹⁻¹⁰ and are not efficient in the direct conversion of cellulose or raw lignocellulose. Therefore, it would be highly desired to selectively produce LA from simple oxygenates like acetol³² or levoglucosan, which can be readily produced at large scale from staged condensation or pyrolysis of abundant raw biomass.

Levoglucosan is a type of dehydrated C6 sugar monomer, which can be readily hydrolyzed to form glucose using Brønsted acid catalysts. Once glucose is produced, Lewis acid catalysts such as Sn- β can be applied for its subsequent conversion toward LA.³³ It appears quite straight forward that a combination of Brønsted and Lewis acid sites can potentially enable such a tandem conversion. However, an initial attempt for such a tandem conversion showed that the presence of Brønsted and Lewis acids can catalyze very complex reactions, leading to low yield of the desired product.³⁴ To circumvent such a dilemma, we report a novel method for the conversion of levoglucosan, where external LA is added as the Brønsted acid and the modified Sn- β was employed as the Lewis

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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COMMUNICATION

counterpart. Since LA itself is the targeted product, there will be no need for post-reaction separation caused by using the homogeneous acid. The stratagem here also simplifies the catalyst design, with the focus of only enhancing the Lewis acidity of Sn- β catalysts as opposed to simultaneously introducing both Brønsted acid and Lewis acid sites. The post-synthesis Sn- β prepared in this work was further modified with ion-exchange of various alkali and alkaline-earth cations to fine-tune the Lewis acid-base properties inside the confined space, achieving the synergetic effect in enhancing LA yield.

2 Results and discussion

2.1 Catalyst characterization

The topology of beta zeolite remained intact after all the treatments, including acid treatment, incorporation of metal and exchange with various cations (Fig.S1). Moreover, no diffraction peaks corresponding to SnO₂ (JCPDS No. 41-1445) exist in Sn- β , indicating the little formation of extra-framework SnO₂ (at least below the detection limit of XRD).³⁴ The reflection peaks of Sn- β remain constant after exchanging with various cations, suggesting no destruction of the zeolite structure. The surface areas of all the zeolites didn't change significantly after acid treatment and exchanging treatment, as shown in Table 1. The contents of metal exchanged onto the zeolite are also measured and listed in the same table.

Table 1 ph	nysiochemical	properties of	different zeolites

Entry	Catalyst	Surface area ^[a] [m²g-1]	Content of metal ^[b] Molar ratio
1	Η-β	460	-
2	deAl-β	498	-
3	Sn-β	467	Si/Sn≈18 ^[c]
4	Sn-β-Na	437	Sn/Na \approx 11.4
5	Sn-β-K	489	Sn/K≈11.1
6	Sn-β-Mg	444	Sn/Mg \approx 14.9
7	Sn-β-Ca	403	Sn/Ca $pprox$ 20 (10 ^[d])

^aSpecific surface areas obtained by BET method.

^bDetermined by ICP.

^cDecided by EDX.

^dExchanged for three times.

Diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy was used to understand if Sn was incorporated in framework positions. Relatively low absorption in deAl- β suggests that little electronic transition occurred (Fig. S2a). The presence of tetrahedrally coordinated Sn in the framework Sn- β zeolites is confirmed by an absorption peak near 200 nm due to the ligand-to-metal charge transfer from O²⁻ to Sn⁴⁺.1³, ²⁷, ³⁵ SnO₂ is present in SnO₂/deAl- β as evidenced by a broad absorption from 250 nm-300 nm.²⁷ the fact that there is no SnO₂ phase in Sn- β zeolites confirms that most Sn has been successfully incorporated into the framework of Sn- β zeolites, which is consistent with our earlier work.³⁴ Cation-exchanged Sn- β zeolites have the same absorption peak except for slightly



Figure 1. CO₂-TPD of Sn- β and exchanged Sn- β

Catalyst's basicity was characterized by CO₂-TPD. As shown in Fig. 1, the basicity of Sn- β was evidently enhanced after exchanging with different cations. The strength of catalyst basicity follows the order of Sn- β < Sn- β -Mg< Sn- β -Ca< Sn- β -Na< Sn- β -K, which is similar to the results reported previously.^{23,37}

2.2 External lactic acid initially added as the Brønsted acid for hydrolysis



Figure 2. Time on stream of conversion of levoglucosan with Sn-β. Reaction conditions: cat. 200 mg; lactic acid 0.2 mmol; levoglucosan 0.05 g; H₂O 20 mL; N₂ 2 MPa; temperature 190 °C.

Levoglucosan conversion was initially attempted with the use of Sn- β only, where lactic acid was found to be a major product with a yield about 30% (Fig.S4). However, it took more than 6 hours to reach complete conversion, even when the temperature was raised to 190 °C. In contrast, the introduction of external lactic acid (0.2 mmol) significantly speeds up reaction, resulting in complete conversion in less than 2 hours

Page 2 of 9

Journal Name

COMMUNICATION

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Journal Name

with even improved selectivity of LA. This provides us a piece of direct evidence that lactic acid i.e. the target product self can effectively function as the Brønsted acid to facilitate the hydrolysis of levoglucosan, which appears apparently as the rate-relevant step in the case of only using Sn-B. The temporal evolution of products from the combination of $Sn-\beta$ and extra lactic acid is shown in Fig. 2. LA exhibited a steady increase in yield with time-on-stream, reaching 34% after 4 hours' reaction. Accordingly, the yield of glucose and fructose exhibited a typical trend of intermediate products, both peaked at around 15% after 25 min and then decreased gradually until complete disappearance. This result is consistent with the postulated reaction pathway depicted in scheme 1a, which proceeds via the isomerization and subsequent decomposition of these two hexoses respectively. However, severe side reactions took place, leading to such a low yield of LA. Among them, a small amount of HMF derivatives (5-(hydroxymethyl furfural and levulinic acid) were produced, apparently due to dehydration of fructose and hydrolysis of HMF, respectively, catalyzed by Brønsted acid. Some decomposition products (formic acid and acetol) were also found, which is consistent with the previous reports.12,17 Moreover, a significant amount of oligomers were detected, which exhibit the identical peaks with the products generated when only using HMF as a reactant by liquid chromatographymass spectrometry (LC-MS). This suggests that these heavy products are mainly derived from HMF, a compound known very vulnerable to rapid condensation and polymerization. 38

The effect of reaction temperature on the conversion of levoglucosan was also studied. At a low reaction temperature of 150 °C, only a small amount of LA was obtained, leaving glucose and fructose accounted for the most dominant products after 4 hours time-on-stream (Fig.S5). This suggests retro-aldol condensation of hexose to triose sugars is the rate-limiting step,²² which would be facilitated at higher temperatures. Indeed, the yield of LA was significantly enhanced when the reaction temperature increased to 170 °C. Further increase of temperature to 190 °C resulted in similar product distribution, but requiring half of reaction time for the complete conversion (about 2h). Hence, the subsequent tests over levoglucosan were conducted at 190 °C, where the combination of external lactic acid and modified Sn- β was studied to evaluate their synergetic effect.

2.3 Sn- β exchanged with various cations

As discussed above, LA was successfully produced from levoglucosan, but with a rather low yield, no matter whether Sn- β was used alone or was combined with external LA. Our previous work suggested that the acid properties inside the confined zeolite pores play important roles over the reactions of methacrolein and ethanol on Sn- β , where the removal of weak Brønsted acid sites derived from the remaining silanol groups could significantly enhance the target products that are catalyzed by the strong Lewis acid sites.³⁴ Alkali cations such as Na⁺ have also been commonly used to exchange the protons of silanol in Sn- β , thus eliminating the weak Brønsted acid and enhancing the LA yield in the conversion of glucose.²⁵ Similarly, Sn- β -Na indeed demonstrated enhanced LA_{iew}selectivity compared to that of parent Sn- β in the 100 Moder and 200 Moder and



Figure 3. Conversion of levoglucosan with different ratio of Lewis acid and base. Reaction conditions: levoglucosan 0.05 g; H_2O 20 mL; N_2 2 MPa; temperature 190 °C; time 2 h.

The ratio of Lewis acid and extra-added Brønsted acid was further studied and results are shown in Fig. 3. By regulating the Lewis acid and external LA added, we show that increasing the amount of Sn- β -Na from 200 mg to 300 mg can notably improve the selectivity of LA, while the side products such as HMF and levulinic acid are significantly suppressed. Further increase of Sn- β -Na to 500 mg with 0.2mmol extra LA does not show appreciable enhancement of LA yield but reduces HMF and levulinic acid to a negligible extent. It appears that the combination of 0.3g Sn- β -Na and 0.2 mmol external LA can achieve the optimal performances. However, a further increase in external LA (from 0.2 mmol to 0.4mmol) would only cause the drop of LA yield and more severed side reactions toward heavy products. Hence, the subsequent comparisons among various cation-exchanged Sn-ß catalysts were all conducted with the addition of external LA fixed at 0.2mmol.



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The more striking effect was even achieved when the same approach aforementioned was extended to other alkali cations such as K⁺ and alkaline earth cations such as Ca²⁺ and Mg²⁺, which are capable of fine-tuning the acid-base properties inside the confined zeolite environment. It can be seen in Fig. 4 that the yield of LA for Sn- β -K is considerably higher than that for Sn- β -Na, while those of Sn- β -Ca and Sn- β -Mg are even better. The results achieved from the exchange of alkaline earth cations appear quite striking, considering their less molar content (Sn/Mg \approx 14.9 and Sn/Ca \approx 20) compared to that of Na or K amount (Sn/Na \approx 11.4 and Sn/K \approx 11.1) exchanged in the modified zeolite as shown in Table 1. Accordingly, the employment of $Sn-\beta-Ca-3$ with comparable cation concentration as that in Sn- β -Na or Sn- β -K can further enhance the yield of LA, which eventually reaching up to 66% under optimized condition (i.e. 0.3g Sn- β -Ca-3 and 0.2 mmol LA).



Figure 5. Conversion of levoglucosan by adding different amount of Ca²⁺. Reaction conditions: cat. 200 mg; lactic acid 0.2 mmol; levoglucosan 0.05 g; H_2O 20 mL; N_2 2 MPa; temperature 190 °C; time 2 h.

Great care was taken to ensure the origin of the catalytic effect is indeed from the heterogeneous active sites. No cation was detected in the post-reaction solution, indicating no catalyst leaching during the reaction. We then conducted a comparison test by using the combination of unmodified Sn- β and homogenous Ca²⁺ (in the form of Ca (NO₃)₂). As shown in Fig. 5, almost 6 times higher amount of homogeneous Ca²⁺ added can reach a comparable yield of LA. Much higher homogeneous Ca²⁺ added results in a higher yield of LA (69%) attributed to a higher amount of Ca²⁺ exchanged onto the Sn- β . This confirms that the catalytic effects are indeed from the exchanged cations in zeolites, rather than the homogenous ones leached into the solution during the reaction.

Journal Name

Page 4 of 9

Overall, the results above demonstrated that the combination of external LA and Sn- β exchanged with alkali/ alkaline earth cations led to the efficient conversion of levoglucosan into LA, which follows the pathway depicted in Scheme 1a. It's quite straightforward that the introduction of an appropriate amount of external LA should work as added homogenous Brønsted acid to facilitate the desired hydrolysis of levoglucosan, while excess LA would enhance the side reactions leading to diminished LA yield. On the other hand, Sn- β exchanged with either alkali or alkaline earth cations will eliminate the remaining weak Brønsted acid, thus appearing beneficial to inhibit the side reactions inside the confined pore environment. Apparently, acid-base properties inside the confined pore area of zeolite and Brønsted acid in the bulk aqueous solution played key roles in achieving maximum performances. The hydrolysis step of levoglucosan probably takes place dominantly in the bulk aqueous solution, which is facilitated by the homogeneous Brønsted acid introduced by the external LA added. Isomerization of glucose and subsequent retro-aldol condensation proceed mainly inside the zeolite pores on the strong Lewis acid site, where the neutralization of neighboring weak Brønsted acid by cations exchanged helps inhibit the side reactions as shown in Fig. 3. The somewhat hydrophobic property of Sn-B would restrict the diffusion of aqueous bulk LA into the pore, thus limiting homogenous Brønsted acid inside the pores.

The more intriguing part lies in the distinguished effect between exchanged alkali and alkaline metal cations, where the latter exhibit more significantly enhanced selectivity toward LA. To shed light on the insight of the reaction mechanism, we employed the glucose and fructose intermediates as the reaction substrates, respectively, where only the various $Sn-\beta$ catalysts were used as catalysts and the catalytic performances were intentionally carried out at a low temperature of 150 °C to better reveal the distinct effects on the retro-aldol reaction. As shown in Fig. S6a, both the Na, K, and Ca-exchanged Sn- β resulted in somewhat loss of activity over the conversion of glucose, but with a different trend of product distributions. Sn-β-Na has higher selectivity of fructose, while barely showing promoting effect toward that of LA. Instead, Sn-B-K exhibits a comparable yield of fructose, but a notable increase of LA yield, which is further enhanced upon the employment of Sn- β -Ca. A similar conclusion can be drawn with the conversion of fructose (Fig. S6b). The selectivity of LA upon Sn- β -Ca is significantly higher than that of Sn- β -K and unmodified Sn-B, while even some decline was evident over that of Sn- β -Na. The kinetic-relevant step of LA production from either glucose or fructose is related with the retro-aldol condensation, as mentioned earlier. All these clearly suggest that $Sn-\beta$ exchanged with Ca and K can catalyze this key reaction, while the counterpart modified with Na seems to lack of such catalytic effect at low temperature.

Journal Name

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Scheme 1. a) Reaction pathway in the conversion of levoglucosan to LA. b) Reaction mechanism over alkaline-earth ion exchanged $Sn\mathchar`\beta$

Considering these results, the possible mechanism of enhanced retro-aldol condensation over alkaline-earth ion exchanged $Sn-\beta$ is then tentatively proposed. As depicted in scheme 1b, the ketonic oxygen of fructose adsorbs onto tetrahedrally coordinated Sn sites first, and the C-C bond is subsequently cleaved to form C3 species, such as dihydroxyacetone and glyceraldehyde that dehydrate and undergo 1,2-hydride shift to form LA. It is probably the synergistic effect of the frustrated Lewis acid and base pair, that plays an important role to promote the reaction. Specifically, the Lewis base site, namely framework O atom of Si-O-M (Ca^{2+} or $Mg^{2+})\!,$ can help abstract the proton of a hydroxyl group attached to C3 of fructose, while Ca2+ or Mg2+ can stabilize the deprotonated alkoxide, thanks to the relatively strong Lewis acidity.37 Such stabilization from the alkaline-earth cation could then facilitate the cleavage of C-C bond and subsequently form LA through two trioses intermediates. It should be noted that the alkali cations exchanged zeolites actually bear stronger Lewis base sites, as revealed in Fig. 1. Similar results have been reported that the replacement of Na⁺ with heavier alkali metal ions like K⁺, Rb⁺ and Cs⁺ would further increase the base strength of the adjacent framework oxygen atoms, while the exchange with alkaline-earth ion like Ba2+ in zeolites results in lower base strength of such oxygen atoms, but leading to stronger Lewis acid site due to the higher positive field of the divalent cations.37 Herein, the presence and the lack of promotional effect toward LA over Sn-β-K and Sn-β-Na respectively suggest that only the stronger basic sites promote the retro-aldol condensation, while the superior effect from Sn- $\beta\text{-}Ca$ is more likely from the stronger Lewis acidity derived from the alkaline-earth cation, which synergistically cooperate with the frustrated base O atom to stabilize the transition intermediate and accelerate the retro-aldol condensation.

COMMUNICATION

It should be mentioned that the synergistic effect, of alkaline, earth ion exchanged Sn- β shows great universality toward enhanced retro-aldol condensation. Such a mechanism is not only limited to the conversion of levoglucosan or glucose to lactic acid in aqueous solution, but also being effective in glucose conversion to methyl lactate (MLA) in methanol environment. As shown in Fig. 6a, the alkaline earth metal exchanged Sn- β presents a much better yield of MLA than the bare one. The yield of MLA increases from 21 to 33% and 35% when Sn- β exchanged with Ca and Mg respectively, suggesting the synergetic effect of Lewis acid-base also plays an important role in boosting the retro-aldol condensation in an alcohol solvent.

The stability of catalysts in varied solvents has also been carefully evaluated. As shown in Fig. S7, the activity decreased drastically over 3 consecutive runs for the conversion of levoglucosan to lactic acid at 190 °C. The decreased crystallinity of catalysts after reacting in hydrothermal conditions³⁹⁻⁴⁰ and the leaching of Ca²⁺ in the aqueous acidic solution should be the two relevant factors toward such a drastic loss of reactivity. Indeed, the content of Ca2+ in the catalysts was substantially declined from 0.3wt% initially to 0.13wt% just after the 2nd cycle. Even when the reaction temperature was lowered from 190 °C to 150 °C, the deactivation was still quite significant, where no apparent destruction of crystal structure was observed from the XRD result of the spent catalyst (Fig. S8). Thus, the deactivation at relatively low reaction temperatures should be mainly caused by the leaching of metal cation, which was reversely exchanged with H⁺ derived from lactic acid initially added or gradually produced during the reaction. This suggests that the modified Sn-β catalysts need to be frequently refreshed via ion exchange to make up the leached cation after certain batches of reaction, if applied into practical application for the conversion of levoglucosan or glucose to lactic acid in aqueous solution. Alternatively, one possible solution would be to recycle the aqueous solution with leached metal ions, which can be readily separated after the collection of spent catalyst and the recovery of organic acid products. The application of such recycled solution with concentrated alkaline-earth metal ions would be beneficial to the yield of LA (as shown in Figure 5), and meanwhile limit the extent of ion exchange between H⁺ in the bulk solution and Ca^{2+} in the modified Sn- β catalysts, thus alleviating the deactivation caused by metal ion leaching. However, this stability dilemma confronted in aqueous solution appears not a big concern for the production of methyl lactate from glucose in an organic solvent like methanol. As demonstrated in Fig. 6b, the yield of methyl lactate remained comparable during 5 consecutive runs with Sn- β -Mg, suggesting the good stability of the catalyst in methanol solvent. Accordingly, there was no significant leaching of Mg²⁺ in the recycled catalysts, apparently thanks to the avoidance of organic acid products and the use of an organic solvent that leaves H⁺ barely available in the bulk solution to exchange with alkaline earth cation of the catalyst.

Journal Name



Figure. 6 a) Synergetic effect of Lewis acid base on glucose conversion to methyl lactate. b) Recycling test of glucose conversion to methyl lactate over Sn- β -Mg. Reaction conditions: cat. 400 mg; glucose 0.055 g; methanol 20 mL; N₂ 2 MPa; temperature 160 °C, time 4 h.

3 Conclusions

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A combination of post-synthesis modified $Sn-\beta$ as Lewis acid and externally added LA as Brønsted acid has been shown to be effective in the selective conversion of levoglucosan to LA. The initial introduction of the product LA can efficiently catalyze the first hydration step to accelerate the overall process without sacrificing the net LA yield. Sn-ß exchanged with alkali ions can neutralize the remaining Brønsted acid sites and tune the framework oxygen as stronger Lewis basic reactivity-structure-relationship sites. The a nal vsis demonstrated that $Sn-\beta-Na$ can benefit the LA yield probably via suppressing the side reactions, while Sn-β-K can effectively facilitate the retro-aldol condensation. The exchange with alkaline earth cations such as Ca^{2+} and Mg^{2+} can further enhance the selectivity to LA, which may result from the synergetic effect of their stronger Lewis acid that can stabilize the oxygen atom of deprotonated alkoxide during the conversion of fructose intermediate. The optimum yield of LA can reach up to 66% in the case of $Sn-\beta$ -Ca-3. The same synergistic effect on retro-aldol condensation can be also

applied to the conversion of glucose in methapola Solvent, where Sn- β exchanged with Ca and Mg Significantly entranced the yield of methyl lactate and retained good stability during the recycle tests. Drastic deactivation occurred in the conversion of levoglucosan, mainly due to the severe leaching of alkaline earth cation in the aqueous acidic solution.

4 Experimental

4.1 Chemicals and materials

cellulose, glucose, fructose, mannose and 5-hydroxymethyl furfural were obtained from Aladdin Reagent Co. Ltd. (Shanghai, China). Tin (II) acetate (99%), levoglucocan (99%) were purchased from J&K Chemical Technology. Lactic acid (85.0%-90.0%), acetol (95.0%) and inulin were obtained from Alfa Aesar. Sodium nitrate (99.0%), potassium nitrate (99.0%), calcium nitrate (99.0%), magnesium nitrate (99.0%) and commercial H- β zeolite (Si/Al=12.5), HNO₃ (65%-68%) and formic acid (98%) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). N₂ (99.999%) was obtained from Linde Industrial Gases. Levulinic acid (99%) was supplied by Macklin Reagent Co. Ltd. (Shanghai, China). HF was supplied by Xilong Scientific Co. Ltd. (Shantou, China). Ballmilled cellulose was prepared via ball-milling the microcrystalline cellulose at 60 rpm for 48 h by using a QM-3S P04 planetary ball miller.

4.2 Catalyst synthesis

The preparation of zeolites $Sn-\beta$ follows the similar methods previously reported by Hermans and Hammond et al. 30-31 Specifically, H- β (Si/Al=12.5) was dealuminated by treatment in HNO₃ solution (65%-68% HNO₃, 373K, 20 h, 20 mLg⁻¹ zeolite). The acid-treated powder was then filtered, washed thoroughly with deionized water, and dried at 383 K overnight. The dealuminated zeolite (denoted as deAl- β) was subsequently grafted with tin with the solid-state ion exchange (SSIE) method, i.e. by grinding with the appropriate amount of tin (II) acetate in a pestle and mortar. The obtained mixing powder was finally calcined in a tubular reactor to obtain the Sn- β , which was heated up to 823 K (10K min⁻¹ ramp rate) firstina flow of N₂ (6 h) and subsequently in air (3h) for a total of 9 h. A series of ion-exchanged Sn-B were prepared postsynthetically, where the calcined $Sn-\beta$ was soaked into a 1.0 M M(NO₃)_n solution (50 mLg⁻¹ zeolite, M= Na⁺, K⁺, n=1; M= Ca²⁺, Mg²⁺ n=2) and the mixture was stirred at 353 K for 12 h. The solid sample was recovered by filtration and washed with distilled water. After being dried, the sample was calcined at 773 K for 5 h, named Sn $-\beta$ -M. Sn- β exchanged with MNO₃ for one time is denoted as Sn- β -M, three times as $Sn-\beta-M-3$. The deAl- β supported tin oxides (denoted as SnO2/deAl- β) were also prepared through solid state mixing of de Al- β with SnO2, followed by calcination at 823 K for 12 h.

4.3 Catalyst characterization

The surface areas of the samples were measured by nitrogen physisorption on a Micromentics ASAP 2020 M instrument. Before the adsorption, samples were degassed at 573 K for 3h. The total surface area was calculated via the Brunauer-Emmett-Teller (BET)

Journal Name

equation. Scanning electron microscope (SEM) was conducted by Zeiss sigma microscope, with Energy Dispersive X-ray Spectroscopy (EDS) measurements analyzing the chemical compositions. X-ray diffraction (XRD) patterns of samples were recorded on Rigaku Ultima IV X-ray diffractometer with CuKa radiation source (40kV and 30mA) from 5° to 60° and a scan speed of 2θ =10.0° /min. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was employed to measure the amount of K, Na, Ca, and Mg loaded on the support. CO₂ temperature programmed desorption (TPD) was used to measure the basicity of samples. The samples were subjected to heat-treatment at 673 K for 1 h under flowing N2 at a rate of 30 mL min⁻¹ and cooled to 318 K. CO₂ gas was adsorbed for 30 min. Desorption was conducted by increasing the temperature from 318 to 1073 K at a rate of 10 °C min⁻¹ under flowing N₂at a rate of 30 mL min⁻¹. Diffuse reflectance ultraviolet-visible (UV-vis) spectra of samples were recorded in the region of 200-400 nm on a Varian Cary 5000 UV-vis spectrophotometer in Kubelka-Munk units using BaSO₄ as reference.

4.4 Catalytic Evaluation

The catalytic reactions were performed in a batch-type Teflon-lined stainless-steel autodave reactor (50 ml). In a typical procedure, the vessel was charged with reactants, catalysts (solid Lewis acid and lactic acid), and deionized water, after which the autodave was purged five times with N₂ and then pressurized to 2.0 MPa with N₂ at room temperature. Next the autodave was heated to the desired reaction temperature and held at that temperature for required time with stirring at 800 rpm. After a fixed time, the reaction was quickly terminated by cooling the reactor to room temperature in cold water. As for the conversion of glucose to methyl lactate, the solvent is changed to methanol without extra lactic acid added. During the recycling tests, the spent catalyst after each batch was filtered and dried in an oven at 383K ovemight, followed by calcination in a muffle fumace for 5 hours at 823 K (5 K min-1 ramp rate), before employed for the subsequent use.

4.5 Product analysis

Sample products were first qualitatively analyzed by an Agilent GC-MS equipped with a 1701-ms column. The crude product was dissolved in a silvlating agent (bis-(trimethylsilyl) trifluoroaceta mide +1% trimethylchlorosilane). This solution was maintained at 65 °C for 2 h to ensure the complete silvlation which was subsequently injected into the GC-MS. Some peaks in Agilent HPLC were further identified using LC-MS. Quantitative analysis was then performed on an Agilent HPLCsystem equipped with a RI and UV-Vis detectors and a Bio-Rad Aminex HPX-87H ion exclusion column (300 × 7.8 mm), using 0.005 M H₂SO₄ as the mobile phase at a flow rate of 0.6 mL min⁻¹. The column temperature was 50 °C and the detector was set to 50 °C. The amount of product was determined using calibration curves generated with standard solutions. The products collected from glucose conversion to MLA were quantitatively analyzed by gas chromatography (model GC 2060 by Shanghai Ruimin Instruments, Inc.) equipped with a DB-WAXETR capillary column (50 m \times 0.32 mm \times 1.0 μ m) and a flame ionization detector (FID), where 1,4-dioxane was always added as an external standard.

Conflicts of interest

There are no conflicts to declare

View Article Online DOI: 10.1039/D0CY00089B

Acknowledgements

This work was supported by the Major Research Plan of National Natural Science Foundation of China (No. 91545114, and No. 91545203), the National Natural Science Foundations of China (No.21576227) and the 985 Program of the Chemistry and Chemical Engineering disciplines of Xiamen University.

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