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Methyl lactate production from levoglucosan by using Sn-Beta and H-Beta catalysts

Dan Luo,^a Shengnan Liu,^a Wang Yin^b and Shuqian Xia^{a*}

Abstract

BACKGROUND: Fast pyrolysis of lignocellulosics has provided an abundant sugar source for production of value-added chemicals, and levoglucosan is the most representative sugar in pyrolysis liquid (bio oil). This paper explored the potential for producing methyl lactate from levoglucosan by employing the mixed catalysts of zeolite tin beta (Sn-Beta) and zeolite hydrogen beta (H-Beta).

RESULTS: Under the optimal conditions (at 200 °C and mixed catalysts with H-Beta:Sn-Beta ratio of 1:5), the yield of methyl lactate obtained from levoglucosan conversion was as high as 35%. And the yield was comparable to that of methyl lactate obtained from glucose conversion under the similar conditions (at 200 °C and pure Sn-Beta). In order to investigate the reason, a contrasting experiment with glucose as substrate also was carried out with the mixed catalysts. The results indicated that during the levoglucosan conversion process, 'the methanolysis of levoglucosan' was likely to compete with 'the dehydration of glucose' for the Brønsted acid sites of H-Beta. In addition, the catalytic functions of H-Beta and Sn-Beta, and the reaction pathway were deeply investigated through tracking and comparing the conversion of levoglucosan over mixed H-Beta/Sn-Beta and over pure Sn-Beta catalysts, respectively.

CONCLUSION: The appropriately lower ratio of H-Beta:Sn-Beta and relatively higher temperature were favorable for the reaction. H-Beta containing Brønsted acid could remarkably accelerate the conversion of levoglucosan and methyl-glucosides to glucose. Sn-Beta containing Lewis acid mainly promoted the retro-aldol condensation of glucose and formation of methyl lactate.

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Supporting information may be found in the online version of this article.

Keywords: levoglucosan; methyl lactate; glucose; Sn-Beta; H-Beta

INTRODUCTION

Lactate esters are important commodity chemicals, which can be used as food additives, flavour chemicals and green solvents, etc.¹ They also are promising precursors, from which various chemicals, such as lactic acid, acrylic acid and lactide, can be produced.² Their hydrolysate lactic acid also has widespread applications, for example as the platform molecule for producing various bulk chemicals and as the monomer for synthesizing biodegradable plastics.³ Currently, there are two main approaches for producing lactic acid: fermentation and chemical catalytic conversion of sugars. Fermentation generates a substantial amount of waste, which limits its application and has resulted in extensive focus on chemical catalysis.

At present, many researches have been devoted to producing lactic acid or its esters through the chemical catalytic conversion of simple sugars (trioses and C5/C6 monosaccharide), and various homogenous and heterogeneous catalysts have been proposed. West et al. first found that the zeolite H-USY was quite active for the triose-to-lactate conversion.⁴ Since then, Holm et al. first reported that the heterogeneous zeolite tin beta (Sn-Beta) was an excellent catalyst for the conversion of glucose to methyl lactate, in which a yield of 43% was obtained at 160 °C.⁵ However, these simple sugar substrates were obtained through enzymatic hydrolysis of cellulose, which was not only a slow process, but also required costly separation.⁶ In addition, only a few studies have reported

production of lactic acid or its esters directly from cellulose due to its robust crystalline structure. Deng et al. achieved a 65% yield of lactic acid by using the bifunctional Al(III)-Sn(IV) catalyst in water at 190 °C.⁷ Wang et al. found that Erbium(III) trifluoromethanesulfonate [Er(OTf)₃] can effectively convert cellulose to lactic acid with 89.6% yield under hydrothermal conditions.⁸ For these homogenous processes, the toxicity of metal ions and difficulty of separation limited their application. Yang et al. employed an heterogeneous mesoporous zirconium-doped silica (Zr-SBA-15) catalyst and yielded 33% ethyl lactate at 260 °C in a supercritical mixture of ethanol and water.⁹ Verma et al. gave a 58% yield of methyl lactate over the gallium-doped zinc (Zn)/H-nanozeolite Y catalyst at 280 °C in supercritical methanol.² Nevertheless, it is worth noting that these heterogeneous processes require harsh reaction conditions, and hence, it is highly desirable to find an alternative

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sugar precursor, which is not only easily obtained but also simple in chemical structure.

For the degradation of lignocellulosic biomass, fast pyrolysis is an appealing process and the pyrolysis product was commonly known as bio oil. During pyrolysis, various C5 and C6 monomeric sugars were released from lignocellulosic and concentrated into bio oil.¹⁰ Among them, levoglucosan was the most familiar to researchers. The amounts of these monomeric sugars in bio oil vary, which depend on feedstock types, pyrolysis conditions and reactor configuration.¹¹ Moreover, some efforts have been made to increase sugar yields in bio oil. Kuzhiyil et al. used pure cellulose as the feedstock and reported a 60% yield of levoglucosan in bio oil.¹² By using staged condensation of the vapours, Rover et al. first recovered the heaviest fraction of bio oil, which consisted of water-soluble sugars and water-insoluble phenolic oligomers. Then this sugar-rich solution was separated through a simple washing procedure.¹³ In brief, fast pyrolysis of lignocellulosic biomass could provide an abundant sugar resource. The use of pyrolytic sugars as the substrate for the production of valuable chemicals also has been reported in the literature. For example, Santhanaraj et al. reported the production of gluconic acid from a levoglucosan-rich stream, which was obtained through sequential condensation of pyrolysis vapours and water extraction.⁶ Yin et al. reported the one-step synthesis of sorbitol from levoglucosan and cellobiose, which could represent the low-molecular-weight sugars in bio oil.¹⁴ Their selective conversions for the production of levulinic esters, bioethanol also have been reported.^{15–18} However, little information is available about the production of lactic acid and its esters from pyrolytic sugars; given their abundance and structural simplicity, conversion of pyrolytic sugars to valuable lactic acid and its esters seems to be very meaningful.

The present paper reports on the production of methyl lactate from levoglucosan, which is the most representative sugar in bio oil. According to Holm's report, Sn-Beta is an excellent Lewis acid catalyst and can efficiently catalyze the conversion of monosaccharides into lactic acid or its esters, but it cannot catalyze the hydrolysis/methanolysis of disaccharides into monosaccharides.¹⁹ Although levoglucosan is a C6 sugar, it has a similar structure to disaccharides with glycosidic bonds in the molecules. The Brønsted acid-containing zeolite hydrogen beta (H-Beta) is known as an efficient catalyst for cleavage of the glycosidic bonds.^{20,21} Therefore, the intention was to convert levoglucosan into methyl lactate with mixed H-Beta/Sn-Beta as catalysts.

MATERIALS AND METHODS

Chemicals

Levoglucosan (>99%, LG) was purchased from TCI Development Co., Ltd (America). Glucose, methyl- α -glucoside (99%, MG), methyl- β -glucoside (99%, MG), methyl lactate (>98%, ML), methyl levulinate (>99%, MLU), 5-(methoxymethyl)furfural (97%, FUR), nitric acid (65–68%), methanol and naphthalene were purchased from Shanghai Aladdin Industrial Co., Ltd (China). H-Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) was purchased from Nankai University Catalyst Co., Ltd (China). Dimethyltin dichloride (98%) and 1,1,2-trimethoxyethane (98%, GA) were purchased from Tianjin Heowns Biochem Technologies Co., Ltd (China). Methyl DL-2-hydroxy-3-butenate (95%, MVG) was purchased from Enamine Co., Ltd (Ukraine).

Catalyst preparation

The Sn-Beta was synthesized according to the method described by Tang et al.²² The parent H-Beta was dealuminated with 65–68%

HNO_3 at 100 °C for 20 h (20 mL g⁻¹ H-Beta). The resulting dealuminated zeolite was filtered, washed thoroughly with ample water, and then dried at 150 °C overnight. Afterward, 0.3004 g of the dried dealuminated zeolite was ground with 0.0223 g of $(\text{CH}_3)_2\text{SnCl}_2$ for 30 min. The mixture was calcined in air according to the following procedure: ramp 2 °C min⁻¹ to 200 °C, 200 °C for 6 h, ramp 2 °C min⁻¹ to 550 °C, 550 °C for 6 h.

Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8-Focus diffractometer with a Cu-K α X-ray source, and the results are shown in Fig. S1. The Sn content of Sn-Beta was determined by ICP. Nitrogen (N_2)-adsorption/desorption was performed on an Autosorb-IQ2-MP system. Before the measurements were taken, the samples were degassed at 300 °C for 4 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation, and the micropore volume was calculated by applying the t-plot method. Acidities of the samples were evaluated by ammonia temperature-programmed desorption (NH_3 -TPD). In a typical experiment, the samples were first pretreated at 350 °C for 1 h, and then cooled down to 100 °C to adsorb NH_3 . After the baseline was steady, the samples were heated from 100 °C to 800 °C at a rate of 10 °C min⁻¹ and the process was monitored using TCD. The Brønsted and Lewis acid sites of the samples were characterized by Fourier transform infrared (FTIR) spectra of pyridine adsorption on a Bruker VERTEX 70 spectrometer. The self-supporting wafers first were degassed at 450 °C for 2 h, and then cooled down to 60 °C. Subsequently, trace pyridine was injected and exposed to the sample for 0.5 h. Before measuring, the wafers were evacuated at 150 °C for 0.5 h. The spectra were collected at evacuation temperature.

Reaction procedure and product analysis

Reactions were carried out in a 100 mL high pressure batch reactor. In a typical experiment, 0.5 g levoglucosan (or 0.5556 g of glucose), 0.3 g catalyst and 50 mL methanol were introduced into the reactor. Then the reactor was sealed and purged with N_2 six times. After charging with 0.2 MPa N_2 , the reactor was heated to the desired temperature with a stirring rate of 500 rpm. When the reaction was finished, the reactor was cooled down to the ambient temperature and its internal pressure dropped back to 0.2 MPa. This indicated that few or no gaseous products were produced during the reaction.

The reaction products were identified by gas chromatography-mass spectrometry (GC–MS). It was Thermo ISQ (America), with capillary column DB-1 (30 m $\times$ 0.25 mm $\times$ 0.25 μm), injector temperature 300 °C, detector temperature 300 °C, and oven temperature initially of 55 °C (held for 5 min), then raised to 230 °C (at 10 °C min⁻¹, kept for 5 min). ML, MLU, GA and MVG were quantified by a GC-flame ionization detector (FID) with naphthalene as the internal standard (Beijing Beifen SP-3420A, China), with capillary column (DB-1, 30 m $\times$ 0.25 mm $\times$ 0.25 μm), and a temperature program consistent with that used in the GC–MS. Levoglucosan, glucose and MG were quantified by high-performance liquid chromatography (HPLC) using a Shimadzu LC-20AT equipped with an Aminex HPX-87H column and a differential detector. The mobile phase was an aqueous solution of H_2SO_4 (5 mmol L⁻¹) with a flow rate of 0.6 mL min⁻¹ and column temperature 50 °C. 5-(methoxymethyl)furfural also was quantified by HPLC (Thermo Syncronis C18 column, UV-visible detector). The mobile phase was methanol with a flow rate of 1 mL min⁻¹ and the detector was

used at 280 nm. In addition, the conversion of LG and the yields of all products were calculated using Eqns (S1–S7) in the Supporting Information. Carbon balance could not be calculated accurately due to the formation of ‘humins’ that could not be quantitative.

RESULTS AND DISCUSSION

Catalyst characterization

The XRD patterns of all the samples (H-Beta, dealuminated Beta and Sn-Beta) are presented in Fig. S1. It could be observed that they exhibited similar diffractions peaks, which indicated that the synthesis process did not cause significant changes in Beta structure. Fig. S2 shows the nitrogen physisorption of all the samples (H-Beta, dealuminated Beta and Sn-Beta) and Table S1 shows the physicochemical properties of all the samples. It can be seen that they had similar adsorption–desorption isotherms, micropore volumes and BET surface areas, which further confirmed that the Beta structure remained fully intact during the preparation process. The Sn loading on Sn-Beta was 3.8 wt%, which was approximate to the expected value (4 wt%).

Additionally, Fig. S3 displays the NH_3 -TPD curves of H-Beta and Sn-Beta; the total acid amounts are listed also. Sn-Beta showed less NH_3 adsorption (0.61 mmol g^{-1}) than H-Beta (1.23 mmol g^{-1}). Fig. S4 illustrates the pyridine-IR spectra of H-Beta and Sn-Beta. The band at 1445 cm^{-1} was assigned to Lewis acid sites, the band at 1545 cm^{-1} was assigned to Brønsted acid sites, and the band at 1490 cm^{-1} was the combination of both acid sites. The results indicated that H-Beta had both Brønsted acid and Lewis acid sites, whereas Sn-Beta had only Lewis acid sites.

Levoglucosan conversion

Fig. 1(a) and (b) showed the conversion of LG and glucose in methanol using pure Sn-Beta as catalyst at different reaction temperatures, respectively. The detailed data are summarized in Table S2. Fig. 1(a) shows that at lower reaction temperature (160°C), LG was not completely converted (78%) and it only gave a minor amount of ML (3%). In addition, the yields of other retro-aldol products (MVG, GA) and dehydration products (MLU, FUR) were also very low. It was noted that most of the LG was converted to intermediate MG (the selectivity of which was 80%). As the temperature increased, the LG was almost completely converted, but the ML yield was not significantly increased, which was only 11% even at 200°C . However, the conversion results of glucose, shown in Fig. 1(b), reveal that glucose could be completely converted with high ML yield (34%) even at relatively lower reaction temperature (160°C). Increasing temperature had an insignificant effect on glucose conversion and product distribution. It can be inferred from the comparison above that using the pure Sn-Beta as catalyst, the methanolysis of LG was rate-limiting. Therefore, in order to obtain more ML from LG conversion, H-Beta containing Brønsted acid sites was used as catalysts together with Sn-Beta.

Fig. 2(a)–(d) shows the results of LG conversion with different H-Beta:Sn-Beta ratios at different reaction temperatures (160 , 180 , 200 and 220°C). The detailed data are summarized in the Table S3. From Fig. 2(a) it can be seen that at 160°C , the conversion of LG increased as the ratio of H-Beta:Sn-Beta increased, which reached 98% as the ratio reached 1:11. The yield of MG firstly increased with increasing H-Beta:Sn-Beta ratio and then decreased as it exceeded 1:11. The selectivity of MG decreased continuously with increasing H-Beta:Sn-Beta ratio (from 80% to 37%). It also is worth noting that MG was always the major product under the investigated ratios at 160°C and its yield was still as

Figure 1. Conversions of LG (a) and glucose (b) and the yields of products over the pure Sn-Beta at different temperatures for 18 h.

high as 36% even if the ratio was increased to 1:1. This indicated that a higher H-Beta:Sn-Beta ratio was beneficial to the further conversion of MG; however, at the lower reaction temperature of 160°C , a very high ratio ($>1:1$) was required to achieve its complete conversion. The yields of ML and other retro-aldol products (MVG, GA) increased as the H-Beta:Sn-Beta ratio increased, but the increases were very slight. The yield of ML was always very low, which was only 10% even when the ratio was 1:1. This can be attributed to two factors: at lower ratio the conversion of intermediate MG was not obvious whereas at higher ratio the dehydration pathway would compete. The yields of dehydration products (MLU, FUR) also increased with the increasing H-Beta:Sn-Beta ratio, and the increase became more significant as the ratio got higher. In addition, the proportion of dehydration products in the total products (retro-aldol products and dehydration products) was calculated and summarized in Table S3. It could be found that the proportion significantly increased as the H-Beta:Sn-Beta ratio increased, indicating that relatively higher H-Beta:Sn-Beta ratio would promote the conversion of more intermediate MG towards

Figure 2. Conversion of LG and the yields of products over the various ratios of H-Beta and Sn-Beta at different temperatures [(a) 160 °C, (b) 180 °C, (c) 200 °C or (d) 220 °C] for 18 h.

the dehydration pathway, and then reduce the selectivity of ML and other retro-aldol products. Thus, in light of the fact that at 160 °C, the conversion of MG required a higher H-Beta/Sn-Beta ratio, however, the higher ratio would reduce the selectivity of ML, it was impossible to obtain the high yield of ML at the relatively lower reaction temperature (160 °C).

Fig. 2(b) and (c) shows that at relatively higher reaction temperatures (180 °C and 200 °C), LG was almost completely converted. At the two temperatures, the yield of MG decreased with increasing H-Beta/Sn-Beta ratio. Yet at different temperatures, the lowest H-Beta/Sn-Beta ratios required for complete conversion of MG varied: at 200 °C the lowest ratio required for complete conversion of MG was 1:5, whereas at 180 °C the ratio was 1:3, and it was >1:1 at 160 °C (mentioned in previous paragraph). This indicated that the higher the reaction temperature, the smaller the lowest ratio required for complete conversion of MG. At these two temperatures, the yields of ML and other retro-aldol products (MVG, GA) both showed the trend of first increasing and then decreasing with rising H-Beta/Sn-Beta ratio. When the reaction temperature was 200 °C and the ratio was 1:5, the highest yield of ML (35%) was obtained, whereas at 180 °C, it achieved 28% at the ratio of 1:3. It is worth noting that at the two temperatures, the H-Beta/Sn-Beta

ratio required for the highest yield of ML (i.e. the optimal ratio) was exactly consistent with the minimum ratio that ensured the almost complete conversion of MG. It indicated that the yield of ML was limited by two factors: one was the incomplete conversion of intermediate MG at lower H-Beta/Sn-Beta ratio, the other was the preferable dehydration pathway at higher H-Beta/Sn-Beta ratio. The yields of dehydration products (MLU, FUR) increased with the increasing H-Beta/Sn-Beta ratio. As reported by Hu et al.,¹⁷ higher H-Beta/Sn-Beta ratio (or more H-Beta) would enhance the conversion of glucose (or its methylated form MG) to FUR and MLU, and cause a decline in the selectivity of retro-aldol products. Thus, to obtain the highest yield of ML, the ratio should be as low as possible with the precondition of guaranteeing the complete conversion of MG.

Fig. 2(d) shows that at 220 °C, the conversion of LG catalyzed by pure Sn-Beta could yield 19% ML and 26% MG. However, at 220 °C the mixed catalysts gave some unreasonable phenomena. For example, when the H-Beta/Sn-Beta ratio of 1:11 was applied, the yield of ML (25%) obtained at 220 °C was similar to that (24%) obtained at 200 °C. With H-Beta/Sn-Beta of 1:5, the yields of dehydration products (3%) obtained at 220 °C were much lower than those (7%) obtained at 200 °C. Actually, at 220 °C and with

the mixed catalysts, only the clarified liquid product was observed after the reaction and the catalysts were all adhered on the reactor wall. This indicates that very high reaction temperatures would cause deactivation of the mixed catalysts; thus, using the mixed catalysts, the reaction temperature should be $\leq 220^\circ\text{C}$ for this reaction system.

In brief, the yield of ML was mainly affected by the conversion degree of MG and the competitiveness of the dehydration pathway. Increasing the reaction temperature or the H-Beta:Sn-Beta ratio would both promote conversion of MG, but higher H-Beta:Sn-Beta ratio also would promote the reaction towards the dehydration pathway. Thus, higher reaction temperature and the appropriately lower H-Beta:Sn-Beta ratio were favorable for the production of ML. The highest yield (35%) of ML was obtained at 200°C with H-Beta:Sn-Beta of 1:5.

Glucose conversion

As mentioned above, under the optimum conditions (200°C and mixed catalysts with H-Beta:Sn-Beta of 1:5), the highest yield of ML (35%) obtained from LG conversion was comparable to that (37%) obtained from glucose conversion under similar conditions (200°C and pure Sn-Beta catalyst). This result was exciting, but also confusing.

In order to investigate the reason for the intriguing result, conversion of glucose was carried out with various H-Beta:Sn-Beta ratios at 200°C . The results are summarized in Table S4, which can be used to contrast with the results of LG conversion under the same conditions in Table S3. Fig. 3 shows the change of the yield ratio between retro-aldol products and dehydration products with the change of H-Beta:Sn-Beta ratio during the LG and glucose conversion processes, respectively. It can be observed that the yield ratios between retro-aldol products and dehydration products during the LG conversion process were always larger than those during the glucose conversion process. Furthermore, the difference between the ratios of two processes gradually decreased with the increasing H-Beta:Sn-Beta ratio. In other words, LG showed a higher selectivity towards retro-aldol

products than glucose under the same reaction conditions. This indicates that during the LG conversion process, 'the methanolysis of levoglucosan' might compete with 'the dehydration of glucose' for the Brønsted acid sites of H-Beta, and thus the Brønsted acid sites available for the side reaction of dehydration of LG were insufficient. As a result, LG was converted through the main reaction path of retro-aldol condensation. In addition, with the increase of H-Beta:Sn-Beta ratio, the available Brønsted acid sites exceeded the amount required by the methanolysis step, which were then provided to the side reaction of dehydration pathway. Hence, with the increase of H-Beta:Sn-Beta ratio, the yields ratio between main and by-products obtained from LG conversion was gradually approximate to that obtained from glucose conversion.

This comparison and analysis may explain the results. At the lower H-Beta:Sn-Beta ratio (1:5), the methanolysis of LG would occupy most Brønsted acid sites, and then the sites available for further conversion of glucose were mainly Lewis acid sites of Sn-Beta and very few Brønsted acid sites of H-Beta. Thus, at 200°C , the LG-to-ML conversion catalyzed by mixed catalysts with a ratio of 1:5 was very close to that of glucose-to-ML catalyzed by pure Sn-Beta.

Reaction pathway

In order to gain deeper insight into the reaction pathway of LG conversion to ML, a time-course experiment was conducted at 200°C with the mixed catalysts with H-Beta:Sn-Beta of 1:5. Fig. 4(a) presents the reaction progress curves. It can be observed that LG was rapidly converted to MG during the temperature-ramping stage (≈ 0.8 h), and then MG was converted mainly to retro-aldol products (ML, MVG, GA) and small amounts of dehydration products (MLU, FUR). It is worth noting that the yield of MG first increased with time, reaching a maximum after 0.8 h, and then decreasing. This indicated that MG is an important intermediate and its further conversion was rate-limiting. After 9 h reaction time, the yields of all products no longer changed with reaction time, which indicated that 9 h was sufficient to obtain the highest yield (35%) of ML.

In addition, in order to clarify the catalytic function of H-Beta containing Brønsted acid, a time-course experiment also was conducted at 200°C with pure Sn-Beta. Fig. 4(b) and (c) compares the performance of the two catalysts. Fig. 4(b) shows that with pure Sn-Beta as catalyst, the conversion of LG was much slower; it took 9 h to achieve complete LG conversion, whereas it took only 0.8 h using the mixed catalysts with a ratio of 1:5. This indicates that the Brønsted acid sites of H-Beta could promote LG-to-MG conversion. The MG yield shown in Fig. 4(c), which first increased and then decreased with time, and the two changing trends with the two kinds of catalysts were consistent. However, the further conversion of MG catalyzed by pure Sn-Beta was much slower than that catalyzed by the mixed catalysts. For example, with pure Sn-Beta, the significant yield (44%) of MG was still observed after reaction for 18 h. Yet using the mixed catalysts with a 1:5 ratio, the yield of MG was $\approx 0\%$ after 9 h. This indicates that the Brønsted acid sites of H-Beta could significantly accelerate the further conversion of MG.

Based on the experimental results above, the plausible reaction pathway for the LG conversion using the mixed catalysts with a ratio of 1:5 is displayed in Scheme 1. Initially, LG underwent methanolysis to form MG over the Brønsted acid sites of H-Beta. Then MG was further hydrolyzed to glucose under the action of H-Beta, which has been explained in related reports.^{5,23} Thus, there

Figure 3. The ratio of retro-aldol products yields to dehydration products yields for LG and glucose conversion over the various ratios of H-Beta and Sn-Beta at 200°C for 18 h, respectively. The yields (Y_r) of retro-aldol products were calculated by $[Y_{ML} + Y_{GA} + Y_{MVG}]$, the yields (Y_d) of dehydration products were calculated by $[Y_{MLU} + Y_{FUR}]$.

Figure 4. (a) Time profile of LG conversion at 200 °C over the mixed catalysts with H-Beta:Sn-Beta ratio of 1:5. (b) Time-courses for LG conversion over Sn-Beta combined with H-Beta, and pure Sn-Beta, respectively. (c) Time-courses for MG yield over Sn-Beta combined with H-Beta, and pure Sn-Beta, respectively.

were two paths for glucose conversion. The major pathway was through retro-aldol condensation of glucose and fructose over the Lewis acid sites of Sn-Beta. Fructose was converted from glucose via isomerization, which could decompose into glyceraldehyde and dihydroxyacetone. There was an equilibrium between glyceraldehyde and dihydroxyacetone and they could interconvert with each other. The Brønsted acid sites of H-Beta promoted glyceraldehyde to dehydrate into 2-hydroxypropenal, which was further rearranged into pyruvaldehyde through keto-enol tautomerization. And then pyruvaldehyde was converted to pyruvic aldehyde methyl hemiacetal, which was further converted to ML via a hydride shift over the Lewis acid sites of Sn-Beta. In a similar way, glucose underwent decomposition to form erythrose and glycolaldehyde. Erythrose was converted to MVG through a reaction pathway similar to the pathway of converting trioses to ML. Glycolaldehyde was converted to form GA. The other glucose conversion was a side-reaction pathway initiated by the Brønsted acid sites of H-Beta. As shown in Scheme 1, glucose underwent dehydration, forming FUR, which was further decomposed to MLU.

Catalyst reusability

The catalyst reusability was evaluated for LG conversion. Five consecutive reaction cycles were carried out at 200 °C using the mixed H-Beta and Sn-Beta with a 1:5 mass ratio. After each run, the used catalyst was regenerated by washing and calcination in air at 550 °C for 6 h. The product yields were presented in Fig. 5. It showed that as catalyst cycles increased, the yield of ML steadily decreased from 35% to 25%, whereas the yields of the by-products MLU and FUR increased continuously from 6 to 14%. This meant that the simple physical mixtures of H-Beta and Sn-Beta were not very stable in the recycling study.

In order to investigate the reasons for deactivation, the acidic properties of mixed catalysts with H-Beta:Sn-Beta of 1:5 were investigated by NH_3 -TPD and pyridine-IR before and after regeneration, respectively. Fig. S5 displayed the pyridine-IR spectra of two samples (fresh and regenerated catalysts). It could be observed that after regeneration, the absorption intensity of Lewis acid sites at 1445 cm^{-1} reduced significantly, whereas the absorption intensity of Brønsted acid sites at 1545 cm^{-1} changed little. Additionally, the Brønsted and Lewis acid sites of two samples were quantified by integrating. The results indicated that after regeneration, the ratio of the Brønsted to the Lewis acid sites (B:L ratio) increased from 0.17 (fresh catalysts) to 0.2 (regenerated catalysts). This may explain why the ML yield steadily decreased while the yields of by-products continuously increased with the catalyst cycles increasing. Fig. S6 displayed the NH_3 -TPD curves of two samples (fresh and regenerated catalysts). It can be observed that the total acid amount (1.1 mmol g^{-1}) of regenerated catalysts was lower than that of fresh catalysts (1.3 mmol g^{-1}). This indicates that some acid sites were unavailable after regeneration. Combined with the results of NH_3 -TPD analysis, it can be concluded that the lost acid sites were mainly Lewis acid sites. Considering that Sn-Beta was the major provider of Lewis acid sites, these characterization results indicate that the deactivation of mixed catalysts is attributed mainly to the instability of Sn-Beta. Some literature^{24,25} has mentioned that the chelating properties of substrate (e.g. glucose) aided Sn loss, and then led to catalyst deactivation; the fresh and regenerated catalysts also were analyzed by ICP and the results confirmed Sn loss. Therefore, Sn loss of Sn-Beta was the primary factor causing the deactivation of mixed catalysts.

Scheme 1. Proposed reaction mechanism for the conversion of LG to ML at 200 °C using the mixed catalysts with a H-Beta: Sn-Beta ratio of 1 : 5

CONCLUSIONS

In this study, the ML production from LG conversion at different temperatures with various H-Beta:Sn-Beta ratios was investigated. The results showed, first, that the relatively higher reaction temperature and the appropriately lower H-Beta:Sn-Beta ratio were favorable for the production of ML, which could not only promote the conversion of LG and its intermediate MG, but also restrain the formation of dehydration products (FUR, MLU). The highest yield (35%) of ML was obtained at 200 °C with H-Beta:Sn-Beta of 1:5, and the optimal H-Beta:Sn-Beta ratio required for the highest yield of

ML was exactly the same with the minimum ratio that guaranteed the almost complete conversion of MG. Second, the highest yield of ML obtained from LG conversion was 35% under the optimum conditions, which was comparable to the yield of 37% obtained from glucose conversion under the similar conditions (at 200 °C and pure Sn-Beta catalyst). Results from an investigation into the conversion of glucose, also at 200 °C with the mixed catalysts, indicated that during the LG conversion process, 'the methanolysis of levoglucosan' was likely to compete with 'the dehydration of glucose' for the Brønsted acid sites of H-Beta. Third, a time-course

Figure 5. Recycling of H-Beta combined with Sn-Beta catalyst in the catalytic conversion of LG to ML.

study carried out with pure Sn-Beta and mixed H-Beta:Sn-Beta catalysts, suggested the following plausible reaction pathway: (i) the methanolysis of LG to intermediate MG and the hydrolysis of MG to glucose were catalyzed mainly by H-Beta containing Brønsted acid sites; and (ii) the retro-aldol reaction of glucose (fructose) to ML was mainly catalyzed by Sn-Beta containing Lewis acid sites. Finally, reusability analysis indicated that the mixed catalysts underwent deactivation due to Sn loss. Hopefully the results and inferences herein can provide guidance for the future production of ML from bio-oil or its sugar-rich fraction.

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Supporting Information

Supporting information may be found in the online version of this article.

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