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Synergistic Production of Methyl Lactate from Carbohydrates Using an Ionic Liquid Functionalized Sn-Containing Catalyst

Fenfen Wang,[a] Yi Wen[a], Yanxiong Fang*[a] and Hongbing Ji*[b]

Abstract: Considerable progress has been made recently in the catalytic conversion of renewable biomass resources to methyl lactate (MLA). However, conceiving eco-friendly and effective catalytic systems for the production of MLA from biomass carbohydrates remains a key challenge. Herein, we report a multifunctional catalyst Sn(salen)/IL, consisting of a Sn(salen) complex and an imidazolium-based ionic liquid (IL), which acts via an intramolecular synergistic effect to convert carbohydrates to MLA in methanol. The versatile properties of the resultant catalyst were revealed to be responsible for the conversion of fructose to MLA and the efficient suppression of undesired side reactions. This catalyst displayed outstanding catalytic activity, high selectivity, and excellent recyclability, giving an MLA yield of up to 68.9% at 160 °C after 2 h. The results of this study will contribute to new approaches for designing synergistic catalysts for producing liquid fuels and chemicals from biomass resources.

Introduction

There has been an unprecedented international interest in the efficient utilization of renewable biomass resources for the sustainable production of liquid fuels and chemicals in view of establishing sustainable social development and improving climate conditions.[1–4] Therefore, the exploration of highly efficient and environment-friendly catalytic routes for the selective conversion of biomass carbohydrates to liquid fuels and valuable chemicals has high strategic significance and great urgency.[5–11]

Methyl lactate (MLA) is a very important platform chemical that has been extensively applied in the food, pharmaceutical, cosmetics industries and as a green solvent.[9,12,13] Currently, MLA is produced from biomass carbohydrates using traditional homogeneous Lewis acid, alkali metal hydroxides, solid acid, or inorganic solid base catalysts in methanol.[3,14–16] For example, a series of metal salts have been employed for the conversion of carbohydrates to MLA. In particular, Sn^{4+} exhibits excellent catalytic performance in the conversion of biomass derivatives to MLA.[17] However, some side reactions occur concurrently with the main pathway during this process. Thus, it is very important to inhibit the side reactions for improving the selectivity toward MLA.[18-20] It has been recently reported that the yield of MLA was found to be significantly enhanced by using $SnCl_4$ with NaOH as a cocatalyst, which neutralized the acidity of the solution and efficiently inhibited the undesired side reactions, such as isomerization, dehydration, and rehydration.[16,21] Although the reaction rate was accelerated remarkably by the addition of a stoichiometric amount of NaOH, the liquid waste generated in this process would cause serious environmental pollution, which was disadvantageous for industrialization. Furthermore, the catalyst recycling process was very intricate and difficult.[22]

Ionic liquids have been widely applied in the conversion of biomass resources because of their unique properties, including negligible vapor pressure, and high thermal as well as chemical stability. For example, the weakly basic ionic liquid [OMIm]Br with the strongly nucleophilic Br^- showed strong interactions with carbohydrates.[23,24] However, to overcome the drawbacks encountered with homogeneous catalysts, various heterogeneous catalysts have been explored in recent years.[16,25–28] In particular, Taarning et al. developed a Sn-β solid acid catalyst with Lewis acid to directly convert sucrose into MLA, which provided a satisfactory MLA yield of 68% at 160 °C for 20 h.[20] Unfortunately, the synthesis of Sn-β catalyst was complicated and time-consuming (generally more than 10 days). Moreover, as various polar products were readily adsorbed inside the pores of molecular sieves, and the catalytic activity and recyclability of catalysts would gradually decrease. Taarning et al. subsequently reported MLA yield of up to 75% from sucrose over the Sn-β solid acid catalyst via post-treatment method involving K_2CO_3, which was supposed to neutralize the Brønsted acid sites in zeolites, and efficiently enhanced the yield of MLA.[13] However, the reaction system was possibly contaminated by the addition of alkali metal ions. In a recent report, a Ga-doped Zn/H-Y catalyst was described that gave excellent MLA yield because of its finely tuning Lewis acid and Brønsted acid sites, MLA yield was produced in 57.8% yield from cellulose in near-critical methanol conditions, whereas the harsh reaction conditions facilitated the occurrence of side reactions.[29] Additionally, solid base catalysts such as MgO, has also been utilized for the production of MLA from carbohydrates. However, it shows poor catalytic activity and results in low MLA yield (29.5%).[30] Based on the above results, it can be concluded that Sn^{4+}-containing catalysts facilitate the formation of MLA from biomass carbohydrates in methanol. Moreover, both acid and base sites play important roles in the catalytic conversion of carbohydrates to MLA. Therefore, it is highly desirable to develop novel and multifunctional catalysts for

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efficient catalytic conversion of carbohydrates to MLA in methanol.

Recently, biomimetic metallosalen complexes have received widespread attention owing to their unique properties.[31–33] In particular, metallosalen complexes show excellent catalytic performance because of the presence of binary or ternary catalytic active sites in each catalyst molecule.[34–38] Therefore, we integrated a Lewis acid Sn(IV) metal center, a salen ligand, and an imidazolium-based ionic liquid to obtain an ionic liquid-functionalized Sn(salen) catalyst for the catalytic conversion of carbohydrates to MLA.

In this study, an eco-friendly, multifunctional catalyst was developed by combining a Sn(salen) complex with an imidazolium-based ionic liquid. The resultant catalyst, Sn(salen)/IL, exhibited outstanding catalytic activity and chemoselectivity as well as excellent cycling performance for the conversion of carbohydrates to MLA. This catalyst inhibited side reactions, efficiently improved the yield of MLA, and showed a synergistic effect for producing MLA from carbohydrates. The experimental results suggest that this catalyst has promising potential for transforming biomass feedstocks into liquid fuels and chemicals.

Results and Discussion

Catalytic Conversion of Fructose to MLA

It has been widely reported that the Sn^{4+} ion acts as Lewis acid metal center and exhibits unique properties that mainly stem from its capability to selectively coordinate with the carbonyl oxygen atom and chelate with oxygen atoms from the alcohol groups. Furthermore, it exhibits superior catalytic performance in catalyzing the isomerization, retro-aldol condensation, and dehydration of glucose or its isomers as well as intramolecular 1,2-hydride shift to MLA, which is considered as state-of-the-art active site that favors the formation of MLA from carbohydrates in methanol. It is most likely related to the coordination ability of the unoccupied orbital of Sn^{4+}, which results in the activation of an oxygen in fructose.[18,39] To investigate the influence of various types of ligands and compositions on the catalytic activity of Sn^{4+}-based catalysts, a series of experiments relating to the conversion of fructose to MLA were conducted to evaluate the catalytic performance. Various Sn^{4+}-based catalysts, such as $SnCl_4$, SnTPP, Sn(salen), and Sn(salen)/IL, were studied systematically under identical reaction conditions, and the experimental results were summarized in Table 1.

Table 1. Performance of various catalysts for the catalytic conversion of fructose into MLA.

Entry	Catalyst	Conversion (%)	Y_{MLA} (%)	Y_{MLE} (%)	Y_{PADA} (%)	Y_{MMF} (%)	Y_{MG} (%)	S_{MLA} (%)	Carbon balance (%)
1	Blank	19.2	1.5	2.3	2.4	3.1	--	7.8	9.3
2	$SnCl_4$	100	26.2	16.5	4.2	11.8	--	26.2	58.7
3	Sn(salen)	100	42.4	6.4	5.2	6.5	0.3	42.4	60.8
4	[OMIm]Br	46.5	1.3	--	0.2	--	--	2.8	1.5
5	Sn(salen)/IL	100	68.9	4.1	4.6	5.4	0.6	68.9	83.6
6	SnTPP	100	32.7	3.5	11.0	7.0	--	32.7	54.2
7	Al(salen)/IL	96.2	32.1	3.5	0.7	8.9	--	33.4	45.2
8	Zn(salen)/IL	94.3	21.6	--	--	--	--	22.9	21.6

Reaction conditions: 0.3 g of fructose, 0.05 g of catalyst, 12.0 g of methanol, 2 MPa N_2, 160 °C, 2 h. MLA: Methyl lactate, MLE: Methyl levulinate, PADA: Pyruvic aldehyde dimethyl acetal, MMF: 5-methoxymethylfurfural, MG: Methyl glycolate.

Interestingly, the examined catalysts exhibited significant differences in catalytic activity, which strongly depended on the ligands coordinated to Sn^{4+}. However, similar product distributions were observed for all the tested catalysts. Sn(salen)/IL exhibited notable catalytic activity, affording MLA in up to 68.9% yield, together with methyl levulinate (MLE) in 4.1% yield, pyruvic aldehyde dimethyl acetal (PADA) in 4.6% yield, 5-methoxymethylfurfural (MMF) in 5.4% yield, and methyl glycolate (MG) in 0.6% yield (Table 1, entry 5). In contrast, the Sn^{4+}-based catalyst containing an N_4-chelating ligand, namely tetraphenylporphyrin (SnTPP), gave MLA in a relatively low yield of 32.7%, in addition to PADA in 11.0% yield, MLE in 3.5% yield, and MMF in 7.0% yield (Table 1, entry 6). The pronounced diversity in catalytic activities can likely be attributed to the coordination ligands, with an appropriate choice of structure, such as salen ligand, and exhibited outstanding catalytic performance.[40] Furthermore, the Sn(salen)/IL catalyst gave a higher yield of MLA, which could be the result of an intramolecular synergetic effect between Sn(salen) and the ionic liquid moieties within one molecule. Equivalent to a binary catalytic system, this multifunctional catalyst took advantage of the characteristics of both Sn(salen) and the imidazolium-based ionic liquid, resulting in excellent catalytic performance for the examined reaction.

The catalytic activities of $SnCl_4$ and Sn(salen) as alternative catalysts were assessed under identical reaction conditions (Table 1, entries 2 and 3). Although $SnCl_4$ provided MLA as the principal product in 26.2% yield, MLE was also obtained in

16.5% yield, together with MMF in 11.8% yield and PADA in 4.2% yield. Interestingly, the Sn(salen) complex directly catalyzed fructose to MLA with a higher MLA yield of 42.4%, MLE in 6.4% yield, PADA in 5.2% yield, and MG in 0.3% yield. The catalytic activity of Sn(salen) was significantly superior to that of $SnCl_4$, but obviously inferior to that of Sn(salen)/IL. The experimental results indicated that the decreasing catalytic activity trend of the examined Sn-based catalysts as follows: Sn(salen)/IL > Sn(salen) > $SnCl_4$. Interestingly, the yields of both MLE and MMF could be increased depending on the coordination environment of Sn^{4+}, which confirmed that salen ligand played a pivotal role in improving the catalytic activity.

To gain a deeper insight into the interaction between fructose and the Sn(salen)/IL catalyst that possessed the strong nucleophile Br^- and an imidazolium-based cation, we investigated the influence of ionic liquid [OMIm]Br on the catalytic performance. [OMIm]Br alone exhibited extremely low catalytic performance, giving a negligible MLA yield of 1.3% and MLE yield of 0.2% (Table 1, entry 4). This was likely due to weaker hydrogen-bonding interactions between [OMIm]Br and fructose, as well as the lack of an active metal center for the activation of fructose.[41] However, covalently grafting the imidazolium-based ionic liquid [OMIm]Br to the Sn(salen) complex resulted in excellent catalytic performance for the conversion of fructose to MLA. This behavior could be attributed to the formation of hydrogen bonds between the component ions of [OMIm]Br and OH of fructose, which promoted proton transfer from $[OMIm]^+$ to the OH leaving group in fructose. Subsequent nucleophilic attack of the least sterically hindered C atom in the fructose molecule by Br^- led to intramolecular cleavage of a C–C bond in fructose. Notably, the side reactions were effectively suppressed owing to the weak basicity of the ionic liquid. These results indicated that both Sn(salen) and [OMIm]Br were responsible for the catalytic performance of Sn(salen)/IL, exhibiting a concerted promoting effect for the conversion of fructose to MLA.[42]

It has been previously reported that Al and Zn ions with Lewis acid active centers are favorable for the conversion of biomass resources into chemicals. Therefore, the catalytic activities of ionic-liquid-based metallosalen complexes, such as Al(salen)/IL and Zn (salen)/IL, which have similar structures to Sn(salen)/IL, were evaluated to understand the effect of the metal ion center on the catalytic performance. Clearly, both Al(salen)/IL and Zn (salen)/IL exhibited relatively low catalytic activity, with MLA yields of 32.1% and 21.6%, respectively (Table 1, entry 7 and 8). These results indicated that the type of the active metal center was very important, as the breakage of a C–C bond in the retro-aldol condensation reaction required the participation of a suitable Lewis acidic active metal center to realize higher active sites.

The influence of various reaction parameters on the catalytic activity and yields of products were examined. First, the reaction temperature dependence of the conversion of fructose to MLA with the Sn(salen)/IL catalyst was systematically investigated, as shown in Figure 1.

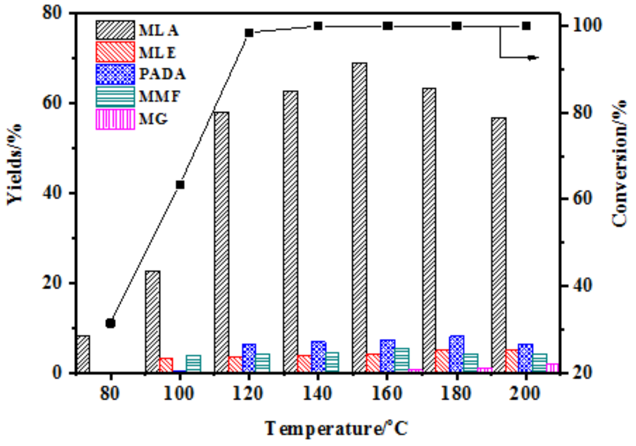


Figure 1. Influence of reaction temperature on the conversion of fructose and the yields of products (Reaction conditions: 0.3 g of fructose, 0.05 g of catalyst, 12 g of methanol, 2 MPa N_2, 2 h).

The experimental results showed that an almost linear increase in the conversion of fructose from 31.4% to 98.5% as the temperature increased from 80 to 120 °C, and the corresponding yield of MLA also increased from 11.2% to 58.0%. However, a further increase in the reaction temperature up to 160 °C resulted in complete conversion of fructose and a slightly increase in MLA yield to 68.9%. The average reaction rate calculated as the number of moles of MLA produced per mole of Sn^{4+} per hour obviously increased from 1.9 h^{-1} at 80 °C to 11.8 h^{-1} at 160 °C. This was probably because the increase in reaction temperature induced further conversion of undetected intermediate products, which promoted the formation of MLA to some extent. The experimental phenomenon was consistent with the previous report.[21] Small amounts of MLE, PADA, and MMF were also formed during the reaction, and concomitantly, the MG yield was also observed at 160 °C. In this reaction, MG was formed by the disproportionation and subsequent esterification of the extremely unstable glycolaldehyde in the retro-aldol condensation of glucose, which was formed by isomerization of fructose.[16] In addition, an obvious change in the color of the reaction solution from brown-red to dark brown occurred gradually, which was attributed the formation of the polymer. Further increase in the reaction temperature to 200 °C resulted in a decrease in the yields of both MLA and MMF, probably because the higher temperature accelerated the retro-aldol condensation reaction and rehydration of MMF to MLE, while simultaneously increased the polymerization of products under acidic conditions.[25,43,44] Clearly, 160 °C is the optimal reaction temperature for the conversion of fructose to MLA.

Based on these promising experimental results, the kinetic behavior of both Sn(salen) and Sn(salen)/IL was investigated in terms of the initial turnover frequency (TOF) at temperatures between 323 and 363 K (Figure S1a). Arrhenius plots were constructed for Sn(salen) and Sn(salen)/IL and their activation energies were calculated at low fructose conversion using the number of molecules converted per mole of Sn^{4+} per hour (Figure S1b). The initial reaction rates obviously increased with increasing reaction temperature. Notably, the TOF value of Sn(salen)/IL dramatically increased from 79 h^{-1} at 323 K to 3599 h^{-1} at 363 K. The kinetic data confirmed that the catalytic performance of Sn(salen)/IL was superior to that of Sn(salen), as the activation energy of Sn(salen)/IL (71.5 kJ mol^{-1}) was considerably lower than that of Sn(salen) (95.9 kJ mol^{-1}), indicating that Sn(salen)/IL was more favorable for the production of MLA from fructose compared to Sn(salen).[45]

A time-course study of the products was also conducted for the catalytic reaction performed at a temperature of 160 °C (Figure 2). The product profiles at different reaction times suggested that the maximum yield of MLA was reached after 2 h and the yield of the by-products increased monotonously over 2 h. However, further prolonging the reaction time to 4 h did not improve the yield of MLA. Instead, the rehydration of MMF to MLE was promoted by the action of Brønsted acid sites from imidazolium-based H^+ in the catalyst.[46] Additionally, the yield of MG increased slowly with longer reaction time. Moreover, the kinetic results showed that the TOFs of Sn(salen)/IL in initial conversion of dihydroxyacetone (DHA) were far higher than that of the initial conversion of fructose. The activation energy from DHA (46.4 kJ mol^{-1}) was much lower than that from fructose to MLA (71.5 kJ mol^{-1}), revealing that the retro-aldol condensation of fructose to C_3 intermediates was the reaction rate-determining step (Figure S2).[47]

The influence of the amount of catalyst on the yields of products was also studied (Figure 3). In the absence of a catalyst, very low catalytic activity was observed, the yields of MLA, MMF, MLE, PADA were 1.5%, 3.1%, 2.3%, and 2.4%, respectively (Table 1, Entry 1). These low yields could be attributed to the H^+ released from methanol solvent. As the amount of catalyst was increased, the yields of both MLA and MMF initially increased and then gradually decreased. In detail, when the amount of catalyst was increased from 0.05 to 0.09 g, the yields of MLA and MMF decreased from 68.9% to 56.5% and from 5.8% to 3.7%, respectively. In contrast, the yield of MLE steadily increased, mainly because the increase in the number of Brønsted acid sites promoted the formation of by-products, such as MLE and polymers. Thus, increasing the number of catalyst sites was unfavorable for the formation of MLA under acidic conditions, and this phenomenon is in agreement with previous reports.[44,48,49]

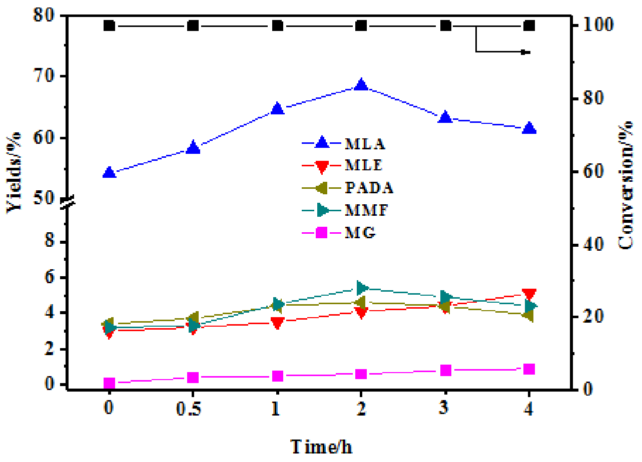


Figure 2. Time-course study of the products from the catalytic conversion of fructose with Sn(salen)/IL (Reaction conditions: 0.3 g of fructose, 0.05 g of catalyst, 12 g of methanol, 2 MPa N_2, 160 °C).

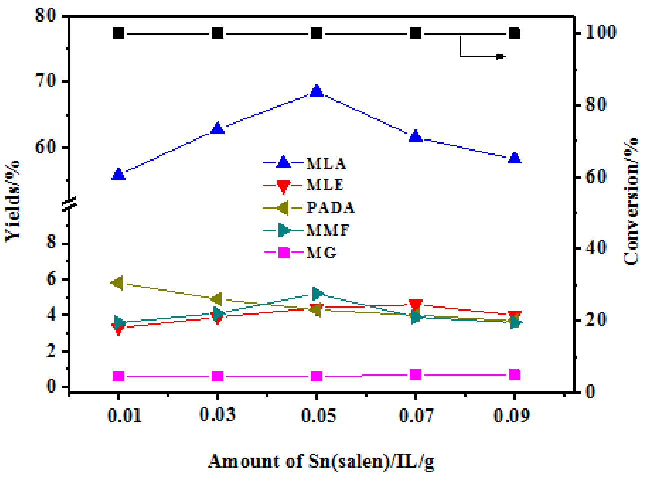


Figure 3. Influence of amount of Sn(salen)/IL on the yields of products (Reaction conditions: 0.3 g of fructose, 12 g of methanol, 2 MPa N_2, 160 °C, 2 h).

Generally, one-pot reactions that can convert large amounts of feedstocks into the target product are desirable. Thus, the influence of the initial amount of fructose on the catalytic performance was investigated at 160 °C for 2 h. As illustrated in Figure 4, in the presence of Sn(salen)/IL, increasing the amount of fructose resulted in a marked increase in the yield of MLA, with a maximum yield of 68.9%. Further increase in the amount of the substrate to 0.3 g resulted in a gradual decrease in the yield of MLA, likely because the active site density was inadequate at higher fructose amounts. Thus, continuously increasing the fructose amount did not enhance the reaction efficiency. Notably, an increasing trend was observed for the yield of MG, whereas the yield of MMF decreased continuously, likely caused by intermolecular polymerization of fructose that led to covering of the active sites, and a relative reduction in available acid sites. Nevertheless, the yield of MLA still exceeded 63.1% at higher substrate amounts (>0.5 g), indicating that the Sn(salen)/IL catalyst was highly efficient for the conversion of fructose to MLA.

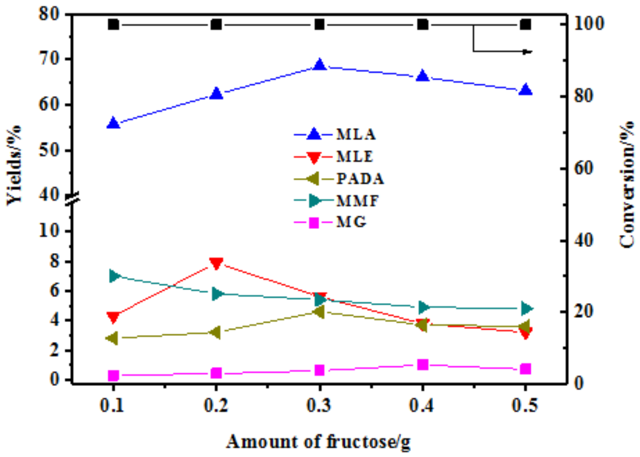


Figure 4. Influence of initial amount of fructose on the yields of products (Reaction conditions: 0.05 g of catalyst, 12 g of methanol, 2 MPa N_2, 160 °C, 2 h).

Conversion of Different Feedstocks to MLA

After optimizing the effect of the various reaction parameters by evaluation of their effect on the conversion of fructose and the yields of different products, a series of other biomass carbohydrates were tested as feedstocks under the optimal reaction conditions. As shown in Figure 5, it was notable that dihydroxyacetone (DHA) and glyceraldehyde gave MLA in 95.5% and 91.7% yield, respectively, which were much higher than those achieved from hexoses (fructose, glucose, and galactose) and disaccharides (sucrose and cellobiose) under identical conditions. Except for DHA and glyceraldehyde, fructose offered the highest yield of MLA (68.9%) compared with sucrose (56.0%), glucose (40.8%), and galactose (35.1%). Additionally, the yield of MLA from inulin (61.8%) was slightly lower than that from fructose, but much higher than that from cellobiose (32.6%). Although the yields of MLA from cellulose and starch were unsatisfactory (<10%) at 160 °C, the MLA yields from these feedstocks increased drastically to 22.4% and 27.9%, respectively, at 180 °C for 2 h. These comprehensive results suggest that the Sn(salen)/IL catalyst has high potential for generating MLA from biomass carbohydrates.[50]

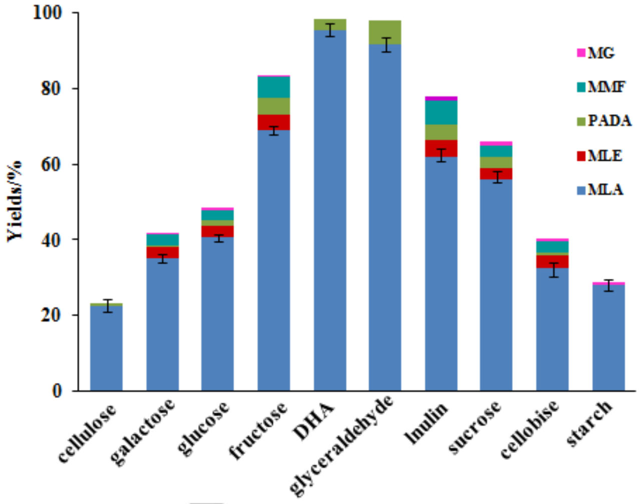


Figure 5. Catalytic conversion of various biomass carbohydrates with Sn(salen)/IL (Reaction conditions: 0.3 g of substrate, 12 g of methanol, 0.05 g of catalyst, 2 MPa N_2, 160 °C, 2 h; cellulose and starch at 180 °C).

Catalyst Recycling

The recyclability and reusability of the catalyst were evaluated using fructose as feedstock under the optimized reaction conditions. After the completion of the reaction, the catalyst was easily separated by centrifugation, followed by washing with ethyl acetate, and used for the next run under identical conditions. As shown in Figure 6, MLA was still obtained in a satisfactory yield after five consecutive cycles, indicating that there was no considerable loss of catalytic activity. Thus, these results confirmed that the Sn(salen)/IL catalyst was recyclable and stable.

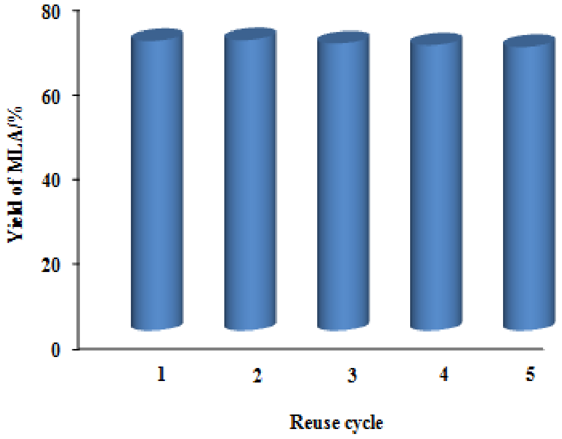
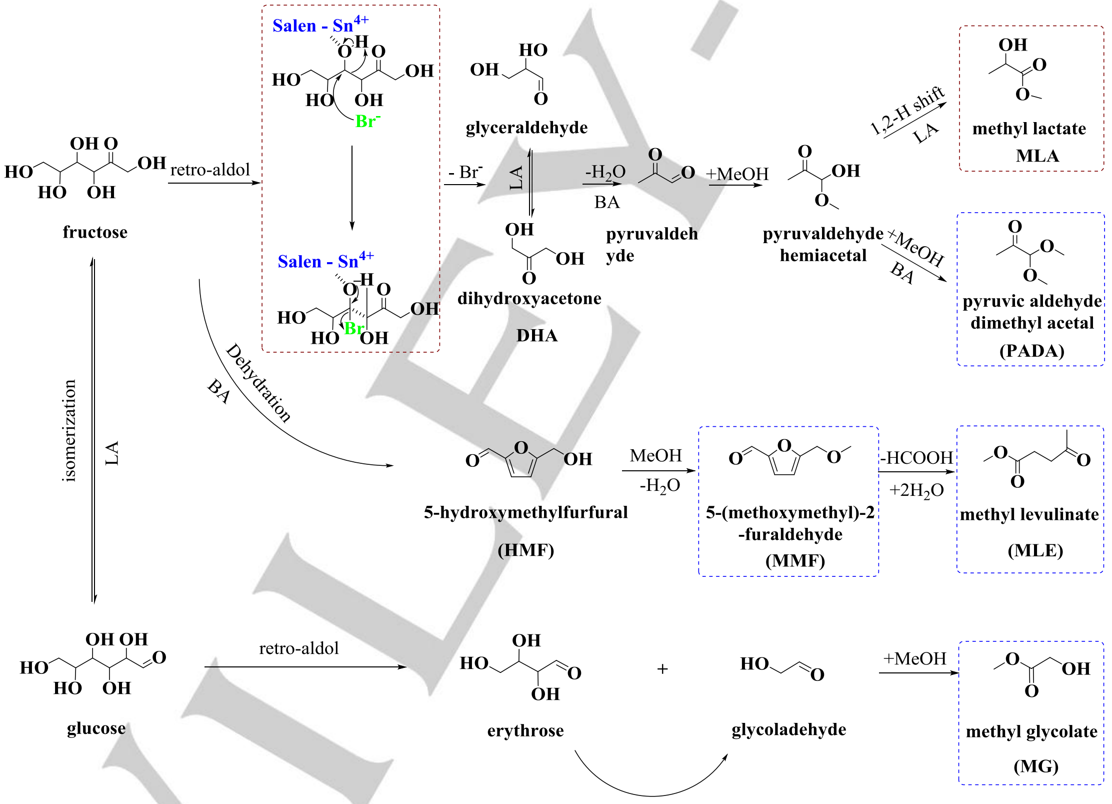


Figure 6. Recyclability of the Sn(salen)/IL catalyst for the catalytic conversion of fructose to MLA (Reaction conditions: 0.3 g of fructose, 0.05 g of catalyst, 12 g of methanol, 2 MPa N_2, 160 °C, 2 h).

Reaction Pathway for the Conversion of Fructose to MLA

Combining the results of the present study and numerous previous reports, a plausible reaction pathway was proposed for production of MLA from fructose catalyzed by Sn(salen)/IL. It is generally accepted that the reaction pathway for converting fructose to MLA involves multistep reactions, including retro-aldol condensation, isomerization, dehydration, and esterification.[9,14,17,21,39,45,51] The experimental results provided a deeper insight into the reaction pathway and mechanism of action of the Sn(salen)/IL catalyst. It was evident that the Sn(salen)/IL catalyst facilitated the retro-aldol condensation reaction. In this reaction, the O atom of fructose coordinated to the Sn^{4+} Lewis acid site through a Sn···O bond. Meanwhile, nucleophilic Br^- attacked the least sterically hindered C atom of fructose. This led to the intramolecular cleavage of the C–C bond in fructose to form DHA and glyceraldehyde, which were further isomerized at Lewis acid sites. Subsequent dehydration at the Brønsted acid sites of the catalyst produced pyruvaldehyde. This compound further reacted with methanol molecule to form pyruvaldehyde hemiacetal, which promptly underwent 1,2-H transfer and esterification, producing MLA under the action of Lewis acid sites. Meanwhile, by-product PADA was obtained through reaction at Brønsted acid sites. In parallel, traces of MG were formed as result of the disproportionation and subsequent esterification of glycolaldehyde which was formed in the retro-aldol reaction of glucose. Thus, it could be concluded that the production of MLA from fructose was the result of a cooperative effect of both Lewis acid and Brønsted acid sites, as well as basic sites in the catalyst. The retro-aldol condensation of fructose to the C_3 intermediates and eventual esterification to formation of MLA was the main reaction pathway, but the retro-aldol condensation of fructose to C_3 intermediates was the reaction rate-determining step in the fructose-to-MLA process. The dehydration and isomerization reaction of fructose were parallel competing reactions. The reaction pathway for the catalytic conversion of fructose to MLA catalyzed by Sn(salen)/IL is summarized in Scheme 1.



Scheme 1. Proposed reaction pathway for the catalytic conversion of fructose to MLA catalyzed by Sn(salen)/IL.

Conclusion

In summary, a novel, high-efficiency ionic liquid functionalized Sn-containing catalyst was developed for producing MLA from biomass carbohydrates in methanol. The Sn(salen)/IL catalyst exhibited excellent catalytic performance owing to an intramolecular synergistic effect resulting from the electrophilic Sn^{4+} unit and the nucleophilic Br^- as well as the imidazolium cation. In particular, this catalyst not only provided Lewis acid sites for the activation of the carbonyl oxygen in fructose and Brønsted acid sites for promoting the initial dehydration of DHA and glyceraldehyde to pyruvaldehyde, but also had basic sites that could effectively suppress the undesired side reactions, resulting in a high MLA yield of 68.9% from fructose. In addition, the catalyst could be easily separated and recycled for five consecutive cycles without significant loss in catalytic activity. However, the Sn(salen)/IL catalyst gave a much lower yield of MLA from glucose and sucrose as compared to the Sn-Beta catalyst, which was probably as result of the different local environment of Sn^{4+} and the lower number of Lewis acid sites in the catalyst. In order to enhance the yield of MLA, further research efforts must comprise tailoring of the structure and Lewis acidity of the catalysts in the conversion of glucose and sucrose.

Experimental Section

Materials

D-Fructose (99%), D-glucose (98%), galactose (98%), glyceraldehyde (99%), MLE (99%), inulin (99%), and starch (98%) were purchased from Sinopharm Chemical Reagents Co., Ltd. MLA (99%), MG (98%), sucrose (99%), MMF (98%), DHA (99%), 5-hydroxymethylfurfural (HMF) (98%), cellobiose (98%), and microcrystalline cellulose (average particle size 20 *μm*) were obtained from Sigma-Aldrich. Pyruvaldehyde (40 wt% solution in water) and PADA (99%) were purchased from Alfa Aesar. All other reagents were of analytical grade and used without further purification.

Catalyst Preparation

The Sn(IV) salen complex functionalized by the imidazolium-based ionic liquid [OMIm]Br (abbreviated as Sn(salen)/IL) was synthesized as previous reported by our group.[40] In this procedure, *N*-octylimidazole was reacted directly with salicycladehyde modified with benzyl halide to afford ionic-liquid-substituted salicycladehyde. Successive Schiff base condensation reactions between the aldehyde groups of the ionic-liquid-substituted salicycladehyde and the amino groups of ethylenediamine led to the formation of the corresponding salen ligand. Subsequently, the ionic liquid functionalized Sn(salen) complex was then obtained via a metallization process under nitrogen protection. The synthesis route for Sn(salen)/IL was depicted in Scheme S1.

Catalyst Characterization

The FT-IR spectrum of Sn(salen)/IL (Figure S3), recorded with a Bruker spectrophotometer, indicated that the imidazolium-based ionic liquid was successfully grafted onto the salen ligand to obtain the Sn(salen)/IL catalyst. The thermogravimetric and differential thermogravimetric (TG-DTG) curves were obtained using a NETZSCH STA 449C thermal analyzer. The sample was heated from room temperature to 800 °C under flowing air at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) demonstrated that the Sn(salen)/IL catalyst was stable to about 218 °C without significant weight loss. The decomposition temperature of the ionic liquid was about 455 °C, reflecting its higher thermostability (Figure S4). The XPS spectra of Sn(salen)/IL and Sn3d of Sn(salen)/IL are illustrated in Figure S5.

Catalytic Reaction Procedure

All experiments were conducted in a 25 mL Teflon-line stainless steel batch reactor. Typically, 0.3 g of fructose, 0.05 g of catalyst, and 12 g of methanol were charged into the stainless steel autoclave equipped with a magnetic stirrer. After the autoclave was sealed and purged three times with N_2, it was pressurized to 2 MPa with N_2. The reaction mixture was then heated to the desired temperature under stirring at 600 rpm. After the completion of the reaction, the reactor was quickly quenched to room temperature by using an ice bath.

The resulting liquid products, such as MLA, MMF, MLE, PADA and MG were identified and qualitatively determined by using a Shimadzu 2010 GC-MS gas chromatograph equipped with a FID and an RTX-5 capillary column (30 m × 0.32 mm × 0.25 μm) using butanol as an internal standard. Fructose was determined with a Shimadzu LC-20 AT HPLC system equipped with a RID-10A detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 × 7.8 mm). Before analysis, the reaction solution was filtered and diluted five times with the mobile phase (0.005 M H_2SO_4). The flow rate was 0.5 mL min^{-1}, the column temperature was 50 °C, and the detector temperature was 40 °C. The conversion of fructose, the yield and selectivity of MLA and the yield (Y_i) of each other product *i* were calculated as follows:

Fructose conversion (mol %):

$$\text{Conversion} = \left(1 - \frac{\text{mole of unconverted of fructose}}{\text{mole of initial frutose}}\right) \times 100\%$$

$$Y_{\text{MLA}} = \frac{\text{mole of MLA}}{\text{mole of initial fructose}} \times \frac{1}{2} \times 100\%$$

$$S_{\text{MLA}} = \frac{\text{yield of MLA}}{\text{conversion of frutose}} \times 100\%$$

$$Y_i = \frac{\text{mole of product } i}{\text{mole of initial fructose}} \times 100\%$$

TOF was calculated as the number of mole of substrate converted per mole of Sn^{4+} per unit time.

$$\text{TOF}(h^{-1}) = \text{mol}_{\text{sub}}/\text{mol}_{\text{Sn}^{4+}}/h$$

where mol_{sub} was the number of moles of substrate reacted in the system, mol_{Sn} was the number of moles of Sn^{4+} in the system, h was the reaction time.

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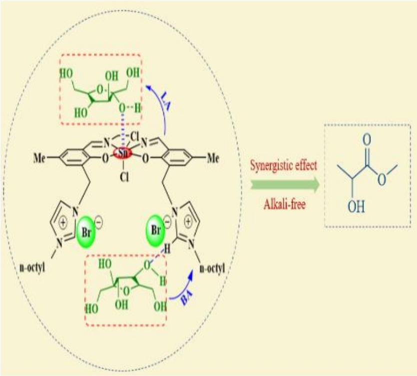
FULL PAPER

A multifunctional catalyst incorporating a Lewis acidic Sn(IV) center, a salen ligand, and an imidazolium-based ionic liquid was developed. This catalyst exhibits intramolecular synergistic effect for catalytic conversion of fructose to methyl lactate in methanol.



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Synergistic Production of Methyl Lactate from Carbohydrates Using an Ionic Liquid Functionalized Sn-Containing Catalyst