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Short Communication

The synthesis of methyl lactate and other methyl oxygenates from cellulose

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ABSTRACT

Light oxygenates, such as methyl lactate (MLA), methyl levulinate (MLE), methyl formate (MFO), methyl acetate (MAC), dimethoxymethane (DMM), and methoxyacetaldehyde dimethyl acetal (MADA) were synthesized from cellulose in the presence of promoted SnX_2 ($X = Cl^-$, Br^-, and I^-) salt catalysts in methanol. The presence of halides in SnX_2-ML_n (ML_n is metal salt) catalysts was found crucial for methyl lactate formation from sugar. The investigation shows that $ZnCl_2$ is an efficient promoter for SnX_2 catalyst in converting cellulose to light oxygenates. Up to 52.2% of total one-pass oxygenate yield was obtained in the presence of $SnCl_2$–$ZnCl_2$ catalyst.

1. Introduction

Carbohydrates, such as sucrose, starch, and celluloses synthesized by plants, are the most abundant renewable carbon sources. The high content of the functional groups in carbohydrate molecule has both priorities and drawbacks in converting carbohydrates to valuable chemicals. The active functional groups make it possible to convert these carbohydrates to liquid fuel [1,2] or fundamental building blocks [3–5]. However, many functional groups on the same molecular also bring in problems in the selective conversion of carbohydrates to specific chemicals. Different reactions could simultaneously occur on different functional groups of the molecular, leading to unwanted by-products, especially the tar like by-products (humins), which make the practice of the process difficult. It is highly desired to develop a simple catalyst that directly decomposes carbohydrates to light oxygenates, such as MLA and MLE. MLA is a versatile platform compound, which could be a potential feed stock for the synthesis of biodegradable polylactic acid plastics [6], 1,2-propanediol [7], allyl alcohol, or acrylic acid.

Presently, large scale production of lactic acid is through fermentation of glucose [8]. However, the biological process generally suffers from low reaction rate and low product concentration, which costs too much energy in product purification.

Aqueous alkali hydroxides were reported to convert carbohydrates to lactate salts [9]. However, the reaction consumes excess amount of alkali hydroxide. Holm et al. demonstrated that glucose, fructose, and sucrose could be directly converted to methyl lactate over Sn^{4+} doped zeolite [10]. The active sites were thought to be the framework tin ions that show Lewis acidity. The disadvantages of the tin-zeolite catalyst are that it is difficult to synthesize (needs more than 48 days) and to separate the zeolite particles from the tar like humins after reaction. Generally, the channels in zeolite could accommodate monosaccharide and disaccharide molecules. Larger molecules, such as starch and cellulose, could not access these Lewis acid sites. Solid catalysts sulfonated carbon (C-SO_3H), H-ZSM-5, H-beta, sulfated zirconia, HY zeolite, tungstated zirconia, and tungstated alumina [11,12] were reported effective in cellulose conversion. However, Chambon and coworkers' work proved that these solid catalysts can only act on the pre-hydrolyzed cellulose fragments (soluble oligomers and polymers) [12]. In order to resolve the problems, we developed a type of simple homogeneous catalyst, which could directly act on cellulose to prepare MLA, MLE, and other oxygenates.

2. Experimental

Microcrystalline cellulose (MCC), sucrose, methanol, NaCl, KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $BaCl_2$, $AlCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$, $CdCl_2$, $BiCl_3$, $ZnCl_2$, SnO, NH_4Cl, SnO, and $PbCl_2$ were bought from Guo Yiao Chemical Group Inc. in China. These compounds are all in analytic purity.

The reactions were carried out in stainless steel batch reactors (having inside volume of 20.0 or 100 mL) lined with poly tetrafluoroethylene. Reactant, catalyst, and methanol were charged into the reactors at room temperature. The reactors were then sealed and placed onto a rotation axis in an oven. Rotate the axis to achieve mixing and ramp up the temperature of the oven to desired temperatures to run

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reactions. The scaling up reactions were carried out in a batch reactor with an inside volume of 10 L (when carrying out reaction at 110 °C, the inside pressure is 5.0 atm. The vapor pressure of CH_3OH at 110 °C is 4.8 atm. The difference could be measurement error. When running reactions at 190 °C, the inside pressure is 35.0 atm. The vapor pressure of CH_3OH at 190 °C is 33.0 atm. The difference between the practice pressure and the vapor pressure of methanol at 190 °C is because of the formation of dimethyl ether, which was detected as a by-product in our reactions). After completing the reactions, the batch reactors were cooled to room temperature, and then opened to take samples. The samples were centrifuged to separate the liquid from the solid. The liquid sample was analyzed on a GC and a GC-MS to calculate the yields of products.

The samples were analyzed on a GC-MS (Agilent 6890N/5975B) with a column Agilent DB-1701 (30 m × 320 μm × 0.25 μm) and a GC (Agilent 6820) with a column Agilent DB-WAX (30 m × 0.450 mm × 0.8 mm).

The calculations of the product yields are as follows:

MLA yield: YMLA = (mol number of MLA)/(2 × mol number of $C_6H_{10}O_5$ unit);

MLE yield: YMLE = (5 × mol number of MLE)/(6 × mol number of $C_6H_{10}O_5$ unit);
Methyl acetate yield: YMAC = (mol number of methyl acetate)/(3 × mol number of $C_6H_{10}O_5$ unit);
Methyl formate yield: YMFO = (mol number of methyl formate)/(6 × mol number of $C_6H_{10}O_5$ unit);
DMM yield: YDMM = (mol number of DMM)/(6 × mol number of $C_6H_{10}O_5$ unit);
MADA: YMADA = (4 × mol number of MADA)/(6 × mol number of $C_6H_{10}O_5$ unit).

3. Results and discussion

In the present investigation, a few kinds of metal chlorides were tested as catalysts in converting sucrose to MLA and other oxygenates in methanol (Table 1s). Generally, MLA, MLE, MFO, MAC, DMM, and MADA or some of them (depend on catalyst) were formed as products in the reactions. For easy discussion, only the yields of major products MLA and MLE were given in Tables 1 and 2. The mechanism for MLA formation is generally believed to be the retro aldol reaction [10,13].

Table 1
Catalyst performance in MLA and MLE synthesis from sucrose.[a]

Entry	Catalyst	T (K)	MLA (%)	MLE (%)
1	$SnCl_2 \cdot 2H_2O$	403	23.5	10.3
2	$SnCl_2 \cdot 2H_2O/NH_4Cl$	403	38.5	0
3	$SnCl_2 \cdot 2H_2O/NaCl$	403	39.3	0
4	$SnCl_2 \cdot 2H_2O/NaBr$	403	26.6	1.3
5	$SnCl_2 \cdot 2H_2O/NaI$	403	25.1	0.5
6	$SnCl_2 \cdot 2H_2O/KCl$	403	43.3	0
7	$SnCl_2 \cdot 2H_2O/MgCl_2$	403	42.6	0
8	$SnCl_2 \cdot 2H_2O/MgBr_2$	403	37.8	1
9	$SnCl_2 \cdot 2H_2O/CaCl_2$	403	32.8	0
10	$SnCl_2 \cdot 2\ H_2O/FeCl_3 \cdot 6H_2O$	403	27.0	0.1
11	$SnCl_2 \cdot 2H_2O/AlCl_3$	403	7.4	6.4
12	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$	403	14.4	8.4
13	$SnCl_2 \cdot 2\ H_2O/SbCl_3$	403	27.5	7.1
14	$SnCl_2 \cdot 2H_2O/NiCl_2$	403	36.0	0.7
15	$SnCl_2 \cdot 2\ H_2O/CoCl_2 \cdot 6H_2O$	403	38.0	0
16	$SnCl_2 \cdot 2\ H_2O/PbCl_2$	403	0.4	3.3
17	$SnCl_2 \cdot 2\ H_2O/CrCl_3 \cdot 6H_2O$	403	4.5	14.6
18	$Sn(CH_3SO_3)_2/NH_4Cl$	403	42.0	0
19	$Sn(C_6H_5SO_3)_2/NH_4Cl$	403	38.5	0
20	$Sn(CH_3SO_3)_2/NH_4(CH_3C_6H_5SO_3)$	403	1.2	14.5
21	$Sn(CH_3SO_3)_2/NH_4(C_6H_5SO_3)$	403	0.9	13.1
22	$Sn(C_6H_5SO_3)_2/NH_4(C_6H_5SO_3)$	403	0.6	13.1

[a] Sucrose 0.500 g, SnL_2 0.220 mmol, ML_n 1.87 mmol, CH_3OH 4.000 g, and reaction time 2 h. The yield is in mol. The relative errors are below 4.6%.

Table 2
Catalyst performance in MLA and MLE synthesis from cellulose, glucose, and sucrose.[a]

	Catalyst	T (K)	MLAY (%)	MLEY (%)
1	$SnCl_2 \cdot 2\ H_2O$	453	11.6	4.5
2	$SnCl_2 \cdot 2\ H_2O/NaCl$	453	1.0	0.8
3	$SnCl_2 \cdot 2\ H_2O/KCl$	453	0.8	0.3
4	$SnCl_2 \cdot 2\ H_2O/MgCl_2 \cdot 6H_2O$	453	1.8	0.4
5	$SnCl_2 \cdot 2\ H_2O/CaCl_2$	453	1.0	0.3
6	$SnCl_2 \cdot 2\ H_2O/BaCl_2$	453	6.4	1.9
7	$SnCl_2 \cdot 2\ H_2O/NH_4Cl$	453	1.4	0.5
8	$SnCl_2 \cdot 2\ H_2O/CoCl_2 \cdot 6H_2O$	453	9.4	2.6
9	$SnCl_2 \cdot 2\ H_2O/PbCl_2$	453	9.8	2.8
10	$SnCl_2 \cdot 2\ H_2O/CrCl_3 \cdot 6H_2O$	453	9.9	4.3
11	$SnCl_2 \cdot 2\ H_2O/FeCl_3 \cdot 6H_2O$	453	12.7	4.6
12	$SnCl_2 \cdot 2\ H_2O/AlCl_3 \cdot 6H_2O$	453	15.9	4.4
13	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$	453	15.0	11.0
14	$SnCl_2 \cdot 2\ H_2O$	463	21.6	12.2
15	$SnCl_2 \cdot 2\ H_2O/AlCl_3 \cdot 6\ H_2$	463	20.8	5.9
16	$SnCl_2 \cdot 2\ H_2O/SbCl_3$	463	17.6	7.2
17	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$	463	23.7	13.8
18	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$[b]	463	27.0	4.0
19	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$[c]	463	31.2	6.0
20	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$[d]	463	15.7	11.9
21	$SnCl_2 \cdot 2\ H_2O/ZnCl_2$[e]	463	14.7	11.8

In the reaction of sugar cane bagasse, the yields of products were calculated based on the composition of 45% of cellulose, 27.5% of half cellulose, and 2.0% of sucrose. The composition of the bagasse is 19% of lignin, 45% of cellulose, 27.5% of half cellulose, 2.5% of protein, 2.5% of ash, 1.5% of pectic, and 2.0% of sucrose.

[a] The yield is in mol. The relative errors are below 4.6%. Reactions were run at 180 °C for 4 h. The amount of microcrystal cellulose is 0.400 ± 0.001 g for all of the reactions. The amount of methanol is 8.000 g. The amount of other salt (except $SnCl_2$) was 0.736 mmol, respectively. The amount of $SnCl_2 \cdot 2H_2O$ was 0.200 g (0.886 mmol).

[b] The reactant was sugar cane bagasse (0.400 g). The amount of methanol is 8.000 g. The amount of $ZnCl_2$ was 0.736 mmol. The amount of $SnCl_2 \cdot 2H_2O$ was 0.200 g (0.886 mmol).

[c] The reactant was sugar cane bagasse. The $SnCl_2 \cdot 2\ H_2O/ZnCl_2$ is 0.30 mmol/1.0 mmol, and reaction time is 6 h. The amount of methanol is 8.000 g. The amount of $ZnCl_2$ was 0.736 mmol.

[d] The reactant was glucose (0.400 g). The amount of methanol is 8.000 g. The amount of $ZnCl_2$ was 0.736 mmol. The amount of $SnCl_2 \cdot 2H_2O$ was 0.200 g (0.886 mmol).

[e] The reactant is sucrose (0.400 g). The amount of methanol is 8.000 g. The amount of $ZnCl_2$ was 0.736 mmol. The amount of $SnCl_2 \cdot 2H_2O$ was 0.200 g (0.886 mmol).

Among the mono-component catalysts, $SnCl_2$ gave the highest MLA and MLE yields (23.5% and 10.3%, respectively) at 403 K (Table 1), while the other metal chlorides did not show much selectivity to form MLA (Table 1s). The results indicate that the Sn^{2+} cation and halides are necessary for MLA formation (Table 1, entries 1–15, 18–19). Without halides, the major product is MLE (Table 1, entries 20–22). Of course, as shown in Table 1, entries 18 and 19, even the tin salts do not contain halides, and the catalysts $Sn(CH_3SO_3)_2$-NH_4Cl and $Sn(C_6H_5SO_3)_2$-NH_4Cl still gave high MLA yields. The reason could be that the halides could come from the promoter by anion exchange between the tin salts and the halide containing salts. We speculate that, possibly, the halides are involved in the MLA formation steps (the study is still in progress regarding to the role of halides).

It was found that adding promoters could either enhance or inhibit the catalytic activity of $SnCl_2$ for MLA formation. The addition of relatively weaker Lewis acid (weak acceptors, such as NH_4^+, Co^{2+}, Ni^{2+}, alkaline metal cation, and alkaline earth metal cation) into $SnCl_2 \cdot 2H_2O$ catalyst improves the MLA yields. The $SnCl_2 \cdot 2HO$ catalyst promoted by NH_4Cl, KCl, or $MgCl_2$ (Table 1, entries 6, 7, and 18) gave relatively higher MLA yields (>40%). The addition of relatively stronger Lewis acids (such as $FeCl_3 \cdot 6H_2O$, $AlCl_3$, and $ZnCl_2$) into $SnCl_2 \cdot 2H_2O$ gave much low MLA yields.

In a kilogram level reaction (Section 1s) carried out in the presence of $SnCl_2 \cdot 2H_2O$-$MgCl_2 \cdot 6H_2O$ catalyst, 50% of MLA yield with 1.0% of MLE yield was obtained. When reducing the amount of $MgCl_2 \cdot 6H_2O$ to 41.6 g, 47.1% of MLA yield and 1.5% of MLE yield were obtained. However, further reducing the amount of $SnCl_2 \cdot 2H_2O$ led to MLA yield dramatically decreasing. The drawback of the reaction is to form large amount of dark tar. Generally, the formation of MLE and tar is catalyzed by BrØnsted acid. In the present cases, the hydrolysis of $SnCl_2 \cdot 2H_2O$ (H_2O is also a by-product in the formation of MLA, MFO, MAC, DMM, and MADA) could generate BrØnsted acid HCl, which might catalyze the dehydration reaction of sucrose to form MLE and humins.

It is known that the tin dihalides could combine with halide to form SnX_3^- type anions [14]. Our results indicate that the weak accepting salts promote the MLA yield in sucrose reactions. It is known that the Lewis acidity of Sn^{2+} in SnX_3^- is weaker than that in $SnCl_2$ (also see PH value in Section 1s). The results indicate that relatively higher MLA yield was obtained over $M(SnX_3)_n$, in which, M^{n+} has relatively weaker acidity. Hence, reasonably reducing the Lewis acidity of Sn^{2+} (by adding alkaline or alkaline earth metal halides) favors the MLA formation from sucrose. High acidity leads to low MLA yield (Table 1, entries 10–13) and favors the formation of dark tar.

Several metal salt catalysts were also tested for the purpose of converting cellulose to light oxygenates. $SnCl_2 \cdot 2H_2O$ gave the highest MLA yield, while $CrCl_3 \cdot 6H_2O$ gave the highest MLE yield (Table 2s). Comparing with the reaction results from the sucrose reactions, the $SnCl_2 \cdot 2H_2O\text{-}MCl_n$ catalyst behaves differently in catalyzing cellulose conversion. In the reaction of microcrystal cellulose, $SnCl_2 \cdot 2H_2O$ gave 11.6% of MLA yield and 4.5% of MLE yield at 453 K. The addition of NH_4Cl, alkaline metal chloride, or alkaline earth metal chloride into $SnCl_2 \cdot 2H_2O$ reduced the MLA yields (Table 2, entries 2–7). Adding metal chlorides with medium accepting capability (Table 2, entries 8–10) into $SnCl_2 \cdot 2H_2O$ did not impact much on the MLA yields. Stronger Lewis acids show improving effects on the activity of $SnCl_2 \cdot 2H_2O$ catalyst for MLA formation (Table 2, entries 11 to 13). The results indicate that the combination of $SnCl_2 \cdot 2H_2O\text{-}ZnCl_2$ is the most efficient catalyst in converting cellulose to MLA and MLE. At elevated temperature (210 °C), up to 32.1% of MLA and 10.6% of MLE yields were obtained (Fig. 1). The catalyst also performed well in converting sugar cane bagasse to MLA and MLE (31.2% and 6.0% yields, respectively, Table 2, entries 18–19). However, these catalysts are not good for monosaccharide and disaccharide involved reactions (Table 2, entries 20–21). The strong acidity of these catalysts turned too much of monosaccharide and disaccharide to humins.

In order to check the influence of mechanical ball milling on product yields, the cellulose was milled (ball milled at 200 rotations/min for 10 h, see pictures in Supplement material, see Fig. 1Sa and 1Sb), and then run reaction at the same conditions as that in Table 2, entry 13. The reaction gave 18.5% of MLA yield and 7.3% of MLE yield. Without milling the cellulose, the reaction gave 15.0% of MLA yield and 11.0% of MLE yield (Table 2, entry 13). The milled cellulose gave higher MLA yield, but lower MLE yield than that not milled.

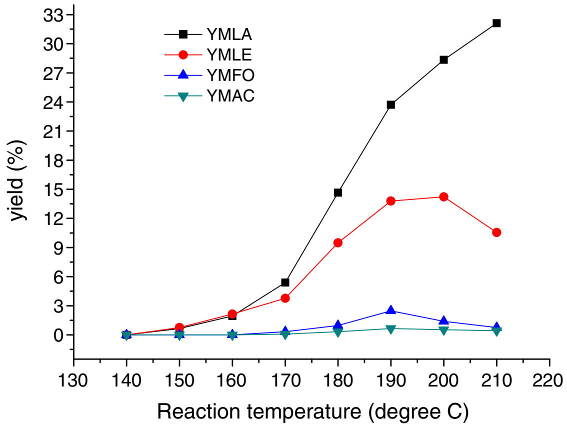

Fig. 1. The influence of reaction temperature on the yields of products. YMLA stands for the yield of MLA. YMLE stands for the yield of MLE. YMFO stands for the yield of MFO. YMAC stands for the yield of MAC. Reaction conditions: microcrystal cellulose 0.400 ± 0.001 g, CH_3OH 8.000 ± 0.001 g,$ZnCl_2 \cdot 2H_2O$ 0.100 ± 0.001 g (0.736 mmol), $SnCl_2 \cdot 2H_2O$ 0.200 ± 0.001 g (0.886 mmol), and reaction time 4 h.

In the reaction of cellulose, it was found that there was dark solid formation. The formation of dark compounds might be one of the reasons that retard the reaction. Although, we cannot confirm if the whole used solid is cellulose, the XRD characterization shows that there was still cellulose in the used cellulose (Fig. 1Sc). It was found that high catalyst concentration turned cellulose to dark (Fig. 2). In order to reduce the formation of dark compound, the reaction was run at more diluted condition (cellulose 0.400 ± 0.001 g, CH_3OH 20.000 ± 0.001 g, $SnCl_2 \cdot 2H_2O$ 1.50 mmol, $ZnCl_2$ 1.00 mmol, reaction temperature 190 °C) and for longer time (7.0 h instead of 4 h). Even higher MLA yield (33.5%) and MLE yield (14.3%) were obtained (comparing with that of Fig. 2A) and the rest of the cellulose was not turned into dark (Fig. 2B). Clearly, the formation of dark compound over cellulose particles is one of the reasons that retard the reaction. However, prolonging the reaction time to 8 or 9 h, the yields of MLA and MLE did not increase any more. The results indicate that the catalyst did not continue acting its rule. One of the possible reasons could be that some of the products poison the catalyst. We speculated that the most possible component that poisons the catalyst might be MLA, since that the hydroxyl group bearing compounds could easily coordinate to Sn^{2+} [15,16]. In order to verify our speculation, MLA was added to microcrystal cellulose to run reaction at the optimized conditions. When small amount of MLA was added, much low MLA yields were obtained. Adding more MLA could fully stop the MLA formation reaction (see Section 2s for detail). However, the MLA addition only slightly reduces the MLE yield. The results indicate that the addition of MLA poisons the MLA formation pathway.

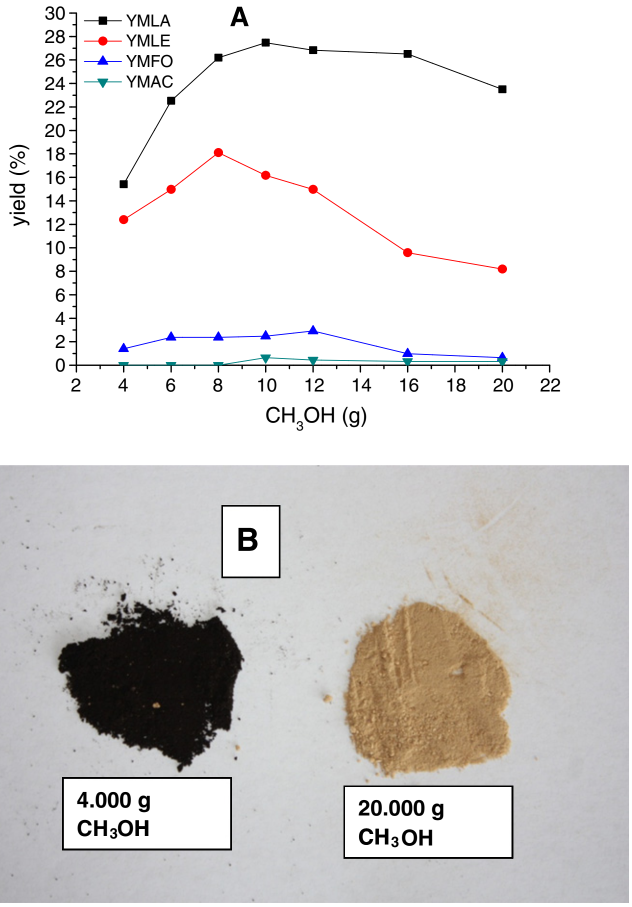

Fig. 2. A: The influence of CH_3OH amount on the yields of products. YMLA stands for the yield of MLA. YMLE stands for the yield of MLE. YMFO stands for the yield of MFO. YMAC stands for the yield of MAC. Reaction conditions: microcrystal cellulose 0.400 ± 0.001 g, $SnCl_2 \cdot 2H_2O$ 1.50 mmol, $ZnCl_2$ 1.00 mmol, reaction temperature 190 °C, and reaction time 4 h. B: The cellulose samples after reaction with 4.000 ± 0.001 and 20.000 ± 0.001 g of methanol.

The possible reason could be that MLA might react with Sn^{2+} through the hydroxyl group to form a more stable coordination complex and kikes out Cl^- ligands from the coordination sphere of Sn^{2+} ions. The resulted Sn^{2+} complexes (without halides) are not active for the topic reaction (consistent with the results in Table 1, entries 20–22).

As mentioned previously, the dark compound formation could be one of the reasons that retard the reaction. If the dark layer was broken, the reaction should be able to continue over the newly generated surface. In order to verify the idea, reaction was run with fresh microcrystal cellulose at optimized conditions (2.000 g of MCC, 7.50 mmol of $SnCl_2 \cdot 2H_2O$, 5.00 mmol of $ZnCl_2$, 100.0 g of CH_3OH, reaction time 7 h, temperature 190 °C). The reaction gave 33.6%, 9.2%, 1.2%, 0.3%, 3.7%, and 4.2% of MLA, MLE, MFO, MAC, DMM, and MADA yields, respectively (total carbon yield of 52.2%). There was about half of the solid left. The left solid is defined as used MCC. Without milling the used MCC, even if we loaded it with fresh catalyst, there were still not much MLA and MLE detected. After the used MCC was milled, the reaction of the used MCC gave 6.1%, 7.8%, 0.7%, and 0.5% of MLA, MLE, MFO, and DMM yields, respectively. The results indicate that the formation of the dark compounds is one of the reasons that retard the reaction in some degree. In our investigation, it was found that high reaction temperature and high catalyst concentration usually lead to dark solid formation in cellulose reaction. In order to obtain relatively higher MLA yield and without turning cellulose to dark, we run the reactions at relatively lower catalyst concentration and reasonably lower reaction temperature (190 °C) for longer time (Fig. 2s).

In conclusion, our investigations show that if $SnCl_2 \cdot 2H_2O$ was promoted by suitable slats (ML_n), it could be an efficient catalyst to catalyze carbohydrate conversion to prepare light oxygenates, such as MLA and MLE, in methanol. The $MgCl_2$ promoted $SnCl_2 \cdot 2H_2O$ catalyst is efficient to catalyze monosaccharides and disaccharide conversion to produce MLA and MLE, while the $ZnCl_2$ promoted $SnCl_2 \cdot 2H_2O$ catalyst is efficient to catalyze cellulose conversion to produce MLA, MLE, MFO, MAC, DMM, and MADA. These products are easily separatable high value oxygenates. The catalyst is simple metal chlorides, which could be easily regenerated (Section 3s). The process has potential to be scaled up to commercial stage. Research in this aspect is in progress.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.02.012.

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