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.

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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$_3$H), 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$_2$ · 6H$_2$O, CaCl$_2$, BaCl$_2$, AlCl$_3$ · 6H$_2$O, CrCl$_3$ · 6H$_2$O, FeCl$_3$ · 6H$_2$O, CoCl$_2$ · 6H$_2$O, NiCl$_2$ · 6H$_2$O, SnCl$_2$ · 2H$_2$O, CdCl$_2$, BiCl$_3$, ZnCl$_2$, SnO, NH$_4$Cl, 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

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

MLE yield: $Y_{MLE} = $ (5 × mol number of MLE)/(6 × mol number of $C_6H_{10}O_5$ unit);

Methyl acetate yield: $Y_{MAC} = $ (mol number of methyl acetate)/(3 × mol number of $C_6H_{10}O_5$ unit);

Methyl formate yield: $Y_{MFO} = $ (mol number of methyl formate)/(6 × mol number of $C_6H_{10}O_5$ unit);

DMM yield: $Y_{DMM} = $ (mol number of DMM)/(6 × mol number of $C_6H_{10}O_5$ unit);

MADA: $Y_{MADA} = $ (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	$SnCl_2 \cdot 2H_2O/FeCl_3 \cdot 6H_2O$	403	27.0	0.1
11	$SnCl_2 \cdot 2H_2O/AlCl_3$	403	7.4	6.4
12	$SnCl_2 \cdot 2H_2O/ZnCl_2$	403	14.4	8.4
13	$SnCl_2 \cdot 2H_2O/SbCl_3$	403	27.5	7.1
14	$SnCl_2 \cdot 2H_2O/NiCl_2$	403	36.0	0.7
15	$SnCl_2 \cdot 2H_2O/CoCl_2 \cdot 6H_2O$	403	38.0	0
16	$SnCl_2 \cdot 2H_2O/PbCl_2$	403	0.4	3.3
17	$SnCl_2 \cdot 2H_2O/CrCl_3 \cdot 6H_2O$	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	$SnCl_2 \cdot 2H_2O$	453	11.6	4.5
2	$SnCl_2 \cdot 2H_2O/NaCl$	453	1.0	0.8
3	$SnCl_2 \cdot 2H_2O/KCl$	453	0.8	0.3
4	$SnCl_2 \cdot 2H_2O/MgCl_2 \cdot 6H_2O$	453	1.8	0.4
5	$SnCl_2 \cdot 2H_2O/CaCl_2$	453	1.0	0.3
6	$SnCl_2 \cdot 2H_2O/BaCl_2$	453	6.4	1.9
7	$SnCl_2 \cdot 2H_2O/NH_4Cl$	453	1.4	0.5
8	$SnCl_2 \cdot 2H_2O/CoCl_2 \cdot 6H_2O$	453	9.4	2.6
9	$SnCl_2 \cdot 2H_2O/PbCl_2$	453	9.8	2.8
10	$SnCl_2 \cdot 2H_2O/CrCl_3 \cdot 6H_2O$	453	9.9	4.3
11	$SnCl_2 \cdot 2H_2O/FeCl_3 \cdot 6H_2O$	453	12.7	4.6
12	$SnCl_2 \cdot 2H_2O/AlCl_3 \cdot 6H_2O$	453	15.9	4.4
13	$SnCl_2 \cdot 2H_2O/ZnCl_2$	453	15.0	11.0
14	$SnCl_2 \cdot 2H_2O$	463	21.6	12.2
15	$SnCl_2 \cdot 2H_2O/AlCl_3 \cdot 6H_2$	463	20.8	5.9
16	$SnCl_2 \cdot 2H_2O/SbCl_3$	463	17.6	7.2
17	$SnCl_2 \cdot 2H_2O/ZnCl_2$	463	23.7	13.8
18	$SnCl_2 \cdot 2H_2O/ZnCl_2$[b]	463	27.0	4.0
19	$SnCl_2 \cdot 2H_2O/ZnCl_2$[c]	463	31.2	6.0
20	$SnCl_2 \cdot 2H_2O/ZnCl_2$[d]	463	15.7	11.9
21	$SnCl_2 \cdot 2H_2O/ZnCl_2$[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 $SnCl_2 \cdot 2H_2O/ZnCl_2$ 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