Insights into the Metal Salt Catalyzed 5-Ethoxymethylfurfural Synthesis from Carbohydrates

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Abstract: The use of common metal salts as catalysts for 5-ethoxymethylfurfural (EMF) synthesis from carbohydrate transformation was performed. Initial screening suggested $AlCl_3$ as an efficient catalyst for EMF synthesis (45.0%) from fructose at 140 °C. Interestingly, $CuSO_4$ and $Fe_2(SO_4)_3$ were found to yield comparable EMF at lower temperature of 110 to 120 °C, and high yields of ethyl levulinate (65.4–71.8%) were obtained at 150 °C. However, these sulfate salts were inactive in EMF synthesis from glucose and the major product was ethyl glucoside with around 80% yield, whereas EMF of 15.2% yield could be produced from glucose using $CrCl_3$. The conversion of sucrose followed the accumulation of the reaction pathways of fructose and glucose, and a moderate yield of EMF could be achieved.

Keywords: carbohydrate; 5-ethoxymethylfurfural; catalytic conversion; metal salt; Lewis acid

1. Introduction

Biomass is abundant available and renewable, which has the potential to displace steadily depleting fossil resources for the sustainable supply of fuels and chemicals in the future, especially through the transformation of biomass-derived carbohydrates [1,2]. 5-Ethoxymethylfurfural (EMF) is such a promising carbohydrate-based liquid chemical, and it has received considerable attention purporting its potential use as a transportation fuel [3]. This is because EMF has a relatively high energy density of 8.7 kWh L^{-1}, which is nearly as good as regular gasoline (8.8 kWh L^{-1}) and diesel fuel (9.7 kWh L^{-1}), and apparently higher than widely concerned bioethanol (6.1 kWh L^{-1}) [4,5]. Also, EMF has been tested as a blending component of diesel fuel, giving satisfied results in terms of engine performance, accompanied by a significant reduction of soot and SO_x emissions [6].

In recent years, research on the transformation of carbohydrates to EMF has been reported at an increasing rate. It was revealed that acidic catalyst is crucial to this reaction. Due to its ease of separation from reaction mixture and reusability, much effort using heterogeneous catalyst has been taken to achieve the goal. For example, heteropolyacid [7,8] or its supported nanoparticles [9–13], acid-modified silica mesoporous materials [14,15], graphene oxide [16], and magnetic solid acid catalysts [11,17,18] were found to be efficient in the synthesis of EMF from fructose or fructose-based carbohydrates. By contrast, the transformation of glucose to EMF is much difficult owing to the demand of isomerization into fructose firstly, and the above developed catalysts had low reactivity. Presently, two combined catalyst systems consisting of zeolite and Amberlyst exhibited good catalytic activity for EMF synthesis from glucose [19,20]. Although significant advances have been made from persistent research, obstacles of using the heterogeneous catalysts include the complex preparation of the catalyst,

expensive catalyst cost, and/or limited substrate adaptability. In this context, the production of EMF from carbohydrates with better acceptance at an industrial scale still presents challenges.

Previously, several admirable findings on the catalytic transformation of glucose to 5-hydroxymethylfurfural (HMF) or other chemicals were presented by using metal salts such as $CrCl_2$ [21], $AlCl_3$ [22], and $Al_2(SO_4)_3$ [23]. These metal salts are earth-abundant and commercially available, providing inexpensive and environmentally benign catalyst sources for carbohydrate conversion. It showed that the metal salts with Lewis acidity were effective for isomerization of glucose into fructose to achieve high yield of products. Recently, $AlCl_3$ was developed as an efficient catalyst for the synthesis of EMF from glucose and fructose [24,25]. To better understand the catalytic mechanism of metal salts and find more potential catalyst systems for the selective conversion of carbohydrates to EMF, further studies are required. Herein, the use of a wide range of common metal salts as catalysts for the synthesis of EMF from fructose in ethanol medium was initially evaluated. The study was further extended to glucose and sucrose to get mechanistic insights of the metal salt catalyzed conversion of carbohydrates.

2. Results and Discussion

2.1. Conversion of Fructose in Ethanol Medium over Various Metal Salts

A series of metal salts as catalysts for the conversion of fructose in ethanol medium were tested at 140 °C for 10 h. The liquid-phase products of reaction were identified and quantified using GC and HPLC analysis, and the results are listed in Table 1. A variety of substances were detected after the reaction, namely glucose, fructose, ethyl glucoside (EGO), ethyl fructoside (EFO), HMF, EMF, and ethyl levulinate (EL). Factually, ethyl formate can also be generated along with EL in a serial mode from the reaction of the furan derivatives and ethanol [26–28]. However, ethyl formate was not observed in our tests, probably due to no separation of ethyl formate and solvent ethanol for the equipped GC instrument. Consequently, a parallel key product (EL) was quantified to monitor the degradation of EMF. In addition, the carbon balance of fructose conversion was not conserved for all the cases. This could be because of the carbonization of saccharides and/or polymerization of furans to form insoluble solid substances and/or undetected oligomers by GC and HPLC during the reaction (the solution turned to dark-brown or black).

As for various metal salts, the species and distribution of liquid-phase products were markedly different, suggesting that the chemo-selectivity is a clear function of the type of metal salt. It is fact that some Brønsted acidic sites can be generated from the hydrolysis/alcoholysis of the metal ions with crystalliferous water or alcohol in the reaction mixture [23,29], and may be responsible for the reaction. Hence, the pH value of reaction solution was monitored, as included in Table 1. By and large, there was no obvious difference between alkali metal chlorides and no catalyst for the conversion of fructose (Table 1, Entries 1–4). Fructose was mostly converted, but only trace amounts of the target product (EMF) was detected. The main reaction products were EFO and EGO, which are the products of the etherification and isomerization of fructose, respectively [25]. For alkaline earth metal chlorides ($MnCl_2$ and $CoCl_2$), the major product was HMF, while other substances were obtained in relatively few quantities. The pH value in reaction solution of above-mentioned metal salts was high with near neutral or weak acidity. By contrast, several transition metal chlorides ($CuCl_2$, $FeCl_3$, and $CrCl_3$) and the group IIIA metal chloride ($AlCl_3$) showed good catalytic activity in the synthesis of EMF from fructose. The pH value in reaction solution of these metal chlorides was relatively low (1.2–2.0), indicating strong Brønsted acidity.

Further investigations using these metal sulfates as catalysts showed that EMF yield for all tested sulfates ($Al_2(SO_4)_3$, $CuSO_4$, $Fe_2(SO_4)_3$, and $Cr_2(SO_4)_3$) was lower than that for their corresponding chlorides. Especially, $Cr_2(SO_4)_3$ was almost inactive in the synthesis of EMF. EL was a major product for $Al_2(SO_4)_3$, $CuSO_4$, and $Fe_2(SO_4)_3$, which is from the degradation of EMF. The pH value in reaction

solution of the metal sulfates was higher than that of their corresponding chlorides—this also was obvious for $Cr_2(SO_4)_3$.

All above results pointed to the fact that a certain amount of Brønsted acid sites were indispensable for the production of EMF. However, EMF yield was incompletely consistent with the pH value of reaction solution. It suggests that both Lewis and Brønsted acidity of metal salt might affect the formation of EMF.

Table 1. Conversion of fructose in ethanol medium with various metal salts.

| Entry | Catalyst | Conv., % | Yield, % | | | | | | pH of Reaction Solution |
			Glucose	EGO	EFO	HMF	EMF	EL	
1	-	88.5	0.3	28.2	23.2	1.5	0	0.2	6.8
2	LiCl	89.0	0.2	27.0	26.5	5.5	0.1	0	7.1
3	KCl	79.0	0.5	29.1	34.2	3.3	0.2	0	5.4
4	NaCl	89.9	0.1	24.0	29.1	1.9	0	0	6.5
5	$MgCl_2$	87.3	0.6	2.5	17.8	32.8	5.3	0	5.5
6	$CaCl_2$	74.3	0	9.9	0	16.0	0.9	0	5.3
7	$MnCl_2$	70.3	1.0	5.2	0	22.8	2.5	0	5.3
8	$CoCl_2$	69.9	1.0	6.3	0	16.7	2.7	0	5.6
9	$ZnCl_2$	89.5	1.1	2.2	0	1.0	0	0	6.1
10	$AlCl_3$	99.9	0	0.9	0	4.8	45.0	8.3	1.2
11	$CuCl_2$	98.9	0.5	0.9	0	0.4	34.7	39.0	1.8
12	$FeCl_3$	99.7	4.9	1.9	0	25.1	24.7	2.6	1.8
13	$CrCl_3$	99.6	0.7	1.4	1.3	7.3	36.9	5.8	2.0
14	$Al_2(SO_4)_3$	99.4	0	0.5	0	0.1	20.8	27.2	2.9
15	$CuSO_4$	100	0	0.4	0	0.1	14.7	53.6	2.5
16	$Fe_2(SO_4)_3$	100	0	0	0	0.3	18.2	56.8	2.5
17	$Cr_2(SO_4)_3$	97.1	1.6	22.1	16.1	6.5	0.5	0.6	4.1

Reaction conditions: 0.2 mol/L fructose in ethanol; metal salt dosage of 0.02 mol/L (based on metal ion); temperature of 140 °C; time of 10 h.

It is a fact that the formation of EMF is sensitive to reaction temperature. Figure 1 presents the effect of temperature, ranging from 100 to 150 °C, on the conversion of fructose to EMF. It found that the influence rule of temperature on the formation of EMF was obvious different between metal chlorides and sulfates. In large, for the investigated metal chlorides, there was a remarkable enhance in EMF yield with increasing temperature from 100 to 140 °C. In the case of the metal sulfates except $Cr_2(SO_4)_3$, the formation of EMF grew when the temperature increased from 100 to 120 °C. Then it was observed sharply to decline over 120 °C, and the production of EL was favored. It follows that the required operating conditions in the synthesis of EMF for metal sulfates were milder than that for metal chlorides. Moreover, for $CuSO_4$ and $Fe_2(SO_4)_3$, the optimum yield of EMF was visibly higher than that for their corresponding chlorides. This was indicative of the importance of anions in the conversion of fructose to EMF catalyzed by metal salts.

Based on the above findings, possible reaction pathways for the conversion of fructose in ethanol medium over metal salts are summarized in Scheme 1. The synthesis of EMF from fructose mainly combined with the dehydration of fructose to HMF and the etherification of HMF to EMF. Another possible pathway is that fructose firstly reacted with ethanol by etherification reaction forming EFO, which is then dehydrated to EMF. EMF can be converted to EL when elevating reaction temperature [30]. On the other hand, to a certain extent, some metal salts were found to facilitate the isomerization of fructose into glucose, which is readily etherified with ethanol to form stabilized EGO [25].
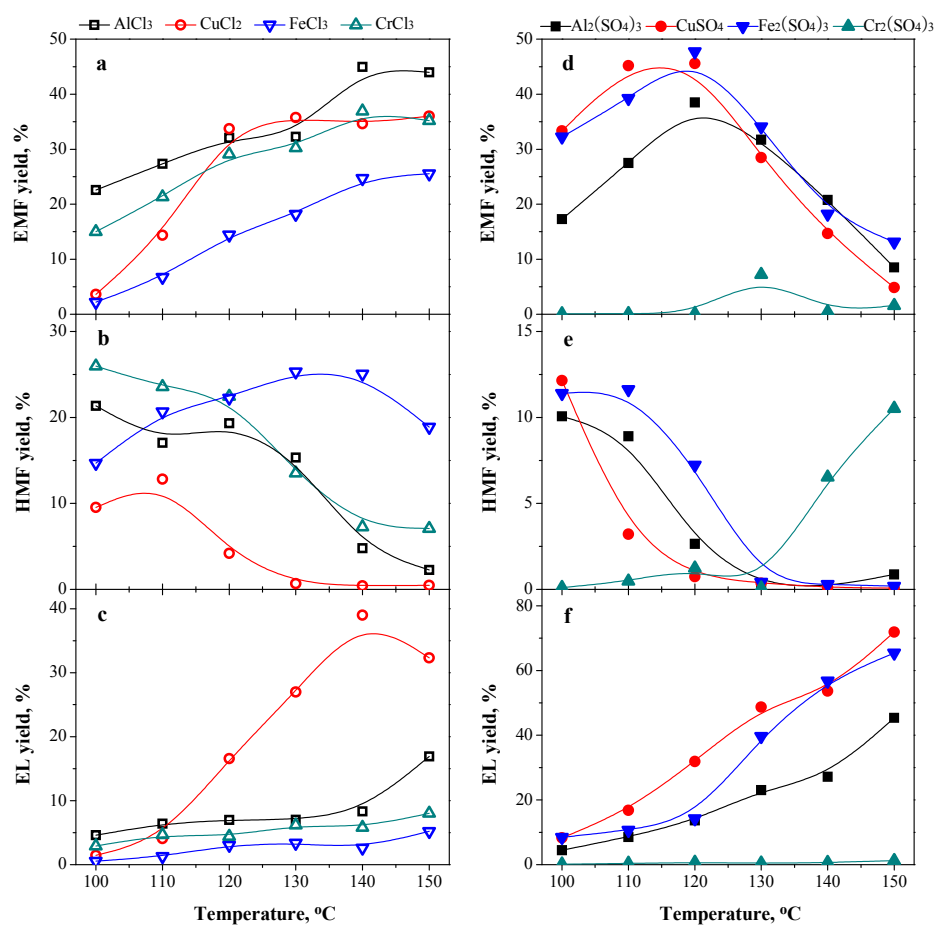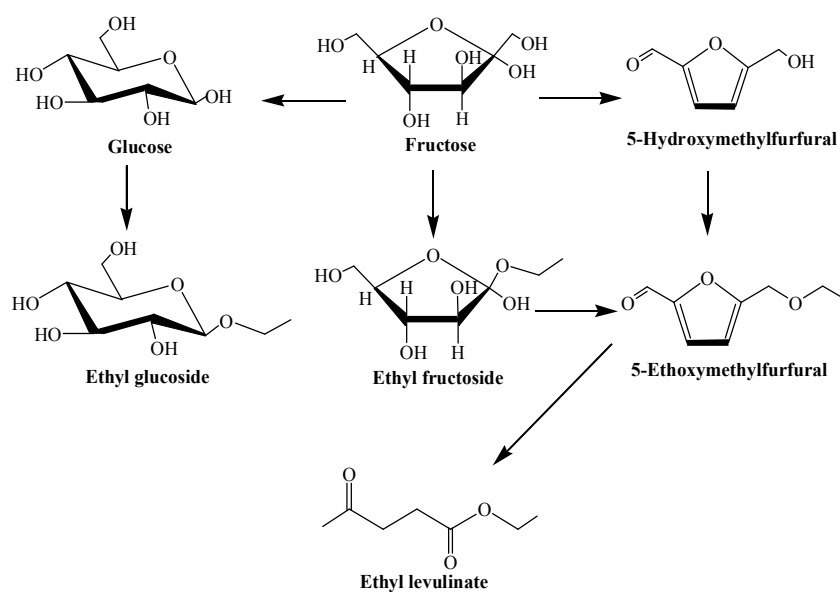
Figure 1. Effect of reaction temperature on the conversion of fructose in ethanol medium over various metal salts. (**a**) EMF yield for metal chloride catalysts; (**b**) HMF yield for metal chloride catalysts; (**c**) EL yield for metal chloride catalysts; (**d**) EMF yield for metal sulfate catalysts; (**e**) HMF yield for metal sulfate catalysts; (**f**) EL yield for metal sulfate catalysts. Reaction conditions: 0.2 mol/L fructose in ethanol; metal salt dosage of 0.02 mol/L; reaction time of 10 h.

Scheme 1. Reaction pathways for the conversion of fructose in ethanol medium over metal salts.

2.2. Synthesis of EMF from Other Saccharides Catalyzed by Specific Metal Salts

Although EMF has obtained better yield from fructose, it would be attractive to employ cheap and abundant glucose/sucrose as the starting material. Figure 2 presents the results of the conversion of glucose catalyzed by several specific metal salts. Glucose was found to react readily with ethanol in the presence of metal salts to form EGO. For the metal chlorides such as $AlCl_3$ and $CrCl_3$, EMF could be produced in the yields of 11.2% to 15.2%, however, the yields were significantly lower than those from fructose. The yields of EGO were between 42.6% and 51.8% with nearly 100% glucose conversions. These findings lead to the conclusions that partial isomerization of glucose to fructose occurred in the presence of metal chlorides, and EGO was formed preferentially from glucose transformation and fairly stable in the reaction system. As a result from Figure 1, the examined metal sulfates except $Cr_2(SO_4)_3$ were quite efficient in the conversion of fructose to EMF at 120 °C. However, when using glucose instead of fructose as substrate under the same operating conditions, hardly any EMF was formed although glucose was almost completely converted. The major product was EGO with the yield of around 80%. Increasing reaction temperature to 140 °C, the results of the reaction were not fundamentally changed. It follows that metal sulfates did not work for the isomerization of glucose to fructose. The above conclusions were further confirmed when sucrose was used as a substrate, as shown in Figure 3.

In the case of all tests with various metal salts and temperatures, the EMF yield was in good agreement with the predicted yield of EMF that was based on the results of fructose and glucose as substrate, respectively (Figure 4). The conversion of sucrose followed the accumulation of the reaction pathways of fructose and glucose and a moderate yield of EMF could be achieved.
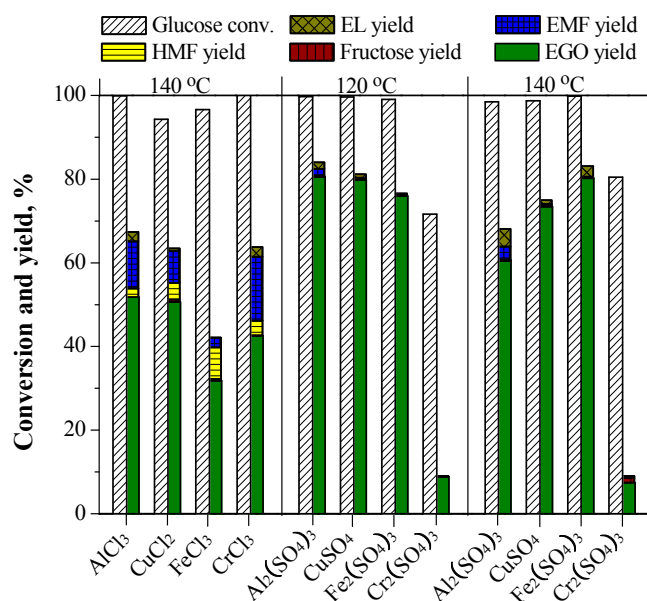

Figure 2. Conversion of glucose in ethanol medium with several specific metal salts. Reaction conditions: 0.2 mol/L glucose in ethanol; metal salt dosage of 0.02 mol/L; time of 10 h.
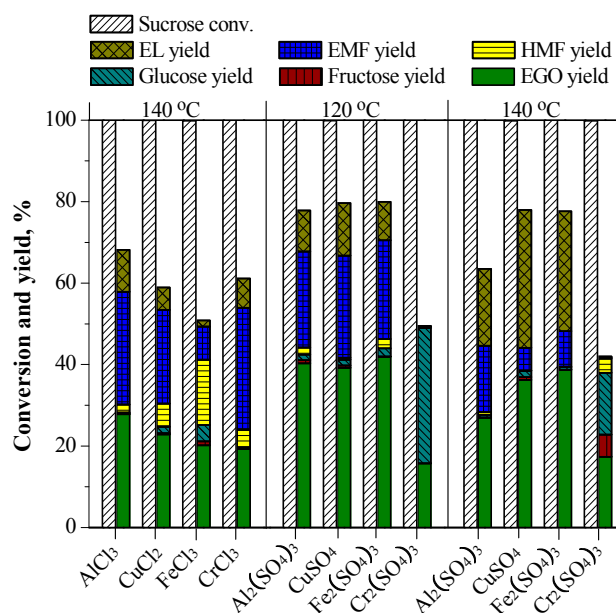
Figure 3. Conversion of sucrose in ethanol medium with several specific metal salts. Reaction conditions: 0.2 mol/L sucrose in ethanol; metal salt dosage of 0.02 mol/L; time of 10 h.
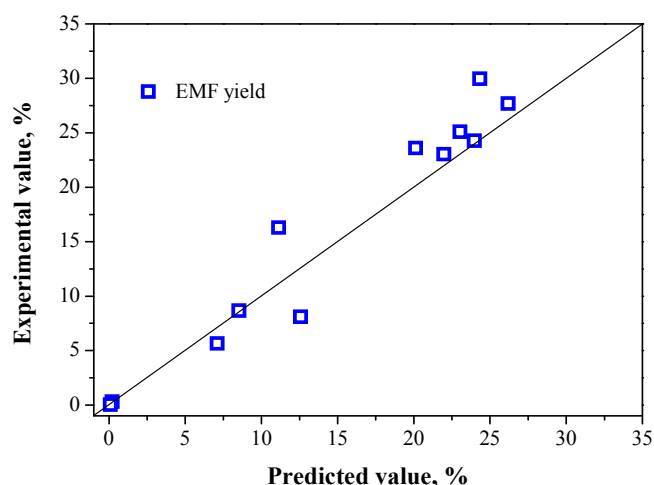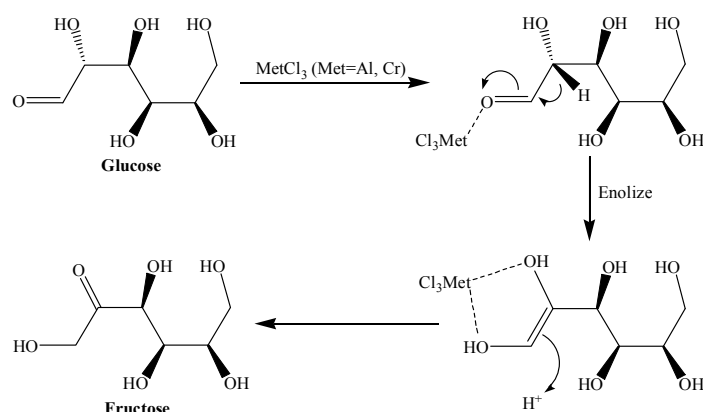

Figure 4. Relationship between the experimental and predicted EMF yield from the conversion of sucrose in ethanol medium over various metal salts. Predicted EMF yield from sucrose = (EMF yield from fructose + EMF yield from glucose)/2.

Obviously, certain metal chlorides such as $AlCl_3$ and $CrCl_3$ were active in the isomerization of glucose to fructose, and the previous experimental evidences supported a 1,2-hydride-shift as a major contributor in this process [21,31,32]. As illustrated in Scheme 2, the metal chloride in the solution approaches the carbonyl group of glucose and affects the electronic cloud density of the carbonyl group by the unoccupied orbits of metal ion. The hemiacetal portion of glucose forms an enolate anion complex with a metal ion that leads to isomerization of glucose to fructose.

Scheme 2. Mechanism of glucose isomerization to fructose over metal chlorides.

3. Materials and Methods

3.1. Materials

LiCl, KCl, NaCl, $MgCl_2$, $CaCl_2$, $MnCl_2$, $CoCl_2$, $ZnCl_2$, $AlCl_3$, $CuCl_2$, $FeCl_3$, $CrCl_3$, $Al_2(SO_4)_3$, $CuSO_4$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, glucose, fructose, sucrose, HMF, and EL were purchased from Aladdin Reagent (Shanghai, China). EMF was obtained from Sigma-Aldrich (Shanghai, China). EGO and EFO were supplied by Chemsynlab Pharmaceutical Science & Technology Co., Ltd. (Beijing, China). Ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The above reagent and chemicals were all of analytical grade and used without further purification or treatment.

3.2. General Reaction Procedure

The reaction of carbohydrates with ethanol were carried out in a 50 mL cylindrical stainless steel pressurized reactor with an oil-bath heating and magnetic stirrer. The typical procedure of the synthesis of EMF from fructose is described as follows: 1.09 g fructose (0.2 mol/L working concentration) and 30 mL ethanol solution contains metal salt (0.02 mol/L working concentration) were loaded into the reactor. After the reactor was sealed, the reaction was carried out at a set temperature and continuously stirred at 800 rpm with a magnetic stirrer. Zero time was taken as soon as the reaction vessel was put into the oil bath. After the desired reaction time, the reactor was quickly removed from the oil bath and placed into cool water to quench the reaction. Then, the reaction mixture was diluted and filtered with a 0.22 μm syringe filter. Finally, the obtained mixture was analyzed by high-performance liquid chromatography (HPLC) and gas chromatography (GC) analysis, respectively.

3.3. Analytical Methods

Quantitative analyses of EMF, HMF, fructose, glucose, sucrose, EGO, and EFO were performed by a Shimadzu HPLC (LC-10AVP). A Copsil C18 column (250 × 4.6 mm) with a UV detector at the wavelength of 280 nm was employed to detect the EMF and HMF. The mobile phase was composed of methanol and deionized water at a volume ratio of 1:1 with a flow rate of 1.0 mL/min. For the analysis of fructose, glucose, sucrose, EGO, and EFO, a Copsil NH_2 column (250 × 4.6 mm) with a refractive index detector was used with a solution of acetonitrile and deionized water at the volume ratio of 7:3 with a flow rate of 1.0 mL/min as the mobile phase. The temperature of the above columns was maintained at 30 °C. The amount of EL was quantitatively analyzed by GC on an Agilent 6890 instrument equipped with a DB-5 capillary column (30.0 m × 320 μm × 0.25 μm) and a flame-ionization detector. The following operating conditions were used in the analysis: the carrier gas was N_2 with a flow rate of 1.0 mL/min, the injection port temperature was 250 °C, the oven temperature was programmed from 60 to 200 °C at a heating rate of 20 °C/min, and the detector temperature was 250 °C. The amounts of detected substances were calculated based on external

standard curves constructed with their authentic standards. Substrate conversion was defined as the ratio of the moles of substrate converted to the moles of substrate loaded in the feed. The yields of products were defined as the ratio of the moles of products obtained to the moles of substrate loaded in the feed.

The pH value of the reaction solution with metal salt was measured at ambient temperature using a model PHS-3C pH meter (Leici Analytical Instrument Factory, Shanghai, China) calibrated with standard buffer solutions.

4. Conclusions

The species and distribution of products from carbohydrate conversion in ethanol medium were clearly different in the presence of various metal salts. Both Lewis and Brønsted acidity of metal salts affect the formation of EMF. $AlCl_3$ showed good catalytic activity in the synthesis of EMF from fructose at 140 °C. $CuSO_4$ and $Fe_2(SO_4)_3$ were found to yield comparable EMF at lower temperatures of 110 to 120 °C, and EL formation was favored over 120 °C. However, these sulfate salts were inert for EMF synthesis from glucose, and the major reaction product was EGO. $AlCl_3$ and $CrCl_3$ were effective in the isomerization of glucose to fructose resulting in EMF yields of 11.2 to 15.2% from glucose. The conversion of sucrose followed the accumulation of the reaction pathways of fructose and glucose, and a moderate yield of EMF could be achieved. This work provides insights for the metal salt catalysis mechanism of selective synthesis of biofuel components from biorenewable carbohydrates in ethanol medium.

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Conflicts of Interest: The authors declare no conflict of interest.

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