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Microwave-assisted rapid conversion of carbohydrates into 5-hydroxymethylfurfural by ScCl₃ in ionic liquids



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ABSTRACT

In this study, synthesis of HMF from carbohydrates was carried out in ionic liquids 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) catalyzed by ScCl₃ under microwave irradiation. Under the optimal reaction conditions, HMF was obtained in a high yield of 73.4% in 2 mins with the microwave power at 400 W. Compared with the conventional oil-bath heating manner, the use of microwave irradiation not only reduced reaction times from hours to minutes, but also improved HMF yield. This catalytic system could be reused several times without losing its catalytic activity. This efficient catalytic system will generate a promising application strategy for biomass transformation.

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1. Introduction

With the diminishing of fossil fuel reserves, there is a growing interest in the development of alternative sources for energy and chemicals. Renewable biomass, in particular carbohydrates, has been widely regarded as a promising alternative to fossil resources to supply fuels and chemicals.^{1–3} Recently, much effort has been devoted to develop new catalytic routes for the conversion of carbohydrates into valuable chemicals.⁴ Among the various bio-based chemicals, 5-hydroxymethylfurfural (HMF), the acid-catalyzed dehydration product of C6-based carbohydrates, is considered to be one of top building-block chemicals.⁵ HMF can be used as a versatile and key precursor for the synthesis of pharmaceuticals, furan based polymers, and fine chemicals.^{6,7} In recent years, synthesis of HMF has been extensively studied. Generally, fructose is the preferable feedstock for the synthesis of HMF with high efficiency and selectivity. However, the large-scale synthesis of HMF from fructose is limited due to the high price of fructose. Therefore, it is desirable to use the cheap and renewable glucose based carbohydrates for the synthesis of HMF.

Sucrose is widely present in plants with an estimated annual production of 167 million metric tons.⁸ As the most common disaccharide, sucrose is consisted of glucose and fructose units. Sugarcane and sugar beet are the two main sugar crops resource for the industrial production of sucrose. Compared with the price of fructose and glucose, the price of sucrose is relative lower. Therefore, sucrose shows a great potential in the large-scale synthesis of HMF.9 To date, there were some reports on the synthesis of HMF from sucrose. Synthesis of HMF from carbohydrates was usually carried out in water, polar organic solvents, and biphasic water-organic systems.¹⁰ Although a high HMF yield of HMF was usually obtained from fructose, these systems were not very effective for the conversion of glucose into HMF. Recently, ionic liquids (ILs) have been widely used as convenient and popular solvents for many chemical reactions, due to their excellent properties such as negligible vapor pressure, nonflammability, and high thermostability.¹¹ Synthesis of HMF from sucrose was reported to be effective in ILs with metallic chlorides as a catalyst.^{12,13} Recently, Wang et al.¹⁴ developed an efficient method for the synthesis of HMF from sucrose with a yield of 87% using CrCl₃ as a catalyst and NH₄Br as a co-catalyst. Although a good result was achieved, the high toxicity of CrCl₃ inevitably resulted in a risk of the contamination of the final product HMF and the environment.

In recent years, the use of microwave irradiation (MI) has been widely applied in many fields such as organic chemistry, medical chemistry, and material synthesis.¹⁵ One of the most important advantages in the use of MI is that MI always improves the reaction rate, reducing the reaction time from hours down to minutes. In some cases, the 'microwave effect' also improves the reaction selectivity. It is well-known that developing more environmentally friendly catalytic system is still remained an issue of scientific interest and industrial significance. Some of the rare earth element



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Scheme 1. Conversion of sucrose into HMF catalyzed by ScCl₃ in ILs under microwave irradiation.

based compounds are believed to be non-toxic and are widely utilized for the replacement of toxic heavy metals in technological applications.¹⁶ Herein, synthesis of HMF has been developed in 1-butyl-3-methylimidazole chloride ([Bmim]Cl) catalyzed by scandium(III) chloride (ScCl₃) under microwave irradiation (Scheme 1). This new catalytic system was proved to be effective in the synthesis of HMF with a good yield in a few minutes.

2. Experimental section

2.1. Materials and instruments

1-Butyl-3-methylimidazole chloride ([Bmim]Cl) was synthesized according to the known procedures.¹⁷ Glucose was purchased from ABCR GmbH & Co. (Karlsruhe, Germany). Fructose was purchased from Sanland-Chem International Inc. (Xiamen, China). Sucrose and ScCl₃·6H₂O were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA). All other reagents and solvents were obtained from commercial suppliers (Wuhan Guoyao Chemical Reagent Co., Ltd).

WBFY-205 microwave reactor was purchased from Gongyi City Yuhua Instrument Co. Ltd (Gongyi, China).

2.2. Synthesis of HMF from sucrose

In a typical procedure, sucrose (100 mg) was firstly added into [Bmim]Cl (2.0 g). Then the mixture was violently stirred at 100 °C with a magnetic stirrer until a clear solution was formed. After the dissolution of sucrose in [Bmim]Cl, ScCl₃ (10 mol %) was added into the above solution. Then the reaction mixture in a 10 mL batch reaction vessel sealed with a cap was transformed into a WBFY-205 microwave reactor, and the reaction was carried out under a microwave irradiation at 400 W. At the desired reaction time, samples were withdrawn from the reaction mixture (recorded as M_1), which were then diluted with distilled water to give a crude solution. Then the solution was centrifuged at 12,000 rpm for 5 min to precipitate the insoluble materials, and the upper solution was analyzed by a HPLC method (recorded as V_1).

2.3. Quantification procedure for HMF

HMF was analyzed by external standard calibration curve method, which was carried out on VARIAN ProStar 210 HPLC system. Samples were separated by a reversed-phase C18 column $(200 \times 4.6 \text{ mm})$ at 30 °C. The mobile phase was consisted of acetonitrile and 0.1 wt% acetic acid aqueous solution (v/v 15:85) at 1.0 mL/min, and HMF was detected at a wavelength of 280 nm. The content of HMF in solution was calculated directly by interpolation from calibration curves with a coefficient of 0.999, then we can calculate the actual weight of HMF in the reaction system, based on the volume of the samples. The yield of HMF was calculated as the ratio of actual mass of HMF to the theoretical mass of HMF, which was based on the substrate and the reaction equation.

HMF yield was calculated according to the following equation:

 $M_{\rm T}$ (mg) = HMF concentration (mg/mL) × V_1 × (M_0/M_1)

HMF yield (percent) =
$$M_T$$
/the theoretical weight of HMF (mg) $\times 100\%$

where $M_{\rm T}$ is the mass of HMF in the reaction mixture at a given reaction time (corresponding to the Section 2.2);

HMF concentration (mg/mL) was based on the standard calibration curves.

 M_0 is the total mass of the initial reaction mixture (corresponding to the Section 2.2).

 M_1 is the mass of sample withdrawn from the reaction mixture (corresponding to the Section 2.2).

 V_1 is the volume of the sample after diluted with water for HPLC (corresponding to the Section 2.2).

The theoretical mass of HMF was calculated from the reaction equation of the conversion of carbohydrates into HMF.

For 100 mg of glucose (or fructose) as a substrate, the theoretical mass of HMF was 70 mg.

For 100 mg of glucose (or fructose) as a substrate, the theoretical mass of HMF was 73.6 mg (Scheme 1).

2.4. Recycling of catalyst

At the end of each reaction, the product HMF was extracted using ethyl acetate successively until no HMF was detected by thin layer chromatography (TLC) method. After HMF was completely extracted from the reaction mixture, sucrose was added into the remaining mixture, and otherwise steps were the same as described for the first run.

3. Results and discussion

3.1. Synthesis of HMF from fructose and glucose in [Bmim]Cl catalyzed by ScCl₃·6H₂O

Synthesis of HMF was initially carried out using fructose and glucose as starting materials (Table 1), as sucrose is consisted of glucose and fructose units. Firstly, catalytic dehydration of fructose into HMF was carried out in water (Table 1, entry 1), polar organic solvents (Table 1, entries 2 and 3) and ionic liquids (Table 1, entry 4) at 110 °C with oil-bath heating. HMF was obtained in a low yield of 2.3% when the dehydration reaction was carried out in water (Table 1, entry 1). The bad catalytic performance in water should be attributed to the following two reasons. On the one hand, the solvent waters are released by the dehydration of one molecular fructose into HMF. On the other hand, it is well known that HMF is readily redehydrated into levulinic acid and formic acid in the presence of water.¹⁸

Some polar organic solvents such as DMSO were reported to be a good reaction medium for the synthesis of HMF from fructose.¹⁹ When the dehydration of fructose was carried out in DMSO and DMF with ScCl₃ as catalyst, HMF yields were reached in 85.4%

Ta	bl	le	1

Dehydration of glucose and fructose into HMF under various conditions^a

Entry	y Substrate	Solvents	Reaction conditions	Time (min)	Yields (%)
1	Fructose	Water	110 °C, Oil-heating	120	2.3
2	Fructose	DMSO	110 °C, Oil-heating	120	85.4
3	Fructose	DMF	110 °C, Oil-heating	120	80.7
4	Fructose	[Bmim]Cl	110 °C, Oil-heating	120	93.3
5 ^b	Fructose	[Bmim]Cl	110 °C, Oil-heating	120	30.1
6	Glucose	[Bmim]Cl	110 °C, Oil-heating	120	32.3
7 ^b	Glucose	[Bmim]Cl	110 °C, Oil-heating	120	5.0
8	Glucose	[Bmim]Cl	MI, 400 W	2	55.4
9	Fructose	[Bmim]Cl	MI, 400 W	2	94.7
10	Glucose	[Bmim]Cl	180 °C, Oil-heating	10	22.1
11	Glucose	[Bmim]Cl	180 °C, Oil-heating	15	35.6
12	Glucose	[Bmim]Cl	180 °C, Oil-heating	20	28.7

 a Reaction conditions: To 2.0 g of solvent were added 100 mg of fructose or glucose and 10 mol % ScCl₃, then the reaction was carried out at 110 °C with oilheating or under MI at 400 W for the desired time.

^b The reaction was done under otherwise identical conditions in the absence of catalyst.

and 80.7% for DMSO and DMF, respectively (Table 1, entries 2 and 3). Although high HMF yields were achieved in polar organic solvents, these processes suffered some serious drawbacks such as tedious procedures for the separation of HMF from the reaction mixture, and the risk of the volatile organic solvents to our environment. Recently, ILs have been extensively used as green solvents in biorefinery, as ILs have a good ability to dissolve carbohydrates and catalysts, leading the catalyst and carbohydrates to be contacted with each other effectively. In addition, some ILs such as [Bmim]Cl were not miscible with lower boiling point organic solvents such as ethyl acetate, therefore the product HMF can be separated from the ILs system via extraction method with ethyl acetate. As expected, HMF was obtained from fructose in a high yield of 93.3% in [Bmim]Cl at 110 °C for 2 h in the presence of ScCl₃ (Table 1, entry 4). With the in-depth study of ILs, it was reported that the hydrogen at C2 position in the imidazole ring showed acidic property.²⁰ HMF was obtained in a yield around 40%, when fructose was subjected to be heated at 100 °C in 1-ethyl-3methylimidazole chloride ([Emim]Cl) for 3 h in the absence of catalyst.²¹ Dehydration of fructose into HMF was also carried out at 110 °C in [Bmim]Cl without ScCl₃ for 2 h, and HMF was obtained in a yield of 30.1% (Table 1, entry 5). The results verified that [Bmim]Cl was positive for the conversion of fructose into HMF in comparison with other solvents, but the catalyst ScCl₃ played a key role in achieving a high HMF yield.

Secondly, catalytic conversion of glucose into HMF was also carried out in [Bmim]Cl at 110 °C with ScCl₃ as catalyst, and a moderate yield of 32.3% was obtained (Table 1, entry 6). It indicated that the efficiency of glucose dehydration into HMF was much lower than that of fructose dehydration. It is generally accepted that two successive steps are required during the conversion of glucose into HMF, namely the isomerization of glucose into fructose and the followed dehydration of fructose into HMF. As high HMF yield was obtained from fructose, the relative low HMF yield from glucose should be attributed to the low selectivity of the isomerization of glucose into fructose. As a control experiment, the dehydration of glucose was also carried out at 110 °C in the absence of SeCl₃ for 120 min, and HMF was only obtained in a low yield of 5% (Table 1, entry 7). The results clearly indicated that SeCl₃ played a crucial role in the dehydration of glucose into HMF.

Recently, the use of microwave irradiation (MI) in chemical reaction has attracted great interest by chemists. When the dehydration of glucose was carried out under MI at 400 W, HMF yield was largely increased from 32.3% to 55.4% in 2 min (Table 1, entries 8 vs 6). In parallel, a high HMF yield in 94.7% was also obtained from fructose under the same MI reaction conditions used for glucose (Table 1, entry 9).

The temperature of the reaction system under MI at 400 W for 2 min was detected to be 180 °C. Therefore, in order to exclude the effect of reaction temperature on the yield of HMF, the dehydration of glucose into HMF catalyzed by ScCl₃ was carried out at 180 °C using an oil-bath. As shown in Table 1 (entries 10-12), the maximum HMF yield was obtained in 35.6% at 15 min. Although the high temperature with an oil-bath heating benefited the dehydration process, resulting in higher HMF in a short time (Table 1, entries 6 vs 8), the result was inferior to that under MI (Table 1, entries 8 vs 11). Compared the dehydration results under MI with those using conversional oil-bath heating, the main reason should be attributed to the 'microwave effects'.²² In fact MI produces efficient internal heating or in-core volumetric effect heating by direct coupling of microwave energy with the molecules that may be the solvents, reagents, or catalysts presented in the reaction mixture. Therefore, it circumvented some conventional oil-bath heating drawbacks such as partly overheating. In addition, it is also possible to lower activation energy or increase the pre-exponential factor in Arrhenius law due to orientation effect of polar species in an electromagnetic field, leading to a more effective and clean chemical reaction.

3.2. Microwave-assisted rapid conversion of sucrose into HMF

Glycosidic bonds are usually weakened by H⁺. However, glycosidic bonds were also weakened by Lewis acids though their coordination with oxygen atoms in the glycosidic bonds, which was then attacked by H₂O to release monosaccharides.²³ The good results of the dehydration of glucose and fructose into HMF inspired us to carry out the synthesis of HMF directly from sucrose, which avoids the tedious hydrolysis and separation processes. The dehydration of sucrose into HMF was carried out under MI at 400 W, and the time course of HMF yield was recorded (Fig. 1). The yield of HMF was slowly increased during the first min, and then rapidly increased from 5.1% to 73.4% during 1 to 2.5 min. It indicated that hydrolysis of sucrose was the first step for the one-pot conversion of sucrose into HMF, and the hydrolysis step was mainly performed in the first min. Further prolonged the reaction time from 2.5 to 5 min, the yield of HMF was gradually decreased from 73.4% to 53.2%. The results indicated that HMF was not very stable under our reaction conditions. After the completion of the reaction, some humins were also observed, when the reaction mixture was diluted



Figure 1. Time course of HMF yield during the dehydration of sucrose into HMF. Reaction conditions: To 2.0 g of [Bmim]Cl were added 100 mg of sucrose and 10 mol % ScCl₃, then the reaction was carried out under MI at 400 W.

Entry	Conditions	Solvent	Time (min)	HMF yields (%)	Ref.
1 ^a	MI 240 W, 10 mol % ScCl ₃	[Bmim]Cl	8	67.7	This work
2 ^a	MI 400 W, 10 mol % ScCl ₃	[Bmim]Cl	2.5	73.4	This work
3 ^a	MI 640 W, 10 mol % ScCl ₃	[Bmim]Cl	1.5	61.3	This work
4 ^a	MI 400 W, 5 mol % ScCl ₃	[Bmim]Cl	6	70.3	This work
5 ^a	MI 400 W, 2.5 mol % ScCl ₃	[Bmim]Cl	9	71.5	This work
6	CrCl ₂ , 100 °C	Choline chloride	60	43	Ref. 27
7	CrCl ₃ , MI, 100 °C	[Bmim]Cl	5	76	Ref. 28
8	GeCl ₄ , 120 °C	[Bmim]Cl	30	55.4	Ref. 29
9	SnCl ₄ , 100 °C	[EMIM][BF ₄]	180	65.0	Ref. 30
10	FeCl ₃ -Et ₄ NBr, 90 °C	DMF	180	38.0	Ref. 31
11	AlCl ₃ , MI, 140 °C	DMSO	5	42.5	Ref. 32

Table 2
The results of microwave-assisted catalytic conversion of sucrose into HMF under different conditions

^a Reaction conditions: To 2.0 g of [Bmim]Cl were added 100 mg of sucrose and a set amount of ScCl₃, then the reaction was carried out under MI at a set power for the desired time.

with water. The humins were likely formed through the polymerization and cross-polymerization of HMF.²⁴

Taking the above results into accounts, the combination effect of [Bmim]Cl, ScCl₃, and MI generates the magic power for catalytic conversion of sucrose into HMF. Firstly, complete dissolution of sucrose in [Bmim]Cl makes the sucrose chains accessible to be contacted with catalyst for the chemical transformation. Secondly, [Bmim]Cl has excellent dielectric properties for the transformation of microwave into heat, that was the mentioned 'microwave effects'. More importantly, ScCl₃ would form a series of complex ions such as $[ScCl_4]^-$ and $[ScCl_5]^{2-}$ in [Bmim]Cl in a manner similar to $LnCl_3$,²⁵ due to the high coordination ability of element Sc.²⁶ These complexes played an important role in the isomerization of glucose into fructose, followed by dehydration to produce HMF.

3.3. Microwave-assisted dehydration of sucrose into HMF under various conditions

The effect of MI power on the conversion of sucrose into HMF was further investigated, and the MI power was set at 240, 400, and 640 W, respectively (Table 2, entries 1–3). When the reaction was carried out at 240 W, it required a longer reaction time in 8 min to obtain a maximum HMF yield of 67.7% in comparison with the reaction performed at 400 W (Table 2, entries 1 vs 2). Further increased MI power to 640 W, albeit reduced the reaction time to 1.5 min, the maximum yield of HMF yield was decreased to 61.3% (Table 2, entry 3). Therefore, 400 W was selected as an appropriate MI power to obtain the highest HMF yield of 73.4%.

The effect of catalyst loading on the conversion of sucrose into HMF was also studied. It was found that the catalyst loading had no obvious effect on the maximum HMF yield, and the maximum yields of HMF were 73.4%, 70.3%, and 71.5% for 10, 5, and 2.5 mol % ScCl₃, respectively, (Table 2, entries 2, 4, and 5). But the reaction time for obtaining the maximum HMF yield was decreased with an increase of catalyst loading. The more the catalyst loading was, the higher the dehydration rate was. A higher dehydration rate with an increase in catalyst loading can be attributed to an increase in the availability and number of catalytically active sites.

Our reaction system for the synthesis of HMF from sucrose was compared with other reaction systems catalyzed by other Lewis acid.^{27–32} As demonstrated in Table 2, it can be seen that our reaction system was comparable with some reaction systems, and it was better than some reaction system. The efficiency for the dehydration of sucrose into HMF seems depended on the Lewis acid catalysts, the reaction solvent, the reaction temperature, and the heating manner. It was clearly noted that the reaction time for obtaining a maximum HMF yield under MI was shorter than that



Figure 2. Recycle experiments of ScCl₃/[Bmim]Cl catalytic system.

with an oil-bath heating (Table 2, entries 2, 7, 11 vs 6, and 8–10). It was also observed that ionic liquids were superior to organic solvents for the dehydration of sucrose into HMF (Table 2, entries 1–9 vs 10 and 11). As demonstrated in Table 2, ScCl₃ showed a satisfied catalytic activity as other Lewis acid.

3.4. Catalyst reusability experiment

Finally, the reusability of this novel catalytic system was evaluated. The dehydration of sucrose into HMF at 400 W with 10 mol % ScCl₃ was used as a model reaction. After the completion of the first run, the product HMF was extracted by ethyl acetate successively until no HMF was detected by thin layer chromatography (TLC) method. After HMF was completely extracted, sucrose was then added into the remaining mixture system. The reaction was carried out under the same conditions. These steps were repeated six times, and the reusability results are shown in Figure 2. It was found that there was a slight decrease trend in the HMF yield. As shown in Figure 2, HMF yield was 73.4% in the first run, and it was reduced to 66.8% in the sixth run. In our reuse experiment, the product HMF was extracted by organic solvents from the reaction mixture. Then the fresh sucrose was added into the mixture for the second run. Thus one important reason was that trace amount of ScCl₃ was extracted from the reaction system, leading to a slight decrease in HMF yield. It might also be caused by the combination of byproducts such as humins with the catalyst, leading to decease in the catalytic activity.³³

4. Conclusion

In summary, synthesis of HMF from sucrose has been successfully developed in [Bmim]Cl with ScCl₃ as a catalyst under MI. HMF was obtained in a high yield of 73.4% in a short reaction time of 2.5 min under MI at 400 W. The results indicated that [Bmim]Cl, ScCl₃, and MI showed a synergic effect on the magic power for catalytic conversion of sucrose into HMF. This catalytic system could be reused several times without losing its catalytic activity. Our system should provide a new opportunity for transformation of abundant and inexpensive crop based biomass through a non-fermentative process into biofuels and bio-based products.

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