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Note

Efficient and selective conversion of sucrose to 5-hydroxymethylfurfural promoted by ammonium halides under mild conditions

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ABSTRACT

The highly efficient and selective production of 5-hydroxymethylfurfural (HMF) from sucrose has been achieved in the presence of metal chlorides and ammonium halides under mild conditions. Notably, an 87% yield of HMF from sucrose was obtained with a catalyst system composed of $CrCl_3$ and NH_4Br at 100 °C for 1.0 h in *N,N*-dimethylacetamide (DMAc) solvent. The effect of the reaction temperature and time was investigated in detail, and a possible mechanism for this catalytic process has been proposed. In addition, NH_4Br is an effective promoter in the conversion of glucose and fructose to HMF.

Diminishing fossil fuel reserves, global warming, and the resulting energy security issues have stimulated the search for new renewable energy resources.[1,2] In the chemical industry, abundant biomass resources, including carbohydrates, are being studied as potential renewable carbon sources for liquid fuels and other valuable chemicals.[3–8] In particular, 5-hydroxymethylfurfural (HMF), one of the most important intermediates derived from biomass feedstocks, has gradually become a platform chemical from which a variety of target molecules can be synthesized.[9–12] In recent years, the efficient conversion of sugars into HMF has received a great deal of attention.[13–16] Although fructose has been shown to be the preferred feedstock for a high HMF yield,[17,18] it is clear that generation of ample amounts of HMF will require more inexpensive and abundantly available raw materials, such as glucose and sucrose. Sucrose, a disaccharide consisting of glucose and fructose, is widely present in the plant kingdom. Thus, in addition to glucose, which is derived from starch and cellulose, sucrose is a key low-molecular-weight carbohydrate resource to produce chemicals.[10]

To date, a few investigations on HMF production from sucrose have been reported. Mineral acids,[19,20] solid acids,[21–23] ionic liquids,[24] and metallic compounds[25–28] have been employed as catalysts for the dehydration of sucrose in multiple reaction media, including water, organic solvents, ionic liquids, and biphasic water–organic systems. Chheda et al.[19] studied the conversion of sucrose to HMF using HCl as the catalyst in a biphasic reactor system, and an HMF yield of 50% was achieved. The reactor system was composed of an aqueous phase modified with DMSO and an organic extracting phase consisting of a 7:3 (w/w) MIBK–2-butanol mixture. Takagaki et al.[22] reported that a 54% yield of HMF can be produced from sucrose in a simple one-pot synthesis using a combination of Mg–Al hydrotalcite (HT) and Amberlyst-15. In these reports, the yields of HMF are relatively low. The apparent reason is that only the fructose moiety of sucrose was efficiently converted into HMF, which left most of glucose molecules unreacted.[24] Recently, catalytic systems including metallic halides and ionic liquids were used in the conversion of sucrose, and good results were obtained. Hu et al.[25] found that $SnCl_4$ can efficiently convert sucrose to HMF in 1-ethyl-3-methyl imidazolium tetrafluoroborate ([BMIM]BF_4), and the yield was as high as 65%. Qi et al.[26] studied the production of HMF from sucrose in 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) with $CrCl_3$ as the catalyst, and an HMF yield of 76% was achieved in 5 min with microwave heating at 100 °C. Although promising, these methods depend on the use of expensive ionic liquids as solvents. Therefore, it is important to develop a cost-effective technique that can process both fructose and glucose molecules, thereby making efficient use of carbons in sucrose.

In this paper, a new catalyst system, composed of a metal chloride and an ammonium halide, was employed to form HMF from sucrose under mild conditions. Among the different ammonium halides used as promoters, NH_4Br led to the highest HMF yield from sucrose, which was 87% using $CrCl_3$ as the catalyst.

For the catalytic conversion of sucrose with metal chlorides, $CrCl_3$ was first chosen as the catalyst, and a variety of alkali metal

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Table 1
Dehydration of sucrose with different systems[a]

Entry	Catalyst	Promoter[b]	Yield[c] (%)
1	$CrCl_3$	No	66
2	$CrCl_3$	LiCl	64
3	$CrCl_3$	NaCl	67
4	$CrCl_3$	KCl	63
5	$CrCl_3$	LiBr	77
6	$CrCl_3$	NaBr	79
7	$CrCl_3$	KBr	77
8	$CrCl_3$	NH_4Cl	79
9	$CrCl_3$	NH_4Br	87
10	$CrCl_3$	NH_4I	73
11	$SnCl_4$	NH_4Br	66
12	$SnCl_2$	NH_4Br	48
13	$FeCl_3$	NH_4Br	42
14	no	NH_4Br	40

[a] Reaction conditions: 1.0 g sucrose, 9.5 mol % metal chloride, in 10 mL of DMAc, reaction time 1 h, temperature 100 °C.

[b] The concentration of the promoter was 0.16 M.

[c] The results were obtained by HPLC analysis.

and ammonium halides were used as the promoters. The results are summarized in Table 1. A 66% yield of HMF was obtained with $CrCl_3$ as the catalyst in *N*,*N*-dimethylacetamide (DMAc) (entry 1). When LiCl, NaCl, and KCl were employed as promoters, HMF yields of 64%, 67%, and 63% were obtained, respectively (entries 2–4). These results indicate that alkali metal chlorides do not efficiently promote the conversion of sucrose to HMF. However, when LiBr, NaBr, or KBr were employed as the promoter, the yield of HMF was elevated to 77%, 79%, and 77%, respectively (entries 5–7), which indicates that alkali metal bromides are more efficient promoters than alkali metal chlorides. A variety of ammonium halides were also used as promoters for this process (entries 8–10). To our surprise, the HMF yield was substantially increased (87%—entry 9) when NH_4Br was employed as a promoter. The result for NH_4Cl is also better than those of alkali metal chlorides (entry 8). Similar studies were performed with other metal chloride catalysts (entries 11–13). When $SnCl_4$–NH_4Br was used in the conversion of sucrose, an HMF yield of 66% was achieved (entry 11), which is comparable to results obtained previously.[25] If a metal chloride catalyst is not present, an HMF yield of 40% can still be obtained in the presence of NH_4Br (entry 14).

To explain the good results for NH_4Br, a possible mechanism that is consistent with the data is shown in Figure 1. The conversion of sucrose to HMF involves the following three steps: (1) hydrolysis breaks the glycosidic bond, converting sucrose into glucose and fructose; (2) glucose is isomerized into fructose; (3) fructose is dehydrated to form HMF. As is known, ammonium halides (except NH_4F) formed by the reaction of a strong acid (a hydrogen halide) with a weak base (ammonia). A hydrolysis reaction in which the ammonium ions react with water to yield hydronium ions might occur during the dehydration of the carbohydrate and thereby decrease the pH of the reaction system. Acidic conditions are favorable for the hydrolysis of sucrose and the subsequent conversion of fructose to HMF, because H^+ can contribute to the formation of intermediates I and III. Therefore, NH_4Br is more effective than alkali metal bromides in sucrose conversion. In addition, the halide additive must play two different roles in the conversion of sucrose: serving as a ligand for the catalytic metal center in the chelate complex (intermediate II) and attacking the fructofuranosyl oxocarbenium ion (intermediate IV) to form intermediate V, just like in glucose conversion.[29] Bromide has better coordinating abilities than iodide and better nucleophilicity than chloride, so it is an optimal additive for the conversion of both the glucose and fructose moieties of sucrose. This is the reason why NH_4Br exhibits a better effect than NH_4Cl and NH_4I in the formation of HMF from sucrose (entries 8–10 in Table 1).

To better understand the $CrCl_3$–NH_4Br system, the effects of reaction time on the dehydration of sucrose were investigated

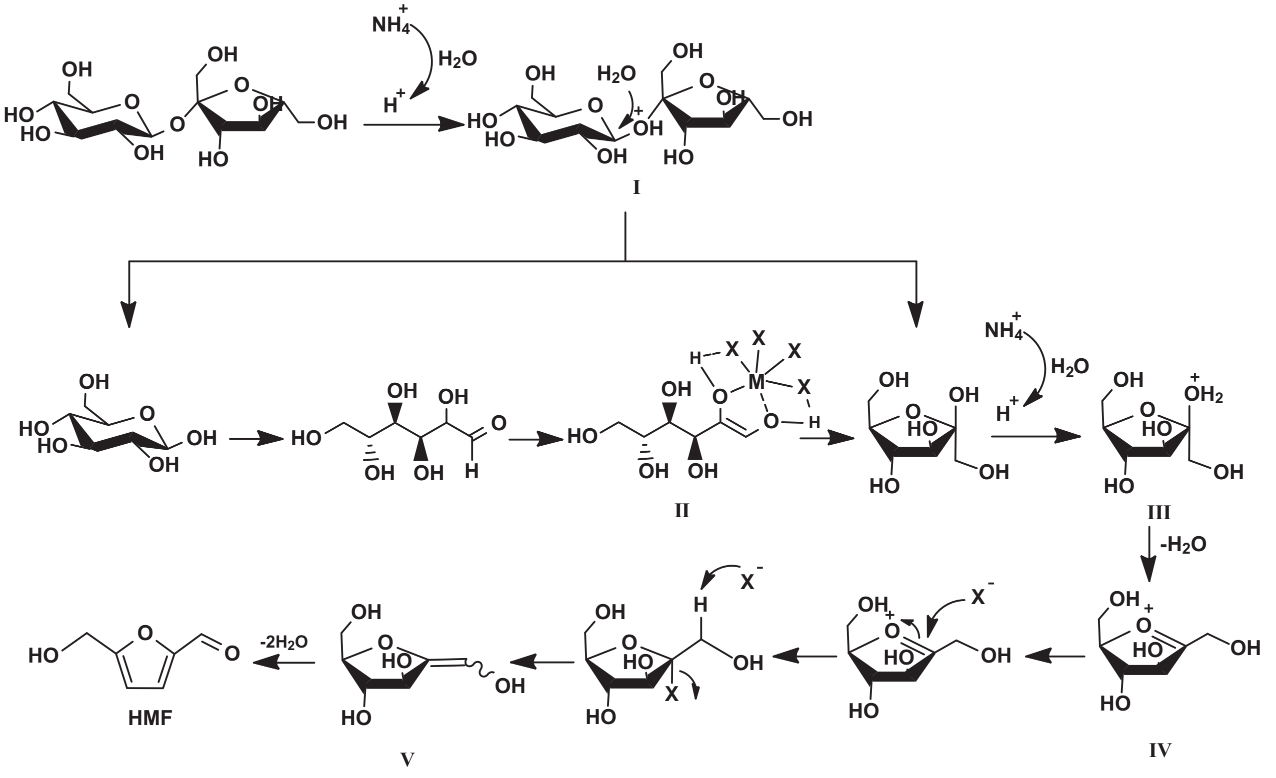

Figure 1. Proposed mechanism for the conversion of sucrose to HMF catalyzed by metal chlorides in the presence of an ammonium halide. (M represents various metal; X^- represents a halide ion).

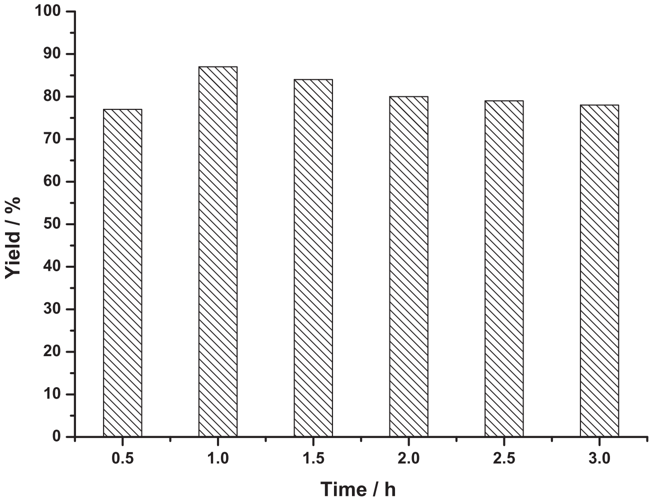

Figure 2. Effect of reaction time on the dehydration of sucrose. (Reaction conditions: 1.0 g sucrose, 9.5 mol % $CrCl_3$, 0.157 g NH_4Br, in 10 mL of DMAc, temperature 100 °C).

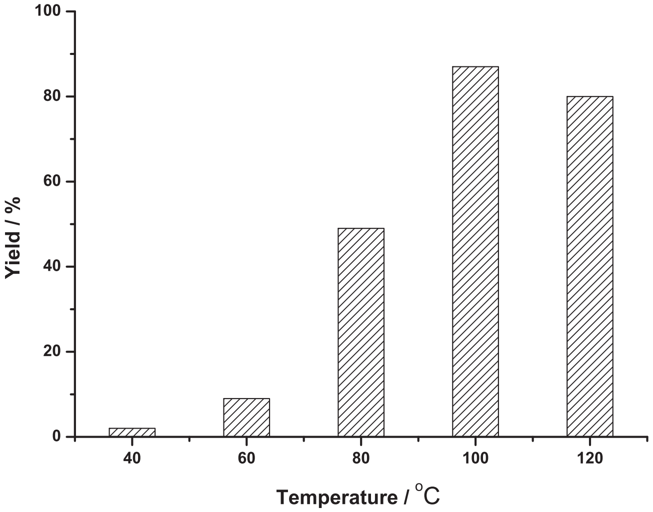

Figure 3. Effect of temperature on the dehydration of sucrose. (Reaction conditions: 1.0 g sucrose, 9.5 mol % $CrCl_3$, 0.157 g NH_4Br, in 10 mL of DMAc, reaction time 1 h).

Table 2
Dehydration of sucrose using different solvents[a]

Entry	Solvent	Yield[b] (%)
1	Water	4
2	Ethanol	13
3	*N*-Methyl-2-pyrrolidone (NMP)	64
4	Dimethylsulfoxide (DMSO)	56
5	Dimethylformamide (DMF)	60
6	Dimethylacetamide (DMAc)	87

[a] Reaction conditions: 1.0 g sucrose, 9.5 mol % $CrCl_3$, 0.157 g NH_4Br, in 10 mL of solvent, reaction time 1 h, temperature 100 °C.

[b] The results were obtained by HPLC analysis.

Table 3
Dehydration of glucose and fructose with different catalyst systems[a]

Entry	Substrate	Catalyst	Promoter[b]	Yield[c] (%)
1	Glucose	$CrCl_3$	No	59
2	Glucose	$CrCl_3$	NH_4Cl	58
3	Glucose	$CrCl_3$	NH_4Br	74
4	Glucose	$CrCl_3$	NH_4I	57
5	Glucose	$SnCl_4$	No	30
6	Glucose	$SnCl_4$	NH_4Br	52
7	Glucose	no	NH_4Br	8
8	Fructose	$SnCl_4$	NH_4Br	73
9	Fructose	$CrCl_3$	NH_4Br	92

[a] Reaction conditions: 1.0 g glucose/fructose, 9.5 mol % metal chloride, in 10 mL of DMAc, reaction time 1 h, temperature 100 °C.

[b] The concentration of the promoter was 0.16 M.

[c] The results were obtained by HPLC analysis.

and the results are shown in Figure 2. The yield of HMF increased when the reaction time increased from 0.5 to 1 h. However, when the reaction time was extended to 1.5 h or longer, the yield of HMF decreased, which indicates that after 1 h, the conversion of HMF to byproducts, such as humins and levulinic acid, is probably more rapid than the generation of HMF. Thus, the optimal reaction time is 1.0 h for this catalyst system.

The effect of temperature on the dehydration of sucrose was also investigated with $CrCl_3$–NH_4Br system and the results are shown in Figure 3. From these results, it can be concluded that for the catalytic dehydration of sucrose, the optimal reaction temperature is 100 °C.

Different solvents, including protic and aprotic ones, were used for the dehydration of sucrose for 1 h at 100 °C (Table 2). Yields of 64%, 56%, 60%, and 87% were obtained with *N*-methyl-2-pyrrolidone, dimethylsulfoxide, dimethylformamide, and dimethylacetamide, respectively. These yields were greatly superior to those for ethanol or water. It can be concluded that aprotic solvents are more suitable for the $CrCl_3$–NH_4Br system, and dimethylacetamide is the most effective.

Furthermore, the reuse of DMAc solvent and $CrCl_3$ has been achieved in the conversion of sucrose. The experimental results showed that the yield of HMF is still high after being recycled four times, which is helpful to decrease the harm of $CrCl_3$ to the environment.

Intrigued by the results for sucrose, the effect of ammonium halides on the dehydration of glucose and fructose was then investigated and the results are summarized in Table 3. For the dehydration of glucose, an HMF yield of 59% was obtained with $CrCl_3$ as the catalyst (entry 1). Then, a series of ammonium halides were tested as promoters for this process. Addition of NH_4Cl or NH_4I to the $CrCl_3$ reaction mixture did not enhance the HMF yield, but using NH_4Br did increase the HMF yield to 74% in DMAc (entries 2–4). These results are in agreement with the halide effect reported by Binder and Raines.[29] That is, the conversion of glucose to HMF is a two-step process: glucose is first isomerized to fructose followed by conversion of the fructose into HMF. Bromide, which offers the optimal balance between coordination ability and nucleophilicity, is more effective as an ionic additive than chloride or iodide. Moreover, NH_4Br also can contribute to the $SnCl_4$ catalyzed conversion of glucose. In combination with $SnCl_4$, NH_4Br greatly increased the yield of HMF up to 52% (entries 5 and 6). A control test was also performed with only NH_4Br and an HMF yield of only 8% was obtained, indicating that NH_4Br has to be combined with a metal chloride to promote the glucose conversion (entry 7). In the dehydration of fructose, the promotion effect of NH_4Br is more significant. For example, $SnCl_4$–NH_4Br and $CrCl_3$–NH_4Br systems produced high HMF yields from fructose, 73% and 92%, respectively (entries 8 and 9). Based on the above results, it can be concluded that both the glucose and fructose moieties of sucrose can be efficiently converted into HMF with metal chloride/NH_4Br systems.

1. Experimental

1.1. Reagents and instruments

Glucose, fructose, sucrose, $CrCl_3·6H_2O$, $SnCl_4·5H_2O$, $SnCl_2·2H_2O$, $FeCl_3·6H_2O$, NH_4Cl, NH_4Br, NH_4I, LiCl, LiBr, NaCl, NaBr, KCl, KBr and DMAc were of analytical grade. A standard sample of HMF was obtained from J&K Co. Ltd. NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. The quantitative analyses of the products were performed on a Waters 1525 HPLC equipped with both UV and refractive index detectors.

1.2. Reaction conditions for the dehydration of sucrose

All the dehydration reaction experiments were performed in a 100 mL flask equipped with magnetic stirring and a condenser. A typical procedure for the dehydration of sucrose is as follows: sucrose (1.0 g, 2.9 mmol), $CrCl_3·6H_2O$ (9.5 mol %), NH_4Br (0.157 g), and 10 mL of DMAc were added into the flask. The mixture was stirred and preheated to 100 °C in an oil bath and then maintained at 100 °C for 1 h. After the reaction, the mixture was decanted to a volumetric flask and pure H_2O was used as the diluent. The mixture was then analyzed by a High Performance Liquid Chromatography (HPLC) equipped with UV and refractive index detectors.

1.3. Separation procedure for HMF

After the dehydration of sugar, the reaction mixture was distilled under reduced pressure (1 mm Hg, 55 °C). The solvent separated from the mixture can be used in the next run. The remaining mixture was extracted with EtOAc (10 mL × 5) after water (0.5 g) was added, and then organic phase was collected, dried with anhydrous sodium sulfate, and distilled to obtain pure HMF as the main product. The isolated yields of HMF were, respectively, 73%, 61%, and 79% when sucrose, glucose, and fructose were used as substrates in the best reaction conditions.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2011.11.013.

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