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Defunctionalization of fructose and sucrose: Iron-catalyzed production of 5-hydroxymethylfurfural from fructose and sucrose

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ABSTRACT

A highly efficient iron-catalyzed production of 5-hydroxymethylfurfural (HMF) from sugar is reported. The dehydration of fructose and sucrose has been studied in the presence of different iron salts and co-catalysts. As a result, it was found that fructose and sucrose could be efficiently and selectively converted to HMF using a combination of environmentally friendly $FeCl_3$ and tetraethyl ammonium bromide (Et_4NBr) as the catalytic system. For instance, 86% HMF yield at full conversion of fructose was obtained for 2 h at 90 °C in air. The effects of catalyst concentration, reaction time and reaction temperature were investigated in detail. The electronic absorption spectra of different catalysts were recorded, and the $FeCl_3Br^-$ ion was considered as the active catalyst species.

1. Introduction

The use of biomass as a source of liquid fuels and chemicals represents a sustainable approach for obtaining energy and carbon-based compounds [1–3]. Conversion of sugars, such as fructose and sucrose, to valuable chemicals is very important in the chemical processing from biomass resources [4–6]. The important compound 5-hydroxymethylfurfural (HMF), which originates from the dehydration of sugar, is a valuable intermediate used in the production of fine chemicals, pharmaceuticals and numerous polymers [7–9]. In recent years, the development of novel and efficient catalytic systems for the dehydration of sugars to HMF has become a hot topic [10–12]. Traditionally, acid catalysts, such as mineral acids [13,14], strong acid cation exchange resins [15–17], H-form zeolites [18,19], and supported heteropolyacids [20], have been employed for the dehydration fructose to HMF. In addition, acidic ionic liquids have been used as catalysts or solvents in sugar dehydration [21–24]. However, these catalysts may have favored the subsequent dehydration of HMF to levulinic and formic acids, which ultimately lowers the yield of HMF [25,26].

Recently, the metal-catalyzed dehydration of sugar has received considerable attention due to the high selectivity of HMF that may be achieved with negligible acid by-product. For example, Zhao et al. [27] have reported a metal chloride/1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) system that gives moderate to good HMF yields from fructose (ca. 83% with Pt or Rh chloride) and glucose (ca. 68% with $CrCl_2$); Yong et al. [28] further found that a system based on *N*-heterocyclic carbene-Cr/1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) was more efficient for the dehydration of sugars to HMF. However, in these catalytic systems, only noble metals (Ru and Pt chloride) or potentially toxic metals (Cr chlorides) resulted in a good catalytic performance. It is well-known that developing more cost-efficient and environmentally friendly metal catalysts remains an issue of scientific interest and industrial significance. In this respect, iron salts are ideal candidates due to their low cost, non-toxicity, ready availability and environmentally benign character [29,30].

Iron-based catalysis is effective in the cross-coupling [31–33], oxidation [34,35] and hydrogenation reaction [36], as well as in the Fischer–Tropsch synthesis [37]. However, iron-catalyzed sugar conversion remains a challenge and warrants further investigation. In this paper, we describe the iron-catalyzed dehydration of fructose and sucrose to HMF. It was found that a $FeCl_3$–tetraethyl ammonium bromide (Et_4NBr) system resulted in a high catalytic performance and HMF was obtained in good yield under mild conditions. Moreover, the catalytic system was further optimized and attempts to delineate the nature of the active catalyst were made.

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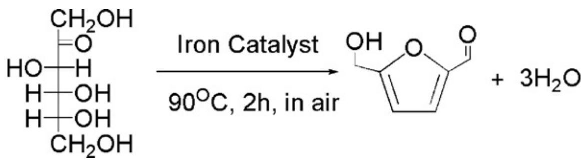

Scheme 1. Synthesis of HMF from fructose.

2. Experimental

2.1. Reagents

Fructose, glucose, sucrose, iron salts, Et_4NBr and other co-catalysts are of analytical quality and were obtained from Tianjin Guangfu Fine Chemical Research Institute. NMP, DMF and DMSO were purified by distillation prior to use. Pure H_2O was prepared using a Ultrapure Water System (electrical resistivity = 10^{-12} mΩ cm). The HMF used as the standard sample was purchased from Alfa Aesar.

2.2. General procedure for the dehydration of sugars and the products analysis method

All the dehydration reaction experiments were performed in a 100 mL flask equipped with magnetic stirrer and a condenser. A typical procedure for dehydration of fructose is as follows: a solution of fructose (1.0 g, 5.6 mmol), $FeCl_3$ (0.56 mmol), co-catalyst (1.0 mmol) and solvent (10 mL) were charged into the flask. Under stirring, the flask was heated to 90 °C in an oil bath for 2 h in air. After 2 h the reaction mixture was decanted to a volumetric flask with pure H_2O or ethanol, and then analyzed by an HPLC equipped with UV and refractive index detectors.

The HPLC measurements are conducted using an Agilent 1200 HPLC with UV and Refractive Index detector. The Eclipse Plus-C18 (4.6 mm × 150 mm) column and an Aminex HPX-87C (300 mm × 7.8 mm) column are employed to separate the reaction mixture. General HPLC conditions for analysis of HMF yield: variable UV detector; C18 column temperature: 30 °C; eluent: 0.5 mL/min H_2O: CH_3CN (1:4); injection amount: 1 μL. General HPLC conditions for analysis of fructose and sucrose conversion: Refractive Index detector; Aminex HPX-87C column temperature: 30 °C; eluent: 0.2 mL/min water; injection amount: 2.5 μL.

2.3. Purification of 5-hydroxymethylfurfural

The reaction mixture was transferred into a flask and was distilled under reduced pressure. The remaining mixture was extracted with ethyl acetate (10 mL × 4) and afterwards water (0.5 g) was added, and then the organic phase was collected. After drying with anhydrous sodium sulfate, the organic layer was distilled under reduced pressure to obtain HMF as the main product. The total isolated yield of HMF is about 78% with $FeCl_3$–Et_4NBr system, and the purity was more than 97% from HPLC analysis. ^{1}HNMR spectrum (DMSO-d_6): 3.396–3.438 (d, 1H, *J* = 7.078), 4.483 (s, 2H), 6.580–6.586 (d, 1H, *J* = 3.417) 7.466–7.473 (d, 1H, *J* = 3.417), 9.522 (s, 1H); ^{13}CNMR spectrum (DMSO-d_6): δ 56.524, 56.650, 110.385, 152.413, 162.805, and 178.667.

3. Results and discussion

3.1. Dehydration of fructose to 5-hydroxymethylfurfural

Initially, the dehydration of fructose was evaluated with different iron salts and co-catalysts in *N*-methylpyrrolidone (NMP), see Scheme 1 and Table 1. HMF was obtained in 1% yield using $FeCl_2$ (Table 1, entry 1) under the employed conditions. In the presence of 10.0 mol% $FeCl_3$ the yield of HMF increased to 42% (Table 1, entry 2), and HMF was obtained in 84% yield with ammonium bromide (NH_4Br) as a co-catalyst (Table 1, entry 3). Further investigations showed that the coupled $FeCl_3$–Et_4NBr system exhibited a better catalytic activity, with an 86% yield of HMF at full fructose conversion (Table 1, entry 4). Note, the yield of HMF was <1% when only Et_4NBr was used as the catalyst (Table 1, entry 5), and a blank experiment was also carried out in the absence of any catalyst and nearly no reaction occurred (Table 1, entry 6).

Table 1
Dehydration of fructose with different catalysts[a].

Entry	Catalyst	Time (h)	Yield (%)[b]	Sel. (%)[b]
1	$FeCl_2$	2	1	–
2	$FeCl_3$	2	42	43
3	$FeCl_3$–NH_4Br	2	84	84
4	$FeCl_3$–Et_4NBr	2	86	86
5	Et_4NBr	3	<1	–
6	no	3	0	–
7	$FeCl_3$–LiCl	2	65	70
8	$FeCl_3$–NaCl	2	69	70
9	$FeCl_3$–KCl	2	61	64
10	$FeCl_3$–LiBr	2	77	80
11	$FeCl_3$–NaBr	2	80	82
12	$FeCl_3$–KBr	2	74	76
13	$FeCl_3$–Et_4NCl	2	82	82
14	$Fe(NO_3)_2$–Et_4NBr	2	<1	–
15	$Fe(NO_3)_3$–Et_4NBr	2	<1	–

[a] Reaction conditions: 1.0 g D-fructose, 0.56 mmol iron salt, and 1.0 mmol co-catalyst in 10 mL NMP solvent, temperature = 90 °C, in air.

[b] The yield and selectivity are obtained by HPLC analysis and product separation method.

In order to further understand the reaction characteristics, different alkali metal halides were also used as co-catalysts in place of Et_4NBr. Lower yields of HMF were obtained with LiCl, NaCl or KCl co-catalyst (Table 1, entries 7–9). Moreover, when LiBr, NaBr or KBr were employed, HMF yields of 74%–80% were obtained (Table 1, entries 10–12). The bromide ion appears to exhibit a superior activity, especially when coupled with the tetraethyl ammonium cation, which is probably linked to the weaker ion pairing present in this salt compared to the others used in the study. In agreement with this hypothesis, further investigations showed that the yield of HMF reached 82% employing Et_4NCl as a co-catalyst (Table 1, entry 13). In addition, other combinations of iron salts with Et_4NBr were evaluated and conversions to HMF were very low (Table 1, entries 14–15). Overall, the $FeCl_3$–Et_4NBr system proved to be the best catalyst system. Here, the obtained yield of HMF is analogous to that with Cr [27,28], La [38], Sn [39] and W catalyst [40]; however, the low cost and non-toxicity of Fe catalyst is more competitive in a large scale production.

Furthermore, the separation and reusability of Fe catalyst has been examined. The investigations are performed at 90 °C for 2 h. After the dehydration reaction, the mixture is first distilled under the reduced pressure. The pure NMP is collected and the left mixture is extracted four times by 10 mL of ethyl acetate after adding 0.5 g of water. The fructose and Fe catalyst are found to be almost insoluble in ethyl acetate; thus, the amount of HMF in ethyl acetate is accounted as total separation yield of HMF. The obtained mixture after extraction is heated at 75 °C for 12 h in a vacuum oven to remove water and residual ethyl acetate. It is then used directly in the next run by adding the distilled NMP and an equal amount of fructose. The results indicated that the HMF yield gradually decreased a little in three recycle reactions, which can be attributed to the partial lose of catalyst during the separation process. This is accord with a common feature of homogeneous catalyst.

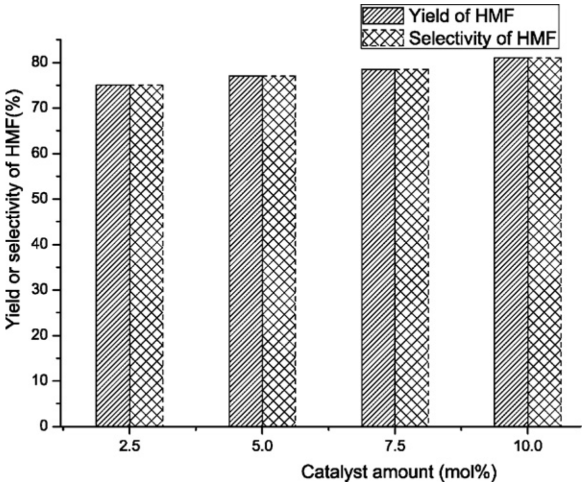

Fig. 1. The effect of catalyst concentration in the dehydration of fructose (reaction conditions: 1.0 g fructose, 90 °C, 2 h, 10 mL NMP, the molar ratio of $FeCl_3$ and Et_4NBr is 1:1).

3.2. Effect of catalyst concentration

The effect of catalyst concentration was investigated, see Fig. 1, and it was found that good yields of HMF could be obtained at lower catalyst loadings. In the presence of 2.5 mol% catalyst the yield of HMF still reaches 75%.

3.3. Effect of reaction time and reaction temperature

The effect of reaction time is presented in Fig. 2. As expected, the yield of HMF increases rapidly and the selectivity decreases appreciably during the first 30 min. After 1 h the yield and selectivity of HMF remains almost unchanged showing that further dehydration of HMF to unwanted acid by-products is not favored by the catalyst.

The reaction temperature proved to be critical with very low yields observed below 70 °C and the system becoming very efficient above 75 °C.

3.4. Dehydration of sucrose and glucose to 5-hydroxymethylfurfural

The dehydration of sucrose and glucose were also studied using the $FeCl_3$–Et_4NBr system. In Table 2, it can be seen that a 40% yield of HMF is obtained for the dehydration of sucrose (Table 2, entry 1), in keeping with results obtained using mineral acid catalysts [41]. However, in the dehydration of glucose the yield of HMF is only 3% (Table 2, entry 2). Furthermore, when the mixture of fructose and glucose is used as a substrate HMF is obtained in 41% yield (Table 2, entry 3). These data show that the ketose is more easily dehydrated than aldose using this catalytic system. On the way from glucose to HMF the first step is probably the isomerization of glucose to fructose, which should be the reason for low yield. For the conversion of sucrose, it can be firstly hydrolyzed to one molecule of glucose and one molecule of fructose, and then the glucose and fructose are dehydrated to produce HMF. Seen from the obtained data, it can be concluded that the hydrolysis of sucrose occurs with good yield but only fructose dehydration takes place. Furthermore, the NMP solvent is replaced by *N*,*N*-dimethyl-formamide (DMF) or dimethylsulfoxide (DMSO). In DMF, a 62% or 38% yield of HMF is obtained for the dehydration of fructose or sucrose, respectively (Table 2, entries 4 and 5). In DMSO, the yield of HMF is 53% or 27% in the dehydration of fructose or sucrose, respectively (Table 2, entries 6 and 7). In addition, when the mixture of NMP and water (1:1, volume ratio) is used as the reaction medium, the yield of HMF from fructose and sucrose is 70% and 21%, respectively (Table 2, entries 8 and 9). It is noteworthy that water does not decrease the yield too much and also ensures the reaction may be conducted without precautions to exclude air or moisture.

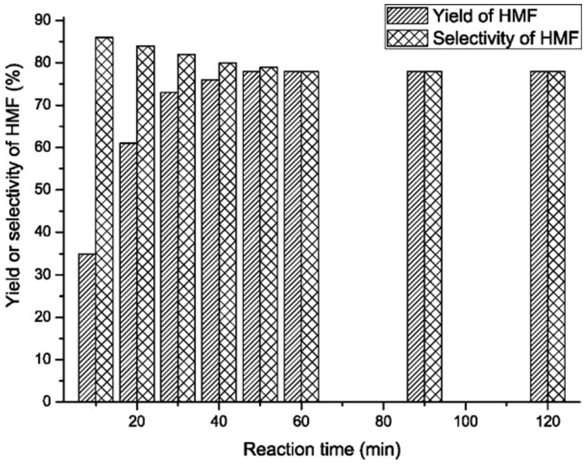

Fig. 2. The influence of reaction time in the dehydration of fructose (reaction conditions: 1.0 g fructose, 5.0 mol% $FeCl_3$, 7.5 mol% Et_4NBr, 90 °C, 10 mL NMP, in air).

Table 2
Dehydration of sugar with $FeCl_3$–Et_4NBr system[a].

Entry	Substrate	Solvent	Time (h)	Yield (%)[b]
1	Sucrose	NMP	3	40
2	Glucose	NMP	3	3
3[c]	Fructose + Glucose	NMP	3	41
4	Fructose	DMF	2	62
5	Sucrose	DMF	3	38
6	Fructose	DMSO	3	53
7	Sucrose	DMSO	5	27
8[d]	Fructose	H_2O + NMP	2	70
9[d]	Sucrose	H_2O + NMP	5	21

[a] Reaction conditions: 1.0 g substrate, 0.56 mmol $FeCl_3 \cdot H_2O$, and 1 mmol co-catalyst in 10 mL solvent, temperature = 90 °C, in air.

[b] The yield of HMF is obtained by HPLC analysis and product separation method.

[c] The mass ratio of fructose and glucose is 1:1.

[d] The volume ratio of H_2O and NMP is 1:1.

3.5. The investigations on the active catalyst species

To gain the insights into the nature of the active catalyst, the electronic absorption spectra of $FeCl_3$, $FeCl_3$–Et_4NCl and $FeCl_3$–Et_4NBr in NMP were recorded. The addition of Et_4NCl or Et_4NBr to $FeCl_3$ results in a change in the absorption spectra, indicating the formation of new species (Fig. 3). Moreover, the obtained spectrum of $FeCl_3$–Et_4NCl corresponds to that of the $FeCl_4^-$ anion, i.e., the peaks centered at 310 and 364 nm belong to the lowest-energy charge transfer (CT) transitions $^6A_1 \rightarrow {}^6T_2$ (literature data: 312 and 361 nm in acetonitrile) and the very weak absorption bands at 530, 616 and 686 nm (literature data: 530, 616 and 686 nm in acetonitrile) corresponding to d–d forbidden transitions [42]. For the $FeCl_3$–Et_4NBr system the spectrum may be tentatively assigned to the $FeCl_3Br^-$ anion. Replacing one chloride with a bromide in the tetrahalogeno-ferrate (III) anion should lead to a decrease in the ligand field strength and the transition energies are expected to increase according to the Tanabe–Sugano diagram [43], as observed in our experiments, with the bands for $^6A_1 \rightarrow {}^6T_2$ transitions for $FeCl_3$–Et_4NBr undergoing a blue shift in comparison with those of $FeCl_{30}$–Et_4NCl (304, 358 nm compared to 310 and 364 nm, see Fig. 3). Additionally, the molar extinction coefficient for $FeCl_3$–Et_4NBr in the visible region is significantly higher than that

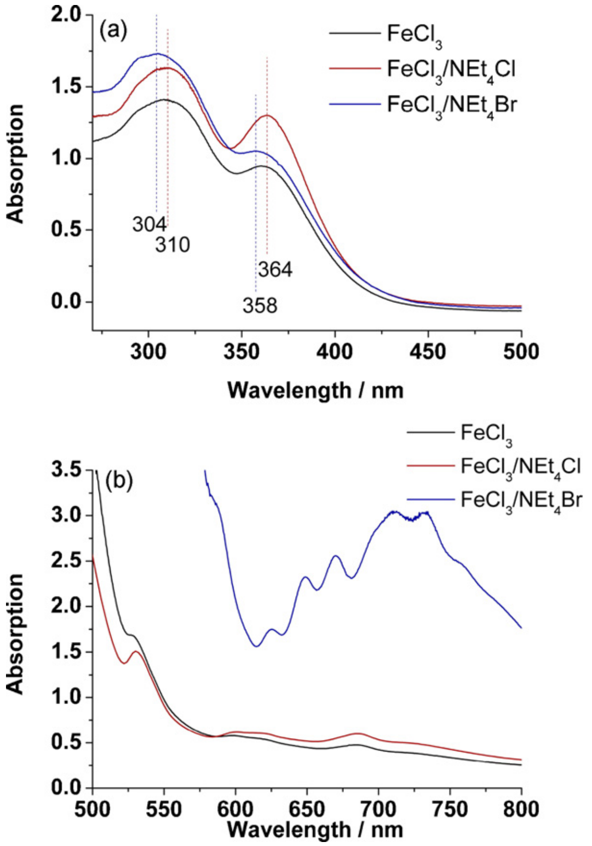

Fig. 3. Electronic absorption spectra of $FeCl_3$, $FeCl_3$–Et_4NCl and $FeCl_3$–Et_4NBr in NMP (concentration: (a) 0.5 mM. (b) 0.5 M).

of $FeCl_3$ or $FeCl_3$–Et_4NCl, which is also indicative of the presence of bromide in the ligand sphere. Consequently, we propose that upon addition of Et_4NBr or Et_4NCl, the major iron species in solution are $FeCl_3Br^-$ and $FeCl_4^-$, respectively, which probably corresponds to the active catalyst. Moreover, based on the experimental data in Table 1, it is also found that the addition of NH_4Br, Et_4NBr, LiBr, NaBr or KBr (Table 1, entries 3, 4, 10, 11, 12) can obviously promote the dehydration of fructose. These results are consistent with the existence of active $FeCl_3Br^-$ species in the dehydration reaction.

4. Conclusions

In summary, a new $FeCl_3$–Et_4NBr system has been developed which can catalyze efficiently the selective dehydration of fructose to HMF; moreover, the conversion of sucrose to HMF with moderate selectivity is also obtained with this catalytic system under mild conditions. It will therefore generate a promising strategy in the utilization of renewable biomass.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.03.003.

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