

Catalytic Conversion of Carbohydrates into 5-Hydroxymethylfurfural by Germanium(IV) Chloride in Ionic Liquids

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Direct conversion of carbohydrates into 5-hydroxymethylfurfural (HMF) catalyzed by germanium(IV) chloride in ionic liquids has been investigated in search of an efficient and environmentally friendly process. Monosaccharides D-fructose and D-glucose, disaccharides sucrose and maltose, and even the polysaccharide cellulose were successfully converted into HMF with good yields under mild conditions (yield up to 92% in 5 min in the case of fructose). The structure of ionic liquids,

catalyst loading, reaction temperature and water content had noticeable effects on this catalytic system. Addition of 5 Å molecular sieves during the dehydration of glucose resulted in an increase in HMF yield from 38.4% to 48.4%. A mechanism for glucose conversion to HMF catalyzed by germanium(IV) chloride was proposed according to ¹³C NMR spectra obtained in situ under different conditions using D-glucose-2-¹³C as the substrate.

Introduction

Concerns about global warming and energy security have led to the exploration of alternatives for fossil resources to supply chemicals and energy.^[1] Biomass with an estimated global production of around 1.0×10^{11} tons per year has attracted considerable attention as an alternative source for both fuels and chemicals.^[2] Carbohydrates make up the majority of biomass, and it is estimated that up to 30% of raw materials for the chemical industry will be produced from renewable sources by 2025.^[3] To achieve this goal, it is pivotal to develop more efficient and environmentally friendly methods to convert carbohydrates into useful chemicals.^[4]

5-Hydroxymethylfurfural (HMF) has been recognized as a versatile and key precursor for the production of fine chemicals, polymeric materials, and biofuels.^[5] In the past few years, the preparation of HMF through the dehydration of biomass-based sugars has received much attention. In the case of fructose, excellent yields were achieved using many methods.^[6] Although fructose is the preferred feedstock for high HMF yield, it is clear that large scale, sustainable production of HMF requires cellulosic biomass as the feedstock. However, dehydration of glucose is much more problematic, and considerable efforts have been devoted to this area.^[7]

A recent study demonstrated that the conversion of glucose into HMF may include consecutive steps, namely, mutarotation and isomerization of glucose into fructose followed by dehydration of fructose.^[8] Both the catalyst and the reaction environment had a major effect on the efficiency of the conversion of glucose into HMF.^[9] In 2007, Zhao et al. reported that chromium(III) chloride catalyzed the dehydration of glucose into HMF in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) in a good yield.^[10] Later on, conversion of carbohydrates into HMF was realized with less toxic catalysts. For example, Hu et al. reported that the common Lewis acid SnCl₄ could catalyze glucose conversion into HMF in about 60% yield at 100 °C

for 3 h in 1-ethyl-3-methylimidazolium tetrafluoroborate.^[11] Stahlberg et al. used the lanthanide salt-based system for the reaction at 140 °C for 6 h, affording HMF in 24% yield.^[12] Regardless of these developments, it remains a challenge to obtain HMF from carbohydrates in terms of efficiency and greenness. Herein, we report a germanium(IV) chloride-based catalytic system that promotes efficient HMF production under mild conditions with a variety of carbohydrates as the substrates.

Results and Discussion

Catalyst screening

We initiated our study using fructose as the substrate and screened several metal salts that had rarely been considered as catalysts for HMF production in ionic liquids. HMF yields were largely dependent on the catalysts (Table 1). An excellent yield of 92% was achieved in 5 min when GeCl₄ was employed (Table 1, entry 2). Only moderate yields (Table 1, entries 5 and 6) or low yields (Table 1, entries 1, 3, 4, and 7) were obtained with other choices of catalyst. Zhao et al. reported that HMF could be produced from fructose without a catalyst in

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Table 1. The results of fructose dehydration to HMF catalyzed by different catalysts.^[a]

Entry	Catalyst	Yields [%]
1	SnCl ₄ ·4H ₂ O	5.5
2	GeCl ₄	92.1
3	BiCl ₃	8.1
4	ScCl ₃ ·6H ₂ O	4.0
5	ZrCl ₄	43.8
6	HfCl ₄	57.7
7	CeCl ₃	0.9
8 ^[b]	–	ND

[a] Reaction conditions: Fructose (100 mg) was added to [BMIM]Cl (2.0 g) at 100 °C, then catalyst (10 mol%) was added. The reaction was stopped after 5 min. [b] The reaction was done under otherwise identical conditions in the absence of a catalyst. ND=not detected.

[EMIM]Cl especially at a high temperature for a long time.^[10] For a control experiment in which fructose was held at 100 °C in the absence of a catalyst, we did not detect any HMF after 5 min (Table 1, entry 8). All of the results clearly indicated that GeCl₄ was a superior catalyst for the dehydration of fructose.

Chan et al. recently reported that the dehydration of fructose catalyzed by WCl₆ at 50 °C for 4 h gave HMF in 63% yield.^[13] Inspired by that study, we reduced the reaction temperature. At 80 °C, the HMF yield reached 90.2% in 5 min (Figure 1). The time course of HMF formation at 80 °C was almost identical to that at 100 °C. However, when the reaction temperature was 50 °C, it took 20 min to reach a yield of 84.3%, and thereafter HMF yield increased only marginally over time. It should be pointed out that fructose conversion was 96.1% at 50 °C after 20 min, and reached over 99.1% after 30 min. To our knowledge, this result is the best reported to date for the production of HMF from fructose in a Lewis acid–ionic liquids system. The low reaction temperature should facilitate an extraction of HMF using a low boiling point solvent (e.g., ethyl acetate), providing much potential to develop a more economical and sustainable process for HMF production^[14].

Moreover, the reusability of [BMIM]Cl/GeCl₄ (BMIM = 1-butyl-3-methylimidazolium) system was estimated. In this experiment, HMF was extracted with ethyl acetate prior to the addition of fructose into the system for the next run under essentially identical conditions. Our results demonstrated that the [BMIM]Cl/GeCl₄ system could be reused five times without significant activity loss (Figure 2).

Effect of catalyst loading

Although fructose has been the preferred feedstock for HMF production, its occurrence in nature is limited. We decided to use more abundant carbohydrates, glucose and cellulosic biomass, as the raw material in our system. When glucose was treated at 100 °C for 75 min in the presence of 10 mol% GeCl₄, the maximal yield was 38.4% with a glucose conversion of 92.5%. Because the yield was lower than those of other catalytic systems,^[10,11] we changed the reaction conditions to im-

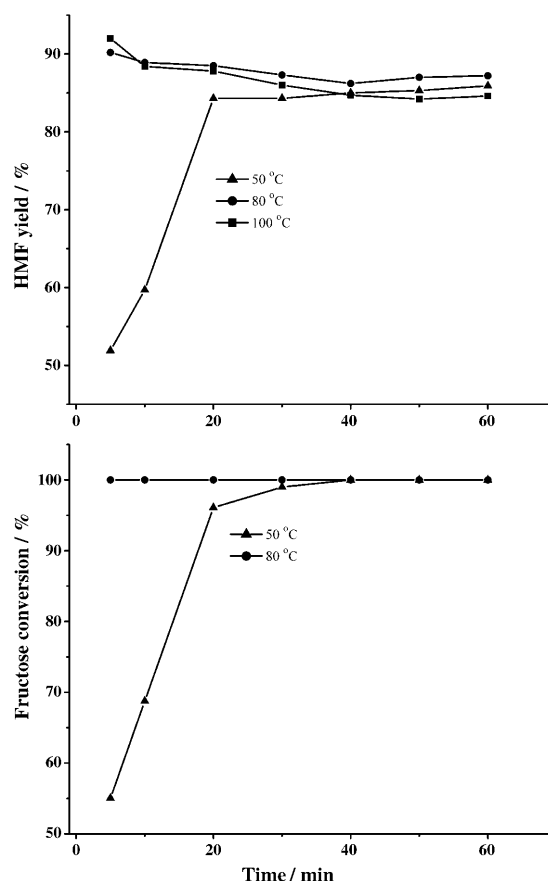


Figure 1. The results of fructose dehydration into HMF catalyzed by GeCl₄ at different temperatures. Reaction conditions: Fructose (100 mg) was added to [BMIM]Cl (2.0 g), then GeCl₄ (10 mol%) was added.

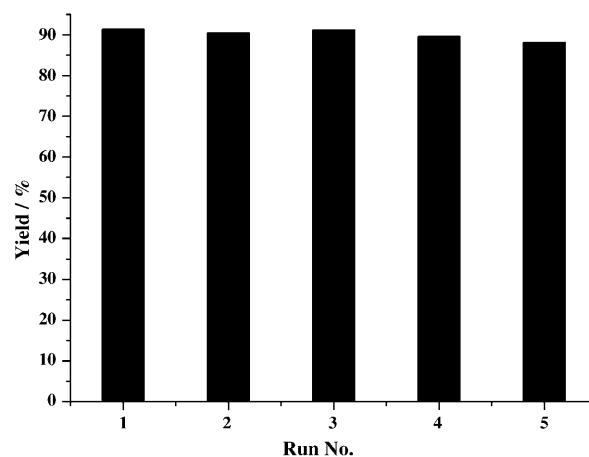


Figure 2. Reuse of the GeCl₄/[BMIM]Cl system. Reaction conditions: Fructose (100 mg), [BMIM]Cl (2.0 g), GeCl₄ (10 mol%), *T* = 100 °C, *t* = 5 min.

prove the HMF yield. Firstly, the effect of catalyst loading was studied. Increasing the catalyst loading from 5 mol% to 15 mol% resulted in an increase in glucose conversion (Figure 3). For example, glucose conversion at 120 min reached 87.3% and 98.5% in the presence of 5 mol% and 15 mol% GeCl₄, respectively. It was clear that the maximal HMF yields were almost identical regardless of whether the catalyst was

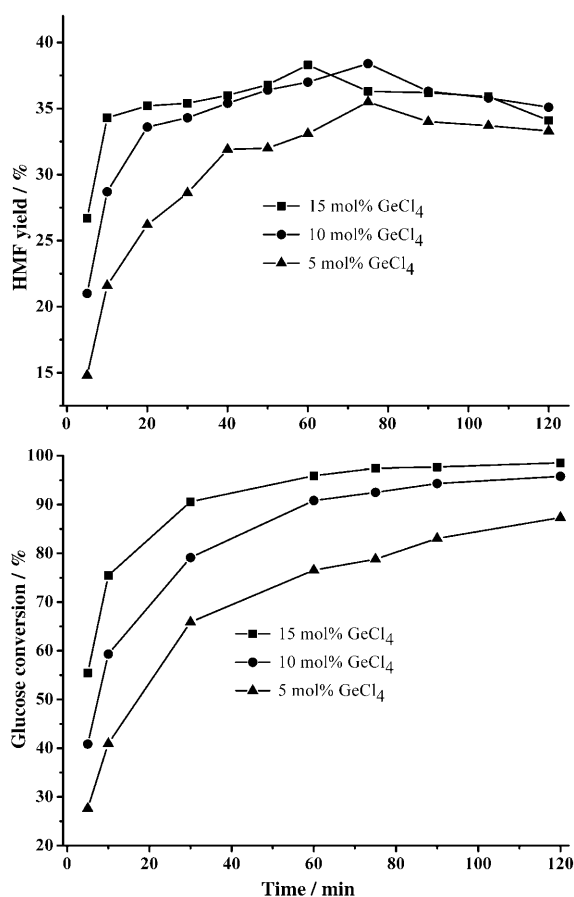


Figure 3. The results of glucose dehydration to HMF catalyzed by GeCl_4 with different catalyst loadings. Reaction conditions: Glucose (100 mg) was added into [BMIM]Cl (2.0 g) at 100 °C, then GeCl_4 was added.

loaded at 10 mol% or 15 mol%. However, at the early stage higher HMF yields were found for the reaction with 15 mol% GeCl_4 . These results indicated that increasing the catalyst loading led to a faster reaction, whereas the reaction selectivity did not change. Because the maximal HMF yield was achieved using 10 mol% GeCl_4 , we used this catalyst loading for the subsequent experiments.

Effect of reaction temperature

Experiments were carried out at 80, 100, and 120 °C. Higher reaction temperatures clearly gave higher glucose conversions and HMF yields (Figure 4). At 120 °C, glucose conversion and HMF yield increased rapidly in the early stage, and the maximal HMF yield of 47.5% was received with 99.1% glucose conversion at 30 min. At 100 °C, the maximal HMF yield of 38.4% was detected after 75 min. In both cases, HMF yields dropped over time beyond the maximal point, indicating that degradation of HMF was significant at higher temperatures. However, glucose conversion and HMF yield were 71.8% and 28.6%, respectively, at 80 °C for 120 min, indicating that the reaction was suppressed at a lower temperature. Fructose was converted at a lower temperature than glucose (Figure 1 versus Figure 4).

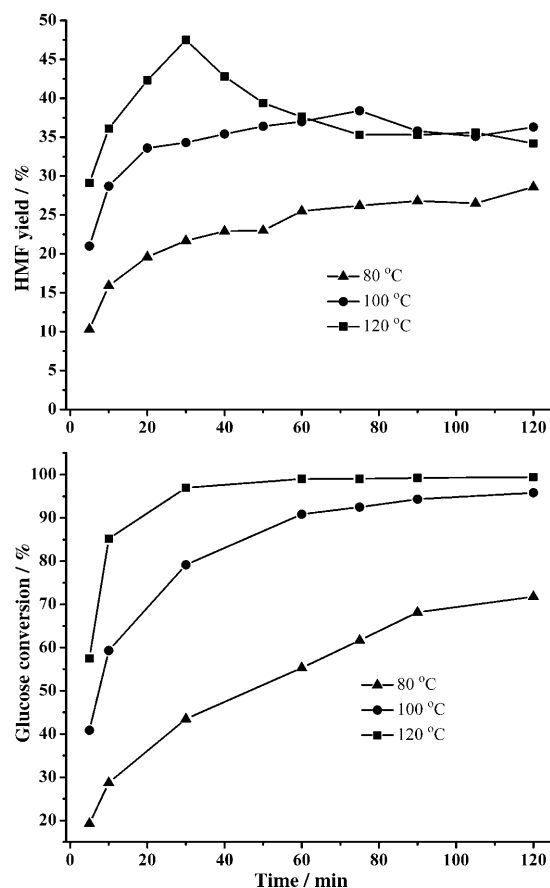


Figure 4. The results of glucose dehydration to HMF catalyzed by GeCl_4 at different temperatures. Reaction conditions: Glucose (100 mg) was added to [BMIM]Cl (2.0 g), then GeCl_4 (10 mol%) was added.

Effect of water content

We also investigated the effect of water content on the reaction, because water could promote rehydration of HMF and other side reactions. Both glucose conversion and HMF yield decreased with increasing water content (Figure 5). For example, when 2 equivalents of water were added, glucose conversion and HMF yield after 120 min were 79.2% and 20.0%, respectively, whereas those values were 92.5% and 38.4% without water addition (see above). Levulinic acid and formic acid are usually the main byproducts of the dehydration of hexoses in an aqueous solution. However, levulinic acid was not detected in this work, indicating that rehydration of HMF was inhibited. In our experiment, we observed the formation of humins, which were likely generated through the polymerization and cross-polymerization of HMF and intermediates.^[14] The decreased glucose conversion in the presence of water may be ascribed to the reaction of GeCl_4 with water. A further experiment was carried out in the presence of 5 Å molecular sieves to remove water from the system. The HMF yield was found to increase moderately, from 38.4% to 48.4%, in the presence of 0.5 g of 5 Å molecular sieves.

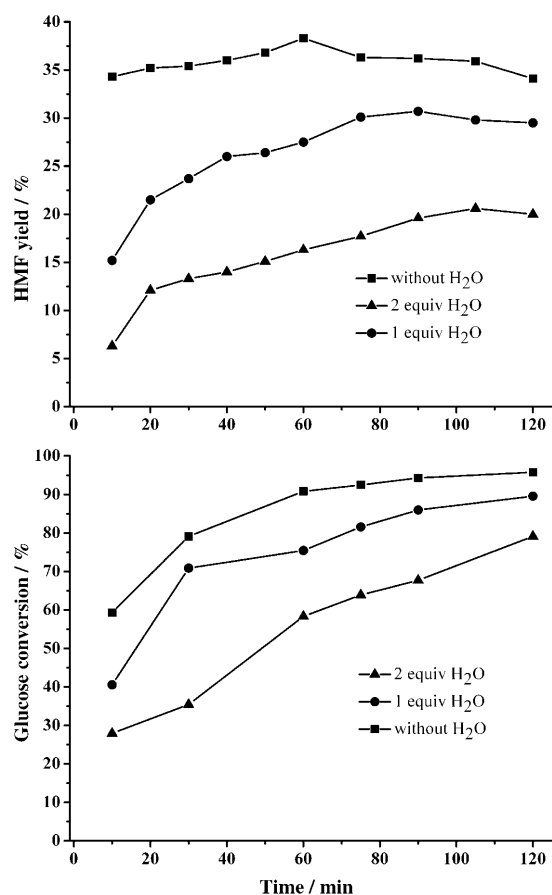


Figure 5. The results of glucose dehydration to HMF catalyzed by GeCl_4 with different amounts of water. Reaction conditions: Glucose (100 mg) was added to [BMIM]Cl (2.0 g) at 100 °C, then water and GeCl_4 (10 mol %) were added.

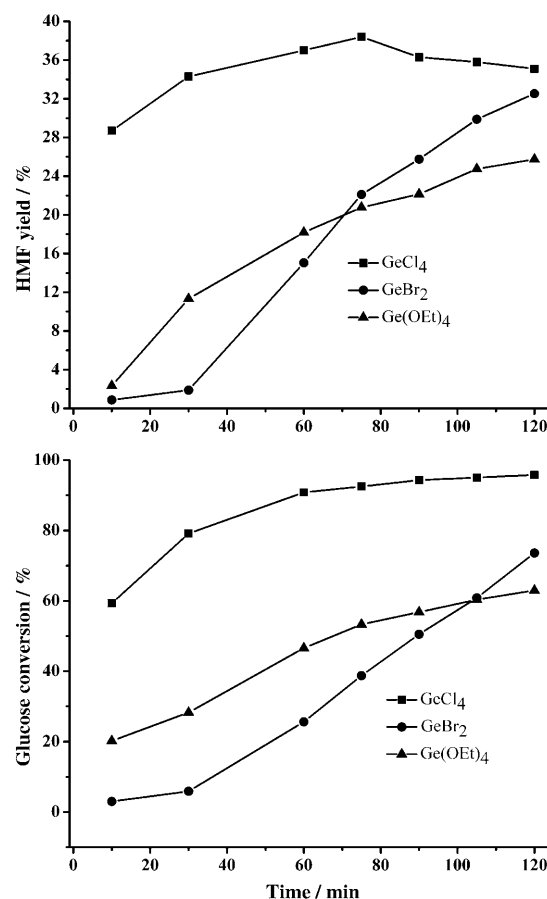


Figure 6. The results of glucose dehydration to HMF catalyzed by different germanium salts. Reaction conditions: Glucose (100 mg) was added to [BMIM]Cl (2.0 g) at 100 °C, then germanium salt (10 mol %) was added.

Conversion of glucose catalyzed by different germanium salts

We then tested two other commercially available germanium salts, Ge(OEt)_4 and GeBr_2 , for the dehydration of glucose. Ge(OEt)_4 was clearly less competent for HMF production (Figure 6). Glucose conversion and HMF yield were 63.0% and 25.7%, respectively, after 120 min in the presence of 10 mol% Ge(OEt)_4 . The difference may be explained by the anion effect. When using Ge(OEt)_4 as the catalyst, the EtO^- group is much larger than Cl^- , presenting more steric hindrance for the coordination between glucose and the catalytic center. Furthermore, EtO^- is more nucleophilic than Cl^- , leading to a stronger interaction with Ge^{IV} , which inhibited the interaction between glucose and Ge^{IV} . When GeBr_2 was used, it was interesting to note that both glucose conversion and HMF yield were low by the first 30 min. However, HMF yield increased linearly after 30 min, and the result was slightly better than that with Ge(OEt)_4 . Ge^{II} is liable to be oxidized aerobically to Ge^{IV} .^[15] Therefore, apparent catalytic activity when GeBr_2 was used might have been the result of the formation of Ge^{IV} species during the reaction process. The fact that HMF yield was reduced to 2.1% was in line with our speculation when the

reaction was performed with 10 mol% GeBr_2 under a N_2 atmosphere.

Conversion of glucose in different ionic liquids

Ionic liquids are regarded as tunable solvents, and their structures have a remarkable effect on their properties.^[16] The interactions among cation, anion and carbohydrates play a key role during the process. Thus we tested a variety of ionic liquids as solvents for GeCl_4 -promoted HMF production from glucose (Figure 7). Besides [BMIM]Cl, 1-hexyl-3-methylimidazolium chloride ([HMIM]Cl), 1-octyl-3-methylimidazolium chloride ([OMIM]Cl), and 1-decyl-3-methylimidazolium chloride ([DMIM]Cl) were also proved as reasonably good solvents for the reaction. These ionic liquids all incorporated chloride as the anion, in which HMF yields ranged from 23.3% in [DMIM]Cl to 38.4% in [BMIM]Cl. It was interesting to scrutinize the effect of the chain length of the alkyl group of these liquids on the reaction. Although glucose conversions were close, HMF yields decreased from 38.4% to 23.3% when the alkyl group changed from butyl to decyl. The opposite phenomena were recently published for the reaction at 160 °C using lanthanide chlorides as catalysts in ionic liquids.^[12] Therefore, a gen-

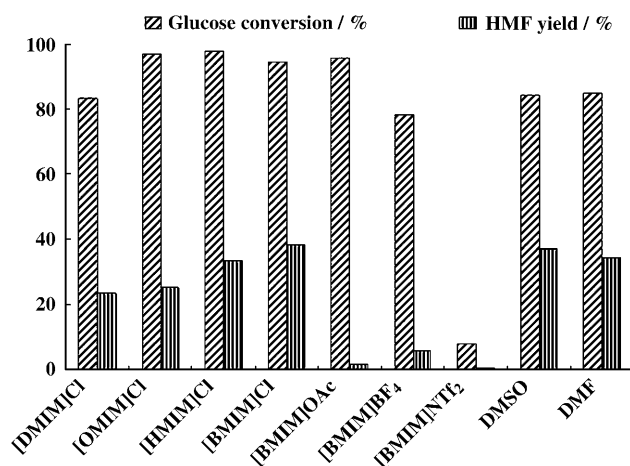


Figure 7. The results of glucose dehydration to HMF catalyzed by GeCl_4 in different solvents for 75 min. Reaction condition: Glucose (100 mg) was added to the solvent (2.0 g) at 100 °C, then GeCl_4 (10 mol%) was added.

eral relationship between the chain length of the alkyl group and HMF yields was not clear, and the catalyst and operational conditions should also be taken into consideration. However, ionic liquids with different anions, including 1-butyl-3-methylimidazolium acetate ([BMIM]OAc), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄), and 1-butyl-3-methylimidazolium bistriflate imide ([BMIM]NTf₂) were found to form catalytically inactive systems. Although the glucose conversion in [BMIM]OAc was high, the selectivity of HMF was rather low, which may be due to possible side reactions between glucose and the imidazolium ring induced by the strongly basic acetate group.^[17] [BMIM]BF₄ was found to be a poor solvent for the reaction, even though it was a good solvent for the SnCl_4 -based system. Both glucose conversion and HMF selectivity were low in the hydrophobic ionic liquid [BMIM]NTf₂. Our results indicated that anions in the ionic liquids had a major effect on the HMF yield, and were consistent with the fact that a moderate basicity of the anion was required to obtain a satisfactory glucose conversion and HMF selectivity.^[18] Other polar aprotic solvents, dimethylsulfoxide (DMSO) and dimethylformamide (DMF), were also effective, giving HMF yields of 37.1% and 34.3%, respectively, under otherwise identical reaction conditions (Figure 7). DMSO is known to give similar yields of HMF if monosaccharides are used as the substrates.^[11] It is likely that DMSO and DMF provided similar environments to ionic liquids to dissolve the catalyst and sugar. However, using ionic liquids such as [BMIM]Cl had two obvious advantages in terms of HMF recovery by extraction with ethyl acetate and direct conversion of cellulose (see below).

Conversion of various substrates into HMF with [BMIM]Cl/ GeCl_4

Next, we sought to explore the substrate scope of this catalytic system. HMF was obtained in 55.4% yield when sucrose was used (Figure 8). This result was slightly lower than previous results (64% HMF yield for [BMIM]BF₄/ SnCl_4 ^[11] and 73% for

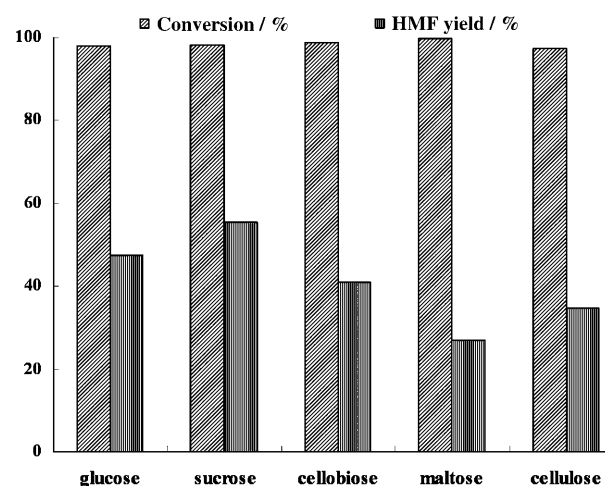


Figure 8. The results of HMF production from various sugars. Reaction conditions: Sugar (100 mg) was added to [BMIM]Cl (2.0 g) at 100 °C followed by GeCl_4 (10 mol%). The reaction mixture was then stirred at 120 °C for 30 min. Maltose monohydrate was used because anhydrous maltose was unavailable.

[BMIM]Cl-IBMK/ CrCl_3 ^[19]; IBMK = isobutyl methyl ketone). When cellobiose was utilized, HMF yield was 41.0%, which was comparable to that in a previous study.^[19] When maltose monohydrate was used, HMF yield was clearly lower than with the other two disaccharides, cellobiose and sucrose. We reasoned that the water introduced with maltose spoiled the reaction. It should be noted that water also inhibited the conversion of glucose into HMF (see above). More interestingly, when cellulose was used, HMF yield was 35.0%. Although the yield was a little lower than that for glucose conversion, the use of cellulose avoided tedious hydrolysis and glucose separation processes. Clearly, the GeCl_4 -based system deserves further investigation to facilitate sustainable biorefining of cellulosic materials.

Possible mechanism for glucose conversion with [BMIM]Cl/ GeCl_4

Much effort has been devoted to revealing the mechanism of the conversion of glucose into HMF catalyzed by Lewis acids. However, in-depth understanding of this process remained scarce. To attain more insights into this transformation, we recorded a series of in situ ¹³C NMR spectra at different temperatures using D-glucose-2-¹³C as the substrate (Figure 9). Based on these data, we have formulated a putative mechanism for the GeCl_4 -promoted HMF production from glucose (Scheme 1).

The ¹³C NMR spectra indicated that glucose was in the forms of α -pyranose (**2**) and β -pyranose (**1**; Scheme 1) in [BMIM]Cl at room temperature in the absence of GeCl_4 (Figure 9a). However, when 1 equivalent of GeCl_4 was added into the mixture, a new peak at $\delta = 76.4$ ppm appeared (Figure 9b). The ability of heavier main-group elements to accommodate more than eight electrons in their valence shells, thus forming so-called hypervalent or hypercoordinate compounds, is well established.^[20] The cations of Group 14 elements can be stabilized

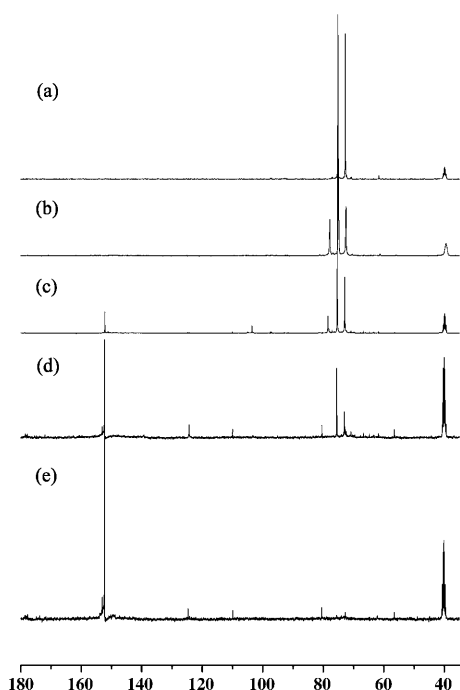
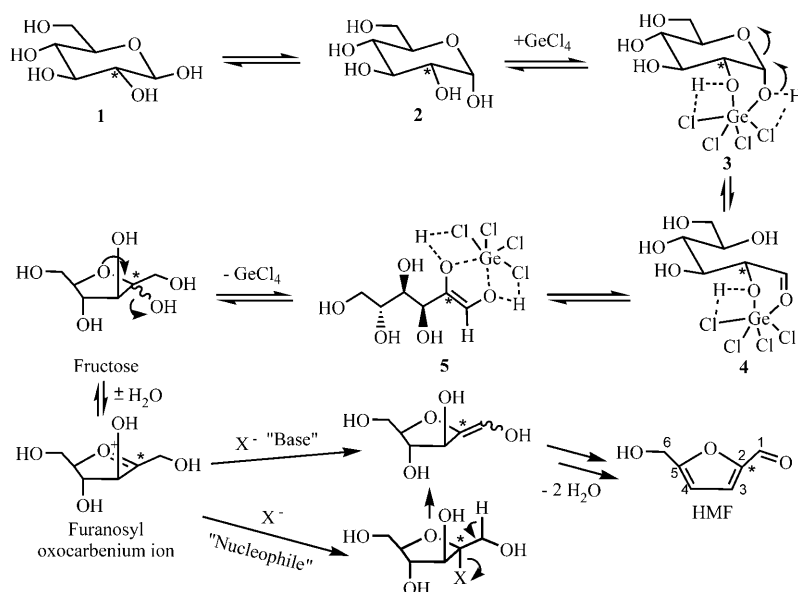


Figure 9. ^{13}C NMR spectra of 5 wt% D-glucose-2- ^{13}C in $[\text{D}_6]\text{DMSO}$ under different conditions: a) Without GeCl_4 at 25 °C; b) in the presence of 1 equivalent GeCl_4 at 25 °C; c) in the presence of 1 equivalent GeCl_4 at 50 °C; d) in the presence of 1 equivalent GeCl_4 at 80 °C; e) in the presence of 1 equivalent GeCl_4 at 100 °C.



Scheme 1. Proposed mechanism of HMF formation from glucose catalyzed by GeCl_4 .

thermodynamically by introduction of auxiliary NR_2 or OR groups, the lone electron pairs of which could, in principle, be capable of bonding to the empty p orbital of the Group 14 element.^[21] Therefore, we speculated that Ge^{IV} interacted with the two O atoms of 1,2-dihydroxy group of α -glucose to form a stable intermediate **3** (Scheme 1). When the ^{13}C NMR spectrum was recorded at 50 °C, the relative intensity of the peak at $\delta = 76.4$ ppm decreased, and two new peaks at $\delta = 152.1$ and

103.6 ppm appeared. The intensity of the signal at $\delta = 152.1$ ppm increased when the reaction was held at higher temperatures (Figure 9d and e) and also increased over time (data not shown). Therefore, this signal was assigned to the ^{13}C -labeled carbon of HMF at the 2-position. Assignment of the signal at $\delta = 103.6$ ppm was more tricky. Because this signal was found only at 50 °C, it should be associated to a relatively stable intermediate with a short lifetime along the reaction pathway to HMF. In other words, at higher temperature, the turnover of this intermediate was greatly accelerated. Therefore, we suppose it was from fructose,^[22] which indicated that the intermediate fructose was formed through glucose isomerization. Moreover, the signal at $\delta = 76.4$ ppm was missing at 80 °C, indicating that the conversion of **3** was fast. As proposed by Zhao et al., fructose was formed from glucose through an enediol intermediate catalyzed by GeCl_4 .^[10] Fructose then lost one water molecular to form the fructofuranosyl oxocarbenium ion.^[18] Due to the basicity and nucleophilicity of the halide ion (X^-), the oxocarbenium ion lost HX to form the enolic species through the nucleophile or the base pathway, followed by loss of two water molecules to form HMF.

Our results also suggested that increasing the reaction temperature would enhance the interaction of glucose and GeCl_4 , and thus promote a ring-opening step of the intermediate **3** to form the straight-chain intermediate **4** through hydrogen transfer, which could be enolized to form **5**, followed by the

release of GeCl_4 to give fructose (Scheme 1). At 80 °C, three new signals at $\delta = 56.1$, 110.9 and 124.3 ppm appeared, which were attributed to C6, C4 and C3, respectively, of HMF. A new peak at $\delta = 80.1$ ppm was also observed at 80 °C and 100 °C, which was attributed to a by-product formed during the reaction.

Additional mechanistic investigation was done using the "germanium reagent" phenylfluorone (Figure 10). When the reaction was run with glucose at 100 °C for 2 h in the presence of 10 mol% GeCl_4 and 30 mol% phenylfluorone, glucose conversion and HMF yield were 33.3% and 3.5%, respectively. Apparently, phenylfluorone significantly inhibited glucose conversion

and HMF production. As phenylfluorone could form stable complexes with Ge^{IV} , there would be much less catalytic species available for the turnover of glucose.

3. Conclusion

In this study, a new catalytic system based on germanium(IV) chloride has been established for the conversion of carbohy-

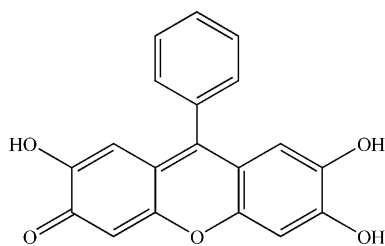


Figure 10. The structure of phenylfluorone.

drates into HMF. This system was excellent for fructose and moderate for other carbohydrates, such as glucose, cellobiose, sucrose, and cellulose, in terms of HMF yield. ^{13}C NMR spectroscopy suggested that there was a dedicated interaction between glucose and the catalyst, and that fructose was formed during the reaction. Furthermore, our system is more attractive than many other Lewis acid-catalyzed systems, as inorganic germanium species are of low toxicity.^[23] Our system should provide a new opportunity for the transformation of abundant and inexpensive cellulosic biomass through a nonfermentative process into biofuels and bio-based products.

Experimental Section

Materials

All of the ionic liquids except [BMIM]OAc were synthesized according to the known procedures.^[24] [BMIM]OAc was supplied by Lanzhou Greenchem ILS, LICP, CAS (Lanzhou, China). Glucose was purchased from ABCR GmbH & Co. (Karlsruhe, Germany) and fructose was from Sanland-Chem International Inc. (Xiamen, China). Avicel PH-101 (Cat. No. 11365) was purchased from Sigma (St. Louis, USA), and was dried under vacuum at 100°C for 24 h before use. Acetonitrile (HPLC grade) was purchased from Merck & Co. (Darmstadt, Germany). All of the metal salts were supplied by J & K Co. Ltd. (Beijing, China). All other chemicals were supplied by local suppliers and used without further purification.

HMF production

In a typical run, glucose (100 mg) and GeCl_4 (10 mol% based on glucose) were added into [BMIM]Cl (2.0 g). The mixture was heated at a specified temperature for the desired time under atmospheric pressure with a magnetic stirrer. Samples were withdrawn, diluted with water, centrifuged at 10000 rpm for 5 min and analyzed by HPLC.^[25]

Determination of HMF

HPLC analysis of HMF was done on a Dionex system (Dionex Co., CA, USA) equipped with Dionex P680 four-unit pump and PDA-100 photodiode array detector. The samples were separated using a reversed-phase C18 column (200×4.6 mm) at 280 nm. The column temperature was maintained at 30°C . The optimized mobile phase consisted of acetonitrile and 0.1 wt%

acetic acid aqueous solution with the volume ratio 15:85. The flow rate was set at 1.0 mL min^{-1} .

Determination of glucose

The ion chromatography system was from Dionex. The hardware consisted of an ICS-2500 system equipped with a GP50 gradient pump, an ED50 A integrated amperometry detector, a CarbonPac PA10 guard column ($4 \text{ mm} \times 50 \text{ mm}$), a high capacity CarbonPac PA20 analytical column ($3 \text{ mm} \times 150 \text{ mm}$), a $25 \mu\text{L}$ sample loop. Samples were eluted with 30 mM NaOH at a rate of 0.5 mL min^{-1} .

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Keywords: carbohydrates • germanium • ionic liquids • oligosaccharides • sustainable chemistry

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