Selective Dehydration of Glucose into 5-Hydroxymethylfurfural by Ionic Liquid-ZrOCl$_2$ in Isopropanol

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Abstract: In this work, a heterogeneous catalytic system consisting of [HO$_2$CMMIm]Cl and ZrOCl$_2$ in isopropanol is demonstrated to be effective for 5-hydroxymethylfurfural (HMF) synthesis with glucose as the feedstock. Various reaction conditions for HMF synthesis by glucose dehydration were investigated systematically. Under optimized reaction conditions, as high as 43 mol% HMF yield could be achieved. Increasing the water content to a level below 3.17% led to the production of HMF with a higher yield, while a lower HMF yield was observed when the water content was increased above 3.17%. In addition, the data also showed that ZrOCl$_2$ could not only effectively convert glucose into intermediate species (which were not fructose, in contrast to the literature) but also catalyze the intermediate species' in situ dehydration into HMF. [HO$_2$CMMIm]Cl was used to catalyze the intermediate species' in situ conversion to HMF. The kinetics data showed that a temperature increase accelerated the intermediate species' dehydration reaction rate. The reaction of glucose dehydration was a strong endothermic reaction.

Keywords: glucose; 5-hydroxymethylfurfural; dehydration; [HO$_2$CMMIm]Cl; ZrOCl$_2$; kinetics

1. Introduction

Carbohydrates, as a renewable and abundant biomass feedstock, represent a promising carbon source. Therefore, an efficient and economical process that can convert carbohydrates into useful chemicals is highly desirable. Production of 5-hydroxymethylfurfural (HMF) with carbohydrates as the feedstock is one of the hot points in the process of material resources' comprehensive utilization. HMF has been proposed by the US Department of Energy to be one of the top 12 platform chemicals, having the potential to be a building block in the synthesis of furanic-based polyamides, polyesters, and polyurethanes analogous to petroleum-based terephthalic acid [1–6].

HMF can be produced from glucose and fructose through acid catalysts [7]. In the past decade, HMF synthesis from fructose has been studied widely, and as high as 90% HMF yields have been readily achieved [8–22]. Glucose is the most abundant and cheap C6 sugar, so the syntheses of HMF from glucose is more attractive. A variety of solvents have been investigated for converting glucose into HMF, such as water [23,24], organic solvents (e.g., DMSO) [2], organic/aqueous binary mixtures [25–29], and ionic liquids [17,30–34]. Many more catalyst systems have also been developed for glucose dehydration, such as Lewis acid catalysts [35], tantalum compounds [36], boric acid [37],

ionic liquids (ILs) [38], ion exchange resins [39], zeolites [40,41], chromium(0) nanoparticles [42], Sn–Mont catalyst [4], bifunctional SO_4^{2-}/ZrO_2 catalysts [43], mesoporous tantalum phosphate [44], and so on.

Recently, HMF synthesis by sugar dehydration with ionic liquids (ILs) as solvents or using acidic ionic liquids [45–47] as catalysts has grown rapidly because of its unique and tunable properties. In fact, a 70% HMF yield with 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as the reaction solvent can be obtained over a chromium (II) chloride catalyst [17]; a 83.4% HMF yield can be obtained over a chromium (II) chloride catalyst in 1,8-diazabicyclo [5.4.0]undec-7-ene-based ionic liquids [32]; a 48.4% HMF yield was observed over a germanium (IV) chloride catalyst in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) with glucose as the feedstock [34]; a 58.3% HMF yield can be obtained over a tin phosphate catalyst with the ionic liquid EMIMBr as the solvent [48]; a 67.3% HMF yield was reported over a 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ionic liquid catalyst in DMSO [38]. Only a 50.6% HMF yield with glucose as the feedstock was achieved in DMSO over the 1-carboxypropyl-3-methyl imidazoliumchloride ([CMIm]Cl) and $ZrOCl_2$ catalyst system by Hu et al., although a 95.7% HMF yield can be obtained with fructose as the feedstock over a [CMIm]Cl catalyst [16].

It is well known that the isomerization of glucose into fructose is a key step in the synthesis of HMF from glucose (Scheme 1). Recently, it was reported that the isomerization of glucopyranose to fructofuranose could be effectively catalyzed by $ZrOCl_2$ [49]. Hu et al. also reported that the isomerization of glucose into fructose could be obtained with $ZrOCl_2$ as the catalyst [16].

Recovery of ionic liquid is usually done by extraction with diethyl ether (Et_2O) [50]. However, diethyl ether is easily volatized, so developing a new method of recovery of the ionic liquid without an organic solvent is highly desirable. In our previous work, [HO_2CMMIm]Cl could be recovered by centrifugation. A 91.2% HMF yield for fructose dehydration could be obtained with [HO_2CMMIm]Cl as the catalyst in isopropanol [51], but only a 6.7% HMF yield could be obtained for glucose dehydration. Thus, a catalytic system with $ZrOCl_2$ and [HO_2CMMIm]Cl was developed in this study to catalyze glucose conversion to HMF.
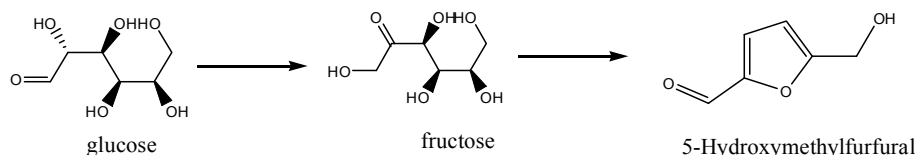
Scheme 1. Dehydration of glucose into 5-hydroxymethylfurfural (HMF).

In this work, a [HO_2CMMIm]Cl–$ZrOCl_2$–isopropanol system was reported to catalyze glucose conversion into HMF, as shown in Scheme 2. Interestingly, no fructose was found in the reactions, and more than 90% glucose conversion with less than 3% HMF yield was observed in a few minutes. $ZrOCl_2$ was used not only for glucose conversion but also for production of HMF; [HO_2CMMIm]Cl was used for production of HMF. These data suggest that glucose was first converted into intermediate species, but the intermediate species were not fructose; therefore, the possible reaction route was not in agreement with the route reported in the literature [16,52]. Increasing the water content (below 3.17%) led to a higher HMF yield, but only a 4.9% HMF yield was obtained with 60% water content. Furthermore, the catalyst system could be recovered by centrifugation without an organic solvent.
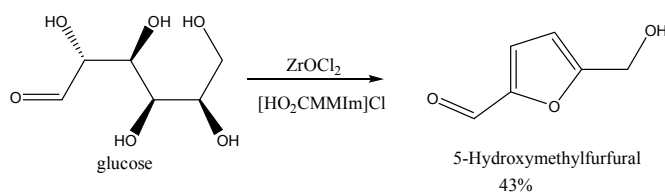
Scheme 2. Glucose dehydration by [HO_2CMMIm]Cl ionic liquid (IL)–$ZrOCl_2$ in isopropanol.

2. Results & Discussion

2.1. Effect of IL [HO₂CMMIm]Cl Loading on the Catalytic Performance

In our previously works, a 91.2% HMF yield for fructose dehydration could be obtained with [HO$_2$CMMIm]Cl as the catalyst in isopropanol [51]. Therefore, a reaction of glucose dehydration was carried out, but only a 6.7% HMF yield with 92% glucose conversion was observed. Based on the literature [16], ZrOCl$_2$ was introduced into the catalytic system. A 25% HMF yield with 95.8% glucose conversion was achieved in a 3 h reaction at 150 °C, with 0.15 g ZrOCl$_2$ and 0.1 g [HO$_2$CMMIm]Cl as the catalyst. Therefore, we studied the effect of IL [HO$_2$CMMIm]Cl loading on the catalytic performance, and the results are listed in Figure 1. It can be seen that the selectivity of HMF increased gradually with the increase of the amounts of [HO$_2$CMMIm]Cl; HMF yield first increased with [HO$_2$CMMIm]Cl loading increase, reached a maximum of 29.3% at 50 mg [HO$_2$CMMIm]Cl, then decreased with further increases of [HO$_2$CMMIm]Cl loading. This suggested that [HO$_2$CMMIm]Cl could increase HMF selectivity, and that ZrOCl$_2$ not only was favorable to the conversion of glucose, but also could increase the yield of HMF.
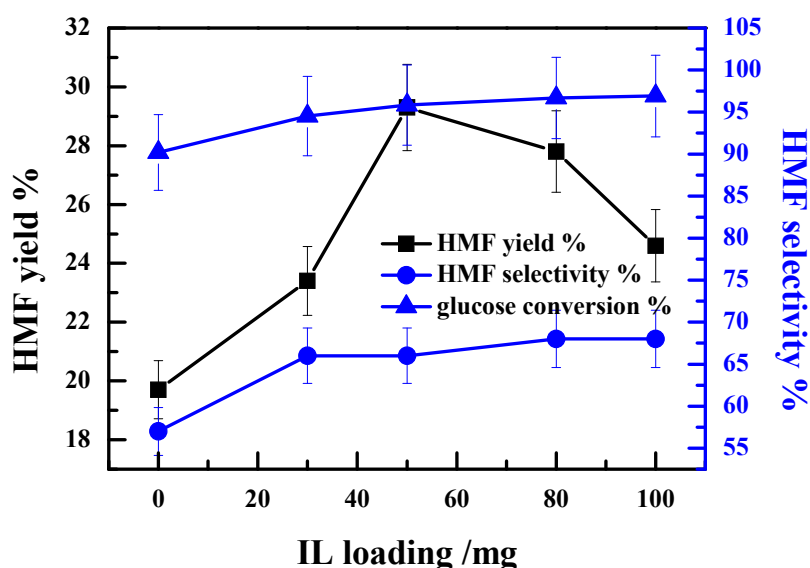

Figure 1. Effect of IL [HO$_2$CMMIm]Cl loading on glucose dehydration.Experimental conditions: 0.15 g ZrOCl$_2$, 0.1 g glucose, 3.0 g isopropanol, 3 h reaction time, 150 °C reaction temperature.

2.2. Effect of ZrOCl$_2$ Loading on the Catalytic Performance

In the above section, ZrOCl$_2$ was not only favoring the conversion of glucose, but also increasing HMF yield. So, the effects of ZrOCl$_2$ loading on the catalytic performance were examined with 50 mg [HO$_2$CMMIm]Cl as the catalyst, and the results are summarized in Figure 2. it can be seen that the yield of HMF increased dramatically with ZrOCl$_2$ loading at the beginning, with up to 30% HMF yield achieved at 200 mg ZrOCl$_2$ loading when the reaction was conducted at 150 °C. While the yield of HMF decreased as ZrOCl$_2$ loading increased to 250 mg, the selectivity of HMF first increased, then decreased.
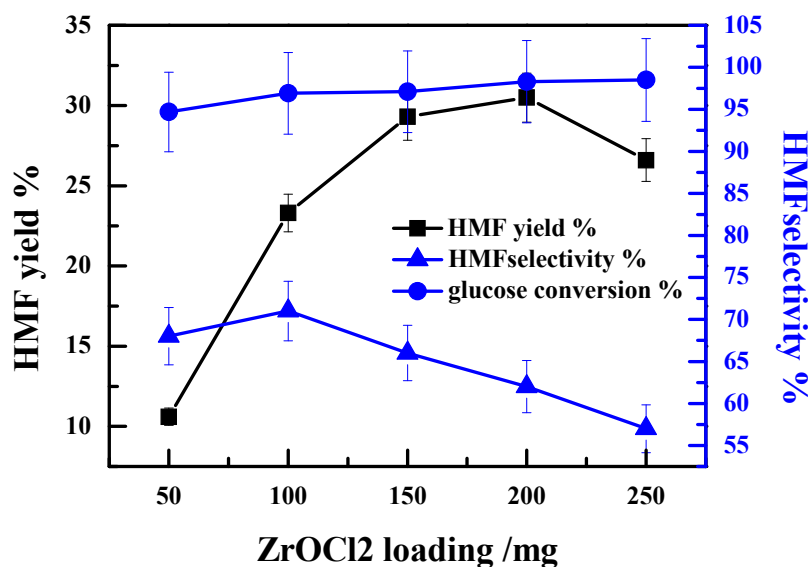
Figure 2. Influence of ZrOCl$_2$ loading on glucose conversion. Reaction conditions: 0.05 g [HO$_2$CMMIm]Cl, 0.1 g glucose, 3.0 g isopropanol, 3 h reaction time, 150 °C reaction temperature.

2.3. Influence of the Reaction Time on the Catalytic Performance

The influence of the reaction time on glucose conversion, HMF yield, and selectivity was also investigated, and the data are summarized in Figure 3. It can be seen that the conversion of glucose increased sharply to 93% in the first 5 min, then increased gradually from 93% to 98% in the following 3 h, while the yield of HMF was only 1% in the first 5 min and then gradually increased to 29.3% in the following 3 h; HMF selectivity gradually decreased from 90% to 66% in 3 h. These data suggested that glucose could be converted into intermediate species within a short time. The intermediate species were not fructose according to the results from HPLC, and a longer reaction time was necessary for HMF production from the intermediate species by the [HO$_2$CMMIm]Cl–ZrOCl$_2$–isopropanol system.
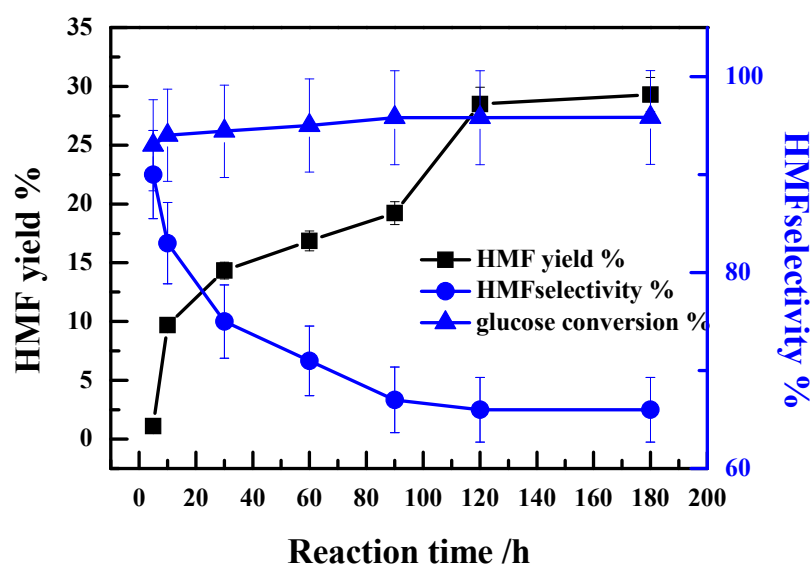

Figure 3. Effect of reaction time on glucose dehydration Reaction conditions: 0.15 ZrOCl$_2$, 0.15 g [HO$_2$CMMIm]Cl, 0.1 g glucose, 3.0 g isopropanol, 150 °C reaction temperature.

2.4. Effect of the Reaction Temperature on the Catalytic Performance

The effect of the reaction temperature on glucose dehydration in isopropanol over the [HO$_2$CMMIm]Cl–ZrOCl$_2$ catalyst system (reaction time of 3 h) was also examined, and the data are listed in Figure 4. The conversion of glucose gradually increased from 80% to 95.8% when increasing the temperature from 120 °C to 160 °C, while the yield of HMF increased to 29.3% from 6.7% with a reaction temperature increase from 120 °C to 150 °C and remained unchanged as the reaction temperature further increased to 160 °C. The change in the selectivity of HMF was very limited, ranging from 68% to 66% under the studied reaction temperature.
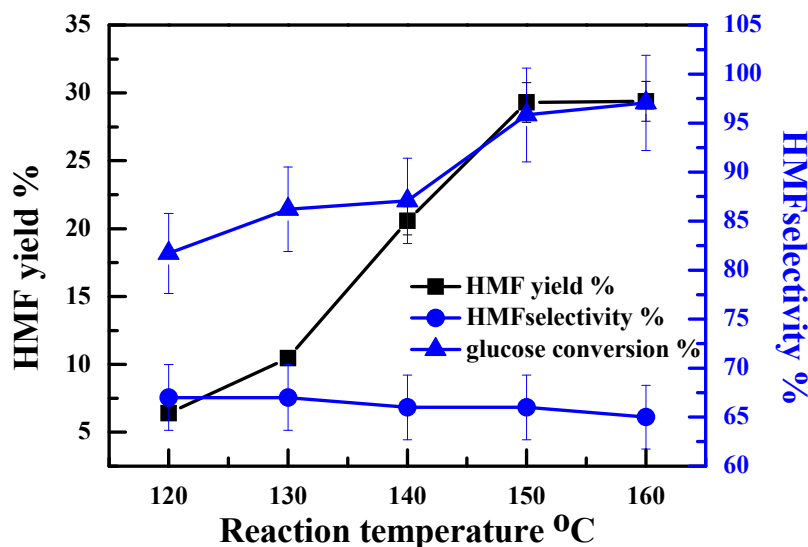

Figure 4. Effect of the reaction temperature on HMF yield, during glucose conversion. Experimental conditions: 0.15 g ZrOCl$_2$, 0.05 g [HO$_2$CMMIm]Cl, 0.1 g glucose, 3.0 g isopropanol, 3 h reaction time.

2.5. Effect of Substrate Loading on HMF synthesis

The effect of the glucose loading on glucose dehydration was also examined under the conditions of 0.05 g [HO$_2$CMMIm]Cl, 0.15 g ZrOCl$_2$, 150 °C reaction temperature, and 3 h reaction time, and the data are listed in Figure 5. HMF yield decreased from 43% to 27% with the increase of glucose loading from 30 mg to 120 mg. This could arise from increased glucose concentration in isopropanol, which likely favored side reactions such as polymerization and rehydration, producing humins as the main by-product. The selectivity of HMF showed a similar trend. The conversion of glucose decreased gradually.

2.6. Effect of Water Content on the Catalytic Performance

Figure 6 shows the influence of water on glucose dehydration in isopropanol at 150 °C. In isopropanol, glucose was firstly converted into the intermediate species, and the intermediate species were subsequently converted to HMF. A 29.3% HMF yield was achieved after a 3 h reaction. The conversion of the intermediate species to HMF was dramatically enhanced by the addition of 3.17 wt % water. The yield of HMF increased to 35.2% with the addition of 3.17 wt % water to the isopropanol. The intermediate species convertion to HMF was inhibited in the presence of more than 10 wt % water. Only a 4.9% HMF yield was observed in the presence of 60 wt % water. These data suggested that the catalytic reaction could be accelerated, and the concentration of the catalytic active species could be decreased by increasing the water content to a certain range.
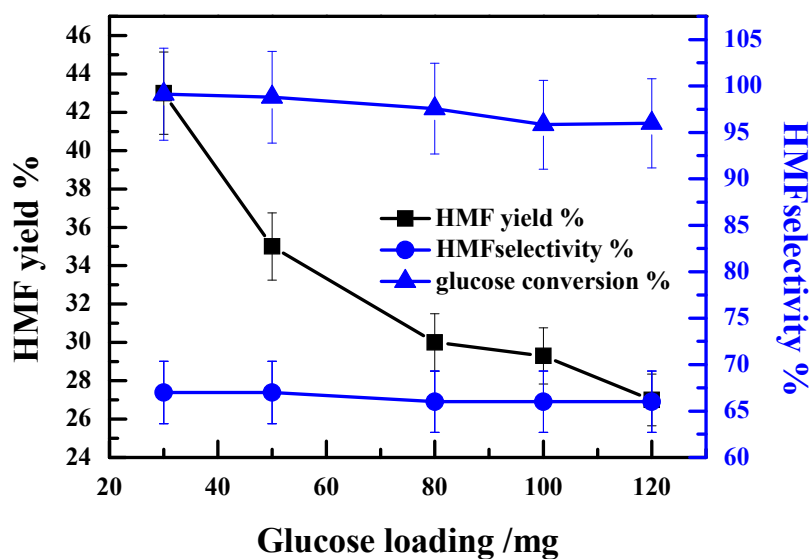
Figure 5. Effect of Substrate loading on glucose conversion.Reaction conditions: 0.15 g ZrOCl$_2$, 0.05 g [HO$_2$CMMIm]Cl, 3.0 g isopropanol, 3 h reaction time, 150 °C reaction temperature.
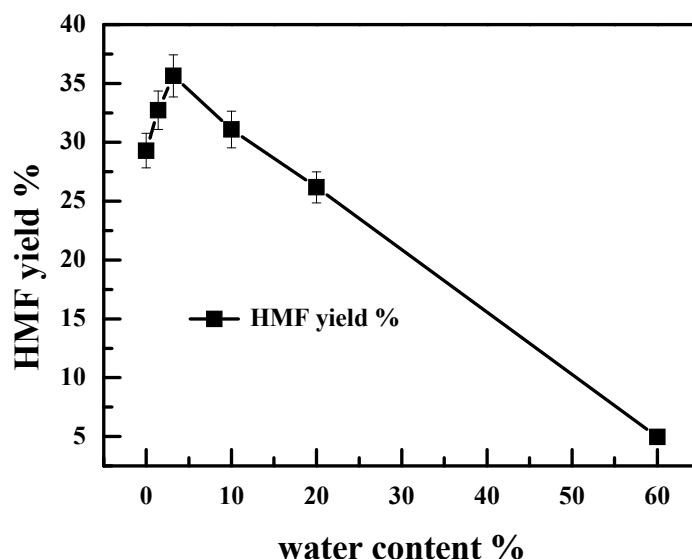

Figure 6. Effect of water content% on glucose dehydration.Experimental conditions: 0.1 g glucose, 0.15 g ZrOCl$_2$, 0.05 g [HO$_2$CMMIm]Cl, 3.0 g isopropanol, 3 h reaction time, and 150 °C reaction temperature.

2.7. Kinetics Studies

We considered that, in our work, glucose dehydration consisted of two processes, the first of which was glucose convertion into the intermediate species, and the second was the intermediate species convertion into HMF, which could be assumed to be the rate-determining step. As shown elsewhere, in this case, the overall rate can be written in terms of a product of equilibrium constants for the steps that are not rate-determining, multiplied by the equilibrium constant for the formation of the transition state for the rate-determining step [53,54]. Accordingly, the overall rate can be expressed in terms of a single equilibrium constant (k, which is a product of the individual equilibrium constants, for example, for HMF) for the formation of the rate-determining transition state from the reactant R [55].

Therefore, in our work, the kinetics of glucose dehydration was analyzed according to the HMF yield. The first few intermediate species (IS) $[IS]_t$ data points were used to construct liner $\ln([IS]_t/[IS]_0)$ versus t plots (Equation (1)), and the first-order rate constants, k, were obtained from the slope

(the glucose dehydration reaction was established to occur as follows: glucose was first converted into fructose, then fructose was converted into HMF; the rate constant of fructose conversion to HMF was described as first-order in the literature; therefore, a first-order rate constant was assumed for glucose dehydration in this work):

$$\ln \langle \frac{[IS]_t}{[IS]_0} \rangle = -kt \tag{1}$$

where $[IS]_t$ = IS concentration at time t, $[IS]_0$ = initial IS concentration, k = observed rate constant, and t = time in minutes.

As summarized in Table 1, the value of k increased with the reaction temperature increase, indicating that the dehydration reaction of the intermediate species would be accelerated by a higher reaction temperature:

$$\ln k = -\frac{E}{RT} + \ln A \tag{2}$$

where k is the observed rate constant, E is the activation energy, T is the temperature in kelvin, R is the ideal gas constant, A is the pre-exponential factor.

Table 1. Reaction rate constants (k) of glucose dehydration at various reaction temperatures [a].

Entry	Temperature °C	$k \times 10^3$ (min^{-1})	Correlation Coefficient
1	140	89.1	0.986
2	150	118.7	0.989
3	160	152.4	0.977

[a] Experimental conditions: 3 h reaction time, 0.05 g [HO$_2$CMMIm]Cl, 0.15 g ZrOCl$_2$, 0.1 g glucose, and 3 g isopropanol.

An Arrhenius plot was obtained, as shown in Figure 7. Based on these data, the kinetic parameters for [HO$_2$CMMIm]Cl–ZrOCl$_2$-catalyzed glucose dehydration could be calculated. An apparent activation energy of 48.01 KJ/mol was calculated.
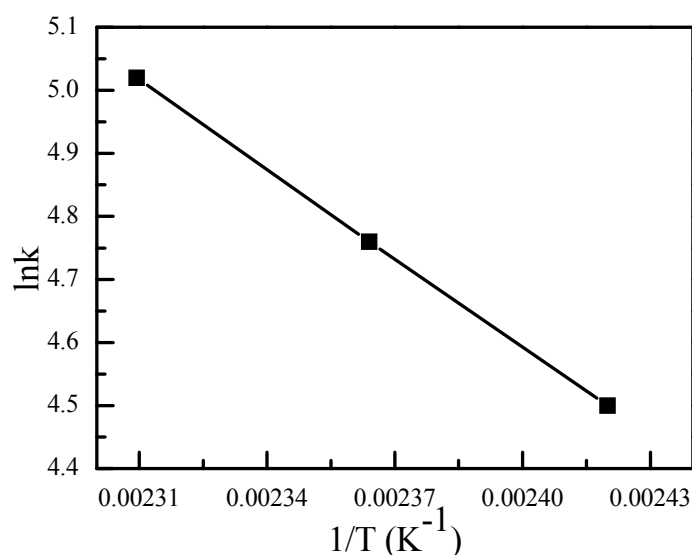

Figure 7. Arrhenius plot for glucose dehydration in isopropanol over [HO$_2$CMMIm]Cl–ZrOCl$_2$.

Jack M. Carraher [56] reported that $\Delta H = Ea - RT$. On the basis of this equation, ΔH at different temperatures could be obtained, and the results are listed in Table 2. Obviously, all values of ΔH were higher than 47 kJ mol^{-1}, suggesting that the reaction of glucose dehydration was a strong endothermal reaction, and thus a high reaction temperature was favorable to obtaining the intermediate species conversion.

Table 2. The values of ΔH at different reaction temperatures.

Entry	Reaction Temperature	$\Delta H/kJ\ mol^{-1}$
1	140	47.976
2	150	47.975
3	160	47.974

2.8. Recycling of the Catalysts

Tests were carried out for the recycling of the catalyst, and the results are summarized in Table 3. It can be seen that there was only a slight decrease of the catalytic performance of the catalyst, suggesting that the catalyst could be recycled and reused. A possible reason for the decreased yield of HMF may be that a certain amount of catalyst was not recycled by centrifugation.

Table 3. Recycling of the catalyst.

Run	Glucose Conversion %	HMF Yield %
1	99	43
2	99	41
3	99	40
4	99	39
5	99	38

Reaction conditions: 0.15 g $ZrOCl_2$, 0.05 g [HO_2CMMIm]Cl, glucose 0.03 g, 3.0 g isopropanol, 3 h reaction time, 150 °C reaction temperature.

3. Experimental Section

3.1. Materials

The IL [HO_2CMMIm]Cl) was supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. All the other materials, such as glucose, fructose, $ZrOCl_2$, isopropanol, were analytic-grade, purchased from Alfa Aesar and used as received without further purification.

3.2. Reaction Testing

Glucose dehydration was carried out in a 10 mL thick-walled glass reactor made by Alltech. An oil bath with an Isotemp digital stirring hot plate was used to heat the reactor rapidly to the desired reaction temperature. In addition, a triangular stir bar was placed in the bottle of the reactor before adding the reactants, so as to give an adequate agitation. A typical experiment was as followed: 0.1 g glucose, 0.05 g [HO_2CMMIm]Cl, 0.15 g $ZrOCl_2$, and 3.0 g isopropanol were introduced into the reactor. Then the reactor was sealed and immersed in the oil bath at 150 °C and stirred at 400 rpm. After 120 min, the reactor was removed from the oil bath and then cooled rapidly to room temperature with water. Other reactions were carried out by changing the reaction temperature, reaction time, glucose loading, [HO_2CMMIm]Cl and $ZrOCl_2$ amounts. For all the reactions, some amounts of brownish humins formed. Humin formation precluded a closed carbon balance analysis, and thus the only product analyzed was HMF. Each reaction was repeated at least three times, and the average yield was reported.

3.3. Sample Analysis

All the liquid samples were precipitated by centrifugation. The upper liquid was analyzed with a Shimadzu LC-20A liquid chromatography. HMF was measured with a SPD-20A UV detector at 280 nm and an InterSustain C18 column at 313 K, with a methanol/5 mM H_2SO_4 (8:2 *v/v*) binary solvent as the mobile phase at a flow rate of 0.6 mL/min. The amount of glucose was analyzed by introducing 2 mL of water into the upper liquid and then measured with a refractive index (RI-20A)

detector, under the conditions of 333 K, with 5 mM H_2SO_4 at a flow rate of 0.6 mL min^{-1} as the mobile phase, with an Aminex HPX-87H Column.

In this manuscript, conversion and selectivity are defined as follows: conversion of glucose is defined as the amount of reacted glucose divided by the moles of initial glucose added; selectivity of HMF is defined as the moles of HMF produced divided by the amount of reacted glucose. The yield of HMF is defined as converted glucose multiplied by HMF selectivity.

4. Conclusions

In summary, a combination of the [HO$_2$CMMIm]ClZrOCl$_2$ catalyst system and isopropanol for HMF synthesis with glucose as the feedstock was developed. A series of experiments was examined over a broad range of conditions (reaction temperature, reaction time, water content, and catalyst and substrate loadings) to explore the rate and selectivity of glucose dehydration. Up to 43% HMF yield could be obtained with 0.03 g glucose, 0.05 g [HO$_2$CMMIm]Cl, 0.15 g ZrOCl$_2$ in 3 mL isopropanol, at 150 °C reaction temperature and in 3 h reaction time.

It was demonstrated that [HO$_2$CMMIm]Cl could increase HMF selectivity and that ZrOCl$_2$ not only was favorable to glucose conversion but also increased HMF yield under the examined reaction conditions. ZrOCl$_2$ affected the reaction in two opposite ways, and these opposite factors resulted in the highest yield corresponding to twice the mass loading of ZrOCl$_2$. Glucose could be converted to intermediate species within a short time (about 5 min), and the intermediate species were not fructose according to the HPLC results; a longer reaction time (3 h or longer) were needed for HMF production from the intermediate species over the [HO$_2$CMMIm]Cl-ZrOCl$_2$ catalyst. The conversion of the intermediate species to HMF was dramatically increased by the addition of 3.17 wt % water. The performance of the catalytically active species could be enhanced by increasing the water content, and the concentration of the catalytically active species could be decreased by increasing the water content to a certain range. The kinetics data showed that a higher temperature accelerated the intermediate species dehydration reaction rate [51]. The glucose dehydration reaction was a strong endothermal reaction, thus a high reaction temperature was favorable to glucose and intermediate species conversion.

Author Contributions: Y.M., L.W., and R.Z. performed the experiments; H.L. and T.W. conceived the idea. All the authors contributed to the writing of the manuscript.

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