

Article

Catalytic Conversion of Glucose into 5-Hydroxymethylfurfural by Hf(OTf)₄ Lewis Acid in Water

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Abstract: A series of Lewis acidic metal salts were used for glucose dehydration to 5-hydroxymethylfurfural (HMF) in water. Effect of valence state, ionic radii of Lewis acidic cation, and the type of anions on the catalytic performance have been studied systematically. The experimental results showed that the valence state played an important role in determining catalytic activity and selectivity. It was found that a higher glucose conversion rate and HMF selectivity could be obtained over high valent Lewis acid salts, where the ionic radii of these Lewis acidic metal salts are usually relatively small. Analysis on the effect of the anions of Lewis acid salts on the catalytic activity and the selectivity suggested that a higher glucose conversion and HMF selectivity could be readily obtained with Cl⁻. Furthermore, the recyclability of high valence state Lewis acid salt was also studied, however, inferior catalytic performance was observed. The deactivation mechanism was speculated to be the fact that high valence state Lewis acid salt was comparatively easier to undergo hydrolysis to yield complicated metal aqua ions with less catalytic activity. The Lewis acidic activity could be recovered by introducing a stoichiometric amount of hydrochloric acid (HCl) to the catalytic before the reaction.

Keywords: glucose; HMF; Lewis acids; dehydration

1. Introduction

Growing concerns about global warming and depletion of fossil-derived carbon resources has prompted the exploration of developing sustainable alternative energy sources to lessen human dependence on the finite fossil reserves. Lignocellulosic biomass, one of the most abundant and renewable carbon resources occurring in nature, has been widely considered as a promising alternative to non-renewable resources for the production of fuels and chemicals [1–5]. Cellulose (a polymer of C6 sugars) and hemi-cellulose (a polymer of C5 sugars) are the most abundant part of nonedible biomass, accounting for about 75% of the renewable and lignocellulosic feedstock. Recently, several efficient approaches for the conversion of carbohydrates into useful platform chemicals have been reported. One of the most promising conversion routes involves the synthesis

of the biomass-derived platform chemical 5-hydroxymethylfurfural, (HMF) from biomass. The HMF molecule, which has been included in the list of the top 12 platform chemicals with the potential to be produced at scale by the US Department of Energy, is a versatile platform intermediate which could possibly be converted to make fine chemicals, plastics, pharmaceuticals, and transportation fuels [6–11].

In the past decades, the preparation of HMF through the dehydration of biomass-based sugars has received much attention, especially in the case of C6 sugar (glucose or fructose) dehydration [12]. Many researchers have studied the production of HMF from C6 carbohydrates such as fructose, and excellent HMF yields have been achieved [13–26]. Since glucose is the more abundant and economical monosaccharide in nature compared with fructose, the production of HMF from glucose is more attractive from a cost-competitiveness perspective.

Examining the literature would lead to the finding that organic/aqueous binary mixtures [23,24,27–29], water [26,30], organic solvents [7], ionic liquids [22,25,31–34], etc., have been used as the solvent to carry out glucose dehydration. Among these solvents, an organic/aqueous binary mixture system is one of the most appealing systems that could effectively solve the dilemma of catalytic activity and product selectivity. Since Dumesic and co-workers reported that fructose dehydration could be conducted in a biphasic reactor with excellent yields [24], much effort has been devoted to developing a more efficient and environmentally friendly process for the conversion of glucose into HMF in a biphasic system by adding the catalytic functionality of glucose isomerization to the fructose step. For instance, a 63% HMF yield was reported by Huang *et al.* [35] by the use of a two-step reaction system where glucose is first converted to fructose by enzymes in aqueous media, and the produced fructose could be subsequently dehydrated to HMF with HCl as a catalyst in a biphasic reactor. HMF yields of 57% were achieved from glucose with Sn-Beta zeolites and HCl as catalysts in an aqueous/Tetrahydrofuran (THF) biphasic reaction system [36]. Wang *et al.* [29] reported that the pH value of the aqueous solution played an important role in controlling the Lewis acidity of MCl_x -type metal salts in water. In addition, in that report, an HMF yield greater than 60% could be achieved by using a combination of $AlCl_3$ and HCl in a biphasic system.

Up to now, many more catalysts, such as Lewis acid catalysts [37], boric acid [38], tantalum compounds [39], Sn-Mont catalyst [9], ion exchanged resins [40], bifunctional SO_4^{2-}/ZrO_2 catalysts [41], ion exchanged zeolites [42,43], chromium(0) nanoparticles [44], ionic liquids (ILs) [45], and mesoporous tantalum phosphate [46] have been reported for glucose dehydration. In addition, Lewis acidic metal salt catalysts, including Al^{3+} , Ga^{3+} , In^{3+} , Sn^{4+} , La^{3+} , Dy^{3+} , Yb^{3+} , Zn^{2+} , Ge^{4+} , Cr^{3+} , Cr^{2+} , and Cu^{2+} have been reported as active catalysts for glucose conversion [23,47–54]. Integrating the Lewis acid properties of the metal for the isomerization of glucose to fructose, and the protons resulting from the metal hydrolysis as a Brønsted acid to catalyze the fructose dehydration reaction were commonly explored in most of the abovementioned literatures. For example, a higher than 60% HMF yield was achieved by using a combination of $AlCl_3$ and HCl in a one-pot biphasic system, as reported independently by three research groups [29,47,52]. However, there has been quite limited study in the literature to systematically examine the influence of the Lewis acid salts, such as the valence state, ionic radii of Lewis acid salts, metal type, and the anion type of the Lewis acid salts, etc., on the catalytic performance of glucose dehydration.

In our previous work [29], the effect of the reaction conditions, such as Lewis acidic metal type, pH values of the reaction media, temperature, etc., were systematically studied; the glucose conversion kinetic profiles and HMF product selectivity were used to examine the importance of the Lewis acid character for the different metal ions. In order to further understand the characteristics of the Lewis acid salts, such as the valence state, ionic radii of Lewis acid salts, the metal and anion type of the Lewis acid salts, the recyclability of these catalysts under reaction conditions, in this work the glucose dehydration reaction was carried out with various Lewis acid salts in an aqueous/sec-butyl phenol biphasic reaction system to explore these parameters. Furthermore, the recyclability of high

valence state Lewis acid salt was carried out and the deactivation mechanisms were also explored with possible catalytic activity recovery strategies being developed.

2. Results and Discussion

Based on our previous work regarding the effect of reaction conditions, such as Lewis acidic metal type, pH values of the reaction media, temperature, *etc.*, on the glucose dehydration [29], in the present work we seek to further explore the effect of the valence state, ionic radii of Lewis acid salts, and metal and anion type of the investigated Lewis acid salts. Subsequently, we continue to study the most highly active catalyst, emphasize the recyclability of these Lewis acid salts, and examine the deactivation mechanism and propose appropriate methods to recover the catalytic activities.

2.1. Effect of Ionic Radii of Lewis Acidic Metal Salts on the Catalytic Performance

In this work, two kinds of Lewis acidic metal salts were selected to examine the effect of ionic radii of these cations on catalytic performance. One type involved cations with a trifluoromethanesulfonic anion, and the results of catalysis are shown in Figures 1 and 2. Another type was chosen with chloride as the anion, with the data being plotted in Figures 3 and 4. As shown in Figures 1 and 2 the highest glucose conversion (60%) and yield of HMF (49%) were observed over the $\text{Al}(\text{OTf})_3$ catalyst, which has the smallest ionic radii of metal. The yield of HMF decreased following the order of $\text{Sc}(\text{OTf})_3 > \text{La}(\text{OTf})_3 > \text{Yb}(\text{OTf})_3$. A similar rule was observed with catalysts where Cl^- was the anion (Figures 3 and 4).

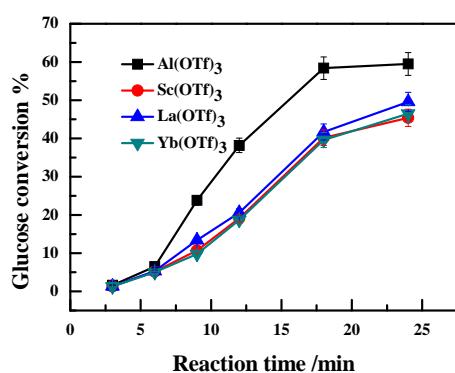


Figure 1. Effect of ionic radii of Lewis acidic metal salts on the conversion of glucose. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

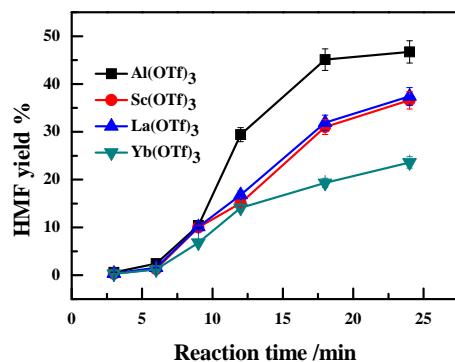


Figure 2. Effect of ionic radii of Lewis acid salts on the yield of HMF. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

All these results collectively suggest that the ionic radii of Lewis acid salts had an important role in controlling catalytic activity of glucose dehydration, with the yield of HMF decreasing upon increasing the ionic radii of Lewis acidic metal salts. The possible reason for the increased catalytic activity with decreasing ionic radius of the Lewis acid is due to stronger electrostatic attraction between the glucose molecule and the smaller cations, owing to their higher effective surface charge density.

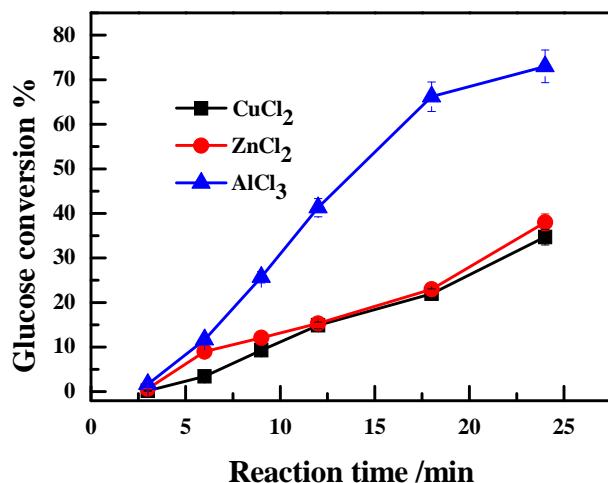


Figure 3. Effect of ionic radii of Lewis acid salts on the conversion of glucose. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

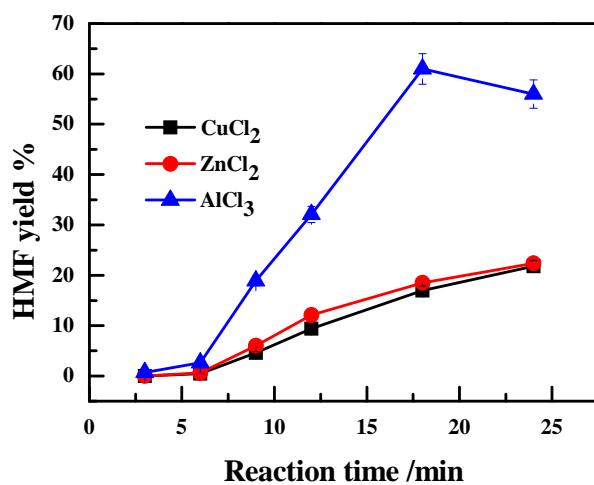


Figure 4. Effect of ionic radii of Lewis acid salts on the yield of HMF. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

2.2. Effect of the Anion Type of Lewis Acidic Metal Salts on the Catalytic Performance

The effect of the anion type of Lewis acidic metal salts on the catalytic performance was also examined over 25 mM Lewis acids under the following reaction conditions: reaction temperature of 160 °C and reaction time of 25 min. The data are summarized in Figures 5 and 6. It can be seen that a higher glucose conversion and HMF yield was achieved with Cl^- as the anion, which was in agreement with the data obtained in our previous work [29]. Furthermore, the reaction rate and HMF selectivity were also better with Cl^- as the anion. It has been demonstrated that under low pH

conditions, AlCl_3 speciation in aqueous media is composed of primarily Al^{3+} , AlCl^{2+} , and Al(OH)^{2+} , which are active Lewis species for the glucose-to-fructose isomerization [29]. The difference in glucose conversion rate and HMF selectivity may be attributed to the fact that the trifluoromethanesulfonic anion might be involved in some side reaction to alter aluminum cation speciation and/or to react with HMF, thereby resulting in slower glucose conversion kinetics and a lower HMF yield.

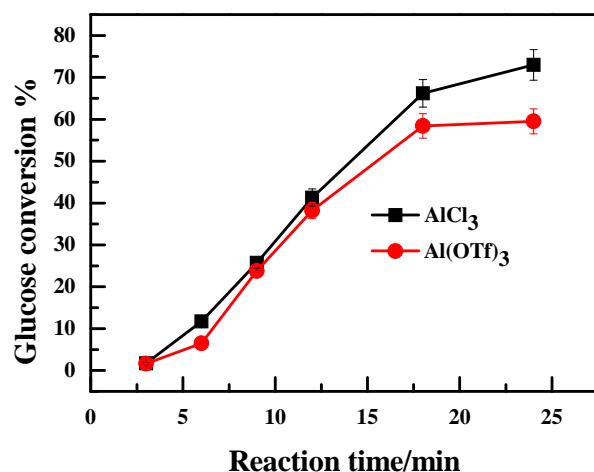


Figure 5. Effect of the anion style of Lewis acid salts on the conversion of glucose. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

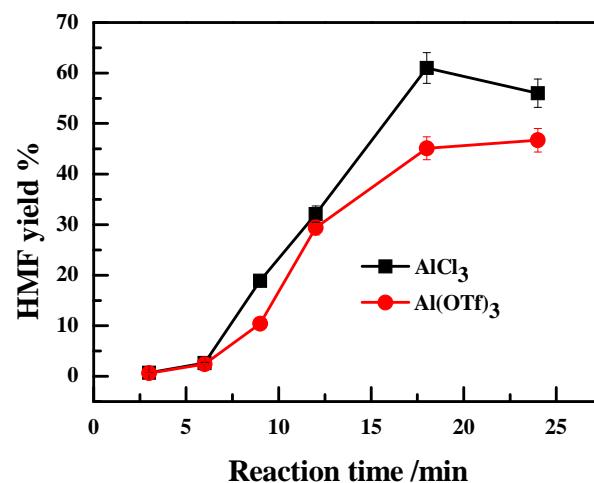


Figure 6. Effect of the anion style of Lewis acid salts on the yield of HMF. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

2.3. Effect of Valence State of Lewis Acidic Metal Salts on the Catalytic Performance

The effect of valence state of Lewis acidic metal salts on the catalytic performance was carried out over different valence states of trifluoromethanesulfonic acid salt catalysts under the reaction conditions of 160 °C reaction temperature and 25 min reaction time, and the results were plotted in Figures 7 and 8. As shown in Figures 7 and 8 a higher glucose conversion rate and HMF yield were obtained with a higher valence state of the Lewis acid salt ($\text{Hf}(\text{OTf})_4$) as the catalyst. This suggested that the valence state of Lewis acid salts played an important impact on the catalytic activity and the selectivity, and a higher glucose conversion could be obtained over high valence state of Lewis acid

salts. This observation likely originates from the fact that for higher valence state Lewis acidic metal salts, its strong Lewis acidity renders its binding with the Lewis basic C–O bond present in the glucose molecule, thereby increasing the glucose conversion rate. A higher glucose conversion rate could be correlated with higher HMF yield as it can minimize the chemical and/or thermal decomposition of HMF under the reactive medium.

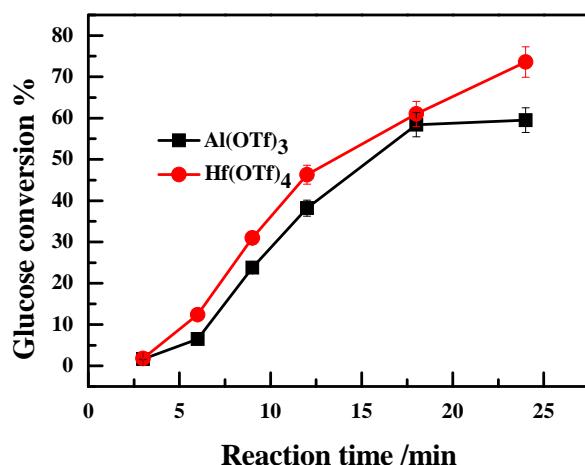


Figure 7. Effect of valence state of Lewis acid salts on the conversion of glucose. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

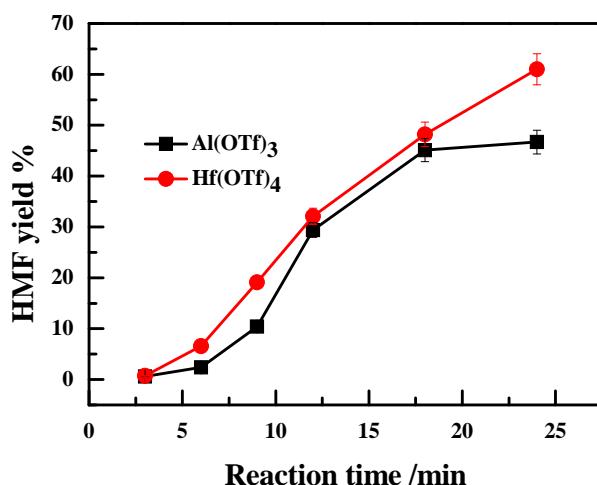


Figure 8. Effect of valence state of Lewis acid salts on the yield of HMF. Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol.

2.4. The Recyclability of Hf(OTf)₄ Catalyst and Its Deactivation/Reactivation Mechanism

As the Hf(OTf)₄ catalyst was found to be the most effective catalyst for glucose dehydration from the abovementioned catalyst screening, the recyclability of Hf(OTf)₄ catalyst was examined, and the results were shown in Table 1 (first row). It can be seen that HMF yield decreased sharply from 60% at the first run to 26% when the catalyst was used for the second time, and an HMF yield of only 4% was obtained after the 5th time. This trend suggested that the catalyst could not be reused due to some sort of deactivation. According to the facile hydrolysis capability of the Hf cation, we conjectured that the possible reason for the deactivation of the Hf(OTf)₄ catalyst might be attributed to the transformation of the Hf(OTf)₄ catalyst into complicated Hf complexes. Therefore, FTIR spectroscopic analysis was

conducted for the Hf(OTf)₄ catalyst before and after the reaction. The data is shown in Figure 9. It is clear that Hf(OTf)₄ might have been converted to some other form, because the peak at 1635 cm⁻¹ completely disappeared after the reaction. If this hypothesis is valid, it should be possible to recover the catalytic activity, since Hf hydrolysis/speciation is highly dependent on pH values, and as such, addition of an appropriate amount of HCl was introduced to the Hf(OTf)₄ system after each reaction. Subsequently, the reaction was carried out under the same reaction conditions of 160 °C reaction temperature and 25 min reaction time; the results are summarized in the second row of Table 1. A decrease in HMF yield of only 3% was observed when the catalyst was used for the second time. Similarly, it was found that almost no drop in HMF yield was observed, even if the catalyst was used for a 5th time. This suggested that the deactivation of the Hf catalyst was highly reversible, meaning that appropriate treatment of the used catalyst, such as acidification, could effectively recover the catalytic activity.

Table 1. The recyclability of 25 mM Hf(OTf)₄ catalyst for glucose dehydration in an aqueous/sec-butyl phenol biphasic reaction system.

Catalysts	HMF Yield %				
	1st run	2nd run	3rd run	4th run	5th run
25 mM Hf(OTf) ₄	60	26	16	9	4
stoichiometric HCl	trace	n/a	n/a	n/a	n/a
25 mM Hf(OTf) ₄ + stoichiometric HCl	60	57	56	57	56

Reaction conditions: reaction temperature of 160 °C, reaction time of 25 min, 0.1 g glucose in 1.5 g 25 mM Lewis acids aqueous solution, 3 g sec-butyl phenol. n/a means that the reaction was not run.

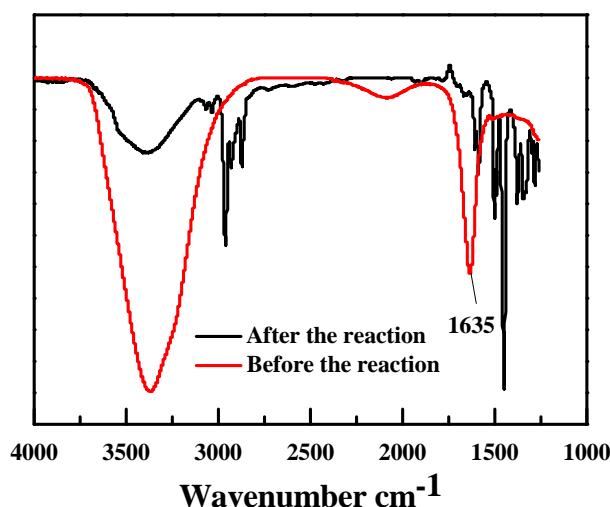


Figure 9. FTIR spectrum of the 25 mM Hf(OTf)₄ catalyst before and after the reaction.

3. Experimental Section

3.1. Materials

Glucose and isopropanol were supplied by Alfa Aesar, Tianjin, China. HMF standard sample was purchased from Aldrich sigma, Beijing, China. All the materials, including AlCl₃, ZnCl₂, FeCl₃, CuCl₂, Al(OTf)₃, Sc(OTf)₃, La(OTf)₃, Yb(OTf)₃, Hf(OTf)₄, HCl, and sec-butyl phenol were of analytic or higher grade and were used as received without further purification.

3.2. Reaction Testing

3.2.1. Preparation of Reaction Solution

The Lewis acid salt solutions were prepared for reaction testing according to a previous method [29]: 25 mM Lewis acid salt aqueous solutions were made by adding the appropriate amount of AlCl_3 , ZnCl_2 , CuCl_2 , $\text{Al}(\text{OTf})_3$, $\text{Sc}(\text{OTf})_3$, $\text{La}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$, and $\text{Hf}(\text{OTf})_4$ into nanopure water. The pH value was adjusted to 1.5 though the addition of HCl. A Titrino automatic titrator was used to measure the pH value of the solutions. The as-made solutions were then saturated with NaCl for further use.

3.2.2. Biphasic Reaction Conditions

All the reactions of glucose dehydration were conducted in a 10 mL thick-walled glass reactor made by Alltech. An oil bath was used to heat the reactor rapidly to the desired reaction temperature, and the temperature and stirring was controlled by an Isotemp digital stirring hot plate (Fisher Scientific). In order to obtain adequate agitation, a triangular stir bar (Fisher Scientific) was placed in the bottom of the reactor before adding reactants and catalysts. Typical experimental conditions were: 1.5 g of an aqueous Lewis acid solution containing 5 wt. % glucose and 3.0 g of organic extracting solvent, sec-butyl phenol (SBP) were successively introduced into the Alltech reactor, sealed and heated to the 160 °C reaction temperature and stirred at 375 rpm for a reaction time of 2–25 min. After the specified time interval, the reactors were removed from the oil bath and then cooled rapidly by ice bath to quench the reaction. For all the reactions, significant amounts of soluble and insoluble brownish humins were formed, of which the production rate was difficult to quantify. The formation of humins 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 for accuracy.

The recyclability of the $\text{Hf}(\text{OTf})_4$ catalyst was carried out as follows: after the reaction, the solution was cooled down and the supernatant was transferred out, leaving 1.5 g of an aqueous Lewis acid solution inside the reactor, and the same amount of sec-butyl phenol and glucose were added for the next run.

$\text{Hf}(\text{OTf})_4$ catalyst reactivation was carried out as follows: after the reaction, the solution was cooled down and the supernatant was transferred out, leaving 1.5 g of an aqueous Lewis acid solution inside the reactor, and the same amount of sec-butyl phenol and glucose, additional stoichiometric HCl (HCl: $\text{Hf}(\text{OTf})_4$ (fresh catalyst) = 4:1) were added for the next run.

3.3. Sample Analysis

After the reaction, the resultant solution was directly analyzed by an HPLC equipped with UV and refractive index detectors according to the previous literature [55]. HPLC analysis was performed using a Shimadzu LC-20A system (Tokyo, Japan) equipped with a SPD-20A UV detector (Tokyo, Japan) at 280 nm and a refractive index (RI-20A) detector (Tokyo, Japan) maintained at 333 K. The unreacted glucose was analyzed by HPLC using an Aminex HPX-87H Column (Beijing, China) at 333 K with 5 mM H_2SO_4 at a flow rate of 0.6 $\text{mL} \cdot \text{min}^{-1}$ as the mobile phase. The amount of HMF was analyzed by HPLC with a Shimadzu UV-Vis SPD-20A detector (Tokyo, Japan) at 280.0 nm, using a InterSustain C18 column maintained 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 glucose conversion/HMF yield being used in this manuscript was calibrated based on the glucose consumption during reaction and HMF formed, respectively. Every sample was injected and analyzed three times for accuracy. The definitions of the conversion of glucose is defined as the moles of glucose reacted divided by the moles of initial introduced glucose added (Equation (1)), the selectivity of HMF is defined as the moles of HMF

produced divided by the moles of glucose reacted (Equation (2)), and the yield of HMF is defined as the moles of HMF produced divided by the moles of initial introduced glucose (Equation (3)).

$$\text{Glucose} = \frac{\text{Mol Glucose}_{\text{in}} - \text{Mol Glucose}_{\text{out}}}{\text{Mol Glucose}_{\text{in}}} \quad (1)$$

where $\text{Mol Glucose}_{\text{in}}$ is the amount of the initial introduced glucose and $\text{Mol Glucose}_{\text{out}}$ is the unreacted glucose remaining in the reaction medium.

$$\text{HMF selectivity} = \frac{\text{Mol HMF}}{\text{Mol Glucose}_{\text{in}} - \text{Mol Glucose}_{\text{out}}} \times 100\% \quad (2)$$

where Mol HMF is the amount of HMF produced in the reaction, $\text{Mol Glucose}_{\text{in}}$ is the amount of the initially introduced glucose, and $\text{Mol Glucose}_{\text{out}}$ is the unreacted glucose.

$$\text{HMF yield} = \frac{\text{Mol HMF}}{\text{Mol Glucose}_{\text{in}}} \times 100\% \quad (3)$$

where Mol HMF is the amount of HMF produced in the reaction and $\text{Mol Glucose}_{\text{in}}$ is the amount of the initially introduced glucose.

4. Conclusions

Glucose dehydration was carried out over various Lewis acidic metal salts under the conditions of 160 °C reaction temperature and 25 min reaction time. The effect of ionic radii, anion type, and the oxidation status of metal salts on the catalytic performance for glucose dehydration were examined systematically. Furthermore, the recyclability of the most active catalyst Hf(OTf)_4 and the deactivation/reactivation mechanisms were also investigated.

The results of ionic radii of Lewis acidic salts on catalysis suggested that the yield of HMF decreased with increases of the ionic radii of Lewis acid salts, which means that salts with stronger Lewis acidic characteristics were more active. The results regarding the anion type indicated that a higher glucose conversion rate and better HMF selectivity could be obtained with Cl^- . The valence state of Lewis acidic metal salts had an important impact on the catalytic activity and the selectivity of the desired product, and a higher glucose conversion could be obtained over higher valence state Lewis acid salts. The deactivation mechanism was that the Hf(OTf)_4 catalyst was transformed into a less-reactive form during the reaction upon contact with water. The catalytic activity, however, could be fully recovered by introducing the appropriate amount of HCl after each reaction.

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Conflicts of Interest: The authors declare no conflict of interest.

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