

Article

Catalytic Upgrading of Biomass-Derived Furfuryl Alcohol to Butyl Levulinate Biofuel over Common Metal Salts

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Abstract: Levulinate ester has been identified as a promising renewable fuel additive and platform chemical. Here, the use of a wide range of common metal salts as acid catalysts for catalytic upgrading of biomass-derived furfuryl alcohol to butyl levulinate was explored by conventional heating. Both alkali and alkaline earth metal chlorides did not lead effectively to the conversion of furfuryl alcohol, while several transition metal chlorides (CrCl_3 , FeCl_3 , and CuCl_2) and AlCl_3 exhibited catalytic activity for the synthesis of butyl levulinate. For their sulfates (Cr(III) , Fe(III) , Cu(II) , and Al(III)), the catalytic activity was low. The reaction performance was correlated with the Brønsted acidity of the reaction system derived from the hydrolysis/alcoholysis of cations, but was more dependent on the Lewis acidity from the metal salts. Among these investigated metal salts, CuCl_2 was found to be uniquely effective, leading to the conversion of furfuryl alcohol to butyl levulinate with an optimized yield of 95%. Moreover, CuCl_2 could be recovered efficiently from the resulting reaction mixture and remained with almost unchanged catalytic activity in multiple recycling runs.

Keywords: biofuel; furfuryl alcohol; catalytic upgrading; metal salt; levulinate ester

1. Introduction

Given the gradual depletion of fossil fuel resources and rising environmental concerns, increasing effort has been devoted to the development of alternative fuels and chemicals from abundant and renewable biomass resources [1–4]. Furfuryl alcohol, one of the most important furan derivatives, is produced industrially via hydrogenation of furfural derived from the hydrolysis and dehydration of xylan contained in lignocellulosic biomass [5]. At present, furfuryl alcohol is not fully utilized and is oversupplied in the chemical market [6]. The development of a feasible and competitive strategy to reform and upgrade furfuryl alcohol is therefore strongly desired. An attractive option regarding the one-pot synthesis of levulinate esters via performing the reaction of furfuryl alcohol with alcohols can be envisioned because the reforming process is atom-economic and convenient, the alcohols suppress humin by-product formation from furfuryl alcohol polymerization [7], and it affords versatile platform chemicals. Concretely, levulinate esters have found applications as fuels or fuel additives [8,9], flavoring agents, solvents, as well as in the area of organic chemistry for the synthesis of γ -valerolactone [10,11], liquid hydrocarbon transportation fuels [12], and other industrial chemicals [13].

In recent years, research on the transformation of furfuryl alcohol to levulinate esters has been reported at an increasing rate [13–15]. Acid catalyst is identified as the key point for the synthesis of levulinate esters, and is thus the focus of the study. Currently, the utilization of solid acid as

a catalyst of the reaction has attracted considerable interest due to environmental friendliness and easy separation from the reaction mixture for reuse. A series of efficient solid acid catalysts including acidic ion-exchange resin [16], organic-inorganic hybrid acid [17], porous aluminosilicate [18], propylsulfonic acid-functionalized mesoporous silica [19], mesostructured zirconium-based mixed oxides [20], carbon and carbon-silica composites containing SO_3H groups [21], graphene oxide [22], organosulfonic acid-functionalized organosilica hollow nanospheres [23], and hierarchical zeolite [24] have been successively developed. Beyond that, acidic ionic liquids were found to be efficient and reusable catalysts for the alcoholysis of furfuryl alcohol to levulinate esters [6,25]. In spite of significant advances from the persistent studies, the main obstacles for the above-mentioned catalysts include the complex preparation of the catalyst, expensive catalyst cost, and/or the deactivation of the recovered catalyst in recycling runs. Consequently, more facile, cheap, efficient and stable catalyst systems are still desirable.

It is well known that many metal salts can endow both strong Lewis and Brønsted acidity in organic or aqueous solvents. Previously, some interesting and admirable findings on the one-pot conversion of biomass carbohydrates into fuels and platform chemicals catalyzed by common metal salts were presented. For example, CrCl_2 in ionic liquid solvents was found to be uniquely effective for glucose conversion, affording a near 70% yield of 5-hydroxymethylfurfural [26]. Analogously, a high levulinic acid yield of 67% was achieved from cellulose catalyzed by CrCl_3 in aqueous medium [27]. $\text{Al}_2(\text{SO}_4)_3$ was highly active in the catalytic synthesis of methyl levulinate from carbohydrates in methanol, giving a 64% yield of methyl levulinate from glucose [28]. These metal salts are earth-abundant and commercially available, providing inexpensive and environmentally benign catalyst sources for biomass conversion. Accordingly, common metal salts are expected to be qualified for the desired purpose in the conversion of furfuryl alcohol to levulinate esters. Recently, Huang et al. [29] reported $\text{Al}_2(\text{SO}_4)_3$ with good catalytic activity for the alcoholysis of furfuryl alcohol under microwave irradiation, affording a 80.6% yield of methyl levulinate. A high butyl levulinate yield of 92% could be achieved for the alcoholysis of furfuryl alcohol catalyzed by indium (III) triflate; however, the catalyst is costly [30]. In order to better understand the catalytic mechanism of metal salts and find more competitive metal salts as alternative catalysts for the conversion of furfuryl alcohol to levulinate esters, further studies are needed. Herein, the use of a wide range of metal salts as acid catalysts for the alcoholysis of furfuryl alcohol to butyl levulinate with conventional heating was evaluated. The results showed that several transition metal chlorides (CrCl_3 , FeCl_3 , and CuCl_2) and AlCl_3 were effective for the synthesis of butyl levulinate. In the case of their corresponding sulfates, the catalytic activity dropped markedly. Among these investigated metal salts, CuCl_2 emerged as a preferred catalyst supplier with unique selectivity for the synthesis of butyl levulinate. Based on its use, the effect of the process variables was further explored in order to determine the optimal conditions for the maximized yield of butyl levulinate. Lastly, the reusability of the CuCl_2 catalyst was performed to demonstrate the versatility of the catalytic strategy.

2. Results and Discussion

2.1. Various Metal Salts' Catalytic Conversion of Furfuryl Alcohol

2.1.1. Catalytic Performance of Various Metal Salts

Firstly, the effect of a wide range of various metal chlorides on the catalytic transformation of furfuryl alcohol to butyl levulinate in *n*-butanol was screened at 110 °C after 60 min reaction time using a 0.3 mol/L furfuryl alcohol solution and a 0.02 mol/L solution of metal chloride as the catalyst. No catalyst was used as the blank for a reference. The results of the furfuryl alcohol conversion and butyl levulinate yield for the investigated metal chlorides are depicted in Figure 1. Hardly any yield of butyl levulinate was observed in the absence of the catalyst. It can also be seen that all alkali and alkaline earth metal chlorides did not lead effectively to the conversion of furfuryl alcohol, and there was no obvious difference with the blank (no catalyst). In contrast, several transition metal chlorides (CrCl_3 , FeCl_3 , and CuCl_2) and AlCl_3 exhibited catalytic activity in the conversion of

furfuryl alcohol to butyl levulinate. Among these four metal chlorides, CrCl_3 gave a relatively low furfuryl alcohol conversion (47%) and butyl levulinate yield (28%). Significantly higher conversions (>97%) and yields (61%–73%) were found under identical operating conditions for CuCl_2 and AlCl_3 . For FeCl_3 , a high conversion of 95% could be achieved; however, the butyl levulinate yield was obviously lower (24%) than that for CuCl_2 and AlCl_3 . The yield of butyl levulinate decreased in the order $\text{CuCl}_2 > \text{AlCl}_3 > \text{CrCl}_3 > \text{FeCl}_3$. These findings suggest that the cation effects in this type of catalyst are quite dramatic for the synthesis of butyl levulinate from furfuryl alcohol. However, further investigations using metal sulfates instead of metal chlorides as the catalysts indicated that the catalytic performance of metal salts is not only correlated with their cation species, but also depends on the anions. Distinct differences in the conversion of furfuryl alcohol to butyl levulinate were observed from Figure 2 between the chloride and sulfate salts of four typical metals (Cr(III), Fe(III), Cu(II), and Al(III)). Furfuryl alcohol conversion and butyl levulinate yield for all the above-investigated metal sulfates were significantly lower than that for their corresponding chlorides, implying that metal chlorides have more potential for the synthesis of levulinate esters from furfuryl alcohol.

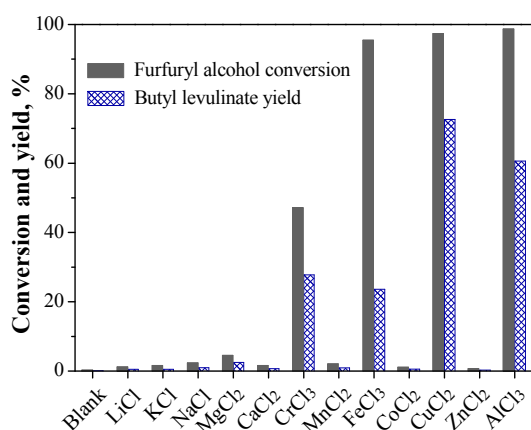


Figure 1. Catalytic comparison of various metal chlorides on the conversion of furfuryl alcohol to butyl levulinate. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; metal chloride concentration of 0.02 mol/L; reaction temperature of 110 °C; reaction time of 60 min.

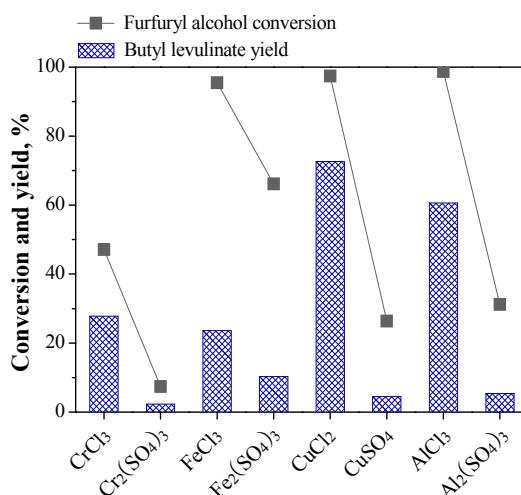


Figure 2. Catalytic comparison of four typical metal chlorides and sulfates on the conversion of furfuryl alcohol to butyl levulinate. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; metal salt concentration of 0.02 mol/L (based on Me^{n+}); reaction temperature of 110 °C; reaction time of 60 min.

2.1.2. Relationship between Reactivity and Acidity of Reaction System

Although many metal salts belong to Lewis acids, the existence of metal salts as the catalysts in the reaction solution can afford Brønsted acidity derived from the hydrolysis/alcoholysis of cations, which may be related to the reaction performance [28,29,31]. Taking metal chloride as an example, the possibility of hydrolysis/alcoholysis in the reaction medium to produce active species was presumed [32,33], as illustrated in Figure 3. In the reaction medium, Lewis acid metal salts dissociate to form complex ions, such as $[\text{Me}(\text{H}_2\text{O})_m]^{n+}$ and $[\text{Me}(\text{ROH})_m]^{n+}$. These ions can be further hydrolyzed/alcoholized, releasing H^+ , leading to a drop in the solution pH. Figure 4 plots the relationship between the butyl levulinate yield (data from Figure 1) and the initial pH value of the *n*-butanol solution with the employed metal chlorides. It can be found that the pH value of the reaction system of four metal chlorides including CrCl_3 , FeCl_3 , CuCl_2 and AlCl_3 with a high yield of butyl levulinate was relatively low, showing strong Brønsted acidity. In comparison, the other investigated metal chlorides presented weak acidity, and did not effect the conversion of furfuryl alcohol to butyl levulinate. It suggests that a certain amount of Brønsted acid sites are required for the synthesis of butyl levulinate. However, this does not mean that the stronger the Brønsted acidity, the better the butyl levulinate formation. For example, the pH value of the reaction system with FeCl_3 was slightly lower (stronger Brønsted acidity) than that with CuCl_2 , but the yield of the butyl levulinate was markedly lower. In the case of the four effective metal chlorides (CrCl_3 , FeCl_3 , CuCl_2 and AlCl_3), further tests were carried out at the two same pH values (1 and 2) adjusted by their dosages. It revealed from Figure 5 that different metal chlorides as the catalysts produced clearly different yields of butyl levulinate, and the yield for CuCl_2 was the highest under the condition of two pH values. Based on these observations, we concluded that the Lewis acidity of metal salts probably plays some role in the synthesis of butyl levulinate in addition to the Brønsted acidity. The combination of Cu^{2+} and Cl^- can afford optimal Lewis and Brønsted acid sites for the synthesis of butyl levulinate from furfuryl alcohol conversion with unique selectivity.

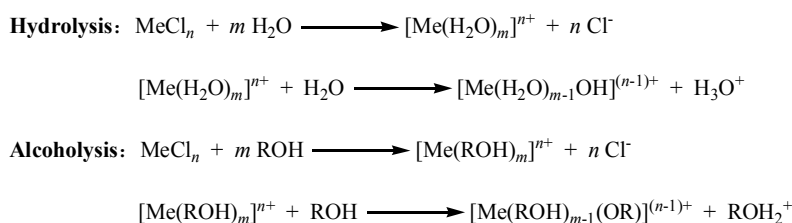


Figure 3. Presumed hydrolysis/alcoholysis reaction of metal chloride in the reaction medium.

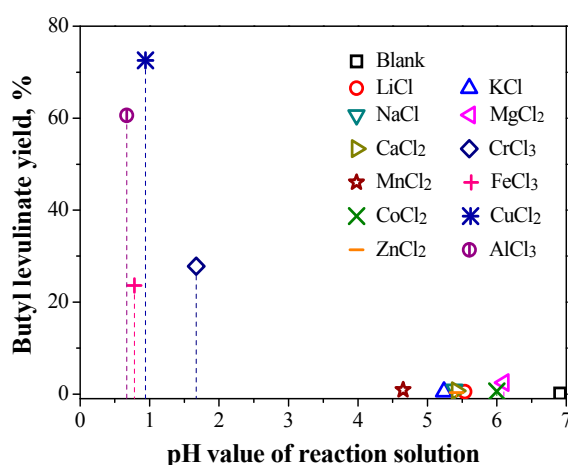


Figure 4. Relationship between butyl levulinate yield (data from Figure 1) and initial pH value of *n*-butanol solution with 0.02 mol/L metal chlorides measured at room temperature.

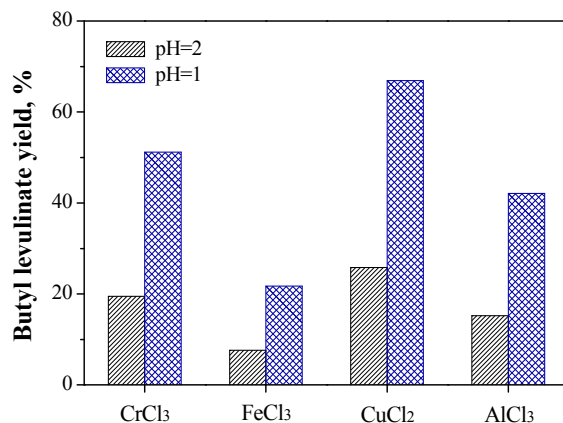


Figure 5. Butyl levulinate yield for four typical metal chlorides at the two same initial pH values of *n*-butanol solution adjusted by metal chlorides dosage. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; reaction temperature of 110 °C; reaction time of 60 min.

Next, Figure 6 presents the relationship between the butyl levulinate yield (data from Figure 2) and the initial pH value of the reaction system with various metal chlorides and sulfates. For all investigated metal sulfates, the butyl levulinate yield was lower than that for their corresponding chlorides. Accordingly, the pH value of the reaction system with metal sulfates was high, and fewer Brønsted acid sites were available for metal sulfates. This finding suggests that there is a good agreement between the reaction performance and Brønsted acidity. However, when we conducted experiments at the same initial pH value of the reaction system for metal chlorides and sulfates, the yield of the butyl levulinate for the sulfates of Cr(III), Cu(II) and Al(III) was still significantly lower than that for their corresponding chlorides (see Figure 7). A possible explanation for these appearances is that the reaction performance depends not only on the Brønsted acidity of the reaction system, but also on the Lewis acidity of the metal salts, and the Lewis and Brønsted acidity for metal sulfates are weaker than those for their corresponding chlorides [34,35]. By and large, the presentation of the optimal Lewis and Brønsted acid sites for the efficient conversion of furfuryl alcohol to butyl levulinate is derived from a valid combination of cations and anions.

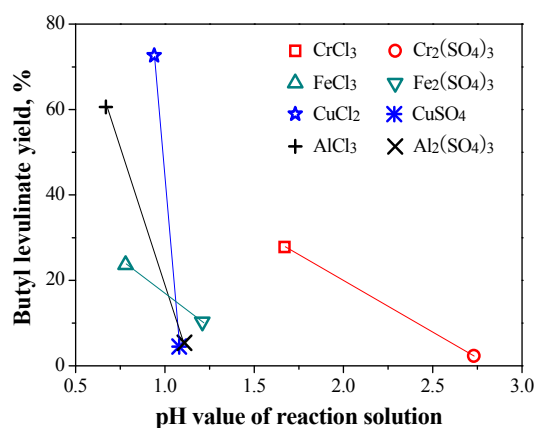


Figure 6. Relationship between butyl levulinate yield (data from Figure 2) and initial pH value of *n*-butanol solution with various metal chlorides and sulfates.

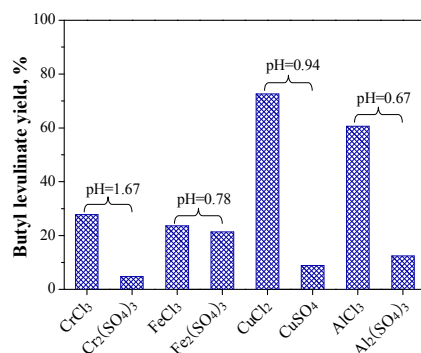


Figure 7. Butyl levulinate yield for metal chlorides and sulfates at the same initial pH value of *n*-butanol solution adjusted by metal salts dosage. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; reaction temperature of 110 °C; reaction time of 60 min.

2.2. Optimization of Butyl Levulinate Production Catalyzed by CuCl₂

Among the tested metal chlorides as the catalysts, CuCl₂ was found to be uniquely effective in the conversion of furfuryl alcohol to butyl levulinate. Therefore, it was chosen as the most suitable catalyst for this purpose and was used in the further exploration. To understand the transformation process of furfuryl alcohol catalyzed by CuCl₂ and to achieve the highest possible yield of butyl levulinate, the effects of the process parameters including the catalyst dosage, reaction temperature and initial furfuryl alcohol concentration on furfuryl alcohol conversion and butyl levulinate yield were studied as a function of time. The results are discussed successively in the following sections.

2.2.1. Catalyst Dosage

Figure 8 illustrates the influence of the CuCl₂ catalyst dosage, ranging from 0.002 to 0.03 mol/L, on the conversion of furfuryl alcohol to butyl levulinate, while the reaction temperature was held constant at 110 °C. As can be seen, the conversion rate of furfuryl alcohol and butyl levulinate yield increased rapidly with increasing the CuCl₂ dosage from 0.002 to 0.02 mol/L. This implies that the synthesis of butyl levulinate from furfuryl alcohol involves a more acidic-demanding step. It is worth noting that furfuryl alcohol was almost entirely consumed after the reaction time of 80 min for all tested catalyst dosages (Figure 8a). However, the CuCl₂ dosage of below 0.01 mol/L cannot seem to offer sufficient acid sites for the synthesis of butyl levulinate from furfuryl alcohol and/or its derived intermediates at a short time, thus giving rise to a low production rate. With increasing the CuCl₂ dosage, the increased total number of available acid sites resulted in a faster reaction rate to promote the synthesis of butyl levulinate. When the CuCl₂ dosage was 0.02 mol/L, the equilibrium conversion for the formation of butyl levulinate was almost reached after 80 min (Figure 8b). The loading of excess CuCl₂ (0.03 mol/L) had little effect, indicating that an optimum CuCl₂ dosage exists for the reaction. The most beneficial CuCl₂ dosage was chosen to be 0.02 mol/L.

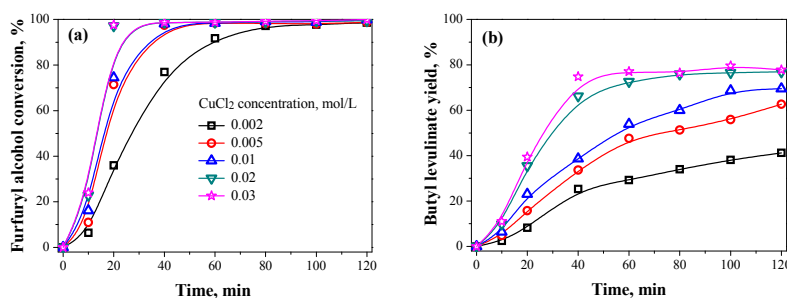


Figure 8. Effect of catalyst dosage on furfuryl alcohol conversion (a) and butyl levulinate yield (b) as a function of time. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; CuCl₂ as the catalyst; reaction temperature of 110 °C.

2.2.2. Reaction Temperature

The effect of the reaction temperature (100–120 °C) on the conversion of furfuryl alcohol to butyl levulinate is presented in Figure 9. It can be observed that the reaction temperature played an important role in the reaction process, which had similar rules as that of the CuCl_2 dosage for furfuryl alcohol conversion and butyl levulinate yield. Under lower temperature conditions, the butyl levulinate yield grew relatively slowly with the prolonging of the reaction time. Only 46% and 67% yields of butyl levulinate were reached after the reaction time of 120 min at 100 °C and 105 °C, respectively. In contrast, furfuryl alcohol was almost totally converted within 60 min. A possible explanation for this appearance is that a large number of intermediates can be accumulated in the reaction process [6,36], which may need a longer time to achieve a complete reaction. Increasing the temperature to 115 °C, the conversion takes place at a faster rate and the yield of butyl levulinate increased rapidly with the extension of the reaction time, and the equilibrium point was reached by 60 min. With an elevated temperature of 120 °C, the reaction rate and final yield of butyl levulinate did not change substantially compared with that at 115 °C. Thus, it can be seen that the elevation of temperature is also unavailing for the extent of the reaction.

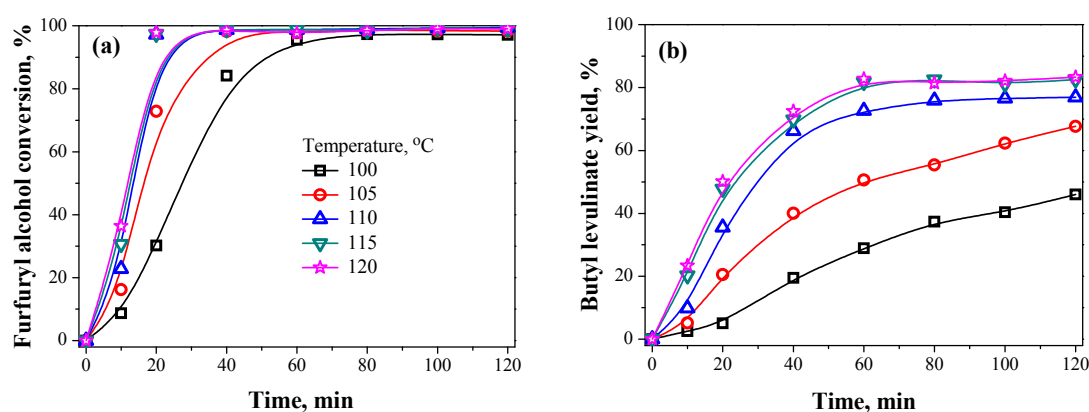


Figure 9. Effect of reaction temperature on furfuryl alcohol conversion (a) and butyl levulinate (b) yield as a function of time. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; CuCl_2 concentration of 0.02 mol/L.

2.2.3. Initial Furfuryl Alcohol Concentration

Theoretically, increasing the initial furfuryl alcohol concentration results in more substrate being available for the efficient conversion to produce butyl levulinate. However, the yield of butyl levulinate dropped clearly with increases in the initial furfuryl alcohol concentration from 0.1 to 2 mol/L (see Figure 10b), implying that the substrate inhibits the kinetics in this process. A similar phenomenon has also been observed in the previous related reports [7,17,25,27]. When the initial furfuryl alcohol concentration was 0.1 mol/L, the yield of butyl levulinate reached a maximum of 95% within 80 min. Unfortunately, the concentration of butyl levulinate in the reaction mixture was fairly low, at around 0.09 mol/L (Figure 10c). In reality, a higher concentration of product is desired because it can not only improve the production efficiency of butyl levulinate, but can also cut down energy consumption in the purification of the product. When the initial furfuryl alcohol concentration increased from 0.1 to 1 mol/L, the concentration of butyl levulinate had risen obviously, from 0.09 to 0.52 mol/L, but its yield was found to decrease. On the other hand, it can be noticed that the furfuryl alcohol conversion was less influenced by its initial concentration, giving close to 100% conversions after 80 min for all tests (Figure 10a). At a higher initial furfuryl alcohol concentration, more intermediates (e.g., 2-butoxymethylfuran, 4,5,5-tributoxypentan-2-one) in the reaction mixture were detected by gas chromatography-mass spectrometer (GC-MS) and the formation of dark-brown insoluble substances known as humins from furfuryl alcohol polymerization was also favored [7,25]. The reason for these

observations is probably due to product feedback inhibition and/or reactivity diminution bringing about an incomplete alcoholysis reaction and the enhancement of the side reaction. Further increasing the initial furfuryl alcohol concentration to 2 mol/L, the concentration of the butyl levulinate was lower than that of 1 mol/L during the initial stage of the reaction (Figure 10c). This may be because of the insufficient acid for the conversion of excess furfuryl alcohol, thus gaining a low production rate of butyl levulinate. Based on these findings, it is necessary to have a comprehensive consideration for choosing an adequate initial furfuryl alcohol concentration in the practical operation.

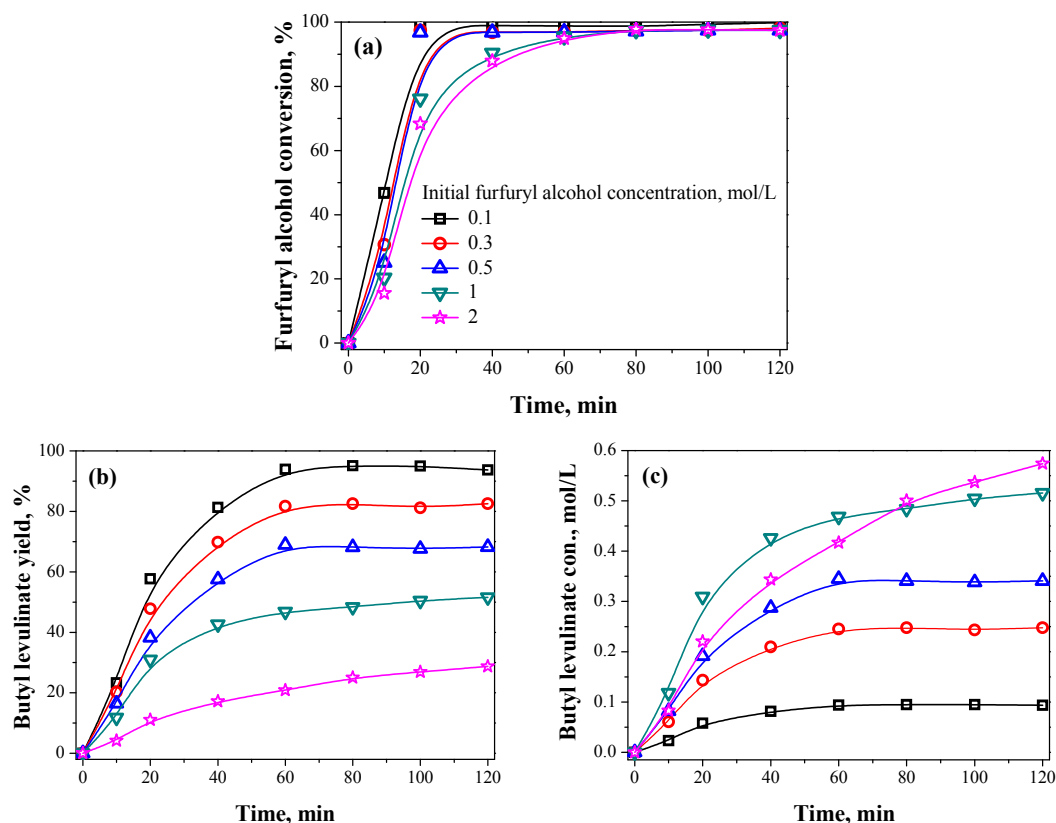


Figure 10. Effect of initial furfuryl alcohol concentration on furfuryl alcohol conversion (a); butyl levulinate yield (b); and concentration (c) as a function of time. Reaction conditions: CuCl_2 concentration of 0.02 mol/L; reaction temperature of 115 °C.

2.3. Reusability of CuCl_2 Catalyst

The reusability and long-term stability of a catalyst are very important characteristics for the practical implementation of the technology to reduce the production cost. Previously, several metal salts such as $\text{Al}_2(\text{SO}_4)_3$ [28,29], AlCl_3 [31,37], and $\text{In}(\text{OTf})_3$ [38] were found to be recoverable from the reaction mixture and exhibited fine catalytic stability in multiple cycles of reuse. Herein, the recycle experiments for the selected CuCl_2 catalyst were carried out under the same reaction conditions. After the reaction was finished, the solvent and products were removed by a distillation technique that combines an atmospheric distillation with a vacuum distillation where *n*-tridecane was added to help distill the heavy fraction. The obtained residue was used as catalyst in the next run. The weight of the residue was around 1.1 times that of the initial added CuCl_2 . This is likely due to the interfusion of humins formed from the partial polymerization of the furfuryl alcohol [7], resulting in an increase in the residue weight. If so, it is reckoned that about 3.5% furfuryl alcohol was polymerized to form the humins. The above recycling process was repeated eight times, and the reusability results of the CuCl_2 are given in Figure 11. The catalytic activity of the recovered catalyst after six cycles was still comparable to that of the fresh CuCl_2 catalyst. Furfuryl alcohol was almost fully converted for all six

runs, giving nearly the same yield of butyl levulinate. In the subsequent two runs, there was a decrease in the yield of butyl levulinate, but the changes were not very noticeable. It suggests that the catalyst species basically appear not to decompose in the reaction, and CuCl_2 can serve as a reusable catalyst with excellent catalytic stability for the synthesis of butyl levulinate from furfuryl alcohol.

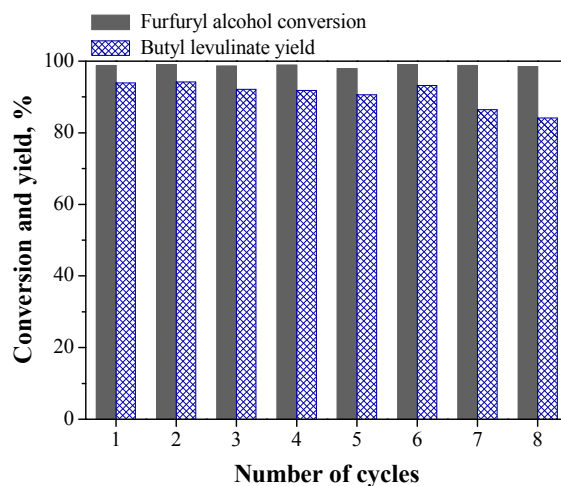


Figure 11. Reusability of the CuCl_2 catalyst. Reaction conditions: 0.1 mol/L furfuryl alcohol in *n*-butanol; CuCl_2 concentration of 0.02 mol/L; reaction temperature of 115 °C; reaction time of 60 min.

3. Materials and Methods

3.1. Materials

Furfuryl alcohol (98% purity) and butyl levulinate (98% purity) were purchased from Aladdin Reagent (Shanghai, China). Metal salts and *n*-butanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The above reagents and chemicals were all of analytical grade and used without further purification or treatment.

3.2. General Procedure for the Synthesis of Butyl Levulinate

The synthesis of butyl levulinate from furfuryl alcohol were conducted in a cylindrical stainless steel pressurized reactor with 50 mL total volume. In a typical experiment, 0.53 mL furfuryl alcohol (0.3 mol/L working concentration) and 19.47 mL *n*-butanol were introduced into the reactor along with 0.4 mmol metal salt (based on Me^{n+}). After the reactor was sealed, the above mixture was then brought to desired temperature by oil-bath heating and was continuously stirred at 800 rpm with a magnetic stirrer. When running the reaction for a desired duration, the reactor was cooled down in an ice water bath to terminate the reaction. Then, the resulting reaction mixture taken from the reactor was diluted with an ethanol solution containing the internal standard of methyl levulinate (0.01 mol/L) for GC analysis.

3.3. Products Analysis

Furfuryl alcohol and butyl levulinate in the reaction mixture after the reaction were analyzed by GC on an Agilent 6890 instrument (Agilent Instruments, Fair Oaks, CA, USA) equipped with a DB-5 capillary column (30.0 m \times 320 μm \times 0.25 μm) and a flame-ionization detector (FID). The following operating conditions were used in the analysis: the carrier gas was nitrogen with a flow rate of 1.0 mL/min, the injection port temperature was 250 °C, the oven temperature was programmed from 60 °C to 90 °C (6 min) at a heating rate of 5 °C/min and then to 190 °C (5 min) at a heating rate of 20 °C/min, and the detector temperature was 250 °C. The amount of furfuryl alcohol and butyl levulinate were determined using internal standard curves constructed with their authentic standards.

Furfuryl alcohol conversion was defined as the ratio of the moles of furfuryl alcohol converted to the moles of furfuryl alcohol loaded in the feed. Butyl levulinate yield was defined as the ratio of the moles of butyl levulinate obtained to the moles of furfuryl alcohol loaded in the feed.

3.4. pH Measurement of the Reaction Solution

The pH measurements of the reaction solution with various metal salts were performed at ambient temperature using a model PHS-3C pH meter (Leici Analytical Instrument Factory, Shanghai, China) calibrated with standard pH buffer solutions.

3.5. Recycling of the Catalyst

To assess the stability of metal salts as catalysts, a selected CuCl_2 was recovered after the reaction and reused for the next run under comparable conditions. The separation of CuCl_2 after the reaction was as follows: the solvent *n*-butanol and low boiling substances in the reaction mixture were firstly removed through rotary evaporation at 120 °C until a dense mixture was formed. Subsequently, high boiling *n*-tridecane was added to the residual component to help distil the heavy products (mainly butyl levulinate), which acted as desorption driving agent for heavy products. At this stage, the heavy products in the residue were separated out by vacuum distillation of 180 °C. This step was repeated three times. Finally, the obtained solid residue (i.e., recovered CuCl_2) was directly dissolved in a certain amount of furfuryl alcohol and *n*-butanol with a specified proportion. The formed mixture was then transferred to reactor for the next run.

4. Conclusions

Different types of metal salts had obviously different impacts on the catalytic conversion of furfuryl alcohol to butyl levulinate. Both alkali and alkaline earth metal chlorides were not effective in the alcoholysis of furfuryl alcohol, while several transition metal chlorides (CrCl_3 , FeCl_3 , and CuCl_2) and AlCl_3 showed catalytic activity for the synthesis of butyl levulinate. For their sulfates (Cr(III) , Fe(III) , Cu(II) , and Al(III)), the catalytic activity was low. The reaction performance was correlated with the Brønsted acidity of the reaction system derived from the hydrolysis/alcoholysis of cations, but was more dependent on the Lewis acidity from the metal salts. The formation of butyl levulinate was favored in the diluted initial furfuryl alcohol concentration at a relatively high catalyst loading and reaction temperature. An optimized yield of butyl levulinate of 95% was achieved when catalyzed by the uniquely effective CuCl_2 . After the reaction, the CuCl_2 could be recovered efficiently and reused multiple times without substantial loss of its catalytic activity. The developed strategy using CuCl_2 as a facile, efficient, and reusable catalyst exhibits a promising prospect for the large-scale synthesis of levulinate ester biofuels from biomass-derived furfuryl alcohol.

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Author Contributions: L.P. conceived and designed the experiments; R.T. and Y.W. performed the experiments; L.P., R.T. and Y.W. analyzed the data; L.P. contributed reagents/materials/analysis tools; L.P. wrote the paper.

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

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