# Metal Chloride Mediated Efficient Conversion of Hydroxymethylfurfural (HMF) into Long-Chain Levulinate Ester

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Levulinate esters are a class of promising alternative fuels derived from biomass. The synthesis of levulinate esters from carbohydrates generally undergoes a route with hydroxymethylfurfural as an intermediate product. The conversion of hydroxymethylfurfural is an intrinsic limiting step for the formation of levulinate esters from carbohydrates. Recent work focuses more on the synthesis of short-chain levulinate esters from biomass, but long-chain levulinate esters have superior properties as fuels. In this work, the synthesis of *n*-hexyl levulinate, a representative long-chain levulinate ester, was investigated with a series of metal chloride catalysts. Iron chloride ($FeCl_3$) and copper chloride ($CuCl_2$) were found to be the most effective amongst the tested catalysts. An *n*-hexyl levulinate yield of approximately 65% with 100% hydroxymethylfurfural conversion could be achieved at a temperature of 160 °C after 240 min. This system was also applied to the conversion of hydroxymethylfurfural and other hexanols such as 2-ethyl-1-butanol, cyclohexanol, 2-hexanol, and 3-hexanol. The catalyst in the system was reusable in a consecutive batch mode. Mechanistic study indicated that the production of levulinate ester from hydroxymethylfurfural probably went through levulinic acid as the intermediate.
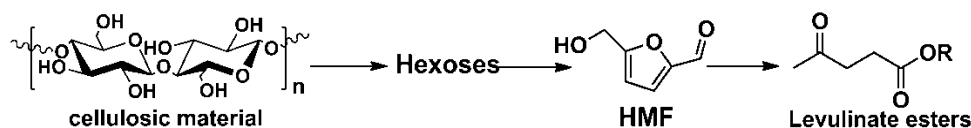
## INTRODUCTION

Due to the great depletion of fossil fuels associated with massive emissions of greenhouse gases, establishing a "carbon neutral" community is becoming a key strategy to respond to global climate change and sustainable development (Sudarsanam *et al.* 2018; Maurya *et al.* 2021). Biomass is considered a promising alternative energy source based on a number of merits, one of which is it conforms to the "carbon neutral" concept. The carbon dioxide emitted by the consumption of biomass is able to be recycled by photosynthesis (Wang *et al.* 2020; Babin *et al.* 2021). As such, the refining of biomass into valuable chemicals has emerged to be an appealing research topic.

Recently, hydroxymethylfurfural (HMF) as a biobased platform compound has attracted a great deal of attention (Xu *et al.* 2020; Hou *et al.* 2021). A wide range of high-value added derivatives can be acquired by the conversion of HMF. These derivatives have shown good potential for supporting the sustainable development of fuels, polymers,

pharmaceuticals, fine chemicals, *etc.* (Kong *et al.* 2018, 2020; Xu *et al.* 2020; Hou *et al.* 2021). Levulinate esters are a class of notable derivatives from levulinic acid (LA), which can be generally produced by the hydration of HMF (Ramli and Amin 2020). Amongst the feasible applications, levulinate esters have been more involved in the area of alternative fuels (Yan *et al.* 2017; Heda *et al.* 2019). Recent studies demonstrate that levulinate esters possess comparable energy densities to traditional fuels. For instance, the energy density of ethyl levulinate (EL) is approximately 31.2 MJ $L^{-1}$, which is similar to that of gasoline (32.4 MJ $L^{-1}$), and obviously higher than that of ethanol (23.5 MJ $L^{-1}$) (Ghosh *et al.* 2018). Much effort has been currently made to determine the efficient synthesis of short-chain levulinate esters, *e.g.*, methyl levulinate (ML) and EL (Fang *et al.* 2018; Liu *et al.* 2018; Lyu *et al.* 2019; Peixoto *et al.* 2021). However, the oxygen contents of ML and EL are relatively high, which leads to high water miscibilities and low heating values (Jia *et al.* 2020). In comparison, long-chain levulinate esters are more desired, since they have similar chemical structures to biodiesel and superior fuel properties (Jia *et al.* 2020). Meanwhile, the ecotoxicities of long-chain levulinate esters are lower than the ecotoxicities of short-chain ones (Lomba *et al.* 2014).

A typical route for producing levulinate esters from cellulosic materials is shown in Fig. 1. As illustrated, HMF is an intermediate product. The route can be divided into two primary stages, including the conversion of cellulosic materials into HMF and the subsequent conversion of HMF into levulinate esters. Presently, a lot of progress has been made on the production of HMF from carbohydrates, and a few works have also achieved the direct production of levulinate esters from carbohydrates (Li *et al.* 2019; Gu *et al.* 2019; Wen *et al.* 2019; Liang *et al.* 2020; Qu *et al.* 2020; Hao *et al.* 2021). However, the conversion of HMF is still an intrinsic limiting step for the formation of levulinate esters from carbohydrates According to the literature, the conversion of HMF into levulinate esters generally suffers relatively low product yields or complicated catalyst preparation or long reaction time. Wang *et al.* (2020) demonstrated that H-beta25 zeolite could catalyze the formation of ML from HMF with a yield of 60% in the presence of molecular oxygen at a temperature of 170 °C for 50 min. Wang and Chen (2016) synthesized a MOF-based polyoxometalate [Cu-BTC][HPM] catalyst for the conversion of HMF into 5-ethoxymethylfurfural (EMF) and EL at a temperature of 140 °C for 12 h, in which EMF was the predominant product accompanied with an EL yield of approximately 20%. Song *et al.* (2021) prepared some mesoporous organosilica catalysts functionalized by Brønsted acidic ionic liquids with a trifluorosulfonate anion for the synthesis of EL from HMF. Under these conditions, greater than a 90% EL yield could be obtained at a temperature of 140 °C for 4 h (Song *et al.* 2021). However, information on the production of long-chain levulinate esters from HMF remains lacking and ignored.



**Fig. 1.** Reaction path for the production of levulinate esters from cellulosic material

This work focused on the efficient preparation of long-chain levulinate esters from HMF. Herein, 1-hexanol was employed as the primary esterification reagent for research. A series of metal chlorides were used as catalysts. By comparison, iron chloride and copper chloride showed better activities among the tested catalysts. Some influence factors, *e.g.*,

catalyst loading, water content, molar ratio of HMF to 1-hexanol, reaction time and temperature, and alcohol type, were investigated in detail. The reusability of this catalytic system was also evaluated in a consecutive batch reaction mode. In addition, a preliminary mechanism is considered at the end of this paper.

## EXPERIMENTAL

### Materials

Hydroxymethylfurfural (HMF, 98%), iron chloride ($FeCl_3$, 99%), aluminum chloride ($AlCl_3$, 99%), zirconium chloride ($ZrCl_4$, 98%), niobium chloride ($NbCl_5$, 99%), tantalum chloride ($TaCl_5$, 99%), tungsten (VI) chloride ($WCl_6$, 99%), tungsten (V) chloride ($WCl_5$, 99%), scandium chloride tetrahydrate ($ScCl_3 \cdot 4H_2O$, 99%), yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$, 99%), 2-hexanol (98%), 3-hexanol (98%), 2-ethyl-1-butanol (98%), and cyclohexanol (99%) were purchased from Energy Chemical (China). Caesium chloride (CsCl, 99%), lithium chloride (LiCl, 99%), zinc chloride ($ZnCl_2$, 98%), vanadium chloride ($VCl_3$, 97%), lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$, 99%), indium chloride tetrahydrate ($InCl_3 \cdot 4H_2O$, 99%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99%), manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 99%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 99%), hafnium chloride ($HfCl_4$, 99%), and 5-ethoxymethylfurfural (EMF, 97%) were purchased from Aladdin (Shanghai, China). Tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 99%), 1-hexanol (99%), and *p*-xylene (99%) were purchased from Sinopharm Group (China). Copper chloride ($CuCl_2$, 97%) and chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, 96%) were purchased from Sigma-Aldrich (China). The purities of all the above chemicals are suitable for the research in this work. Ultra-pure water with a resistivity of 18.2 MΩ-cm was prepared from a water purification system.

### Reaction Procedure

For a typical run, 1 mmol of HMF, 5 mmol of 1-hexanol, and 3 mmol of $H_2O$ were added into a small reaction vial with a catalyst. The vial was then sealed and inserted into a heating block to allow the reaction to occur. Once the reaction time was up, the vial was immediately immersed into an ice-water bath to quench the reaction. The main product was *n*-hexyl levulinate (HL) and *p*-xylene, as the internal standard, was added into the reaction mixture for quantitative calculation. Finally, the above mixture was diluted with acetone and analyzed *via* a gas chromatography (GC) system.

### Catalyst reuse

The used catalyst (*e.g.* $FeCl_3$) can dissolve in the reaction mixture, which actually presents a homogeneous system, so it is difficult to separate it out. As such, a consecutive batch reaction mode was adopted to assess the reusability of the catalyst, which means that fresh HMF would be added after each run for the next cycle, thus avoiding the separation of the catalyst. For a representative test, 1 mmol of HMF, 0.15 mmol of $FeCl_3$, 5 mmol of 1-hexanol, and 3 mmol of $H_2O$ were reacted in a reaction vial at 160 °C for 240 min. After the first run, another 1 mmol of HMF was directly added into the reaction mixture, then the mixture was reacted at 160 °C for 240 min as the second run. The formation of HL in the second run can be obtained by subtracting the HL formed in the first run from the sum of HL formed after two conversion sequences. The subsequent runs were carried out as above.

## Analysis Method

The GC tests were performed on a Hanwei brand (Zhengzhou, China) GC-L96 system equipped with a flame ionization detector (FID). The analysis column was a SE-54 type capillary column (30 m × 0.32 mm × 0.5 μm). Nitrogen was used as the carrier gas. The temperatures of the vaporization chamber and FID were set to 250 °C. The column was initially preheated to a temperature of 120 °C for 1 min, followed by being heated to a temperature of 200 °C with a heating rate of 30 °C·min$^{-1}$, and then the temperature was maintained at 200 °C for 4 min. A typical GC chromatogram is shown in Fig. S1 in the Appendix. Reactant conversions and ester yields were calculated according to Eq. 1 and Eq. 2.

$$HMF\ conversion\ (mol\%) = \left[1 - \frac{residue(HMF)}{initial(HMF)}\right] \times 100\% \qquad (1)$$

$$Ester\ yield\ (mol\%) = \left[\frac{detected\ ester}{ideal\ amount\ of\ ester\ by\ initial\ HMF}\right] \times 100\% \qquad (2)$$

Since excess alcohol was commonly used, the product yields were calculated based on the HMF loading.

## RESULTS AND DISCUSSION

## Catalyst Screening Test

Appropriate metal chlorides have been reported to be good catalysts for the production of HMF using carbohydrates (Zhao *et al.* 2007; Rasrendra *et al.* 2012). Based on this fact, a series of metal chlorides were employed as catalysts to explore the potential possibility of producing levulinate esters in this work. These catalysts were screened at a temperature of 150 °C for 120 min. As illustrated in Fig. 2, some metal chlorides, *e.g.*, TaCl$_5$, WCl$_5$, WCl$_6$, CuCl$_2$, and FeCl$_3$ exhibited relatively good activities for the production of HL with a yield of approximately 30%. The remarkable differences between the HMF conversion and HL yield indicated that HMF underwent considerable side reactions. As such, many black particles were observed during the reaction. The particles were ascribed to the condensation polymers and humins. The formation of *n*-hexyl ether, the intermolecular dehydration product of 1-hexanol, was also detected *via* GC-MS. However, the actual amount of *n*-hexyl ether was low, so it was not calculated. HMF generally undergoes acid-catalyzed hydration into LA with formic acid (FA) as a companion product, both of which can further react with alcohols to yield esters (Chen *et al.* 2014). As can be seen in Fig. S1, *n*-hexyl formate was detected, indicating that HMF was converted into LA and FA. However, the yields of *n*-hexyl formate were not calculated because it is also a companion product of HL. For comparison, sulfuric acid was used as the catalyst, and an inferior HL yield (approximately 20%) was obtained under the same conditions as above. One may expect that these metal chlorides may hydrolyze to form protons as the catalyst. However, the formation of HL did not correlate with the hydrolysis abilities of metal chlorides herein. For example, the hydrolysis ability of FeCl$_3$ was remarkably higher than that of CuCl$_2$, but the catalytic performances remained the same over the two catalysts (Peng *et al.* 2010). Similarly, AlCl$_3$ had a higher hydrolysis ability than CuCl$_2$, but it had an inferior activity (Peng *et al.* 2010). According to a previous study by Quereshi *et al.* (2017), the Lewis acidity of FeCl$_3$ and CuCl$_2$ could be a major reason for the formation of levulinate esters, probably accounting for the results in this work.
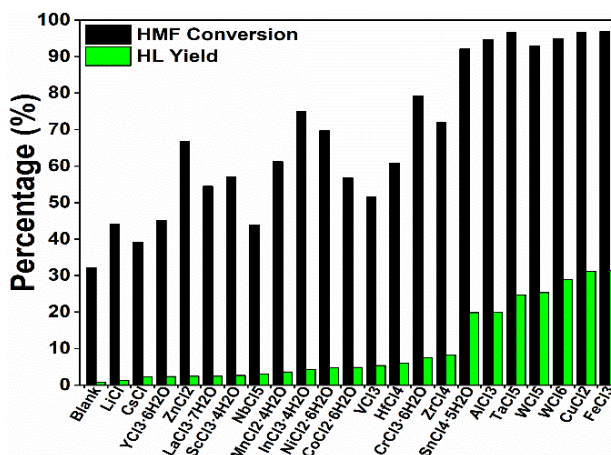
**Fig. 2.** The conversion of HMF into HL in the presence of different metal chloride catalysts and the blank test: Conditions: 1 mmol of HMF, 3 mmol of 1-hexanol, and 0.1 mmol of catalyst at a temperature of 150 °C for 120 min

As shown in Fig. 2, a few metal chlorides exhibited similar activities for the production of HL with almost complete HMF conversion at a temperature of 150 °C. In order to evaluate the actual activities of these catalysts, the reaction was tested at relatively low temperatures and a short reaction time. Figure S2 shows the results for the synthesis of HL at a temperature of 130 °C and 110 °C. Obviously, $FeCl_3$ and $CuCl_2$ still exhibited better activities among the catalysts and were employed for further study.

**Effect of Influence Factors**

As mentioned, HMF can undergo hydration into LA, which is an intermediate to yield levulinate esters (Chen *et al.* 2014). As such, the effect of the water content in the system was first investigated at a temperature of 130 °C for 60 min. As illustrated in Fig. 3, the conversion of HMF with $FeCl_3$ and $CuCl_2$ showed a similar trend. With increasing the water content to three equivalents of HMF, the HL yield slightly increased for both $FeCl_3$ and $CuCl_2$, possibly because the water addition promoted the formation of LA to some extent. However, additional water may also dilute the system, leading to the decrease in HL yield. Furthermore, excess water may also suppress the esterification of LA with 1-hexanol. Thus, a water amount of three equivalents of HMF was used as a fixed variable for the next investigation.
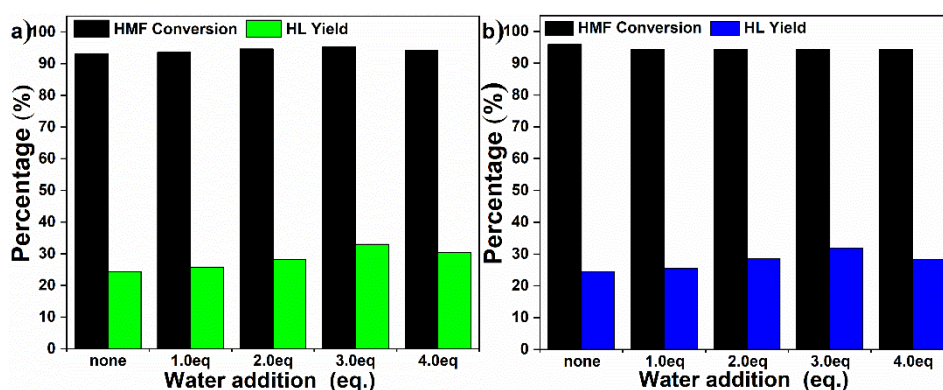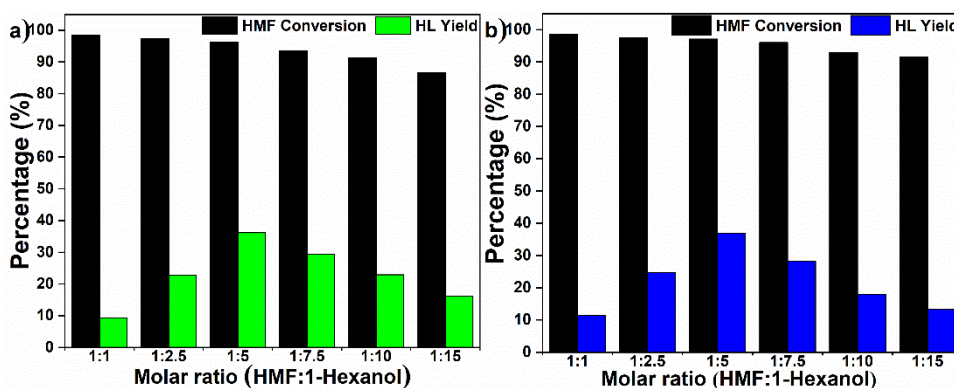


**Fig. 3.** Effect of the water content on the production of HL: Conditions: 1 mmol of HMF, 3 mmol of 1-hexanol, and 0.1 mmol of $FeCl_3$ (a) or $CuCl_2$ (b) at a temperature of 130 °C for 60 min

Figure 4 shows the effect of the catalyst load on the production of HL. As shown, $FeCl_3$ and $CuCl_2$ as the catalysts yielded very close results for the production of HL. When less than 15 mol% of the catalysts were added, the formation of HL showed an upward trend. The HL yield reached a threshold of approximately 37% with a catalyst loading of 15 mol%, indicating that the addition of additional catalyst did not further improve the reaction. Thus, a catalyst loading of 15 mol% was used as an optimal amount.
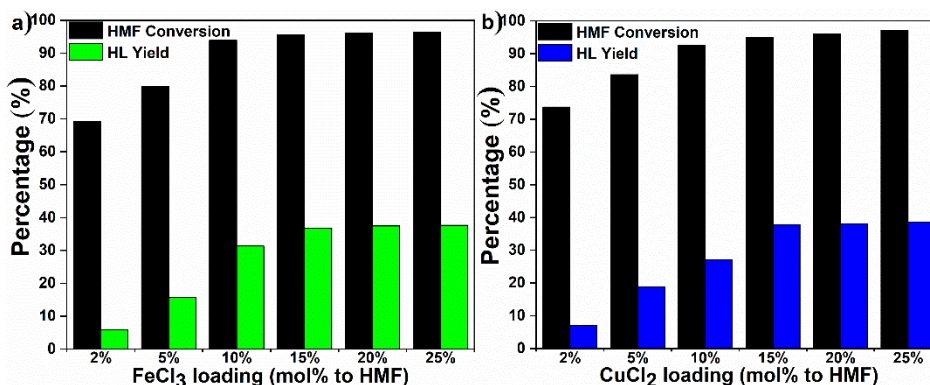


**Fig. 4.** Effect of the catalyst load on the production of HL: Conditions: 1 mmol of HMF, 3 mmol of 1-hexanol, 3 mmol of $H_2O$, and $FeCl_3$ (a) or $CuCl_2$ (b) at a temperature of 130 °C for 60 min

Levulinic acid (LA) is a possible intermediate for the synthesis of levulinate esters from HMF (Chen *et al.* 2014). Once LA is produced from HMF, it would be esterified by alcohols. The effect of the molar ratio of HMF to 1-hexanol was then tested at a temperature of 130 °C for 60 min. As shown in Fig. 5, when equimolar HMF and 1-hexanol were added, the HL yield stayed at a very low level (approximately 10%). By increasing the usage of 1-hexanol, HL yield showed an upward trend followed by a downward trend. According to previous studies, the esterification is a reversible reaction; thus, excess alcohol is generally used to improve the ester yield, which may account for the improvement of HL yield with a change of the HMF to 1-hexanol molar ratio from 1 to 1 to 1 to 5 (Sankar *et al.* 2017; Yang *et al.* 2018). However, too much excess 1-hexanol would further dilute the reaction system, leading to a decreased HL yield, which could be attributed to the decrease in the collision frequency between the reactant and catalyst. As such, a molar ratio of HMF to 1-hexanol of 1 to 5 was set as the optimal value.



**Fig. 5.** Effect of the material molar ratio on the production of HL: Conditions: 1 mmol of HMF, 3mmol of $H_2O$, and 0.15 mmol of $FeCl_3$ (a) or $CuCl_2$ (b) at a temperature of 130 °C for 60 min
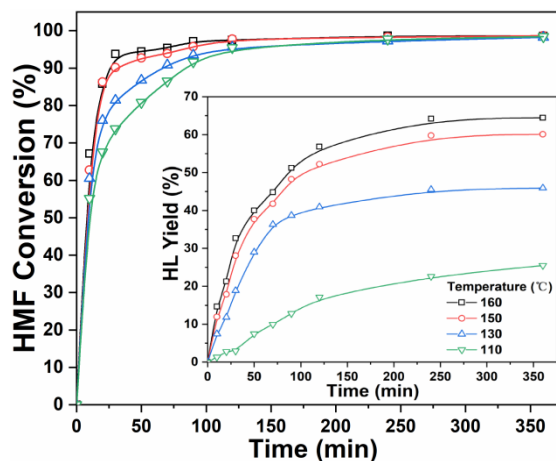
**Fig. 6.** The conversion of HMF into HL with $FeCl_3$ at different temperatures: Conditions: 1 mmol of HMF, 5 mmol of 1-hexanol, 3 mmol of $H_2O$, and 0.15 mmol of $FeCl_3$

Since $FeCl_3$ and $CuCl_2$ basically showed the same performances as above, $FeCl_3$ was used as the catalyst to test the conversion of HMF as a function of reaction time at different temperatures, in order to obtain an optimal HL yield. As illustrated in Fig. 6, the production of HL was remarkably affected by the temperature. When the reaction was run at a temperature of 110 °C, the production of HL proceeded slowly, with a yield of approximately 25% after 360 min. With elevating temperature, the formation of HL considerably accelerated. When compared, the HL yields at temperatures of 130 to 160 °C showed a remarkable increase within 70 min, while the conversions were close to those at a temperature of 110 °C, which indicated that a certain intermediate may be readily converted into HL at high temperatures. When the reaction was carried at a temperature of 160 °C, the maximum HL yield reached up to 65% after 240 min. Figure S3 shows that $CuCl_2$ had similar performance to $FeCl_3$, which was consistent with the above phenomenon.

**Preliminary Mechanistic Insights**

To understand the reaction mechanism, some control experiments were carried out. First, HMF (1 mmol) was heated at a temperature of 130 °C in the presence of $FeCl_3$ (0.15 mmol). However, the reaction mixture was found to be sticky with many black solid particles appearing quite soon, which made it difficult to stir. In this case, a certain amount of water was added to overcome the issue of stirring. A small amount of water (10 mmol) was added as the solvent and the kinetics of HMF conversion was monitored at a temperature of 130 °C. A HMF conversion of 53% and a LA yield of 13% were obtained after 15 min. With extending reaction time, both the HMF conversion and LA yield increased. The HMF conversion reached 69% and 90%, respectively, after 30 min and 60 min. The corresponding LA yields were 20% and 28%, respectively. The above results indicated that the hydration of HMF could occur in the presence of $FeCl_3$ and water. Moreover, the presence of *n*-hexyl formate, as shown in Fig. S1, further indicated that HMF underwent the hydration into LA because FA was a companion product of LA.

Second, 5-ethoxymethylfurfural (EMF) was employed as an intermediate model compound for the formation of EL from HMF and ethanol. As reported, the production of levulinate esters underwent two paths: 1) HMF was converted into LA, and the latter reacted with alcohols to produce levulinate esters; and 2) HMF was etherified *via* alcohols,

then the formed ethers went through a ring-opening process to yield levulinate esters by the elimination of formic acid (Flannelly *et al.* 2015). Herein, EMF (1 mmol) was used as the feedstock and heated at a temperature of 110 °C for 60 min in the presence of $FeCl_3$ (0.15 mmol) and water (10 mmol). However, no considerable EL was detected, which demonstrated that the conversion of HMF in this work possibly followed the first path as mentioned above.

## Conversion of Hydroxymethylfurfural (HMF) with Other Hexanols

The results of this study indicated that LA could be the intermediate from HMF to HL, in which the esterification of LA and 1-hexanol actually produced HL. This study also explored the conversion of HMF with other hexanols. As listed in Table 1, when 2-ethyl-1-butanol was used, the yield of the corresponding levulinate ester could compete with the optimal yield of HL shown in Fig. 6. The esterification of LA and alcohol was considerably affected by the steric hindrance of alcohol (Sankar *et al.* 2017). Since 2-ethyl-1-butanol is a primary alcohol like 1-hexanol, a close yield of levulinate ester can be expected. In contrast, cyclohexanol, 2-hexanol and 3-hexanol are secondary alcohols, which have larger steric hindrances, therefore leading to a lower product yield.

**Table 1.** Results for the Conversion of Hydroxymethylfurfural (HMF) with Other Hexanols

| Entry | ROH | Temperature (°C) | Time (min) | HMF Conversion (%) | Ester Yield (%) |
|---|---|---|---|---|---|
| 1 | 2-Ethyl-1-butanol | 130 | 60 | 85 | 23 |
| 2 | 2-Ethyl-1-butanol | 150 | 120 | 95 | 42 |
| 3 | 2-Ethyl-1-butanol | 160 | 240 | 99 | 58 |
| 4 | Cyclohexanol | 130 | 60 | 87 | 18 |
| 5 | Cyclohexanol | 150 | 120 | 96 | 39 |
| 6 | Cyclohexanol | 160 | 240 | 99 | 55 |
| 7 | 2-Hexanol | 130 | 60 | 82 | 13 |
| 8 | 2-Hexanol | 150 | 120 | 93 | 28 |
| 9 | 2-Hexanol | 160 | 240 | 98 | 41 |
| 10 | 3-Hexanol | 130 | 60 | 80 | 11 |
| 11 | 3-Hexanol | 150 | 120 | 94 | 26 |
| 12 | 3-Hexanol | 160 | 240 | 98 | 39 |
| Note: Conditions: 1 mmol HMF, 5 mmol alcohol, 0.15 mmol $FeCl_3$, 3 mmol $H_2O$. | | | | | |

## Catalyst Reuse and Scale-up Test

The reusability of a catalytic system is highly desirable. The authors employed $FeCl_3$ to assess the reusability of catalyst for the synthesis of HL. The detailed reaction procedure is depicted in the Experimental Section in this work. These tests were run under the optimal conditions. As shown in Fig. 7, the reaction performance remained at a high level after four runs, which demonstrated that the catalyst was stable and reusable in the system. In addition, a scale-up test will be beneficial to the design and development of an industrial process. The authors tested both the five-fold and ten-fold experiments as the regular HMF conversion at a temperature of 160 °C for 240 min in this work. The HMF conversions remained about 100% and HL yields were around 63%, which are very close to the regular results as illustrated in Fig. 6, implying the potential of scaling up such a system.
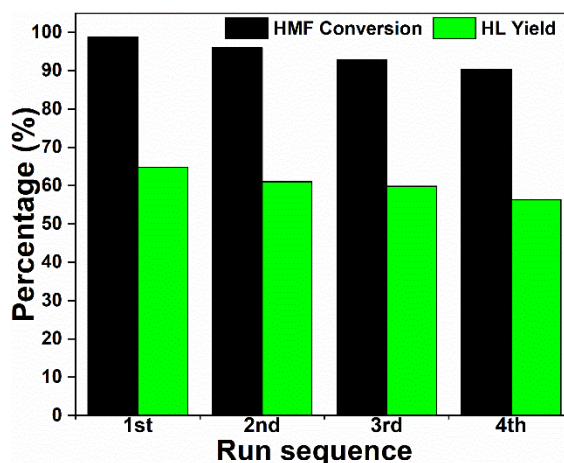
**Fig. 7.** Reusability of the $FeCl_3$ catalyst for the synthesis of HL at a temperature of 160 °C for 240 min

## CONCLUSIONS

1. In this work, the authors demonstrated that $FeCl_3$ and $CuCl_2$ were good catalysts for the synthesis of a long-chain levulinate ester, *n*-hexyl levulinate (HL), from hydroxymethylfurfural (HMF). A maximum HL yield of approximately 65% could be achieved at a temperature of 160 °C after 240 min.

2. The system also worked for conversion with other primary and secondary hexanols, including 2-ethyl-1-butanol, cyclohexanol, 2-hexanol, and 3-hexanol, with reasonable yields of 39% to 58%. The catalyst was reusable in a consecutive batch reaction mode.

3. Control experiments and kinetic experiments demonstrated that the formation of HL possibly was converted to levulinic acid (LA) as the intermediate, but not the etherification of HMF first.

## ACKNOWLEDGMENTS

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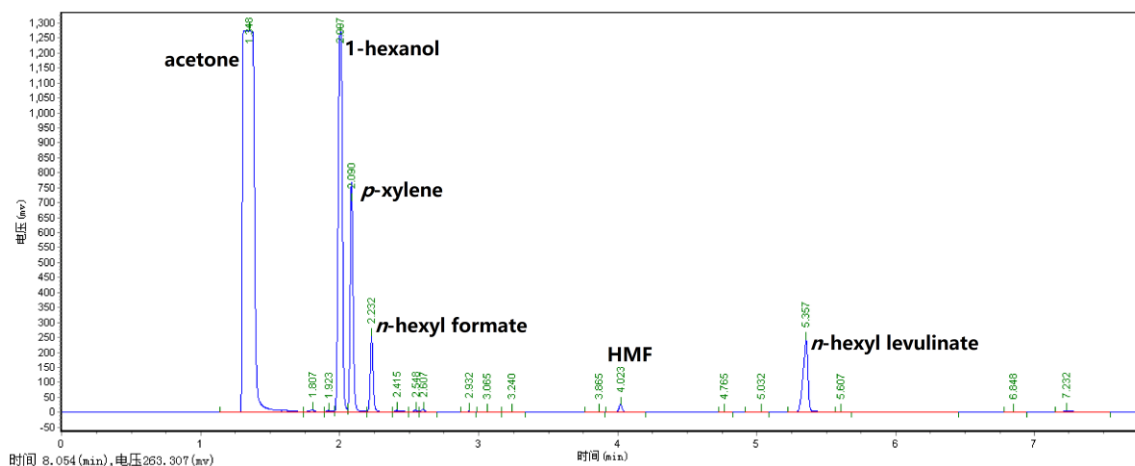
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## APPENDIX



**Fig. S1.** Representative GC chromatogram for the conversion of HMF into HL
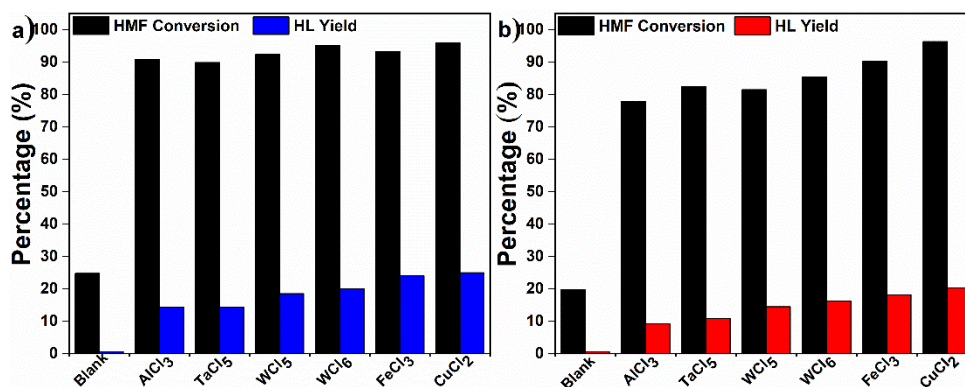


**Fig. S2.** The conversion of HMF into HL in the presence of different metal chlorides and blank test at 130 (a) and 110 °C (b), respectively. Reaction conditions: 1 mmol of HMF, 3 mmol of hexanol, and 0.1 of mmol catalyst at a temperature of 130 (a) or 110 °C (b) for 60 min
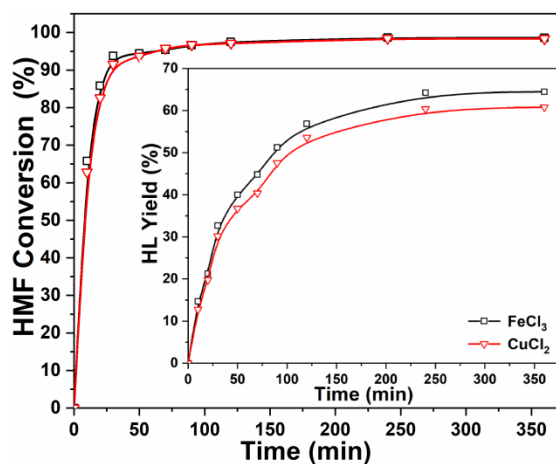


**Fig. S3.** The conversion of HMF into HL with $FeCl_3$ and $CuCl_2$ at 160 °C, respectively. Reaction conditions: 1 mmol of HMF, 5 mmol of 1-hexanol, 0.15 mmol of catalyst, and 3 mmol of $H_2O$ at a temperature of 160 °C