Enhanced Conversion of Furfuryl Alcohol to Alkyl Levulinates Catalyzed by Synergy of $CrCl_3$ and H_3PO_4

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To enhance the yield of alkyl levulinates, a mixed-acid catalyst system consisting of $CrCl_3$ and H_3PO_4 was investigated for the transformation of furfuryl alcohol (FA). The $CrCl_3$−H_3PO_4 system exhibited a positive synergistic catalytic activity for the synthesis of alkyl levulinates, which was especially obvious for *n*-butyl levulinate (BL) synthesis. The strongest synergic effect of mixed-acid system for BL production was achieved at the $CrCl_3$ molar ratio of 0.3 (based on total moles of $CrCl_3$ and H_3PO_4). Furthermore, the mixed-acid systems consisting of Cr-salts combined with H_3PO_4 and its salts in catalyzing FA conversion to BL were evaluated, and the evolution process of FA to produce BL was explored in the presence of $CrCl_3$−H_3PO_4, sole $CrCl_3$, and sole H_3PO_4. A possible synergistic catalytic pathway of $CrCl_3$ combined with H_3PO_4 was proposed. Finally, the key process variables were examined. Under optimal conditions, a high BL yield of 95% was achieved from 99% FA conversion catalyzed by the synergy of $CrCl_3$ and H_3PO_4.

Keywords: Biofuel; Furfuryl alcohol; Alkyl levulinates; Synergistic catalysis

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INTRODUCTION

Biomass is a renewable and reliable source of carbon-based fuels and chemicals; it is a promising alternative to diminishing fossil fuel resources. Due to the complex structure of biomass, its utilization usually involves multiple processing steps in which biomass is first depolymerized and converted to certain platform chemicals. A variety of fuels and valuable chemicals are derived from these platform chemicals. Furfuryl alcohol (FA), an important furan derivative, is produced industrially by hydrogenation of furfural derived from the hydrolysis and dehydration of xylan in lignocellulosic biomass (Lange *et al*. 2012; Ghashghaee *et al*. 2017; Sadjadi *et al*. 2017). To achieve valuable products of the desired fuel properties and commercial applications, further catalytic upgrading of FA is important (Bohre *et al*. 2015; Han *et al*. 2017). An economic and convenient strategy for the synthesis of alkyl levulinates can be envisioned *via* the catalytic reaction of FA with alcohols (Démolis *et al*. 2014). Alkyl levulinates are versatile products with extensive applications, including as transportation fuels or fuel additives (Windom *et al*. 2011), flavoring agents, solvents, and as precursors for the preparation of γ-valerolactone (Tang *et al*. 2014) and other useful chemicals (Démolis *et al*. 2014).

An acid catalyst is required for the transformation of FA into alkyl levulinates. In the past, a variety of heterogeneous catalysts have been tested, and some of them, such as acidic resin (Lange *et al*. 2009), zeolite (Neves *et al*. 2013; Nandiwale *et al*. 2015), organic-inorganic hybrid acid (Zhang *et al*. 2011), mesostructured zirconium-based mixed oxides (Neves *et al*. 2014), graphene oxide (Zhu *et al*. 2014), sulfonic acid-functionalized solid materials (Demma Carà *et al*. 2014; Russo *et al*. 2014; Lu *et al*. 2015; Liu *et al*. 2016), zinc exchanged heteropoly tungstate supported on niobia catalysts (Rao *et al*. 2017), and magnetically separable sulfated zirconia (Tiwari *et al*. 2016), have been found to be active in the synthesis of alkyl levulinates. Heterogeneous catalysts have advantages over homogeneous catalysts regarding catalyst separation and reusability. However, they also suffer from several shortcomings, including the complex synthesis of catalyst, high cost, and/or the deactivation of the recovered catalyst due to the deposition of carbonaceous products in the catalyst pores. In this context, the synthesis of alkyl levulinates from FA with practical acceptance at an industrial scale remains a challenge.

Some metal salts such as $AlCl_3$, $CrCl_3$, and $FeCl_3$ can impart superior Lewis and/or Brønsted acidity in certain organic or aqueous solvents. These metal salts are abundant and commercially available, providing inexpensive and facile catalyst sources for the acid-catalyzed conversion of biomass or its derived compounds into fuels and chemicals. Previously, $AlCl_3$ and $CuCl_2$ were used as efficient and reusable catalysts for the synthesis of alkyl levulinates from FA (Peng *et al*. 2015, 2016). Huang *et al*. (2016) showed that $Al_2(SO_4)_3$ also possesses good catalytic activity for the conversion of FA into methyl levulinate under microwave irradiation condition. In addition, $CrCl_3$ is active in these reaction conditions, but its catalytic activity is considerably inferior to the above-mentioned metal salts (Huang *et al*. 2016; Peng *et al*. 2016). Previous reports showed that $CrCl_3$ combined with H_3PO_4 had a strong synergic catalytic activity for the transformation of glucose to levulinic acid, the yield of which was much higher than that of $CrCl_3$ alone (Yang *et al*. 2013; Wei and Wu 2017). Accordingly, this catalyst system is expected to be qualified for the conversion of FA to alkyl levulinates. The objective of this study was to investigate the feasibility and mechanism of a mixed-acid catalyst system consisting of $CrCl_3$ and H_3PO_4 for improving the synthesis of alkyl levulinates from FA.

EXPERIMENTAL

Materials

The chemicals FA, $CrCl_3$, $Cr_2(SO_4)_3$, H_3PO_4, KH_2PO_4, K_2HPO_4, and K_3PO_4 were purchased from Aladdin Reagent (Shanghai, China). 2-Butoxymethylfuran (BMF) was obtained from Ruisheng Chemical Co., Ltd (Jiangyin, China). The alcoholic reagents including methanol, ethanol, *n*-propanol, and *n*-butanol were acquired from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All reagents used were of analytical grade and used without further purification. The alkyl levulinates (methyl-, ethyl-, *n*-propyl-, and *n*-butyl-) used for calibration, with purity of over 98%, were procured from Sigma-Aldrich (Shanghai, China) and Aladdin Reagent (Shanghai, China).

General Reaction Procedure

The reaction of FA with alcohols was carried out in a 50 mL cylindrical stainless steel pressurized reactor equipped with an oil-bath heating and magnetic stirrer. In a typical experiment, 0.53 mL of FA (0.3 mol/L working concentration) and 19.47 mL *n*-butanol solution containing both 0.01 mol/L $CrCl_3$ and 0.01 mol/L H_3PO_4 were loaded into the reactor. After the reactor was sealed, the above mixture was heated to the desired temperature in an oil-bath and was continuously stirred at 600 rpm with a magnetic stirrer. After running the reaction for a specified duration, the reactor was placed in cool water bath to terminate the reaction. The sample was collected from the cooled reactor after filtration. The liquid fraction was diluted with an ethanol solution containing the internal standard for gas chromatographic (GC) analysis.

Analytical Methods

The reaction products of the FA alcoholysis were quantitatively analyzed by gas chromatography (GC) on an Agilent 6890 instrument (Santa Clara, CA, USA) equipped with a DB-5 capillary column (30.0 m × 320 µm × 0.25 µm) and a flame-ionization detector (FID). The following operating conditions were used: nitrogen as carrier gas at a flow rate of 1.0 mL/min, the injection port temperature of 250 °C, the oven temperature of 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 of 250 °C. The detected compounds were estimated based on internal standard curves constructed with their authentic compounds. The FA conversion was defined as the ratio of the moles of FA converted to the moles of FA loaded in the feed. The yield of alkyl levulinates/intermediates were estimated as the ratio of the moles of alkyl levulinates/intermediates obtained to the moles of FA loaded in the feed. The selectivity of alkyl levulinates was calculated by dividing the yield of alkyl levulinates by the FA conversion.

To judge whether the combination of $CrCl_3$ and H_3PO_4 has a synergistic catalytic effect on the synthesis of alkyl levulinate, a synergy factor (SF) was defined using Eq 1. If the synergy factor of the mixed-acid system is greater than 1, it suggests that the mixed-acid system has a positive synergistic catalytic activity, and *vice versa*.

$$\text{SF} = \text{Yield of alkyl levulinates in the mixed-acid system} / (\text{Yield of alkyl levulinates with sole } CrCl_3 + \text{Yield of alkyl levulinates with sole } H_3PO_4) \quad (1)$$

RESULTS AND DISCUSSION

Evaluation of $CrCl_3$−H_3PO_4 System on the Conversion of FA to Alkyl Levulinates

The catalytic performance of $CrCl_3$−H_3PO_4 system in the formation of alkyl levulinates was examined for the reaction of FA with various alkyl alcohols. The $CrCl_3$ and H_3PO_4 as sole catalysts were also tested for comparison. The results of the reaction are summarized in Table 1. When FA was treated with 0.01 mol/L pure H_3PO_4 in methanol medium, only 24.9% of FA was converted, and the methyl levulinate was formed in a low yield of 3.4%, indicating an extremely low catalytic activity. A slightly better conversion rate of FA and methyl levulinate yield was obtained with sole $CrCl_3$ (0.01 mol/L) up to 76.9% and 24.7%, respectively. The reaction performances for the conversion of FA in ethanol, *n*-propanol, and *n*-butanol media were similar to that in methanol medium with sole H_3PO_4 and sole $CrCl_3$. Nevertheless, a noticeably higher conversion of FA, and good yield and selectivity of alkyl levulinates were achieved for all tested alcohols, when both H_3PO_4 and $CrCl_3$ were used simultaneously. The yield of alkyl levulinates was far greater than the sum of the yields from sole H_3PO_4 and $CrCl_3$ as catalysts. The synergy factors of H_3PO_4 and $CrCl_3$ in all investigated alcohols media were larger than 1, suggesting strong synergistic catalytic effect. Thus, the synergies of H_3PO_4 and $CrCl_3$ were intrinsic to the conversion of FA to alkyl levulinates. Because the reaction of FA with *n*-butanol catalyzed by H_3PO_4−$CrCl_3$ system exhibited the strongest synergistic catalytic activity with a synergy factor of 2.2, it was selected for further exploration.

Table 1. Reaction of FA with Various Alkyl Alcohols to Form Alkyl Levulinates Catalyzed by $CrCl_3-H_3PO_4$ System

Entry	Reaction Medium	Catalyst	FA Conversion (%)	Yield of Alkyl Levulinate (%)	Selectivity of Alkyl Levulinate (%)	Synergy Factor
1	Methanol	$CrCl_3$	76.9 ± 0.5	24.7 ± 1.0	32.1	-
2	Methanol	H_3PO_4	24.9 ± 4.7	3.4 ± 0.1	13.7	-
3	Methanol	$CrCl_3$ + H_3PO_4	95.4 ± 0.4	41.8 ± 2.6	43.8	1.5
4	Ethanol	$CrCl_3$	72.9 ± 0.7	20.9 ± 0.7	28.7	-
5	Ethanol	H_3PO_4	15.2 ± 2.1	0.7 ± 0.1	4.6	-
6	Ethanol	$CrCl_3$ + H_3PO_4	96.9 ± 0.1	38.3 ± 1.1	39.5	1.8
7	*n*-Propanol	$CrCl_3$	65.5 ± 0.2	20.8 ± 0.1	31.8	-
8	*n*-Propanol	H_3PO_4	21.4 ± 2.4	1.4 ± 0.1	6.5	-
9	*n*-Propanol	$CrCl_3$ + H_3PO_4	97.7 ± 0.1	38.4 ± 0.3	39.3	1.7
10	*n*-Butanol	$CrCl_3$	71.3 ± 0.2	21.3 ± 1.6	29.9	-
11	*n*-Butanol	H_3PO_4	14.9 ± 1.8	0.4 ± 0.1	2.7	-
12	*n*-Butanol	$CrCl_3$ + H_3PO_4	99.3 ± 0.2	48.6 ± 0.9	48.9	2.2

Reaction conditions: 0.3 mol/L FA in reaction medium; $CrCl_3$ of 0.01 mol/L; H_3PO_4 of 0.01 mol/L; temperature of 110 °C; time of 2 h

Effect of $CrCl_3$ Ratio in the $CrCl_3-H_3PO_4$ Mixed System on FA Conversion

To better understand the synergistic catalytic activity of the $CrCl_3-H_3PO_4$ system, the effects of $CrCl_3$ ratio in the mixed catalytic system, sole $CrCl_3$, and sole H_3PO_4 on the conversion of FA to *n*-butyl levulinate (BL) were investigated. The $CrCl_3$ ratio was defined as the ratio of the moles of $CrCl_3$ used to the total moles of $CrCl_3$ and H_3PO_4 loaded in the reaction. The results are depicted in Fig. 1. The conversion of FA to BL was closely related to the proportion of $CrCl_3$ in the $CrCl_3-H_3PO_4$ system. The FA conversion and BL yield with 0.02 mol/L H_3PO_4 ($CrCl_3$ ratio of zero) at 110 °C for 2 h was only 19.7% and 2.1%, respectively. When the ratio of $CrCl_3$ was varied from zero to 0.3, a rapid and nearly linear increasing trend for the conversion of FA to BL was observed. The reactant FA was almost totally consumed over 99% at the $CrCl_3$ ratio of 0.3, and the yield of BL was increased to up to 46.3%. The highest BL yield of around 51% was achieved at the $CrCl_3$ ratio of 0.7. At higher ratios of $CrCl_3$, both FA conversion and BL yield were gradually decreased. Hence, optimal Lewis and Brønsted acid sites derived from a valid combination of $CrCl_3$ and H_3PO_4 plays a crucial role in the efficient conversion of FA to BL. When FA was treated with 0.02 mol/L pure $CrCl_3$, FA conversion and BL yield were 82.0% and 34.6%, respectively. This catalytic activity is merely similar to the mixed-acid system with the $CrCl_3$ ratio of 0.1 to 0.2. The conversion rate of FA and BL yield gradually increased with increasing the catalyst dosages from 0.0002 mol/L to 0.02 mol/L for sole $CrCl_3$. In this situation, a higher $CrCl_3$ catalyst dosage and/or longer reaction time may be required to achieve a more effective conversion of FA to BL. In the case of sole H_3PO_4, its dosage had less impact on the conversion of FA to BL, and the BL yield was kept very low (0.4% to 2.1%) for all dosages studied. The conversion rate of FA and yield of BL with the mixed-acid system at various $CrCl_3$ ratios were higher than those with sole H_3PO_4 and sole $CrCl_3$ as catalysts. Also, the calculation of synergy factor from Fig. 1b showed that the synergy factors at all ratios of $CrCl_3$ were larger than 1, indicating the synergy of $CrCl_3$ and H_3PO_4. The synergy factor had a maximum value of 2.5 at the $CrCl_3$ ratio of 0.3, and the trend firstly increased and then decreased as the $CrCl_3$ ratio was increased. Hence, the $CrCl_3$ ratio of 0.3 in the mixed-acid system with the highest synergy factor was employed in the following study.

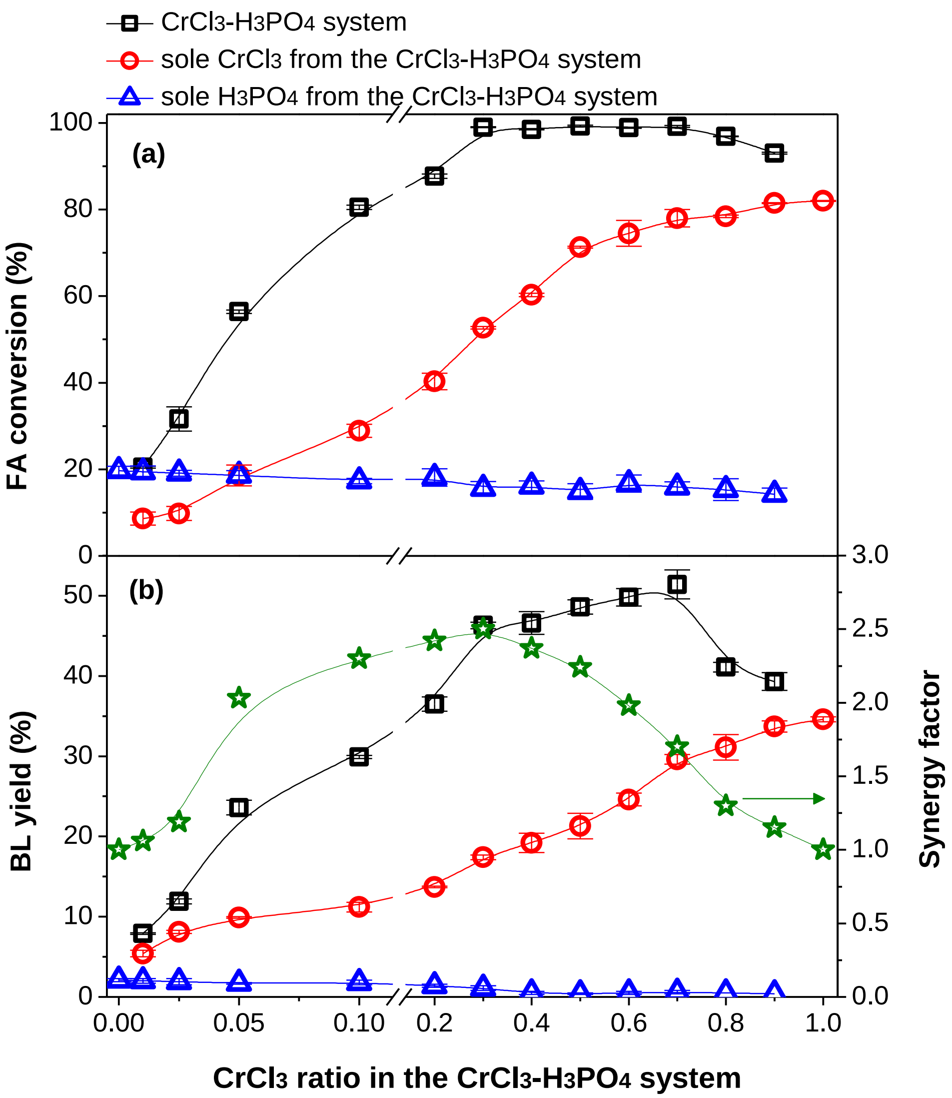


Fig. 1. Effect of $CrCl_3$ ratio in the $CrCl_3$−H_3PO_4 system on FA conversion, BL yield, and synergy factor. Conditions: 0.3 mol/L FA in *n*-butanol; $CrCl_3$−H_3PO_4 concentration of 0.02 mol/L; temperature of 110 °C; and time of 2 h

Comparison of Cr-Salts–H_3PO_4 System and with Other Salts on FA Conversion to BL

To explain the synergic effect in the catalytic performance of mixed acid catalyst system, the efficacy of Cr-salts combined with H_3PO_4 in catalyzing FA conversion to BL was examined, and the results are listed in Table 2. The sole phosphate salts such as KH_2PO_4, K_2HPO_4, and K_3PO_4 did not effectively convert FA to BL, and there were no noteworthy differences with the sole H_3PO_4. For the mixed-acid systems, the conversion rate of FA and BL yield decreased in the order H_3PO_4−$CrCl_3$ > KH_2PO_4−$CrCl_3$ > K_2HPO_4−$CrCl_3$ > K_3PO_4−$CrCl_3$, which seems related to the content of H^+ ions. However, FA conversion and BL yield with $CrCl_3$ combined with KH_2PO_4 and K_2HPO_4 were still higher than those with sole $CrCl_3$, and the synergy factors were 2.4 and 1.5, respectively, displaying synergistic catalytic activity. In contrast, the yields of BL with $CrCl_3$ and K_3PO_4 were slightly lower than that with sole $CrCl_3$, and the synergy factor was less than 1. The ability of K_3PO_4 dissociation to form HPO_4^{2-} ion and to release H^+ ion is the weakest in these phosphates used. Therefore, a possible explanation for these observations is that HPO_4^{2-}, $H_2PO_4^-$, and/or H^+ ions play a critical role in the synergistic catalytic synthesis of BL from FA alcoholysis. Furthermore, when $Cr_2(SO_4)_3$ was used instead of $CrCl_3$, the catalytic activity was markedly decreased. Only 25.9% FA conversion and 0.6% BL yield were obtained with 0.006 mol/L pure $Cr_2(SO_4)_3$. Meanwhile, no synergic effect was observed with combining of $Cr_2(SO_4)_3$ and H_3PO_4, and the synergy factor was only 0.1. It can be concluded that the anion type of metal salt also plays an important role in the conversion of FA to BL in addition to cationic species, and the metal chloride was more appropriate as the catalyst or co-catalyst. The differences in the catalytic activity are probably caused by their different Lewis acid sites in reaction medium, and the Lewis acidity of metal sulfates is usually weaker than that of their corresponding chlorides (Corma and Garcia 2003).

Table 2. FA Conversion, Yield and Selectivity of BL, and Synergy Factor for the Alcoholysis of FA in *n*-Butanol with Cr-Salts Combined H_3PO_4 and its Various Salts

Entry	Catalyst	FA Conversion (%)	BL Yield (%)	BL Selectivity (%)	Synergy Factor
1	H_3PO_4	15.6 ± 1.6	1.1 ± 0.3	7.1	-
2	KH_2PO_4	22.1 ± 2.1	0.9 ± 0.1	4.1	-
3	K_2HPO_4	20.1 ± 0.7	0.9 ± 0.2	4.5	-
4	K_3PO_4	22.1 ± 0.5	0.6 ± 0.1	2.7	-
5	$CrCl_3$	52.7 ± 0.3	17.4 ± 0.3	33.0	-
6	$Cr_2(SO_4)_3$	25.9 ± 2.2	0.6 ± 0.1	2.3	-
7	$CrCl_3$ + H_3PO_4	99.0 ± 0.1	46.3 ± 0.4	46.8	2.5
8	$CrCl_3$ + KH_2PO_4	93.3 ± 1.1	44.1 ± 1.2	47.3	2.4
9	$CrCl_3$ + K_2HPO_4	72.7 ± 0.7	28.0 ± 0.6	38.5	1.5
10	$CrCl_3$ + K_3PO_4	54.2 ± 0.1	13.3 ± 0.1	24.5	0.7
11	$Cr_2(SO_4)_3$ + H_3PO_4	15.0 ± 1.5	0.2 ± 0.0	1.3	0.1

Reaction conditions: 0.3 mol/L FA in *n*-butanol; 0.006 mol/L Cr-salts; 0.014 mol/L H_3PO_4 or its salts; temperature of 110 °C; and time of 2 h

Evolution Process of FA to Produce BL Catalyzed by $CrCl_3$−H_3PO_4 System

The liquid-phase chemical composition that was produced by the reaction of FA with *n*-butanol in the presence of $CrCl_3$−H_3PO_4 was analyzed using GC-MS. Only two main products were detected in the liquid-phase: one is intermediate compound 2-butoxymethylfuran (BMF), and the other is target product BL. To further understand the synergic effect of $CrCl_3$ and H_3PO_4, the changes of FA and the products formed in the reaction were traced for $CrCl_3$−H_3PO_4, sole $CrCl_3$, and sole H_3PO_4 catalyst systems, respectively. As shown in Fig. 2, in the case of sole $CrCl_3$, FA was relatively slowly converted throughout the reaction by forming the intermediate BMF and product BL slowly. In this reaction process, the yield of intermediate BMF monotonically increased with the extension of the reaction time, which was almost as higher as that of BL at the same reaction times. These findings indicated that the etherification of FA to intermediate BMF and the further decomposition of BMF to BL are both difficult with sole $CrCl_3$ as catalyst. In addition, the sole H_3PO_4 was inoperative in the conversion of FA into BMF and then to BL. However, when using the $CrCl_3$−H_3PO_4 catalyst system, FA was rapidly converted at the beginning of the reaction itself, and the yield of intermediate BMF was high during the initial stage of the reaction and then was decreased. The product BL was formed in a fast reaction rate and in a high final yield.

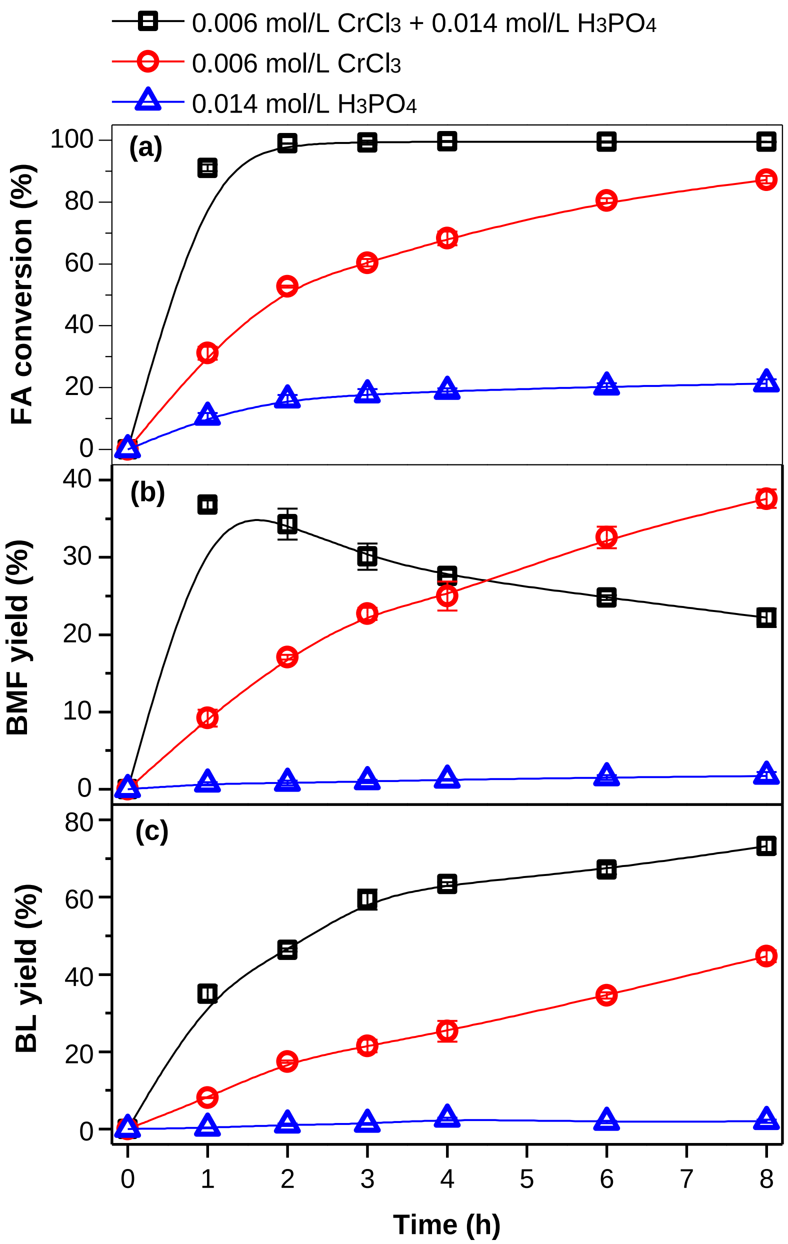


Fig. 2. FA conversion and the major products yield *versus* time for the alcoholysis of FA in *n*-butanol at 110 °C with $CrCl_3$−H_3PO_4, $CrCl_3$, and H_3PO_4, respectively

Experiments were conducted with BMF instead of FA as starting material under the same reaction conditions. As shown in Fig. 3, the synergic effect of $CrCl_3$ and H_3PO_4 in the conversion of BMF to BL was similar to that in the conversion of FA to BL. The intermediate BMF conversion and the final BL yield for the $CrCl_3$−H_3PO_4 mixed system were much higher than those using sole $CrCl_3$ and sole H_3PO_4 as catalysts at the same residence times. Therefore, it can be concluded that the etherification of FA to intermediate BMF and its further decomposition to BL are possibly catalyzed synergistically by $CrCl_3$ and H_3PO_4. By combining these findings with the related literature data (Zhang *et al*. 2011; Maldonado *et al*. 2012; Huang *et al*. 2016), a plausible reaction mechanism for the alcoholysis of FA to BL with $CrCl_3$−H_3PO_4 catalyst system is proposed, as shown in

Scheme 1. In this process, $CrCl_3$ plays a key role in inducing the conversion of FA into BL. FA was first protonated and then an intermediate BMF was formed under the attack of *n*-butanol. After that, the intermediate BMF was further converted to the final product BL through a series of chemical reaction steps, including 1,4-addition, deprotonation, the discharge of *n*-butanol, protonation, electron-pair transfer, and isomerization in sequence. The addition of H_3PO_4 increases the H^+ ion concentration, facilitating the protonation reaction in the scheme, which leads to the acceleration of FA conversion to the intermediate BMF and its decomposition to BL. In the case of the salt K_2HPO_4, the release of H^+ ion was difficult than H_3PO_4 and KH_2PO_4. Therefore, the synergic effect of K_2HPO_4 and $CrCl_3$ on the alcoholysis of FA to BL is weaker than H_3PO_4 and KH_2PO_4.

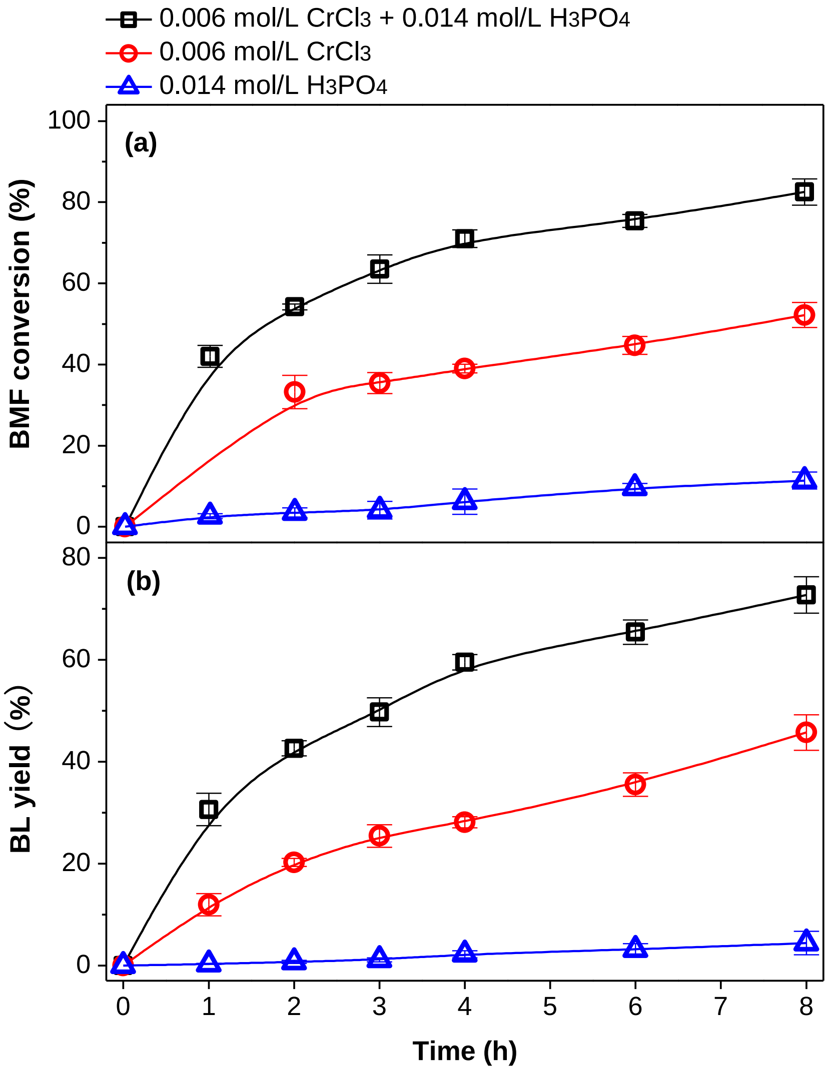
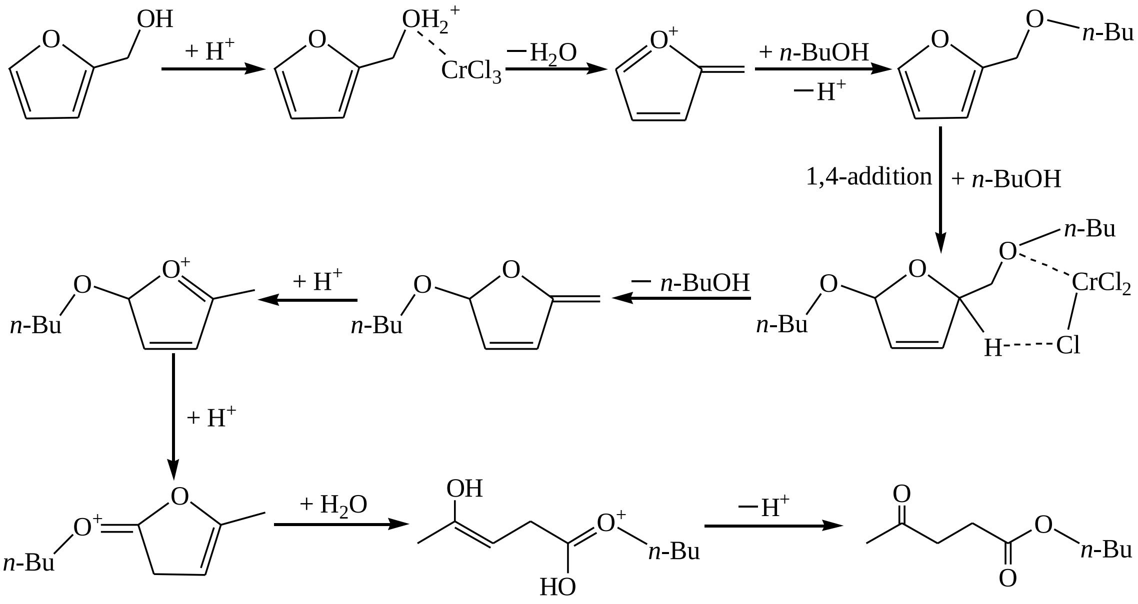


Fig. 3. BMF conversion and BL yield *versus* time for the alcoholysis of BMF in *n*-butanol with $CrCl_3$−H_3PO_4, $CrCl_3$, and H_3PO_4 catalysts



Scheme 1. Proposed mechanism for the alcoholysis of FA to BL with $CrCl_3$−H_3PO_4 catalyst system

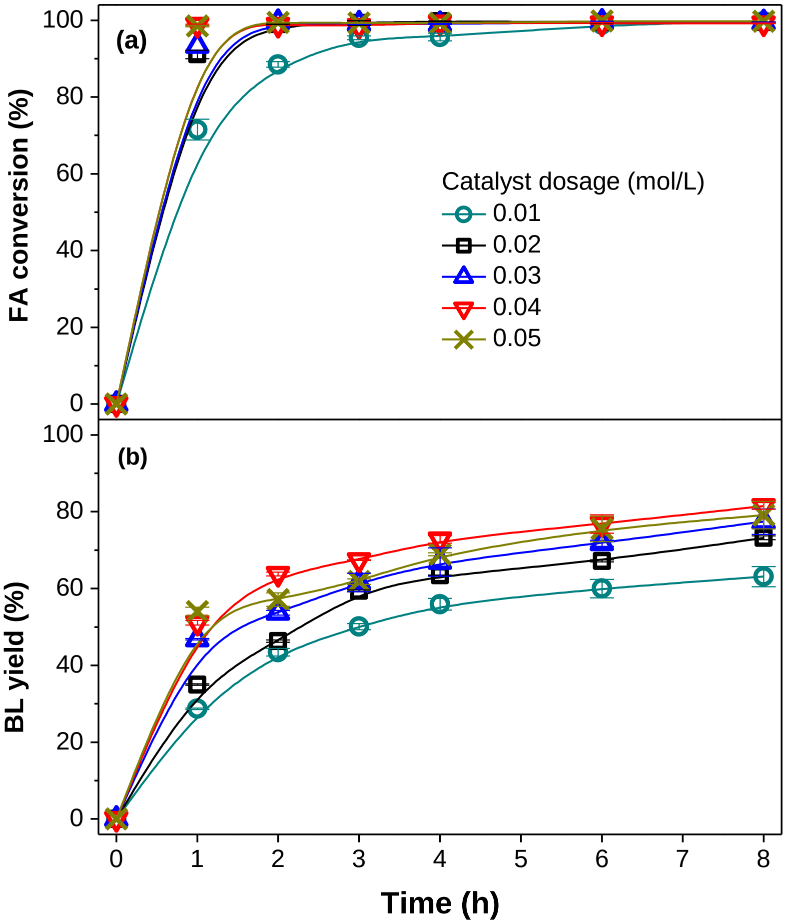


Fig. 4. Effect of catalyst dosage on the conversion of FA to BL as a function of time. Conditions: 0.3 mol/L FA in *n*-butanol; $CrCl_3$−H_3PO_4 system (fixed $CrCl_3$ ratio of 0.3) as the catalyst; and temperature of 110 °C

Optimization of BL Production Catalyzed by Synergy of $CrCl_3$ and H_3PO_4

To achieve the highest possible yield of BL, the effects of the process variables including the catalyst dosage, reaction temperature, and initial FA concentration on the conversion of FA to BL were investigated as a function of reaction time. Figure 4 illustrates the effect of the dosage of $CrCl_3$−H_3PO_4 system (fixed $CrCl_3$ ratio of 0.3), ranging from 0.01 mol/L to 0.05 mol/L, on the FA conversion and BL yield, while the reaction temperature was held constant at 110 °C. By and large, with increasing the catalyst dosage, the total number of available acid sites were increased, which resulted in a faster reaction rate to promote the conversion of FA to form more BL. The starting material FA was almost entirely consumed within a short reaction time of 1 to 2 h when the catalyst dosage exceeded to 0.02 mol/L. The yield of BL grew rapidly during the initial stages of the reaction, and then it was observed slowly to rise over time for all tested catalyst dosages. At the same reaction time, the BL yield with the catalyst dosage of 0.04 mol/L (0.012 mol/L $CrCl_3$ and 0.028 mol/L H_3PO_4) was the highest. The loading of excess catalyst (0.05 mol/L) had a negative impact on the synthesis of BL, suggesting that the reactivity ratio of FA polymerization to its alcoholysis may increase.

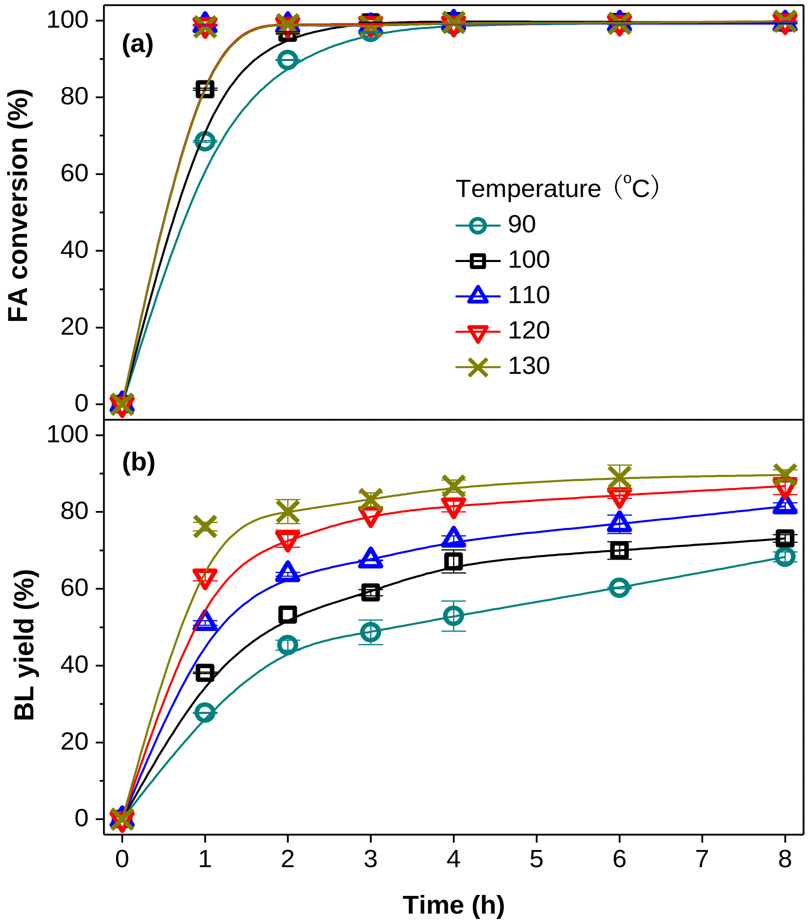


Fig. 5. Effect of reaction temperature on the conversion of FA to BL as a function of time with $CrCl_3$−H_3PO_4 system. Conditions: 0.3 mol/L FA in *n*-butanol; catalyst dosage of 0.04 mol/L (0.012 mol/L $CrCl_3$ + 0.028 mol/L H_3PO_4)

The influence of reaction temperature (90 °C to 130 °C) on the conversion of FA to BL is presented in Fig. 5. Temperature played an important role in the synthesis of BL, and the BL yield was increased when higher temperature was employed at the same reaction time. Under lower temperature conditions, the BL yield grew relatively slowly with the prolonging of time, and only 68.3% yield of BL was achieved after 8 h at 90 °C. In contrast, FA was almost totally converted within 3 h. A possible explanation for this difference is that a great amount of intermediates can be accumulated during the reaction process, which may need a longer time to reach a completion (Maldonado *et al*. 2012; Wang *et al*. 2014). Higher temperature gave rise to a faster reaction rate for the formation of BL at the beginning of reaction. About 76.2% yield of BL could be obtained at 130 °C during 1 h. The yield of BL increased slowly as the time was extended, and the equilibrium point was almost reached by 6 h of reaction, with a BL yield of around 90%.

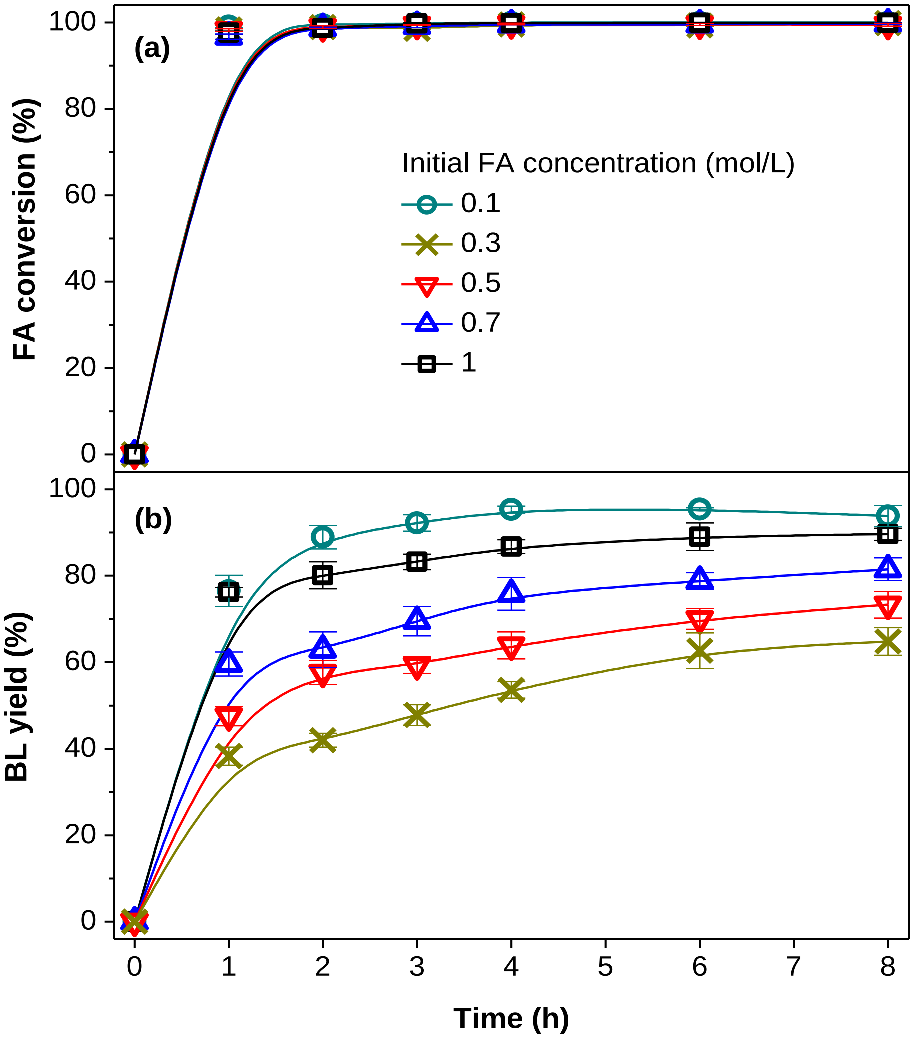


Fig. 6. Effect of initial FA concentration on the conversion of FA to BL as a function of time with $CrCl_3$−H_3PO_4 system. Conditions: Catalyst dosage of 0.04 mol/L (0.012 mol/L $CrCl_3$ + 0.028 mol/L H_3PO_4); temperature of 130 °C

Theoretically, an increase in initial FA concentration results in more substrate availability for the efficient FA conversion to produce BL. However, the yield of BL dropped clearly with increasing initial FA concentration from 0.1 mol/L to 1 mol/L (see Fig. 6), implying that the substrate inhibits the kinetics of this process. When the initial FA concentration was 0.1 mol/L, the BL yield reached a maximum of 95% within 4 h of reaction. When the initial FA concentration increased from 0.1 mol/L to 1 mol/L, the concentration of BL in the reaction mixture had increased, but the actual yield was found to be decreased obviously. Further, it can be noticed that the FA conversion was less influenced by its initial concentration, giving close to 100% conversions after 1 h in all experiments studied. At higher initial FA concentration, more intermediates (*i.e.*, BMF) were detected by GC-MS in the reaction mixture. Additionally the formation of dark-brown insoluble substances known as humins took place as a result of FA polymerization (Gao *et al*. 2015). The reason for these could be attributed to the product feedback inhibition and/or reactivity diminution, which brings about an incomplete alcoholysis reaction and the enhancement of side-reaction products. The optimum yield of alkyl levulinate catalyzed by $CrCl_3$−H_3PO_4 mixed system was equal as those previous obtained using $AlCl_3$ (Peng *et al*. 2015) and $CuCl_2$ (Peng *et al*. 2016) as the catalysts.

CONCLUSIONS

1. The combination of $CrCl_3$ and H_3PO_4 presented an admirable synergistic catalytic activity for the synthesis of alkyl levulinates, especially when the ratio of $CrCl_3$ in the mixed system was 0.3 for *n*-butyl levulinate (BL) synthesis.
2. The reaction of furfuryl alcohol (FA) with *n*-butanol proceeded mainly in two steps−FA was etherified to form the intermediate 2-butoxymethylfuran (BMF), which was further converted to BL. Both steps were catalyzed by the synergic effect of $CrCl_3$ and H_3PO_4.
3. The process variables including the initial FA concentration, catalyst dosage, reaction temperature, and time influenced the formation of BL, and a high yield of 95% was achieved under optimal conditions catalyzed by $CrCl_3$-H_3PO_4 system.
4. This study provides insights for the synergic catalysis mechanism of $CrCl_3$ combined with H_3PO_4 to enhance the synthesis of alkyl levulinates from FA as part of a biorefinery.

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