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Microwave-assisted alcoholysis of furfural alcohol into alkyl levulinates catalyzed by metal salts

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Yao-Bing Huang,[a] Tao Yang,[a] Meng-Chao Zhou,[a] Hui Pan,[a,*] and Yao Fu[b]

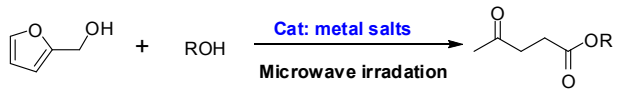
The production of alkyl levulinates from furfuryl alcohol (FAL) were investigated in the presence of metal salt catalysts under microwave irradiation. Various metal salts were tested in the reaction and $Al_2(SO_4)_3$ showed excellent catalytic activity for the FAL alcoholysis, giving a 80.6% yield of methyl levulinate within 5 minutes. Various alcohols were used to obtain different alkyl levulinates. The dielectric properties of these alcohols were also measured to explain their different performances in the reaction. Microwave heating was proved to dramatically increase in the reaction rate of the FAL alcoholysis compared to traditional oil heating. Identification of the reaction intermediates and products provided some insight view of the reaction mechanism, whereas methoxymethylfuran (MMF) and 4, 5, 5-trimethoxypentan-2-one (TMP) were the key intermediates. Finally, the catalyst was recycled and reused for 6 times without much drop in the activity.

Introduction

The utilization of biomass for the production of energy and chemicals has attracted considerable interest during the past few decades.[1] Lignocellulose, the most important source of biomass, is mainly composed of three polymers i.e. cellulose, hemicellulose and lignin.[2] While lignin is reluctant to be degraded due to its inert nature, cellulose and hemicellulose attract more attentions due to their repeated carbohydrate structure units and lower C-O glycoside bond dissociation energies.[3] Hydrolysis of cellulose and hemicellulose can therefore generate sugars such as glucose and xylose.[4] These sugars can be further transformed to platform molecules, for example, 5-hydroxylfurfural (HMF),[5] furfural[6] and levulinic acid (LA),[7] as well as commodity chemicals including furans,[8] esters[9] and polyols.[10] Alkyl levulinates such as methyl levulinate (ML) and ethyl levulinate (EL) are of particular interest due to the wide applications as plasticizing agents, solvents, and fuel additives.[11] In addition, alkyl levulinates possess two functional groups (i.e. a ketone group and an ester group) which make them easier to be valorized for the synthesis of various chemicals and drugs.[12]

To produce alkyl levulinates, the esterification of levulinic acid with the corresponding alcohols over acidic catalysts is the direct route.[13] Although levulinic acid can be produced by acid hydrolysis of lignocellulosic biomass, the separation and purification of the product from the resulting aqueous mixture are costly, which made it unsuitable as the raw material for this purpose.[14] Therefore, efforts were devoted to the development of new methods to produce alkyl levulinates directly from widely available and cheaper sources such as mono- and polysaccharides,[15] raw biomass,[16] and furfural alcohol.[17] Among them, furfuryl alcohol is a preferred starting material due to its easy accessibility from furfural and high reactivity toward the acoholysis reaction to yield alkyl levulinate.

It has been reported that acidic catalysts are crucial to this conversion and various catalysts such as mineral acid,[18] resins,[17] zeolites,[19] organic-inorganic hybrid acids[20,14] and solid superacids[21] have been reported to achieve this goal. For example, Lange *et al.* reported pioneering work on the alcoholysis of FAL to EL with several solid acids such as acidic ion-exchange resins.[17] Zhang *et al.* used several organic-inorganic hybrid solid acids for the conversion of FAL and reached a high EL yield of 93%.[20a] Song[14] and Rode *et al.*[20b] reported ionic liquids functionalized with acid sites or anions for the alcoholysis of FAL and achieved high alkyl levulinate yields. Besides, the mechanism of FAL alcoholysis reaction has also attracted much research interest. For example, Dumesic *et al.* carried out mechanistic studies on the alcoholysis reaction by identifying the intermediates with different characterization methods.[22] These work constitute the main research advances on FAL alcoholysis reaction. However, in consideration of the importance of this reaction, more efficient, inexpensive, and green systems are still desirable.



Scheme 1. Conversion of furfurl alcohol into alkyl levulinates over metal salts catalysts under microwave condition.

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Recently, metal salts such as $CrCl_3$, $SnCl_4$, $ZnCl_2$, and $AlCl_3$ have been widely used as effective catalysts in the conversion of cellulose and glucose to HMF or small molecules and they exhibited strong Lewis or Brønsted acidity in some organic or aqueous solvents.[23] These catalysts, especially the earth-abundant metal salts, provided environmentally benign and inexpensive protocols for the biomass conversion. Thus, it's appealing to use these metal salts as the "acidic catalysts" in a broad spectrum of biomass conversions. Apart from that, microwave (MW) irradiation has been considered as a volumetric and selective dielectric heating resource which has been widely used in the extraction of natural matrices and organic reactions.[24] It can greatly improve the reaction rate and even change the reaction selectivity and has been considered as a green technology for biomass conversion. Combining these two aspects, it is attractive to explore the alcoholysis of FAL with different metal salts as catalysts under microwave irradiation to achieve new cost effective, simple and green catalytic systems.

Herein, we report the alcoholysis of furfuryl alcohol to alkyl levulinates with different metal salts under microwave irradiation. Various metal salts were tested in alcoholysis reaction. The catalyst loading and reaction temperature were optimized. Different alcohols were also used to synthesis different alkyl levulinates and their related dielectric properties were also investigated. Finally, the reaction were traced by GC/GC-MS and the intermediates were identified to get further mechanistic insights.

Experimental

Materials

Furfuryl alcohol (98%), alkyl levulinates were purchased from TCI Chemicals Co. Ltd. Metal salts and alcohols (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the above chemicals were used without further purification.

Alcoholysis of furfuryl alcohol

The alcoholysis of furfuryl alcohol was carried out as follows: furfuryl alcohol (98 mg, 1 mmol), alcohol (14 mL) and a certain amount of catalyst were added into a 100mL sealed Teflon tube. The alcoholysis of furfuryl alcohol was performed in a MILESTONE Ethos A microwave reactor (MA039). The reaction mixture was heated to desired temperature in two minutes under vigorous stirring and allowed to react for a certain time. Upon the end of the reaction time, the reactor was cooled down to room temperature. The resulting reaction mixture was then added to the internal standard naphthalene for GC analysis.

Product analysis

The liquid phase of the reaction mixture was analyzed by GC-MS (Agilent 7890A, Agilent 5975C MSD) or GC (Agilent 7890A) equipped with a FID detector and a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm, Agilent). The temperature of the column increased from 80°C to 200°C at 10°C/min. The temperature of the injection port and detector was 250°C. The peaks were identified by comparison of the retention time of the unknown compounds with those of the standard compounds and quantified based on the internal standard method.

Recycling of the catalyst

The separation of the catalyst after the reaction was as follows: the solvent methanol and the product ML were firstly removed by using rotary evaporation until a viscous mixture was formed. Subsequently, the viscous mixture was treated with dichloromethane to precipitate the solid $Al_2(SO_4)_3$ derives. The solid species were collected by centrifugation and then washed by fresh dichloromethane for several times until the dichloromethane solution became transparent. Then the rest dichloromethane on the catalyst surface was removed by rotary evaporation. Finally, the obtained $Al_2(SO_4)_3$ derives was directly dissolved in a certain amount of furfuryl alcohol and methanol mixture and transferred to reactor for the next run.

pH measurement of the reaction mixture

The pH values of the reaction mixture with different catalysts after the reaction was were measured by a METTLER FE20 pH meter calibrated with standard pH buffer solutions at ambient temperature.

The measurement of dielectric property

The dielectric values of the alcohols were measured with the help of Agilent dielectric probe 85070E. This was attached to the computer controlled Agilent E5071C Vector Network Analyzer. The sample was measured at room temperature and the frequency ranged from 0.3 to 4.5 GHz.

Results and discussion

Catalysts screening

Initially, various metal salts catalysts were tested in the conversion of FAL to ML in methanol media under microwave irradiation. The reactions were conducted at 150 °C for 5 min (Table 1). To our surprise, the firstly selected metal salt $CrCl_3$ gave a full conversion of FAL, with a 62.7% yield of the product ML. Side products methoxymethylfuran (MMF, 17.6%) and 4, 5, 5-trimethoxypentan-2-one (TMP, 4.9%) were also detected by GC-MS. These two compounds have been reported as the key intermediates of the FAL alcoholysis reaction in previous work (Figure S3).[20a,22] Several other side products were also identified by GC-MS and NMR analysis. The carbon balance of FAL was about 94%. The other 6% of the carbon might convert into humin during the reaction (the solution turned to dark-brown), which cannot be detected by GC. All these results pointed to the fact that some Brønsted acidic sites may be generated in the reaction mixture and responsible for the conversion. Therefore, the pH value of the reaction solution was monitored. The $CrCl_3$ system after the alcoholysis reaction was an acidic solution with a pH value of 1.23. The H^+ was probably generated from the hydrolysis/methanolysis of the

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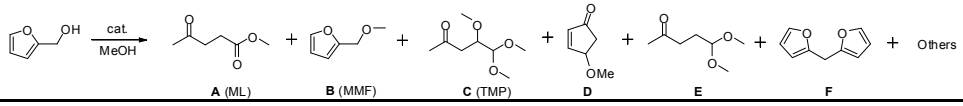
Table 1. Alcoholysis of furfural alcohol with different catalysts.



entry	catalysts	Conv. (%)	Yield (%)							pH
			A	B	C	D	E	F	others	
1	$CrCl_3$	100	62.7	17.6	4.9	2	0	1.1	6.3	1.23
2	$Cr_2(SO_4)_3$	12	0.6	9.3	0	0	0	0.9	0.7	3.90
3	$SnCl_4$	100	74.3	0.5	1.7	4.7	2.1	1.8	7.3	0.69
4	$SnSO_4$	92.8	16.1	50.4	14.1	3.6	0.7	1.9	2.6	2.22
5	$FeCl_3$	100	67.1	1.2	2.9	7.4	1.2	1.0	10.6	1.00
6	$Fe_2(SO_4)_3$	98.9	31.4	18.3	15.6	8.4	0.9	1.3	15.9	1.85
7	$ZnCl_2$	25.5	0	8.9	0	0	0	3.5	10.5	5.03
8	$ZnSO_4$	88.8	9.7	59.1	12.6	1.5	0	1.3	3.7	4.30
9	$AlCl_3$	100	74.5	1.0	2.9	2.2	2	3.2	7.7	0.73
10	$Al_2(SO_4)_3$	100	80.6	0.7	1.5	6.2	1.8	0.9	3.2	0.56
11	$Al(NO_3)_3$	100	48.0	7.0	23.1	2.6	0.7	1.1	11.6	1.35
12	H-beta	10.3	1	0	1.3	0.7	2.2	1.9	2.1	4.27
13	HZSM-5	69.9	4.9	64.7	0.1	0.1	0	0	0	4.60
14[a]	Amberlyst-15	100	89.5	0.2	1.7	2.7	1.1	1.2	0.7	1.52
15[b]	H_2SO_4	100	74.9	0	0.9	7.9	0.7	3.8	4.9	0.35
16[c]	$Al_2(SO_4)_3$	100	71.2	0	0.5	9.5	1.0	4.4	4.3	0.43
17	-	0	0	0	0	0	0	0	0	4.96

Conditions: FAL 1.0 mmol, catalyst loading (metal ions for different salts was kept to 0.4 mmol), 600W, 150 ^oC, 5 min. a: Amberlyst-15 40 mg. b: 0.2 mmol H_2SO_4, c: $Al_2(SO_4)_3$ 0.3 mmol. The conversion and product yields were obtained from GC analysis.

metal ions with crystalliferous water or alcohol, as mentioned in the previous work.[23b,25] Generally, the strength of the acid catalyst played an important role in the conversion of FAL to ML. Therefore, several metal salts were also investigated. When $Cr_2(SO_4)_3$ was used instead of $CrCl_3$, its poor solubility in MeOH prevented it from catalyzing the reaction. Only 12% FAL conversion and 0.6% ML yield were achieved and the pH value of the solution was 3.9. $SnCl_4$ showed superior catalytic activity than $CrCl_3$, providing a 74.3% yield of ML at a full conversion of FAL. A lower pH value of 0.69 of the $SnCl_4$ solution indicated that different metal salts had different Brønsted acidity in the methanol solution.

Based on these results, some other Lewis metal salts were also investigated such as the salts of Fe^{3+}, Zn^{2+} and Al^{3+}. $FeCl_3$, $AlCl_3$ and $Al_2(SO_4)_3$ showed good catalytic performances and achieved 67.1%, 74.5% and 80.6% yield of ML, respectively. The pH measurement of these metal salts' solutions showed that better ML yields were always accompanied with lower pH values, which again confirmed that Brønsted acidity was one of the key factor for the FAL alcoholysis. The difference in catalytic performances for the Al^{3+} salts ($AlCl_3$, $Al_2(SO_4)_3$ and $Al(NO_3)_3$) may also lie in their different Brønsted acidity in methanol solutions (Table 1, entries 9-11). Among all these metal salts, $Al_2(SO_4)_3$ afforded the highest ML yield of 80.6%. In addition, no levulinic acid was detected in the current system though it had been reported as a side product from the hydrolysis of ML in acidic medium. This result suggested that $Al_2(SO_4)_3$ is a preferred catalyst for the synthesis of alkyl levulinates.

For comparison, commercial available solid acid catalysts H-Beta and HZSM-5 were used instead of the metal salts, and lower ML yields were obtained (Table 1, entries 12-13). A commonly used solid acid catalyst Amberlyst-15 was also tested, the reaction reached an 89.5% ML yield at 110 ^oC for 120 min. However, the structure of Amberlyst-15 was destroyed in the reaction, turning to powders, which may be caused by the "hot spots" that generated from MW condition. This problem made it an unsuitable catalyst for FAL alcoholysis under MW condition. When mineral acid H_2SO_4 was used as catalyst, 74.9% ML yield was obtained (Table 1, entry 14). The yield was a little lower than $Al_2(SO_4)_3$, which may be caused by more side reactions due to the over loading of H_2SO_4 (Figure S4). Similarly, for higher concentration of $Al_2(SO_4)_3$, lower ML yield and more side products were observed which may be caused by stronger acidity of the higher concentration of $Al_2(SO_4)_3$ that led to side reactions. The alcoholysis reaction cannot proceed without any catalysts, suggesting that the metal salts are crucial to the FAL alcoholysis reaction.

It is worth noting that the formation of dimethyl ether (DME) was also observed, which may be formed during the conversion of FAL or by the auto-etherification of MeOH itself. The acidity of the catalyst played important role in the formation of DME. Thus, the DME formation in some catalytic systems (Amberlyst-15, H_2SO_4 and $Al_2(SO_4)_3$) were investigated (Table S2).[26] The reactions with different catalysts provided different amounts of DME, so as their blank experiments without FAL. From these results, it can be seen

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that $Al_2(SO_4)_3$ system provided the minimum DME production compared to those from H_2SO_4 and Amberlyst-15 systems, which indicating that $Al_2(SO_4)_3$ was more favorable for the FAL alcoholysis reaction under MW condition.

Influence of temperature

The temperature is crucial to the reaction rate and product yields. Thus, the reaction temperature ranged from 130 °C to 170 °C were tested in the FAL alcoholysis reaction (Figure 1). When the reaction temperature was 130 °C, FAL conversion was 95.2% and ML yield was 40%. The intermediate MMF and TMP were 15.6% and 27.4%, respectively. As the reaction temperature increased to 150 °C, the ML yield gradually increased and reached a maximum point while TMP and MMF decreased to a negligible level. The ML yield slightly decreased when further increasing the temperature to 170 °C. This result may be caused by its side reactions under higher temperatures. The optimized results showed that a moderate temperature of 150°C was necessary to allow full conversion of the intermediates and get the highest yield of ML.

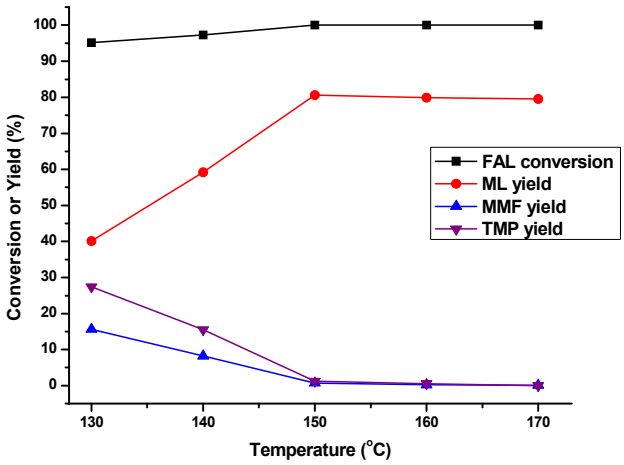

Figure 1. Influence of the reaction temperature. *Condition*: FAL 1.0 mmol, $Al_2(SO_4)_3$ 0.2 mmol, MeOH 14 mL 600W, 5 min.

Influence of catalyst concentration

The catalyst concentration affected the catalytic reaction by changing the H^+ concentration in the alcohol solution. As shown in Figure 2, when the catalyst loading increased from 0.1 mmol to 0.2 mmol while the other reaction parameters remained unchanged, the ML yield increased while the yields of two intermediates gradually decreased. A maximum ML yield was obtained with 0.2 mmol catalyst loading. This was attributed to the increase of the H^+ concentration which can promote the conversions of the reaction. Thus, sufficient acidic concertation was the key to the full conversion of the intermediates and achieving higher ML yields. However, over loading of the catalyst to 0.3 mmol led to a decrease in the ML yield and more side reactions.

To evaluate the amount of H^+ that formed from the hydrolysis of Al^{3+} during the reaction, we used different amount of H_2SO_4 in the FAL alcoholysis reaction as a reference. The results was presented in figure S4. It was found that using 0.16 mmol H_2SO_4 obtained the highest ML yield (78.0%) under the optimized condition. The ML yield was very close to the optimized $Al_2(SO4)_3$ system. It may suggest that during the FAL alcoholysis, 0.4 mmol Al^{3+} may generate ~0.32 mmol H^+, which was approximately equal to that from 0.16 mmol H_2SO_4, when the hydrolysis/alcoholysis of Al^{3+} reached the equilibrium point at the desired reaction temperature.

For the Al species generated from the hydrolysis of Al^{3+}, they did not seem to have any catalytic activity for FAL alcoholysis reaction. Nevertheless, they may play the role of keeping H^+ in a dynamic balance at different reaction stage or different reaction temperature. The generation of H^+ from Al^{3+} was considered as a reversible reaction that was influenced by the reaction temperature.[23b] However, no strong evidence for this hypothesis has been found. Further research on this point is ongoing at our lab.

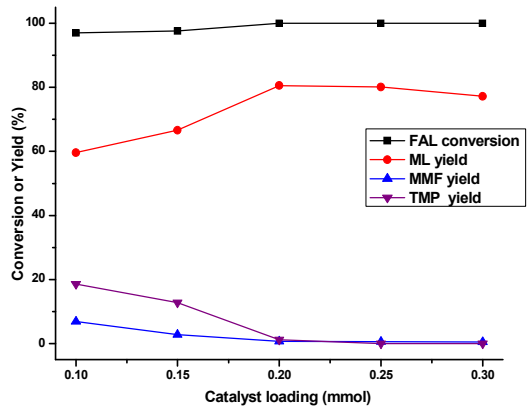

Figure 2. Influence of the catalyst loading. *Condition*: FAL 1.0 mmol, MeOH 14 mL, 600W, 150 °C, 5 min.

Influence of heating methods

To compare the FAL alcoholysis reaction under microwave irradiation and conventional oil heating, typical alcoholysis reaction were carried out in both a batch reactor heated by oil bath and in MW reactor while all the other reaction conditions were identical. As shown in Table 2, with conventional oil bath heating, FAL conversion was 71.2% and the ML yield was only 5.4%. Much of the intermediates MMF and TMP were detected (Table 2, entry 2). However, with MW heating, FAL conversion was 100% and ML yield was 80.6%. The results clearly suggested that MW heating had a dramatic enhancement in the reaction rate on the alcoholysis of FAL compared to the conventional oil heating method. By further prolonging the reaction time to 30 and 60 min with oil heating, FAL and the reaction intermediates gradually converted and the target product ML increased to 58.5% (Table 2, entries 3-4). When the reaction time reached 120 min, a 79.0% yield of ML can be obtained, which was close to that from the reaction with MW heating. This result further revealed that MW condition had

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superior activity over traditional heating for the FAL alcoholysis reaction. On the other hand, the fact that traditional heating provided similar result by prolonging the reaction time indicated that $Al_2(SO_4)_3$ is an effective metal salt catalyst for FAL alcoholysis not only under MW condition but also under conventional heating condition.

Apart from that, the MW condition may affect the reaction selectivity due to its selective heating characteristic. To verify this point, the FAL alcoholysis reaction was conducted with the two heating methods and stopped at the middle stage of the reaction. Prolonged reaction time was used for the conventional oil heating to homogeneous temperature distribution within the reaction system (Figure S6). According to the GC analysis of the two reaction mixtures, no obvious difference in the product selectivity was observed for the two spectrums. It can be concluded that the MW condition can promote the FAL alcoholysis reaction rate without changing the reaction selectivity.

Table 2 Influence of the heating methods on FAL alcoholysis.

	Heat	Time	Conv.(%)	ML(%)	MMF(%)	TMP(%)
1	MW	5	100	80.6	0.7	0
2	Oil bath	5	71.2	5.4	40.5	19.7
3	Oil bath	30	90.0	29.1	18.6	33.4
4	Oil bath	60	98.9	58.5	16.7	19.7
5	Oil bath	120	100	79.0	1.4	5.3

Condition: substrate 0.36 mmol, $Al_2(SO_4)_3$ 0.071 mmol ,150 ^oC, CH_3OH 5 mL.

Substrate screening

The alcoholysis of FAL with different alcohols to synthesis different alkyl levulinates were also investigated. The optimized reaction condition was applied to other alcohols (Table 3). When ethanol was used, a 64.5% yield of ethyl levulinate (EL) was obtained, which was lower than that from the alcoholysis reaction with methanol (Table 3, entry 2). In case of other alcohols (i.e. isopropanol and n-butanol), the target product yields were only 28% and 25.3%, respectively, when the reaction time was 5 min (Table 3, entries 3-4). This may be resulted from two aspects: 1) different reactivities of the alcohols with different alkyl chains which would lead to a little different in the product yields.[20a] 2) different dielectric properties (including dielectric constant ε` and dielectric loss ε``) of the alcohols. These two parameters reflect the abilities of the alcohols in absorbing the electromagnetic energy and turning it into internal heat. According to the previous researches, molecules or functional groups with high dipole moments (high dielectric constant) can easily absorb the microwave energy and create hot spots (local high temperature), together with increaseing the average kinetic energy or collision frequency of the molecule (nonthermal effect). Both of these two aspects would lead to higher reaction rates.[27] For FAL alcoholysis reaction, the two reagents were both with high dipole moments, and therefore would be more reactive under MW condition. For alcohols with different dielectric properties, they may exhibit different performances with MW irradiation. The dielectric properties of different alcohols were list in Table 3 and Figure S1. According to the results in Table 3, we found that alcohols with higher dielectric constant and dielectric loss provided higher ML yields in shorter reaction time (5 min). This was in consistent with the above analysis that alcohols with higher ε` and ε`` would absorb microwave energy more efficiently and create more reactive system for the alcoholysis reaction. To improve the product yields, the reaction time was extended to 15 min or 40 min. And the FAL alcoholysis reaction with EtOH, *i*PrOH and *n*BuOH could achieve satisfied product yields (79.8%, 60.4% and 65.4%, respectively) (Table 3, entry 2-4). In conclusion, the MW assisted alcoholysis reactions showed accelerated reaction rates compared to the conventional heating method and the dielectric properties of alcohols were the key factors in determining the reaction efficiency under microwave condition.

Table 3. Influence of the different solvents on FAL alcoholysis

	Solvent.	ε`[a]	ε``[a]	time	Conv.(%)	Esters(%)
1	MeOH	23.85	12.98	5	100	80.6
2	EtOH	8.11	7.26	5/15	100	64.5/79.8
3	*i*PrOH	4.60	3.24	5/40	100	28.0/60.4
4	*n*BuOH	4.20	2.27	5/40	100	25.3/65.4

Condition: FAL 1.0 mmol, $Al_2(SO_4)_3$ 0.2 mmol, 600W, 150 ^oC, 5 min. [a] dielectric constants and dielectric loss of the pure alcohols were measured at 2.45 GHz.

Reaction pathway and proposed mechanism

During the alcoholysis reaction, two key intermediates were detected by GC-MS which may help us to further explore the reaction mechanism. A typical GC spectrum of the reaction was showed in Figure 3. The product ML, intermediate MMF and TMP can be detected when the reaction was stopped at 1 min. To further understand their changes in the reaction, the reaction was traced and the results were shown in Figure 4. From the figure, we can see that FAL was rapidly converted at the beginning of the reaction by forming the intermediates MMF and TMP, with only a small amount ML product. As the reaction proceeded, the amount of MMF and TMP gradually decreased while ML increased. The ML yield finally reached a maximum point at 5 min and the intermediates reduced to a negligible level. Further prolonging the reaction time resulted in a slight decrease in the ML yield, which might be caused by the side reactions. From the above results, we can conclude that MMF and TMP were the key intermediates of the FAL alcoholysis reaction.

Previous research on the mechanism of FAL alcoholysis reaction revealed that multiple reaction pathways were probably involved in the production of ML. Of all these pathways, the most reported pathways were that FAL was protonated and formed the intermediate MMF and TMP, which took place in parallel to the formation of ML. MMF can also be converted to TMP and then converted to ML during the reaction. Comparing our results with these work, the two main

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intermediates have been confirmed, but whether the intermediate MMF could converted to TMP has not been studied. Therefore, we synthesized the intermediate MMF (in methanol solution) and subjected it to the FAL alcoholysis reaction under optimized condition (Figure 5 and Figure S5). The first step was to synthesize MMF by FAL alcoholysis reaction with Amberlyst-15 catalyst under conventional oil heating. A mixture of MMF (66.9%), TMP (15.6%) and ML (15.2%) was obtained after the filtration of solid catalyst. Directly subjecting the reaction mixture heating to MW heating didn't make much changes in the mixture composition, which indicated that the leaching of the acidic site from Amberlyst-15 can be ignored (Figure S5). Then, the solution mixture from step 1 was subjected to the $Al_2(SO_4)_3$ catalyzed system under MW condition. After reaction, we found that MMF decreased from 66.9% to 23.9%, TMP and ML increased from 15.6% to 21.6% and from 15.2% to 47.3%, respectively. Since there was no FAL in the mixture resulted from step 1, MMF was therefore the only source for the increment of TMP. This result obviously showed that the intermediate MMF could convert to TMP under our optimized reaction condition.

According to the above results, we can conclude that the alcoholysis of FAL mainly proceeded via two important intermediates MMF and TMP to generate the target product ML. And MMF could convert to TMP in the reaction. These findings were consistent with previous researches

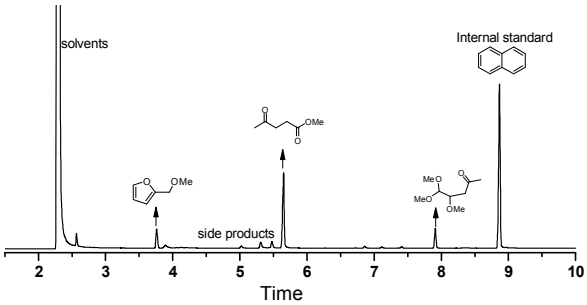


Figure 3. GC analysis of the FAL alcoholysis reaction at 1 min reaction time. *Condition*: FAL 1.0 mmol, MeOH 14 mL, 600W, 150 °C, 1 min.

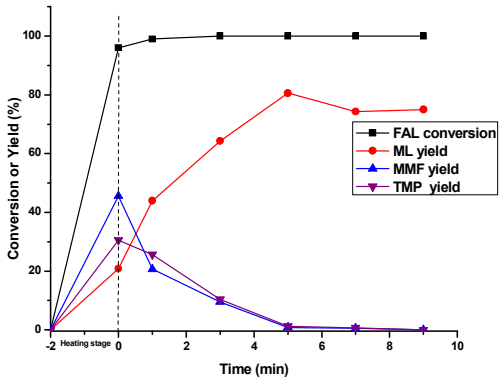


Figure 4. Trace of the FAL alcoholysis reaction. *Condition*: FAL 1.0 mmol, MeOH 14 mL, 600W, 150 °C..

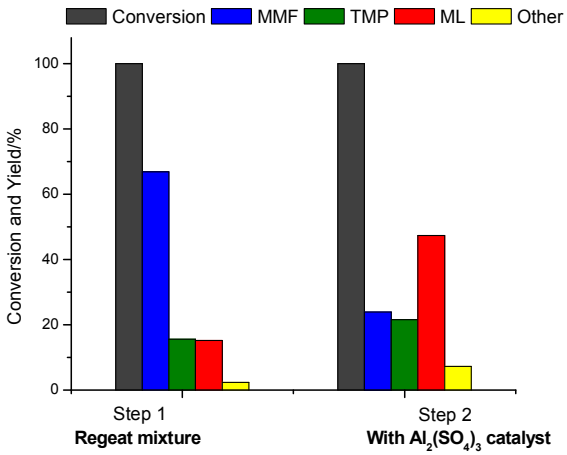
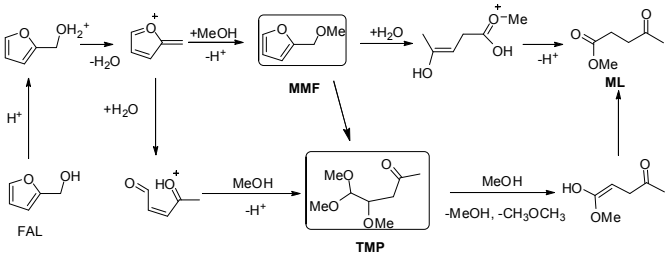


Figure 5. The conversion of MMF to TMP in MeOH. Conditions: Step 1: 1 mmol FAL, 100 mg Amberlyst-15, 14 mL MeOH, 90 °C, 40min, Oil heating. Step 2: $Al_2(SO_4)_3$ 0.2 mmol, MW 600W, 150 °C, 1 min.



Scheme 2. Proposed reaction mechanism of the alcoholysis of FAL.

from Dumesic group.[22] Therefore, a possible mechanism was proposed (scheme 2). FAL was firstly protonated and then formed the two intermediates MMF and TMP under the attack of MeOH or H_2O. Also, MMF can convert to TMP. After that, these two intermediates further convert to the final product ML.

Catalyst recycling

Recycling of the catalyst is an important step for a sustainable and economically feasible catalytic system. Therefore, the recycle experiments were investigated by following procedure reported in literature.[25a] When the reaction was finished, the solvent and ML were removed and previously dissolved catalyst $Al_2(SO_4)_3$ derives were precipitated and washed with dichloromethane. The obtained $Al_2(SO_4)_3$ derives was added into the reactor with furfuryl alcohol and alcohol for the next run. As shown in Figure 6, FAL was almost fully converted for all the 6 runs and the ML yields maintained at a high level. The recycling experiments indicated that $Al_2(SO_4)_3$ is a stable and recyclable catalyst for the alcoholysis of FAL in alcohols.

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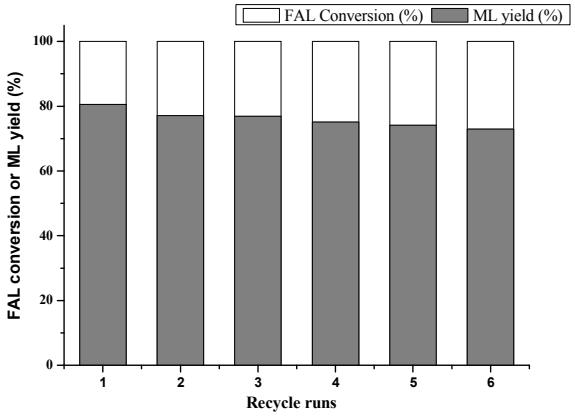

Figure 6. Recycling of the catalysts. *Condition*: FAL 1.0 mmol, MeOH 12 mL, 600W, 150 °C, 5 min.

Conclusions

The productions of alkyl levulinates by alcoholysis of furfuryl alcohol in different alcohols were studied by using various earth-abundant metal salts as the catalysts under microwave irradiation. Upon the optimization, methyl levulinate was obtained in a high yield of 80.6% over $Al_2(SO_4)_3$ catalyst in 5 min. The microwave heating method showed a remarkable enhancement in the reaction rate compared to the conventional heating method. The metal salt catalyst could be easily recycled and reused for six times. Mechanistic study showed that the reaction proceeded via the methoxymethylfuran (MMF) and 4, 5, 5-trimethoxypentan-2-one (TMP) intermediates. The current findings provide a convenient and economically feasible protocol for the production of alkyl levulinates in alcohols mediates. Future study will be devoted to the application of this system to a broader spectrum of biomass conversions.

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Notes and references

[a] College of Chemical Engineering, Nanjing Forestry University, 159 Longpan Road, 210037, Nanjing, China.
Email: hpan@njfu.edu.cn
[b] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, China.

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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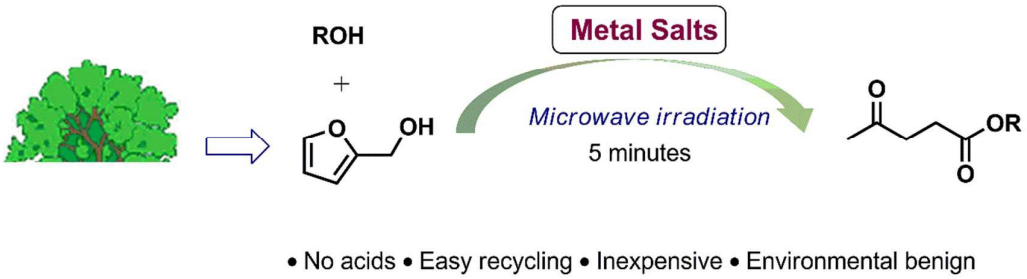

The alcoholysis of furfuryl alcohol with different alcohols was carried out by using metal salt catalysts under microwave condition, achieving high alkyl levulinates' yields in a short reaction time.

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