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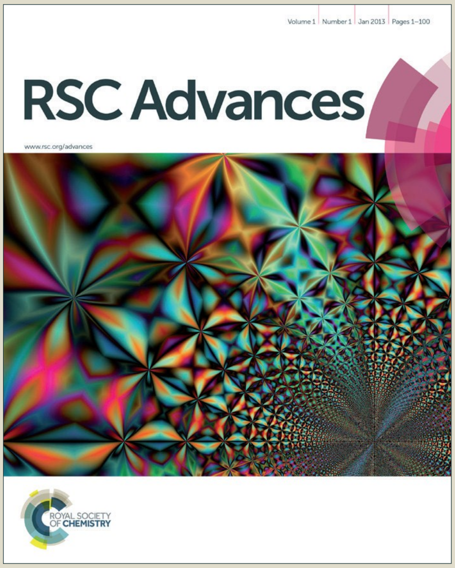

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Highly efficient metal salt catalyst for the esterification of biomass derived levulinic acid under microwave irradiation

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The esterification of levulinic acid (LA) to alkyl levulinates has been investigated in the presence of various metal salts catalysts under microwave irradation. The reaction reached a 99.4% yield of methyl levulinate (ML) in the presence of $Al_2(SO_4)_3$ catalyst in methanol solution under microwave condition. The optimized reaction condition was 110 °C, [illegible] minutes with a 20 mmol% catalyst loading. Alcohols with longer carbon chains showed lower reactivities in the microwave electromagnetic field due to their poorer abilities in absorbing and transimitting the microwave energies. Besides, microwave irradiation provided significantly higher reaction rate compared to conventional oil bath heating. The LA aqueous soluton were also converted to ML with high yields. The $Al_2(SO_4)_3$ catalyst was sucessfully applied to the esterification of other biomass derived organic acids to their corresponding esters in high yields. Finally, the catalyst was recycled for 5 times withour much drop in the activity.

Introduction

The production of fuels and chemicals from renewable lignocellulosic feedstocks has been considered as sustainable ways to replace the traditional fossil resource based industrial systems. Among various chemicals produced from biomass, levulinic acid (LA) and its esters are gaining widely attentions as versatile platform chemicals for their potential applications for biofuel, polymer monomers and pharmaceutical intermediates.[1] Levulinic acid can be produced by acid hydrolysis of (ligno)cellulose. And it can be further converted into a range of important derivatives like levulinate esters,[2] γ-valerolactone[3] and diphenolic acid.[4] In particular, levulinate esters, especially ethyl levulinate (EL), can be as diesel miscible fuel up to 5 wt% in regular car engines.[5] Therefore, the esterification of levulinic acid with different alcohols to produce alkyl levulinates is highly desirable.

In general, esterification of LA with alcohols can be accomplished in the presence of Brønsted acid catalysts such as H_2SO_4.[6] However, the use of liquid mineral acids always suffered from corrosion and disposal problems. On the contrary, heterogeneous catalysts are more favourable due to their easier separability and recyclability. Sulfated oxides,[7] heteropolyacids,[8] zeolites[9] and sulfonic resins[5] were widely used as acid catalysts for esterification reaction. For example, Kuwahara et al.[7a] used sulfated Zr–SBA-15 to catalyze the esterification of levulinic acid in ethanol; 80% yield of ethyl levulinate (EL) was obtained at 70°C for 24h. Baronetti et al.[8c] employed silica-supported Wells–Dawson heteropolyacid ($H_3PW_{12}O_{40}$/ZSM-5) as the catalyst to synthesize ethyl levulinate at 78°C. They obtained 76% conversion of LA within 5h. These works indicated that the acid strength and the dispersibility of the acid sites have a big impact on the overall activity of the catalysts. Recently, Fernandes et al.[5] used several different types of zeolites, sulfated oxides and commercially available resins in the esterification reaction. They found Amberlyst-15 showed the highest activity. Sulfonated carbon nanotube has also been employed in the esterification of LA and achieved moderate to good product yields.[10]

On the other hand, multivalent metal salts such as $CrCl_3$, $SnCl_4$, $ZnCl_2$, and $AlCl_3$ have been widely used in the conversion of carbohydrates (e.g. cellulose, glucose and fructose) into platform molecules (e.g. HMF) through their Lewis acidity and Brønsted acidity.[11] The catalytic effect of these metal salts can be compared to those homogeneous or heterogeneous acid catalysts under specific reaction conditions. Especially, the Brønsted acidic site can be generated through the hydrolysis/alcoholysis of the metal ions in solvents at high reaction temperature.[12] Apart from that, the metal ions of these salts were also preferable catalytic sites for esterification reactions. Combing these two advantages, it's appealing to establish a new catalytic system for the esterification of LA over metal salts catalysts, especially the earth-abundant metal salts.

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Herein, we demonstrated that some inexpensive metal salts have shown outstanding activity, efficiency and stability in the esterification of LA with different primary alcohols. Microwave irradiation, an efficient and green technology for biomass conversion, has also been employed in the model reaction to accelerate the reaction rate. Among all these metal salts we have tested, $Al_2(SO_4)_3$ catalyst gave the highest yield of methyl levulinate (99.4%). In addition, heating from microwave irradiation had dramatically increased the reaction rate compared to the conventional oil bath heating. Finally, the effects of catalyst loading, reaction time, temperature, reusability of catalyst on the esterification of LA were also investigated.

Experimental

Materials

Levulinic acid (97%), methyl levulinate (99%), ethyl levulinate (98%) and butyl levulinate (98%) and were obtained from TCI Chemicals Co. Ltd (Shanghai China). Amberlyst-15 was purchased from Alfa Aester (H^+, ~4.8 mmol/g). Alcohols and $Al_2(SO_4)_3 \cdot 18H_2O$ and other metal salts were all of analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China), and used without further purification.

Esterification of levulinic acid

Esterification of levulinic acid were carried out in a MILESTONE Ethos A microwave reactor (MA039). In brief, levulinic acid (116 mg, 1 mmol), MeOH (14 mL), and a given amount of catalyst were loaded into a 100 mL sealed Teflon tube followed by heating the tube in the microwave reactor, to the desired temperature. The zero time was defined as the reactor was heated to set temperature. Then, the reaction was performed for a given reaction time. After the reaction was finished, the reactor was cooled down to room temperature. All experiments were performed in duplicates and the average values were reported.

For the conventional oil heating reaction, a Parr reactor with a temperature probe was used and the reactor was placed in the oil bath, the zero time was defined as the reaction mixture was heated to the desired reaction temperature. After the reaction was finished, the rector was quickly cooled down in an ice bath.

Analytic methods

Analyses of reaction products were conducted by using a GC system (Agilent, 7890A) equipped with a flame ionization detector (FID) and a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm, Agilent).The injection port and the detector were operating at 250 ^oC. The temperature of the column was programmed to increase from 80^oC to 200^oC at a rate of 10^oC/min. Naphthalene was used as the internal standard to calculate the yield of reaction products.

Recycle and reuse of catalyst

Recycle of the catalyst was as follows: methanol and methyl levulinate were removed from the reaction mixture by rotary evaporation. The catalyst was then washed with dichloromethane (10mL×3). Residue dichloromethane was then evaporated. The dried catalyst was directly dissolved in MeOH and transferred to the reactor.

Measurement of dielectric properties

Measurement of the dielectric properties of different alcohols were carried out on an Agilent E5071C Vector Network Analyzer with Agilent dielectric probe 85070E. The sample was measured at room temperature and the frequency was 2.45 GHz.

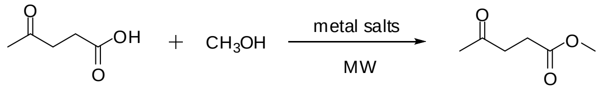
Results and discussion

Esterification of LA with different catalysts

Initially, esterification of LA was carried out with different metal salt catalysts in methanol under microwave irradiation. The results were presented in Table 1. A blank experiment was firstly carried out and only trace amount of methyl levulinate (ML) was detected, suggesting that the esterification of LA reaction cannot proceed without any catalyst (Table 1, entry 1). When $CrCl_3$ was used as catalyst, the esterification reaction afforded 91.5% yield of ML with 96.9% LA conversion at 110^oC for 10 minutes. This result suggested that $CrCl_3$ was a preferable metal salts with both good Lewis and Brønsted acidity in MeOH. A much lower ML yield was observed when $Cr_2(SO_4)_3$was used, which was due to its poor solubility in methanol. Similar result was found for $SnSO_4$. On the other hand, soluble $SnCl_4$ gave a much higher ML yield (96.8%). This result was consistent with many previous literatures that Sn^{4+} was a good Lewis acidic metal ions.[11d] In the case of Fe^{3+} and Cu^{2+} salts, moderate ML yields were obtained. The different Lewis acidity strength of these metal salts may be the main reason for their activities in the esterification reactions. Noteworthy, a near 100% ML yield was obtained when $Al_2(SO_4)_3$ was submitted to the esterification reaction, which could be attribute to the excellent Lewis acidity of Al^{3+} and the *in situ* generated Brønsted acidity, as reported in the previous work.[12a] When the anion changed to Cl^- or NO_3^-, Al^{3+} salts provided lower ML yields compared to that of SO_4^{2-}. This result might be resulted from the different acid strength of these metal salts. Finally, Zn^{2+} salts were tested in the reaction and only achieved a much lower ML yield which was due to their weak Lewis and Brønsted acid strengthen in the reaction media. These results further demonstrated that the Lewis and Brønsted acidity of the reaction system were the key factors to the esterification of LA to alkyl levulinates.

For comparison, commercial available solid catalyst Amberlyst-15 was also tested in the esterification reaction, the reaction achieved a 99% ML yield with an extended reaction time which might be caused by the mass transfer limitation of reactants with the acid sites on the surface of the solid catalyst. However, the structure of Amberlyst-15 was destroyed to powders, which was probably caused by the “hot spots” that generated in the MW condition. For the solid catalyst HNS-$PrSO_3H$,[13] the reaction could also achieve a 98% ML yield in 10 min. However, the high cost may prevent it from wider

Table 1. Esterification of LA over different metal salts. [a]



Entry	catalyst	Conv.(%)	ML yield (%)
1	—	5.0	1.8
2	$CrCl_3$	96.9	91.5
3	$Cr_2(SO_4)_3$	45.2	4.1
4	$SnCl_4$	100	96.8
5	$SnSO_4$	58.6	15.7
6	$FeCl_3$	87.6	89.6
7	$Fe_2(SO_4)_3$	92.7	81.7
8	$CuSO_4$	70.9	49.5
9	$CuCl_2$	71.8	66.1
10	$AlCl_3$	83.7	83.9
11	$Al_2(SO_4)_3$	100	99.4
12	$Al(NO_3)_3$	79.1	70.9
13	$ZnCl_2$	41.4	8.1
14	$ZnSO_4$	44.0	10.8
15[b]	HNS-$PrSO_3H$	100	98.0
16[c]	Amberlyst-15	100	99.6

Conditions: LA 1.0 mmol, catalyst (metal ions, 0.4 mmol), MeOH 14mL (MeOH/metal ions=864 (mole ratio)), 400W, 110 °C, 10 min. a: analysed by GC. b: catalyst 80 mg. c: catalyst 80 mg, 30 min.

application in the industrial production. It is noteworthy that the auto-esterification of methanol in these reactions can be ignored since the reaction temperature was relatively lower. In our previous work, we had revealed that higher reaction temperature (150 °C) would lead to the auto-etherification of alcohols in the reaction. In spite of that, metal salt catalyst provided the minimum etherification side reactions compared to traditional liquid or solid acid catalysts.

Effect of reaction temperature

The effect of reaction temperature on esterification of LA was investigated by using $Al_2(SO_4)_3$ as the catalyst under microwave irradiation from 90 °C to 130 °C (Fig.1). It can be found that the esterification of LA can proceed at lower temperature, with an 84.8% ML yield at 90 °C. Further increase the reaction temperature to 110 °C, a maximum ML yield of 99.4% was obtained, suggesting that higher reaction temperature can promote the reaction rate. The ML yield remained almost unchanged as the reaction temperature was further increased to 130 °C. Thus, the optimum reaction temperature for the esterification of LA is 110 °C.

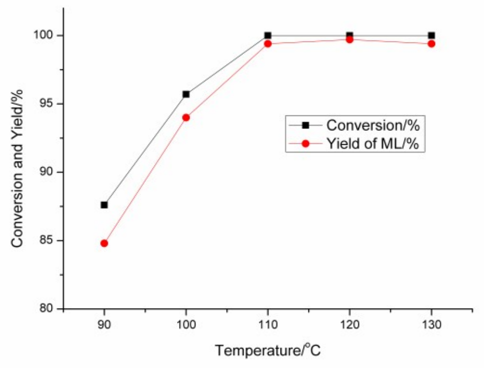


Figure 1. Influence of the reaction temperature. *Conditions*: LA 1.0 mmol, $Al_2(SO_4)_3$ 0.2 mmol, MeOH 14 mL (MeOH/metal ions=864 (mole ratio)), 400W, 10 min.

Table 2. Effect of catalyst loading.

Entry	Catalyst loading (mmol)	Conv.(%)	ML(%)
1	10%	89.4	87.3
2	15%	95.2	94.3
3	20%	100	99.4
4	25%	100	99.6
5	30%	100	98.5

Conditions：LA 1.0 mmol, MeOH 14 mL (MeOH/metal ions=864 (mole ratio)), 400W, 110°C, 10 min.

Effect of catalyst loading

The catalyst loading clearly determines the amount of Lewis and Brønsted acid sites of the methanol solution, and subsequently would affect the yield of ML. In order to find out the optimized catalyst loading, experiments were carried out by changing the $Al_2(SO_4)_3$ loading from 10 mmol% to 30 mmol% while other conditions remained unchanged. As shown in Table 2, the yield of ML firstly increased from 87.3% to 99.4% when the catalyst loading increased from 10 mmol% to 20mmol%. Further increase of the catalyst loading didn't make a significant improvement in the ML yield. In addition, an excess amount of catalyst loading decreased the product yield slightly, which could be due to the formation of side products. To sum up, the catalyst loading of 20 mmol% was sufficient to achieve a high ML yield.

Comparison of two different heating methods

The esterification reactions with microwave heating and conventional oil bath heating were also investigated to compare their heating efficiency. The results were presented in Figure 2. When the esterification reaction was carried out under microwave irradiation condition, a 99.4% yield of ML was obtained in just 10 minutes. For conventional oil bath heating, we used Parr reactor to carry out the reaction with a temperature probe to monitor the reaction temperature of the reaction mixture. The ML yield was lower (74.1% for 10min, 91.4% for 60min and 96.6% for 90min) than that with microwave heating. Even further prolonging the reaction time, the yield of ML remained almost unchanged (97.1% for 120min, 96.6% for 150min). And some of the side products were also detected from the reaction mixture as the reaction time extended and led to a decrease in the reaction selectivity. Thus, a proper reaction time was crucial to maintain a high selectivity of the esterification of LA. These results demonstrated that microwave radiation not only promoted the esterification reaction rate but also improve the selectivity of the target product. Microwave irradiation heating method provides internal heating which can directly couple microwave energy with the molecules (solvents, reagents and catalysts) and promote the reaction rate.

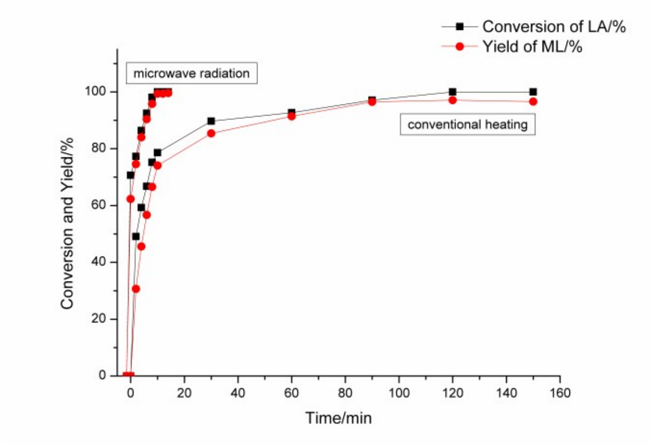


Figure 2. Time course of the esterification of LA by using microwave and conventional heating. *Conditions*: LA 1.0 mmol, $Al_2(SO_4)_3$ 0.2 mmol, MeOH 14 mL (MeOH/metal ions=864 (mole ratio)), 110°C, 10 min.

Preparation of different alkyl levulinates

Different alkyl levulinates were synthesized with the same catalyst and various alcohols. Alcohols with different carbons (e.g. ethanol, n-propanol and n-butanol) were tested in this study. The results are shown in Table 3. A complete conversion of LA and a high selectivity of alkyl levulinates were achieved for all tested alcohols. However, the reaction conditions need to be varied with different alcohols to achieve higher products' yields. This may be caused by two reasons: the different reactivities of alcohols and their dielectric properties. As known, dielectric property of a material determines its heating efficiency when it is subjected to reaction under microwave irradiation. Dielectric constant (ε`) and dielectric loss (ε``) are two key parameters to reflect a medium's abilities of absorbing microwave energy and converting the energy to heat, respectively.[14] Therefore, to figure out the relationship between dielectric properties and reaction efficiency, we carried out the measurement of dielectric properties of different alcohols used in our reactions (Table 3). Dielectric constants of alcohols followed the order of methanol > ethanol > n-propanol > n-butanol, as well as the dielectric loss at a commonly used microwave frequency 2.45 GHz. This result indicated that alcohols with larger polarity have larger dielectric constants/loss, which then can easily absorb the microwave energy and generate internal heat, perhaps with more hot pots (local high temperature). Besides, the collision frequency of the molecular (nonthermal effects) may also be greatly increased in the alcohols with higher dielectric constants.[15] Thus, for alcohols with lower dielectric constants/loss, the "promotion effect" of microwave irradiation were relatively weaker compared with those with higher dielectric constants/loss. Therefore, to achieve higher products' yields, the reaction conditions need to be varied. By increasing the reaction temperature or prolonging the reaction time, high alkyl levulintes' yields could be obtained when ethanol, n-propanol and n-butanol were employed as the solvents.

Table 3. Esterification of LA with different alcohols of different dielectric properties.[a]

Entry	Alcohols	Polarity	ε`	ε``	ester yield/%
1[b]	MeOH	6.6	26.95	14.55	99.4
2[c]	EtOH	4.3	9.21	8.26	97.7
3[d]	n-PrOH	4.0	5.29	3.83	96.5
4[e]	n-BuOH	3.7	4.77	2.64	96.2

Conditions: LA 1.0 mmol, $Al_2(SO_4)_3$ 0.2 mmol, Solvent 14 mL. a: dielectric properties were measured at room temperature. b: 110 °C, 5 min, c: 130 °C, 15 min, d: 150 °C, 20 min, e: 150 °C, 35 min.

Esterification of Levulinic acid in aqueous solution

Generally, esterification of pure LA was not practical for the industrial production of alkyl levulinates because of the high cost to separate LA from the aqueous solution, which was produced by the hydrolysis of sugars. To investigate whether the $Al_2(SO_4)_3$ system could be applied to the direct esterification of carbohydrate hydrolyzate, the esterification of LA aqueous solution with methanol was also carried out. Our previous work on the hydrolysis of glucose in water showed that about 42 wt% of LA aqueous solution could be obtained after simple treatment.[16] Therefore, a LA aqueous solution of the same concentration was prepared to simulate the carbohydrate hydrolyzate resulting from the hydrolysis of glucose. And this mixture was submitted it to esterification reaction with the $Al_2(SO_4)_3$ system. The results were presented in Figure 3. The amount of methanol and the mole ratio of the catalyst $Al_2(SO_4)_3$ to the acid LA were constant. With the increase loading of the LA a.q. in MeOH solution, the ML's yield first decreased slightly and still kept at higher levels (>80%) till the weight ratio reached 17.5:100, which indicated that a proper percentage of water in the reaction system did not have much effect on the esterification reaction. However, when the ratio further increased to 22.5:100, the ML yield decreased to 65.3%. Nevertheless, extension of reaction from 10 min to 30 min could provid a much higher ML yield of 96.7%, implying that the addition of water to esterification system might can decrease the reaction rate and the reaction could reach high product yield at prolonged reaction time. The above results showed that the $Al_2(SO_4)_3$ system is of high potential of being used in the esterification of the acids in the carbohydrate hydrolysate.

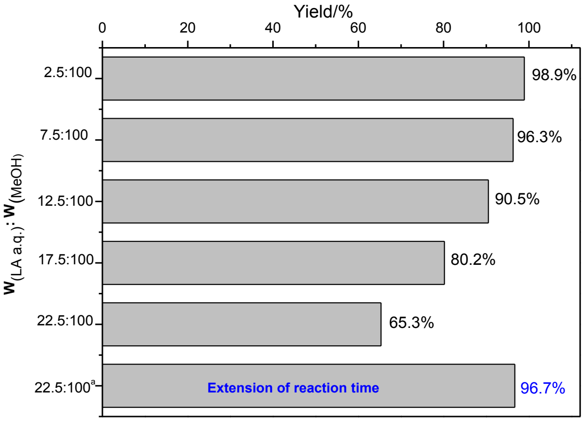
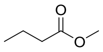
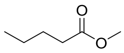
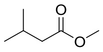
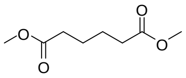
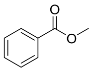
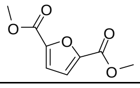


Figure 3. Esterification of LA aqueous soltuion. *Conditions:* LA:H_2O=42:58 (weight ratio), $Al_2(SO_4)_3$:LA= 0.2 (mole ratio), MeOH 11.06g (14 mL), 400W, 110°C, 10 min. a: reaction time 40 min.

Esterification of different carboxylic acids

Given the high conversion and yield of the esterification of LA, the method was applied to the esterification of other biomass derived acids. Straight-chain aliphatic acids could be converted to corresponding esters with high yield under optimized conditions (Table 4, entries 1, 2, 4). For isovaleric acid, increased temperature of 130 °C was necessary to achieve a higher product yield. The esterification of aromatic acid benzoic acid was much more difficult due to its steric hindrance effect of phenyl ring compared to aliphatic acid. Therefore, higher reaction temperature and longer reaction time were used to obtain better result. A good product yield could also be achieved at 150 °C for 25 minutes for 2, 5-furandicarboxylic acid. The above results further suggested that $Al_2(SO_4)_3$ was an effective catalyst with good compatibility for the esterification of different acids.

Table 4. Esterification of different carboxylic acids.

Entry	Product	Conv.(%)	Yield(%)
1[a]		100	99.7
2[a]		100	99.5
3[b]		100	98.1
4[a]		100	97.7
5[c]		100	98.2
6[c]		100	98.5

Conditions: acid 1 mmol, $Al_2(SO_4)_3$ 0.2 mmol, MeOH 14 mL (MeOH/metal ions=864 (mole ratio)), [a]: 400W, 110 °C, 10min, [b]: 400W, 130 °C, 15 min, [c]: 600 W, 150 °C, 25 min.

Alcoholysis/hydrolysis of metal salts in alcohols

The high catalytic activity of $Al_2(SO_4)_3$ in the esterification reaction may be resulted from the alcoholysis/hydrolysis of metal salts in alcohols, which can generate H^+ and then participate in the esterification reaction. Our previous work on the alcoholysis of furfuryl alcohol with metal salt catalyst showed that the solvent became acidic when the reaction mixture was heated to higher temperature, which indicate the generation of H^+.[17] To get further insight into this process, the changes of the dielectric property of the reaction solvent MeOH and MeOH with the catalyst were monitored by a Network Analyzer. The dielectric constants/loss of pure MeOH and MeOH+$Al_2(SO_4)_3$ were measured at a fixed temperature of 60 °C (Figure 4). For dielectric constant, pure MeOH remained almost unchanged during the measuring time. When $Al_2(SO_4)_3$ was added to MeOH at 60 °C, the dielectric constant of the mixture gradually decreased during the first 7 min of the mixing time, and then it remained almost unchanged as time prolonged. Similar trend was also found in dielectric loss of these two systems. The changes of the dielectric properties of the mixture suggested that metal salt underwent a alcoholysis/hydrolysis process in MeOH. The alcoholysis of Al^{3+} in the mixture led to a gradually change of the mixture’s composition (more H^+ and Al species formed), therefore causing the change of the mixture’s dielectric property. When this process reached an equilibrium, the composition of the mixture would remain unchanged and therefore the mixture’s dielectric properties didn’t change, either. These results provided more information about the dielectric properties the alcohol systems with metal salt catalysts, which might be useful when designing microwave assisted reactions with metal salt catalysts.

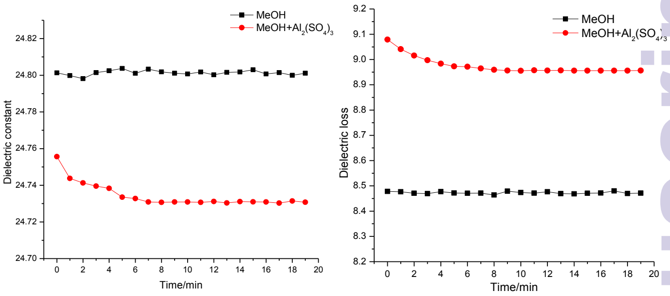


Figure 4. Dielectric properties of MeOH and MeOH+20 mmol% $Al_2(SO_4)_3$ at 60 °C Dielectric constants (left) and Dielectric loss (right).

Reusability of catalyst

The reusability of catalysts is crucial for building a green, economical, and sustainable catalytic system. The reusability of $Al_2(SO_4)_3$ was evaluated by using the esterification of LA in methanol as a model reaction. The catalyst was recycled and reused for 5 times and the results were presented in Fig.5. It was found that the yield of ML can maintain at high level (99.4% yield for fresh, 97.8% after five runs). The recycling experiments further demonstrated that metal salts were economic and efficient catalysts for the esterification of LA for the production of alkyl levulinates.

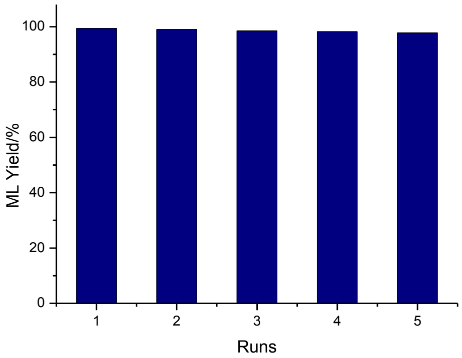


Figure 5. Recycling of the catalyst. *Conditions:* LA 1.0 mmol, $Al_2(SO_4)_3$ 0.2 mmol, MeOH 14 mL (MeOH/metal ions=864 (mole ratio)), 400W, 110°C, 10 min.

Conclusions

In summary, the esterification of LA by using commercially available metal salts as catalysts was studied. A highest ML yield of 99.4% could be achieved over $Al_2(SO_4)_3$ catalyst at 110°C for 10min. Comparison of two heating methods, namely microwave and conventional heating, in the esterification reaction indicated that microwave radiation could significantly enhance the efficiency of the esterification of LA. Other organic carboxylic acids were also successfully converted to their esters with high yields. The esterification of LA aqueous solution in methanol was achieved which provided a potential solution to the esterification of carbohydrate hydrolyzate to generate alkyl levulinates. At last, the catalyst can be easily recycled and reused without much drop in the activity. The current findings provide a new economically viable and environmentally friendly system for the esterification of LA or its aqueous solution to alkyl levulinates.

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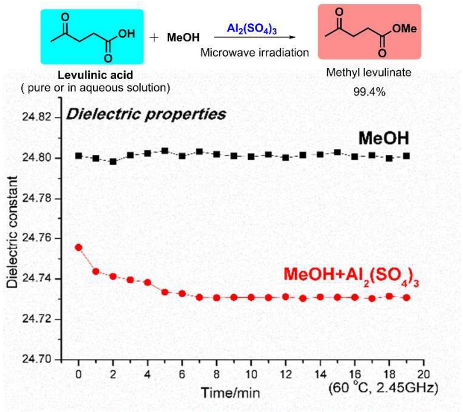

The esterification of biomass derived platform molecule levulinic aicd to its alkyl levulinates were carried out over metal salt catalysts under microwave condition, achieving near-quantitative product yields in few minutes.