# **Green Chemistry**



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### Introduction

In recent years, there has been growing interest in the utilization of renewable resources to produce energy or chemicals to meet the demand of human society. One of the attractive routes, for the chemical industry, is to convert biomass (e.g. lignocellulose) to platform molecules that can serve as starting materials for the production of other value-added chemicals or liquid fuels.<sup>1-3</sup> Of all the components of lignocellulose, cellulose attracts considerable attention due to its widely available, large annual production and highly repetitive structural units that may generate simple depolymerized products.<sup>4</sup> Unlike the general surface modification of cellulose to prepare materials, chemical conversions of cellulose to valued-added compounds require the hydrolysis of the glucosidic bonds of cellulose to release glucose units before the subsequent downstream conversions. However, the high crystallinity and threedimensional hydrogen-bonding networks of cellulose make it reluctant to be hydrolysed, thereby leaving it a challenging



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Efficient production of chemicals from cellulose provides sustainable routes for the utilization of natural renewable resources to meet the requirements of human society. Herein, we reported a highly efficient and simple metal salt catalyst, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, for cellulose conversion to methyl levulinate (ML) under microwave conditions. A highest ML yield of 70.6% was obtained at 180 °C within a very short time of 40 min. The introduction of water could reduce humin/coke formation and solvent consumption, and could also switch the reaction pathway via the more reactive intermediate glucose. Kinetic and mechanistic studies of the subreactions showed that both cellulose hydrolysis and alcoholysis pathways were involved in the cellulose conversion to ML, with the former as the main route in the presence of water. The Lewis acid species  $[Al(OH)_x(H_2O)_y]^{n+}$  and the Brønsted acid species H<sup>+</sup>, generated by in situ hydrolysis of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, were responsible for the reaction conversions. The reaction with microwave heating showed accelerated reaction rates of 25 times the reaction with conventional oil heating, and even more times for the rates of glucose and methyl glucoside (MG) dehydration, resulting in higher reaction selectivity toward ML production. The catalyst was also successfully recycled and applied to the conversion of cellulose to other alkyl levulinates, as well as the conversion of raw biomass to ML with high yields. The homogeneous nature of  $Al_2(SO_4)_{3}$ , together with its high efficiency and excellent recyclability, make it a potential catalyst for the large-scale production of ML in industry.

substrate for chemical conversion.<sup>5</sup> Despite that, tremendous effort has been devoted to the conversion of cellulose to glucose,<sup>6,7</sup> and furthermore to a variety of useful chemicals such as furanics,<sup>8-10</sup> acids,<sup>11,12</sup> esters,<sup>13-15</sup> polyols<sup>16,17</sup> and alkanes,<sup>18,19</sup> which greatly broaden the cellulosic compound family. One particular interest concerns the catalytic conversion of cellulose to alkyl levulinates like (ML) and ethyl levulinate (EL). These esters are a kind of short fatty acid esters which can be used as plasticizing agents, solvents, or as blending fuel additives.<sup>20,21</sup> Apart from that, their reactive ester and carbonyl groups enable them to be used in the synthesis of several downstream chemicals or drugs.<sup>22</sup>

According to the literature,<sup>23,24</sup> both levulinic acid and furfuryl alcohol are the most reported substrates, which undergo esterification and alcoholysis reactions, respectively, to provide alkyl levulinates products. However, these two substrates are also the intermediates of lignocellulose, which require extra reaction steps (*e.g.* hydrolysis and hydrogenation) to be prepared from lignocellulose. These processes obviously add complexity to the whole reaction route and reduce the whole economy. Besides, the associated separation and purification processes are also costly. Therefore, the establishment of new methods to produce alkyl levulinates directly from easily available and cheaper natural biopolymer cellulose is academically and economically more attractive.



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#### Paper

Over the past few years, several catalytic systems have been successfully employed for the conversion of cellulose to alkyl levulinates. Both soluble and solid catalysts could be found in the literature. For example, Fu and Lu et al. examined a series of liquid acids for cellulose methanolysis and found that H<sub>2</sub>SO<sub>4</sub> and *para*-toluenesulfonic acid were the most efficient catalysts, offering the highest ML yield of 55%.<sup>25</sup> Other weak acids such as HCOOH and H<sub>3</sub>PO<sub>4</sub> were inferior in this conversion. However, the undesired etherification of methanol was unavoidable in the presence of these liquid catalysts at elevated reaction temperature, which consumed a lot of solvent. Tominaga et al. reported a mixed catalytic system using 2-naphthalenesulfonic acid and In(OTf)<sub>3</sub> for cellulose conversion and a high yield of 75%, even the highest so far, was obtained.<sup>26</sup> The Lewis acid sites were proposed to promote the rate-determining step of the intermediated MG isomerization to generate ML. In consideration of the recycling and product separation merits of solid catalysts, a few heterogeneously catalysed systems were also reported over the catalysts including sulphated metal oxides, 13,27,28 zeolite<sup>13</sup> and heteropolyacid salts.<sup>29,30</sup> However, the product yields were relatively much lower as compared to the liquid acid systems. Since both cellulose and solid catalyst are insoluble in alcohols, the mass transfer limitation may be the primary factor for the lower efficiency of solid catalysts. Strikingly, Liu and Wang et al. reported the use of mesoporous niobium-based phosphate (NbP) solid catalyst with a proper Brønsted/Lewis (B/L) ratio for cellulose conversion with high reaction efficiency, offering 56% yield of ML at 180 °C for 24 h, which represented a significant advance in heterogeneous systems.<sup>31</sup> Concerning all the above systems, soluble catalysts on average exhibited higher efficiency for cellulose conversion. Besides, it is not difficult to find that both Lewis and Brønsted acid sites, as well as their ratios, are crucial to the final product yields. These advances may provide fundamental principles for the design of new catalytic systems for cellulose conversion to alkyl levulinates.

Several reported studies revealed that metal salts with a proper combination of cations and anions exhibited excellent Brønsted/Lewis acidity in alcoholic solutions, offering inexpensive, simple and efficient methodologies for a variety of biomass conversions.<sup>32-34</sup> Strikingly, our previous studies demonstrated that aluminium sulfate was such a type of catalyst which provided high reactivity for the alcoholysis of furfuryl alcohol to alkyl levulinates.35 These results encouraged us to further apply a metal sulfate catalyst to the conversion of the more challenging substrate cellulose. It is worth noting that Xu et al. had reported the use of aluminium sulfate for glucose conversion to alkyl levulinates.<sup>36</sup> They also tested the conversion of cellulose, but only a moderate ML yield was obtained. Due to the big differences between the chemical properties of glucose and cellulose, the reaction system used for glucose conversion cannot be directly used for cellulose conversion. Besides, detailed information about the influences of reaction parameters and additives on the reaction, kinetics of subreactions and the related mechanism is still lacking.



 $\mbox{Scheme 1}\ \mbox{Al}_2(\mbox{SO}_4)_3$  catalyzed cellulose conversion into ML using microwave heating.

Therefore, it's attractive to establish a comprehensive study on the metal salt catalysed alcoholysis of cellulose.

Apart from that, microwave irradiation is a widely used technology for chemical processes. It is a volumetric and selective dielectric heating, which could greatly accelerate the reaction rate and reduce the requisite time to finish the reaction.<sup>35</sup> It may also save energy consumption, and sometimes reduce undesired side reactions by avoiding the exposure of the reaction mixture to high temperature for a long time. This technology may just be suitable for cellulose conversion, due to the thermal instability of its downstream carbohydrate derived products. Herein, we have reported a facile and economically feasible and high-yield synthesis of ML from cellulose over the metal salt catalyst aluminium sulfate under microwave conditions (Scheme 1). Different metal salt catalysts were investigated in the alcoholysis reaction. The influences of reaction parameters on the product selectivity, as well as the reaction kinetics, were studied. The critical role of additive water in the reaction is discussed. Mechanism studies about the reaction pathway are also proposed.

### Experimental

#### Materials

Microcrystalline cellulose (96%, 20  $\mu$ m, Sigma-Aldrich), ML (99%), EL (98%), butyl levulinate (98%), glucose (98%), MG (98%) and fructose (99%) were supplied by TCI Chemicals Co. Ltd (Shanghai, China). 5-Hydroxymethylfurfural (HMF, 99%) and 5-methoxymethylfurfural (MMF, 97%) were purchased from Adamas-beta Inc. (Shanghai, China). All the metal salts were in the form of crystalline hydrate and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The raw biomass materials (*e.g.* bamboo, bagasse and polar) were collected from the local market.

#### Catalytic reactions

Conversion of cellulose under microwave heating: the alcoholysis of cellulose was conducted in a 100 mL Teflon sealed microwave reactor. Typically, a mixture of 3 mmol microcrystalline cellulose, 14 mL MeOH, a certain amount of  $H_2O$ , and  $Al_2(SO_4)_3$  catalyst was charged into the reactor. Then, the reactor was sealed and heated to the desired reaction temperature in 2 min under microwave irradiation. The time the reactor reached the desired temperature was set as the zero time of the reaction. After the reaction was finished, the reaction was quenched by placing the reactor in an ice cool water bath to stop the reaction. All experiments were duplicated and the average data were recorded.

**Conversion of cellulose with conventional heating.** The reaction was carried out in a stainless steel pressurized reactor with a total volume of 30 mL. Before each run, microcrystalline cellulose (3 mmol), 14 mL MeOH, 0.6 mL H<sub>2</sub>O and a given amount of  $Al_2(SO_4)_3$  were added into the reactor. The reactor was then sealed and heated to the set temperature in 30 min. The zero time was taken when the medium in the reactor was heated to the desired temperature. After the reaction, the reactor was filtered with a 0.22 mm membrane filter before analysis.

**Recycling of the catalyst.** After reaction, the solid particles was firstly separated *via* centrifugation. The liquid reaction solution was evaporated at 50 °C to remove the solvents in a round bottle. Next, the left viscous mixture was treated with 10 mL dichloromethane three times to extract the target product ML. After that, the solid white residual in the bottle was dried and reused for the next reaction. The collected dichloromethane solution was then evaporated to separate ML. All the extraction solvents were recycled after evaporation.

#### **Product analysis**

Analysis of the reaction products and intermediates (ML, 5-methoxymethyl furfural) was carried out by using an Agilent 7890A GC instrument fitted with a DB-5 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu m,$  Agilent) and a FID detector. Naphthalene was used as an internal standard. The other intermediates glucose, MG, fructose and levulinic acid were analyzed on an Agilent 1200 series HPLC system using a Bio-Rad Aminex HPX-87H column operating at 60 °C with a refractive index (RI) detector. 5 mM H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the mobile phase with a flow rate of 0.6 mL min<sup>-1</sup>. The amount of HMF was analyzed on a Waters 1525 series HPLC system equipped with a UV diode array detector at 280 nm and a C18 column at 35 °C (4.6  $\times$  150 mm, 5  $\mu$ m, Agilent). A methanol-water (50/50, v/v) mixture was used as an eluent with a volumetric flow rate of 0.4 mL min<sup>-1</sup>. The content of these reaction intermediates in the samples was calculated by interpolation from calibration curves.

The amount of dimethyl ether was determined by calculating the weight loss of the reactor before and after reaction, as reported in the previous literature.<sup>37</sup> Before the reaction started, all the reagents and catalysts were placed in the reactor and weighed. After the reaction was finished and cooled down to room temperature, the reactor was opened to exclude the gaseous dimethyl ether and then weighed (dimethyl ether has a lower boiling point of -24.9 °C and is gaseous at room temperature). The weight loss before and after the reaction ( $W_1$ ) was approximately equal to the amount of dimethyl ether formed during the reaction, and the yield of DEE was calculated as follows:

DEE yield(%) = 
$$\frac{W_1 \times 64}{W_2 \times 46} \times 100\%$$

where  $W_1$  (mg) = the weight loss before and after the reaction;  $W_2$  (mg) = the initial methanol weight.

**Cellulose conversion.** After the reaction, the solid residue was separated by filtration, washed with 30 mL MeOH and dried under vacuum at 105 °C for 1 h. Then the obtained dry solid residue was weighed (the solid coke and unreacted cellulose,  $W_3$ ). After that, the solid residue was soaked in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution and heated at 433 K for 6 h to remove all unconverted cellulose.<sup>31</sup> Finally, the remaining residue was washed, dried at 105 °C and weighed ( $W_4$ ). The cellulose conversion was calculated using the following formula:

Cellulose conversion(%) = 
$$\left(1 - \frac{W_3 - W_4}{3 \times 162 \times 0.96}\right) \times 100\%$$
.

After the removal of unconverted cellulose, the remaining residue was coke, which was generated from the direct carbonization of cellulose during reaction progress. The elemental composition of the remaining residue ( $W_4$ ) was determined on a CHNS analyzer (Thermo Scientific Flash 2000). The carbon content was determined as  $C_1$ . The yield of coke was calculated using the following equation:

Coke yield(%) = 
$$\left(\frac{W_2 \times C_1}{3 \times 6 \times 12 \times 0.96}\right) \times 100\%$$

were  $W_4$  (mg) = the weight of the remaining residue after the removal of unconverted cellulose;  $C_1$  (%) = the amount of carbon element in the remaining residue.

The humins generated in the reaction mixture were also calculated by carbon yield according to the previous literature.<sup>38</sup> Typically, insoluble products after the reaction were firstly filtered and washed with 30 mL MeOH. All of the filtrate was collected. The solvent methanol and some volatile small molecules were then removed by evaporation at 100 °C for 12 h. The dried residue including humins, (side)products and catalysts was weighed ( $W_5$ ) and characterized by element analysis to obtain carbon content  $C_2$ . Then, the total weights of all the carbons in (side)products were calculated as  $w_6$ . The carbon weight of humins can then be determined as  $W_5 \times C_2 - w_6$ . And the mole yield of humin formation was calculated using the following formula:

Humin yield(%) = 
$$\left(\frac{W_5 \times C_2 - W_6}{3 \times 6 \times 12 \times 0.96}\right) \times 100\%$$

 $W_5$  (mg) = the weight of dried residue;  $W_6$  (mg) = the total weights of all the carbons of reaction intermediates and products including glucose, MG, fructose, HMF, MMF and ML.  $C_2$  (%) = the content of carbon element in dried residue.

### Results and discussion

#### Catalytic performances of varied catalysts

A variety of metal salt catalysts were selected to evaluate their performances in cellulose conversion under microwave conditions. The reaction parameter was firstly set to 180 °C and 40 min with a fixed amount of metal cation loading (Table 1). 1

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Table 1 Direct conversion of cellulose with various catalysts



Reaction conditions: Microcrystalline cellulose 3 mmol, metal salt (M<sup>n+</sup> 1.2 mmol), 0.6 mL H<sub>2</sub>O, 14 mL MeOH, 800 W, 180 °C, 40 min. <sup>a</sup> H<sub>2</sub>SO<sub>4</sub> 1.2 mmol.

To facilitate cellulose conversion, a small amount of water was also added to promote ML yield according to the previous literature.31,39 A blank experiment was firstly tested and no desired ML was detected after the reaction, indicating a catalysing process of cellulose conversion (Table 1, entry 1). Then, a commonly used  $Fe_2(SO_4)_3$  catalyst was investigated and the reaction provided a moderate ML yield of 48.2% at full cellulose conversion (Table 1, entry 2). A small amount of the side products was detected including MMF, glucose and MG. Considerable amounts of humins and coke were obtained. By changing the catalyst to FeCl<sub>3</sub>, a drastic decrease in ML yield was observed (6%) and much cellulose remained unconverted (Table 1, entry 3). This may have originated from the fact that the acidic strength of the FeCl<sub>3</sub> solution was not enough to convert cellulose under the current reaction conditions. Besides, the varied performances of the two metal salt catalysts also highlight the critical role of anions in determining the acidity of a metal salt catalyst in a methanol solution. Encouraged by this promising result, other metal salts including those of different anions were also evaluated. For Cr and Zn salts, they only provided a trace amount of ML under identical conditions (Table 1, entries 4-7). It is noteworthy that the low solubility of  $Cr_2(SO_4)_3$  and  $ZnSO_4$  in methanol solution was most likely be responsible for their poor reactivity in the reaction.<sup>40</sup> For Cu salts, the results were still unsatisfying (Table 1, entries 8 and 9). In the case of Sn salts, the reactions gave no more than 10% yield of ML with lower cellulose conversion (Table 1, entries 10 and 11). This is in accordance with our previous research that the use of Lewis salt SnCl<sub>4</sub> alone was unable to catalyse cellulose conversion in high yield, except in the co-existence of the Brønsted acid H<sub>2</sub>SO<sub>4</sub>.<sup>41</sup> This result enlightened that both Brønsted and Lewis acidic species

were essential to the reaction conversion and product yield. To our surprise, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> exhibited superior catalytic performances for cellulose transformation, providing 70.6% yield of ML at full cellulose conversion (Table 1, entry 12). This yield was close to the highest yield of the mixed-acid system reported by Tominaga,<sup>26</sup> but significantly reduced the reaction complexity. The good result can originate from the synergism of Brønsted and Lewis acid species generated by the hydrolysis of  $Al_2(SO_4)_3$  in the reaction solution. Similarly, when the anion was changed to Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>, the reaction provided much lower ML yields, only 8.2% and 12.6%, respectively (Table 1, entries 13 and 14). The different reactivities of the three Al salts further confirmed the critical role of anions in determining the acid strength of a metal salt in a methanol solution. Based on the above experimental results, only  $Fe_2(SO_4)_3$  and  $Al_2(SO_4)_3$ catalysts offered full cellulose conversions under identical reaction conditions, suggesting the stronger acid strength of these two metal salts in alcoholic solution. But  $Al_2(SO_4)_3$  was the more suitable one with an appropriate B/L ratio to control the product selectivity. Besides, we also carried out the conventional oil heating for cellulose conversion and found that a longer reaction time of 12 h was needed to obtain the highest ML yield of 68.8% (Table S9<sup>†</sup>). This result suggested that the  $Al_2(SO_4)_3$  catalyst could efficiently catalyze cellulose conversion in conventional oil heating, but at a much lower reaction rate. Finally, H<sub>2</sub>SO<sub>4</sub> alone was also tested in the reaction. Although cellulose was fully converted, only 30.4% yield of ML was obtained, associated with much humin and coke formation (Table 1, entry 15). This may be caused by the lack of Lewis acid sites of the system, which cannot efficiently convert sugar intermediates (i.e. glucose and MG from cellulose hydrolysis/ alcoholysis) into the downstream products through the isomer-

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ization step. These hydroxyl-rich sugar intermediates may easily decompose when they are exposed to the thermal reaction mixture for a longer time, and generate humins and coke. This was also verified by the reaction using sugar intermediates as the reaction substrates in the presence or absence of a Lewis acid catalyst as presented in Table S8.† It's not difficult to find that both glucose and MG were fully converted under the standard reaction conditions, but with more humin and coke formation in the case of a lack of Lewis acid, further highlighting the importance of Lewis acid sites in the cellulose-to-ML conversion.

Overall, the simple metal salt catalyst  $Al_2(SO_4)_3$  exhibited the highest reactivity in converting cellulose to ML under microwave conditions, providing a very competitive high ML yield as compared to the literature-reported ones. The hydrolysis of the salt generated the key active Lewis and Brønsted species that enabled the successive reaction steps involved in cellulose conversion. In addition, detailed experiments about the influence of the reaction parameters on the reaction efficiency are also provided in the following part.

#### Influence of the reaction temperature and catalyst loading

The reaction temperature has a profound effect on the reaction conversion and product distribution. Normally, the reported optimal temperature for cellulose conversion ranges from 170 to 220 °C,<sup>22</sup> otherwise it may easily lead to either incomplete cellulose conversion or large production of humins/coke. Since microwave irradiation could generate hot spots in the reaction medium,<sup>42</sup> the reaction temperature needs to be carefully evaluated to avoid the above situations. A lower reaction temperature of 150 or 160 °C only led to lower cellulose conversion even under the microwave conditions, with a maximum 16.2% ML yield at 49.5% cellulose conversion for 2 h (Table S1<sup>†</sup>). By increasing the temperature to 170 °C, the reaction could reach a full conversion at 80 min with a maximum ML of 68.4%, which was close to the highest yield reported in this work (Fig. 1a). The other carbons were mainly converted to humins and coke. A higher reaction temperature of 180 °C could further reduce the reaction time to 40 min and increase the ML yield to 70.6%. Obvious intermediate conversions (e.g. MG, glucose and others) to the products or humins/coke were observed as the reaction proceeded. Although further increasing the reaction temperature to 190 °C could further increase the reaction rate and reduce the reaction time, the maximum ML yield slightly decreased to 66.1% at 30 min of reaction time. Therefore, the suitable reaction temperature was set to 180 °C. The reaction time was 40 min, which has been significantly reduced as compared to the conventional oil heating (e.g. 12-24 h). Besides, a short reaction time was also beneficial for preventing the undesired side reactions to form humins or coke, representing a great advantage of microwave heating over oil heating in cellulose conversion.

The catalyst loading was also found to affect the reaction conversion and product distribution (Fig. 1b). At a lower  $Al_2(SO_4)_3$  loading of 6.7 mol%, the cellulose conversion was only 59% under identical reaction conditions, accompanied by



Fig. 1 Conversion of cellulose with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> with different temperatures (a) and catalyst loadings (b). Reaction conditions: 3 mmol cellulose, 14 mL MeOH, 0.6 mL H<sub>2</sub>O, 800 W; a: 0.6 mmol Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (20 mol% based on cellulose content); b: 180 °C, 40 min (orange squares: cellulose conversion, others refer to fructose, HMF and MMF, see Table S2 and S3† for details).

considerable amount of intermediate products. а Continuously increasing the catalyst loading to 20 mol% resulted in full cellulose conversion and higher ML yield, with much of the intermediate products converted. These results indicated that sufficient catalyst concentration was necessary for maximizing ML yield by promoting the reaction rates. However, excessive catalyst loading may cause an adverse decrease in ML yield, as the formed ML may undergo decomposition to humins over a stronger acidic solution at elevated reaction temperature, which was also verified by the ML decomposition test as presented in Fig. S4.† Thus, 20 mol%  $Al_2(SO_4)_3$  would be the optimal catalyst loading for cellulose conversion.

#### Role of water in cellulose conversion

During our experiments, we noticed that the addition of a certain amount of water into methanol was important to the final ML yield and solvent consumption by the etherification of two methanol molecules. This phenomenon was also found in several reported studies such as by using 95% ethanol or adding water to the cellulose alcoholysis system.<sup>39</sup> However, few studies carried out in-depth research on the role of water in cellulose conversion. According to our experience on metal salt catalyzed systems and the reported literature,<sup>32,39</sup> water

may affect the catalytic sites, the reaction rate or the reaction pathway. To further reveal these aspects, a series of experiments were designed and presented in the following parts.

Firstly, the introduction of water may facilitate the hydrolysis of metal salt to form the active catalytic species. According to work from our and other groups,<sup>32,43,44</sup> a metal salt (*e.g.*  $Al_2(SO_4)_3$ ) tended to hydrolyze with water to generate  $[Al(OH)_x(H_2O)_y]^{n+}$  and  $H^+$ , which were the actual Lewis and Brønsted acid sites that participated in the subreactions involved in cellulose conversion. The water amount in methanol could affect the equilibrium of metal salt hydrolysis, as well as the acid density of the reaction mixture, which would then affect their reactivity in converting cellulose. Thus, a certain amount of water in methanol to form a mixed solvent was beneficial for the formation of active catalytic sites, thereby facilitating cellulose conversion.

Secondly, the introduction of water may also affect the product distribution. This was verified by conducting the reaction with varied water addition to methanol under identical reaction conditions. Fig. 2 shows that the final coke yield was gradually reduced with increasing water amount in the reaction mixture until a relative constant level was obtained from 0.6 mL water content. According to a previous study,<sup>45</sup> coke mainly resulted from the carbonization of cellulose at high reaction temperature for a long time. By adding more water, cellulose was more easy to be attacked by water molecules, moving the reaction towards to the glycosidic C-O bond hydrolysis rather than undergoing thermal decomposition to form coke. At the same time, the yield of humins was firstly reduced and then increased as the water content increased, with a relatively lower level of 14.5% yield around 0.6 mL water content. Apart from that, the addition of water could significantly inhibit the etherification reaction of methanol itself as shown in the figure, which was unavoidable in the presence of acidic catalysts at elevated temperature. When no water was added, over 20% solvent was consumed to generate DME. As the water content increased, the DME yield was quickly decreased to an acceptable level of <5% as the water content exceeded 0.6 mL. The comparison of the etherification of methanol between  $Al_2(SO_4)_3$  catalyst and other commonly used acid catalysts that



Fig. 2 Influence of water content on side products. Reaction conditions: Cellulose 3 mmol, 0.6 mmol  $Al_2(SO_4)_3$ , 14 mL MeOH, 800 W, 40 min (see Table S4† for details).

are typically used for cellulose conversion was also done, as listed in Table S7.† The  $Al_2(SO_4)_3$  system provided the minimum DME production and methanol loss as compared to that with several other equivalent acid catalysts including  $H_2SO_4$ , amberlyst-15 and heteroployacids. This may have resulted from the dynamical equilibrium between the salt and its hydrolysed acidic species that could prevent the system from becoming too acidic. However, further information about this effect is still a topic for further research. From this point,  $Al_2(SO_4)_3$  may have better economic effectiveness in cellulose conversion in methanol at elevated reaction temperature. Based on the above results, it can be concluded that proper addition of water could effectively change the product distribution by inhibiting the undesired side reactions.

Lastly, the addition of water could also change the reaction rates and pathway of cellulose conversion. This was verified by comparing the product distributions of the reactions with varied water addition at the earlier stages (Fig. 3). The conversions of cellulose increased as the water content increased at all the three stages, which indicated the higher cellulose conversion rates as water was gradually added to the reaction. Another important phenomenon related to the reaction pathway that should be noted is that as the water content increased, the ratio of the cellulose alcoholysis intermediate MG to the hydrolysis intermediate glucose (R) was also varied. When no water was added, MG was presented as the major intermediate and R were 1.80, 1.95 and 2.65 at 5, 10 and 20 min, respectively.

These results suggested that cellulose was more readily converted to the intermediate MG in the absence of sufficient water. When 0.2 ml water was added to the reaction, the above R values decreased to 1.11, 1.09 and 1.08, respectively, and further to 0.43, 0.43 and 0.65 as 0.6 mL water was added. These changes in R values clearly showed that the introduction of water had an important influence on the pathways, by switching the main route from cellulose alcoholysis-to-MG to hydrolysis-to-glucose, which was believed to have a big impact on the reaction rate and even the product distribution.



Fig. 3 Products distribution of cellulose conversion with different water contents (orange squares: cellulose conversion). Reaction conditions: Cellulose 3 mmol, 0.6 mmol Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 14 mL MeOH, 800 W, 180 °C (see Table S5† for details).



Fig. 4 ML production from glucose (solid) and MG (hollow). Reaction conditions: Substrate 3 mmol, 0.6 mmol  $Al_2(SO_4)_3$ , 0.6 mL  $H_2O$ , 14 mL MeOH, 800 W, 180 °C.

To verify this point, we carried out the comparison experiments by using MG and glucose as substrates for ML production under the optimized reaction conditions (Fig. 4). As shown, it required less time for glucose to reach a full substrate conversion as compared to MG, which indicated that glucose reacted faster (higher conversion rate) than MG under the same reaction conditions. At the same time, higher ML yield (82.3% vs. 68.1%), as well as its formation rate, was also obtained in glucose conversion. These results all suggested that glucose was more readily converted to ML with higher reactivity and reaction rate.<sup>46</sup> Also, the mutual transformations between these two substrates were observed as both of their intermediates were detected in the reaction, which was consistent with the previously reported work.14 Combining these results, it's not difficult to find that the addition of water may help to alter the reaction pathway via the more reactive intermediate glucose, which provided higher reaction rate and product yield.

Based on the above experiments, it can be concluded that water has three main functions in the alcoholysis of cellulose: (1) provide a reaction medium for metal salt hydrolysis to generate active Brønsted and Lewis acid species, (2) make the reaction proceed mainly through the intermediate glucose instead of MG, accompanied by higher reaction rates and (3) change the product distribution, resulting in higher ML yield, less humin/coke formation and less solvent consumption. These results further highlighted the importance of water in cellulose alcoholysis, and also well explained why water was necessary in the conversion of cellulose.

#### Reaction kinetics and mechanism

During our experiments, a series of intermediates and side products were detected as listed in Table 1. This information provided direct evidence related to the reaction mechanism of cellulose conversion. To further reveal the reaction pathway,



Fig. 5 Product evolution of cellulose conversion. Cellulose 3 mmol, 0.6 mmol  $Al_2(SO_4)_3$ , 14 mL MeOH, 0.6 mL H<sub>2</sub>O, 180 °C, 800 W.

the product evolution of cellulose conversion under identical reaction conditions was monitored (Fig. 5). Cellulose was gradually converted as the reaction proceeded. MG and glucose were firstly increased and then decreased to a negligible level. Other side products such as fructose, HMF and MMF were all detected during the reaction. Based on the product distribution, a skeleton reaction network related to cellulose conversion over  $Al_2(SO_4)_3$  was constructed (Scheme 2).

 $K_1$  is the rate constant of cellulose-to-coke conversion;  $k_2$ and  $k_3$  are the rate constants of cellulose conversion to glucose and MG, respectively;  $k_5$  and  $k_{-5}$  are the rate constants of mutual transformation between glucose and MG;  $k_4$  and  $k_7$  are rate constants of glucose-to-HMF and MG-to-MMF dehydration, respectively;  $k_{10}$  and  $k_{12}$  are rate constants of HMF-to-LA and MMF-to-ML, respectively;  $k_9$  and  $k_{-9}$  are the rate constants of mutual transformation between HMF and MMF, respectively;  $k_6$ ,  $k_{11}$  and  $K_{15}$  are the rate constants of humin formation from glucose, HMF and LA, respectively;  $k_8$ ,  $k_{13}$  and  $k_{16}$  are rate constants of humin formation from MG, MMF and ML, respectively. All the elemental reactions are considered to be pseudo-first-order reactions.

With the increase of water content in the cellulose hydrolysis reaction, the rate of coke formation  $(k_1)$  decreased while that of cellulose conversion  $(k_2 + k_3)$  increased. This indicated that coke formation was suppressed while cellulose conversion



Scheme 2 Reaction pathway and kinetic model for cellulose conversion.

was promoted when water was gradually added. The rate of cellulose-to-glucose  $(k_2)$  was relatively lower than that of cellulose-to-MG  $(k_3)$  without water addition (3.22 vs. 6.42), revealing that the alcoholysis route 2 was the prevalent pathway for cellulose conversion. However,  $k_2$  was continuously increased while  $k_3$  decreased with increasing water content, which indicated that the addition of water could gradually switch the reaction pathway via cellulose hydrolysis route 1 to generate glucose. And this reaction route became prevalent ( $k_2 = 8.21$ vs.  $k_3 = 3.65$ ) under our optimized reaction conditions with 0.6 mL water addition, which was in accordance with our above discussions. The rate constants of mutual transformation between glucose and MG ( $k_5$  and  $k_{-5}$ ) exhibited opposite changes as the water content increased, with a slight increase in  $k_{-5}$  and a decrease in  $k_5$ . This result indicated that more MG was likely to get converted to glucose as the water content increased, which would also contribute to the reaction progress via glucose intermediate. The above results clearly suggested that both of the two reaction routes (routes 1 and 2) were parallelly involved in the cellulose conversion and that the water content played a dominant role in determining which route the reaction would proceed via. The more the addition of water (e.g.  $\geq 0.6$  mL), the more prevalent the hydrolysis route will be.

As for the successive subreactions in route 1 through the intermediate glucose, the rate of glucose-to-HMF  $(k_4)$  was almost invariable with varied water contents, which was due to the independence of the dehydration process that didn't require the participation of water molecules. This was also the case for LA-to-ML esterification  $(k_{14})$ . The rate of HMF-to-LA rehydration  $(k_{10})$  increased significantly as the water content increased and remained at a high level when the water content was 0.6 mL. This was also the case for the ML-to-LA hydrolysis reaction  $(k_{-14})$ , but still at a much lower level as compared to that of LA esterification  $(K_{14})$ . As for route 2, the rates of MGto-MMF dehydration  $(k_7)$  and MMF-to-ML alcoholysis  $(k_{12})$ were unchanged with water addition. This suggested that the subreactions in route 2 wouldn't be affected by water. Apart from that, the glucose conversion rate  $k_4$  was larger than the MG conversion rate  $k_7$ , demonstrating that glucose was more reactive than MG in the conversion. The rate constant of mutual transformation between HMF and MMF showed similar changes to that of the mutual transformation between glucose and MG, further confirming the role of water that effectively switched the reaction progress via route 1. The side reaction rates of humin formation from the two routes  $(k_6, k_{11}, k_{15})$  and  $(k_8, k_{13}, k_{15})$  were comparable and remained almost unchanged under the current reaction conditions.

Finally, by comparing all the reaction rates of the subreactions, the hydrolysis of cellulose and the alcoholysis of cellulose had the lowest reaction rates in the two routes, respectively, thereby being the rate-determining steps of the two reaction routes. The alcoholysis of cellulose into MG was prevalent when no water was added to the reaction  $(k_3 > k_2)$ , while the hydrolysis of cellulose into glucose became prevalent after the introduction of 0.6 ml water  $(k_2 > k_3)$ . Besides, the total rate of cellulose conversion  $(k_2 + k_3)$  with 0.6 mL water content was also higher than that without water addition, further suggesting the acceleration effect of water on cellulose conversion.

To further reveal the apparent activation energies ( $E_a$ ) of each subreaction involved in cellulose conversion, two other reaction temperatures (170 and 190 °C) were used to obtain the rates of subreactions. The Arrhenius rate data plot were recorded and are presented in Fig. S2a.† All *R*-squared values for these reaction steps were higher than 0.98. The apparent activation energies of cellulose hydrolysis ( $E_{a2}$ ) and alcoholysis ( $E_{a3}$ ) were 165.8 and 183.5 kJ per mol, respectively, which were relatively higher than the other subreactions involved in the main route toward ML formation. This result further indicated that these two steps were difficult to proceed and more sensitive to the reaction temperature. The apparent activation energies of the other subreactions of the two main routes were very similar, which further indicated that both of these two routes were parallel reactions in cellulose conversion.

Finally, the accuracy of the kinetic model was examined by comparing the experimental data to the kinetic model (predicted ones) in the parity plot in Fig. S2b.† As seen, a good fit between the kinetic predicted data for cellulose conversion and the experimental data was observed, which further demonstrated the reliability of the current reaction kinetic models.

#### Effect of microwave heating

In our work, microwave conditions are another important factor for the high yield of ML production in a shorter reaction time as compared to the conventional oil heating systems. To further reveal the acceleration effect of microwave heating on cellulose conversion, oil heating for cellulose conversion was carried out and the related reaction rates of the subreactions were also investigated as presented in Table 2, entry 6. The reaction rates were significantly reduced as compared to the reaction conducted under microwave conditions in Table 2, entry 3. As is known, oil heating provides a homogeneous heating in the reaction media, which allows all the subreactions to proceed under the same reaction temperature. However, microwave irradiation is a volumetric and dielectric heating resource which is significantly affected by the dielectric properties of the substrates, namely the dielectric constant  $\varepsilon'$  and the dielectric loss  $\varepsilon''$ . They reflect the abilities of a substrate to absorb the electromagnetic energy and turn the energy into heat, respectively.54 Substrates that possess high dipole moments, as well as the polar chemical bonds or functional groups, can easily absorb the microwave energy and may generate hot spots (local higher temperature or energy), which would greatly accelerate the reaction rates.<sup>42</sup>

To investigate which subreactions in cellulose conversion are more sensitive to the microwave magnetic field, the reaction rates of the subreactions under microwave and oil heating were compared. *R* represents the ratio of the rates with microwave heating to oil heating. As indicated in Fig. 6, most of the rates of the subreaction with microwave heating increased

			Rate cons	tants (×10 <sup>-3</sup>	$^{3} \min^{-1}$ )							
Entry	Add $H_2O(mL)$	$T(^{\circ}C)$	<i>K</i> <sub>1</sub>	$K_2$	$K_3$	$K_4$	$K_5$	$K_{-5}$	$K_6$	$K_7$	$K_8$	$K_9$
1	0	180	1.49	3.22	6.42	15.68	6.24	1.38	1.10	9.01	2.71	8.04
2	0.2	180	1.08	6.74	4.28	15.79	6.02	2.34	1.07	9.07	2.67	7.95
3	0.6	180	0.81	8.21	3.65	15.94	5.81	3.95	1.02	9.10	2.69	7.80
4	0.6	170	0.20	2.55	1.05	7.68	3.95	2.65	0.43	3.64	1.24	5.76
5	0.6	190	3.56	17.78	9.01	29.21	8.38	6.19	2.55	18.11	5.40	10.49
6 <sup>a</sup>	0.6	180	0.02	0.33	0.15	0.48	0.24	0.15	0.056	0.30	0.13	0.31
$E_{\rm a}$ (KJ mol <sup>-1</sup> )			245.4	165.8 <sup>a</sup>	183.5	114.0 <sup>b</sup>	64.1	72.3	151.7 <sup>c</sup>	136.9	125.4 <sup>d</sup>	51.1
			Rate	constants (>	<10 <sup>-3</sup> min <sup>-</sup>	-1)						
Entry	Add $H_2O(mL)$	$T(^{\circ}C)$	<i>K</i> _9	K <sub>10</sub>	<i>K</i> <sub>11</sub>	K	12	<i>K</i> <sub>13</sub>	K <sub>14</sub>	K <sub>-14</sub>	K <sub>15</sub>	K <sub>16</sub>
1	0	180	1.61	15.81	2.	.52 3	2.90	2.35	40.35	1.03	2.58	2.51
2	0.2	180	3.75	28.74	3.	.05 3	2.69	2.87	40.76	2.40	2.63	2.45
3	0.6	180	5.11	35.45	i 3.	.26 3	2.55	3.04	40.85	3.55	2.67	2.38
4	0.6	170	3.67	22.72	2 1.	.47 2	0.80	1.48	32.92	2.58	1.54	1.31
5	0.6	190	7.15	53.32	2. 7.	.11 4	9.98	6.77	51.87	4.76	4.61	4.30
6 <sup>a</sup>	0.6	180	0.20	1.45	<b>0</b> .	.13	1.37	0.12	1.71	0.14	0.11	0.10
E <sub>a</sub> (KJ n	$nol^{-1}$ )		56.8	72.7 <sup>e</sup>	134.	.4 <sup>f</sup> 7	4.7	129.6	38.7 <sup>g</sup>	52.1	93.5 <sup>h</sup>	101.3

Table 2 Estimated kinetic parameters for cellulose conversion under microwave conditions

Reaction conditions: Cellulose (3 mmol), 0.6 mmol Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 14 mL MeOH, 800 W. The apparent activation energy ( $E_a$ ) of each reaction was calculated based on the rate constants in entries 3–5. a: Reaction conducted with conventional oil heating (Table S6). Apparent activation energies in the previous literature: a: 105.6–177.6 kJ mol<sup>-1</sup>;<sup>47,48</sup> b: 86–160 kJ mol<sup>-1</sup>;<sup>49–51</sup> c: 70.97–167 kJ mol<sup>-1</sup>;<sup>49,52</sup> d: 104.2 kJ mol<sup>-1</sup>;<sup>27</sup> e: 57–107 kJ mol<sup>-1</sup>;<sup>49</sup>,<sup>53</sup> g: 29.4–54.3 kJ mol<sup>-1</sup>;<sup>49,53</sup> h: 61.7–150 kJ mol<sup>-1</sup>.<sup>49,53</sup>

24–25 times that with conventional oil heating. A few exceptional subreactions were found to exhibit varied R values. The rate of cellulose-to-coke conversion was more accelerated by about 41 times, which may be caused by the hot spots that led to local higher temperature, making easier the degradation of cellulose to coke due to the poor solubility of cellulose crystals. Despite that,  $K_1$  was still relatively smaller as compared to the rates of the other subreactions. It's worth noting that the rates of glucose-to-HMF ( $k_4$ ) and MG-to-MMF ( $k_7$ ) conversions were also more accelerated while the rates of glucose-to-humins ( $k_6$ ) and MG-to-humins ( $k_8$ ) conversions were less



**Fig. 6** Comparison of the rates of the subreactions with microwave and oil heating. *R* represents the ratio of the rates constants of microwave heating to those of oil heating.

accelerated. These results suggested that microwave heating enabled the reaction to proceed with higher selectivity toward ML production and suppress the undesired side reactions toward humin. This may be originated from the high polarity of glucose and MG that are rich in hydroxyl groups, which would then easily absorb more energy to create a high-energy local reaction environment and increased the reaction rates substantially.<sup>55</sup> The lower R values of  $k_6$  and  $k_8$  were just the result of the higher R values of  $k_4$  and  $k_7$ , respectively. This is because the increased times of the rates of glucose and MG conversion should match that of their formation rates  $k_2$  and  $k_3$ , as these two intermediates (glucose and MG) exhibited similar concentration regularity over the entire reaction time with both microwave and oil heating. Overall, microwave heating did change the reaction selectivity toward higher selectivity to the target product by suppressing the side reaction to humins, as compared to the conventional oil heating, which was also the advantage of microwave heating over conventional heating. This finding may provide preliminary insight into the selective heating of microwaves on a molecular level, which may generate more unique chemistry selectivity.

#### Catalyst reusability

For the application of a catalyst in biomass conversion, its recyclability is very important. Although the current reaction was a homogeneous system, the catalyst could also be efficiently recovered by simple procedures. The recycled catalyst was directly subjected to the next reaction. After recycling five times, the yield of ML decreased by *ca.* 5.3%, from 70.6% to



**Fig. 7** Recycling study of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> catalyst. Reaction conditions: 3 mmol cellulose, 14 mL MeOH, 0.6 mL H<sub>2</sub>O, 800 W, 180 °C,40 min.

65.3%, in the sixth run (Fig. 7). This slight decrease in the product yield may be attributed to the loss of acid species during the recycling process. Despite that, the catalyst still possessed high reactivity for cellulose conversion. Concerning the high reaction efficiency and good recyclability of  $Al_2(SO_4)_3$ , it would be an ideal catalyst for the production of ML from cellulosic biomass, despite its homogeneous nature in the reaction.

#### Applications in biomass conversion

Finally, the established method was applied to the conversion of other carbohydrates and raw biomass (Table 3). Before that, different alcohols were tested for cellulose conversion to produce different alkyl levulinates. The reactions with EtOH, iPrOH and *n*BuOH as solvents provided 53.9, 26.6 and 36.6% yields of alkyl levulinate product, respectively. The lower yields may have resulted from the low reactivity and steric hindrance of these alcohols.<sup>35,40</sup> However, by extending the reaction time, the reactions could also reach satisfying product yields. In addition, different raw biomass resources were also tested for ML production. When sucrose and inulin were used, 83.4% and 64.7% yields of ML were obtained in 15 min, respectively. Another commonly used  $\alpha$ -cellulose could also effectively be

 
 Table 3
 Production of alkyl levulinates (AL) with different alcohols or from different biomass resources

	Substrate	Solvent	Time (min)	AL yield (%)
1	Cellulose	EtOH	40/55	53.9/70.1
2	Cellulose	iPrOH	40/75	26.6/53.7
3	Cellulose	<i>n</i> BuOH	40/75	36.6/63.1
4	Sucrose	MeOH	15	83.4
5	Inulin	MeOH	15	64.7
6	α-Cellulose	MeOH	40	68.9
7	Bagasse	MeOH	35	65.1
8	Poplar powder	MeOH	35	62.7
9	Bamboo powder	MeOH	40	64.2

Reaction conditions: Substrate 500 mg, 0.6 mmol  $Al_2(SO_4)_3$ , 14 mL MeOH, 0.6 mL  $H_2O$ , 800 W, 180 °C. ML yields from bagasse, poplar powder and bamboo powder were calculated based on the cellulose content in dry feedstocks.

converted to ML in 68.9% yield under the optimized conditions. Other raw materials such as bagasse, poplar powder and bamboo powder were also successfully converted to ML with 65.1, 62.7 and 64.2% yields, respectively, based on the cellulose contents of these raw materials. These results further demonstrated the great compatibility of the  $Al_2(SO_4)_3$  catalytic system for the production of ML from different biomass resources.

### Conclusions

In conclusion, we have presented a simple and efficient metal salt  $Al_2(SO_4)_3$  catalyst system for the high yield production of ML from cellulose in methanol solvent under microwave conditions. A high yield of 70.6% of ML, comparable to the reported highest ML yield (75%), was obtained at 180 °C for 40 min with the addition of a certain amount of water. The addition of water can not only effectively increase the rate of cellulose conversions, but also reduce the etherification of solvents and the coke/humin formation during the reaction. Mechanistic and kinetic studies revealed that the reaction proceeds mainly through the cellulose hydrolysis intermediate glucose and the alcoholysis intermediate MG, with the former as the prevalent route for ML production in the presence of the optimized amount of water. Besides, the route through the glucose intermediate showed higher reaction rates as compared to that through the MG intermediate. Microwave irradiation was demonstrated to effectively accelerate the reaction rate ~25 times that of conventional oil heating, with a greater rate of glucose/MG conversion and a lower rate for their side reactions to humins, resulting in higher selectivity toward the target ML product. Finally, the catalyst could be successfully recycled with high reactivity and also showed good compatibility for the conversion of other carbohydrates and raw biomass materials to ML with slightly different reaction times, making Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> a green and practical potential catalyst for industrial ML production from biomass resources.

### Conflicts of interest

There are no conflicts to declare.

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