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Short communication

Conversion of carbohydrates to methyl levulinate catalyzed by sulfated montmorillonite



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A R T I C L E I N F O

ABSTRACT

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Keywords: Carbohydrates Montmorillonite Acid catalysis Methanol Methyl levulinate We reported a highly efficient conversion of carbohydrates such as glucose to methyl levulinate (ML) in methanol with a series of sulfated montmorillonite (MMT) as simple and inexpensive catalysts. Among these catalysts, the MMT treated by H_2SO_4 after calcination (especially the MMT treated by 20% H_2SO_4) showed a high catalytic activity. Under the optimal conditions, the conversion of glucose and fructose was up to 100%, and the ML yields obtained from glucose and fructose were 48% and 65%, respectively. The reaction conditions were optimized. Further, the structure and properties of sulfated MMT were characterized.

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1. Introduction

The increasing need for energy worldwide, namely depleting fossil resources and growing environmental concerns, has triggered great interest in searching for renewable sources of energy and chemicals [1]. Among these resources, biomass attracts enormous attention due to its considerable potential as a raw material for the production of green fine chemicals, fuels and fuel additives [2,3]. In 2004, the US-Department of Energy (DoE) identified 12 kinds of valuable chemicals obtainable via the transformation of biomass [4]. Among these value-added chemicals, levulinic acid (LA) and levulinate esters are used in biofuel chemistry as well as in the petrochemical industry as versatile and key intermediates. Hence, catalytic conversion of biomass into LA [5] and levulinate esters [6] has been one of the focuses in the field of energy and resources.

Homogeneous acid catalysts (such as sulfuric acid and metal salt) were widely adopted to synthesize LA and levulinate esters [7–9]. However, the homogeneous catalysts have many deficiencies, such as catalyst recycling, product separation, and reaction conditions. In recent years, heterogeneous acid catalysts were applied to the synthesis of levulinate esters. There were two main preparation methods reported. One was from biomass-derived feedstocks, such as: LA, furfuryl alcohol and furfural [10–12], which was costly. For this reason, researchers

* Corresponding author. *E-mail address:* tiange@jlu.edu.cn (G. Tian). developed another new and efficient approach to produce levulinate esters by the alcoholysis of cellulosic biomass or carbohydrates under acidic conditions [13–15]. Among various solid acid catalysts, sulfated metal oxides have been widely utilized to convert carbohydrates, such as sulfated titania, and zirconia [16,17]. However, there are still considerable opportunities to improve the catalytic activity and optimize the reaction conditions. In addition, they are expensive and difficult to prepare. Therefore, the development of heterogeneous, cost-effective catalysts is the key to the conversion of biomass-derived feedstocks into levulinate esters and other platform molecules.

Montmorillonite (MMT), a ubiquitous, inexpensive and eco-friendly material, has received much attention as advanced materials in heterogeneous catalysis [18–20]. However, the application of the raw MMT is often limited by its low acid catalytic activity. Many studies have devoted to modify the clay mineral as solid acid catalysts by making use of its special laminated structure [21,22]. Herein, we investigated sulfated MMT, an affordable and easily prepared solid acid catalyst, for the conversion of carbohydrates into ML in methanol through the wellestablished hydro/solvothermal method [23,24]. The detailed process parameters on the reaction and the sulfated MMT were characterized.

2. Experimental

Detailed description of the synthesis, characterization, catalytic test and product analysis was presented in the Supporting material S1 experimental.

Table 1	
Conversions of glucose into ML in methanol catalyzed h	by various catalysts.

	0				
Entry	Catalyst	Catalyst Conversion (%)			
1	Blank	82	0		
2	γ -Al ₂ O ₃	90	0		
3	$Al_2(SO_4)_3$	>99	23		
4	MMT-K10	95	11		
5	5-H-MMT	98	27		
6	10-H-MMT	>99	32		
7	20-H-MMT	>99	34		
8	30-H-MMT	>99	29		
9	$5-SO_4^2$ /MMT	>99	25		
10	10-SO ₄ ²⁻ /MMT	>99	32		
11	20-SO ₄ ²⁻ /MMT	>99	48		
12	30-SO ₄ ²⁻ /MMT	>99	43		
13	$20-SO_4^2 / MMT^b$	93	12		
14	$20-SO_4^2$ /MMT ^c	>99	21		

^a Reaction conditions: 20 mL of methanol, 1 mmol of glucose, catalyst (0.15 g), reaction temperature: 200 °C, reaction time: 4 h.

^b The result obtained after three runs without further treatment.

^c The result obtained after three runs with calcination at 500 °C for 5 h between each experiment.

3. Results and discussion

3.1. The conversion of glucose to ML catalyzed by various acid catalysts

The conversions of glucose into ML in methanol were carried out with various catalysts, as summarized in Table 1. No ML was detected without catalyst (entry 1), or with γ -Al₂O₃ as catalyst under the same condition (entry 2). With $Al_2(SO_4)_3$, the formation of ML showed a moderate yield (23%, entry 3). Among other catalysts (raw MMT (MMT-K10), n-H-MMT and n-SO₄²⁻/MMT), MMT-K10 displayed the lowest catalytic activity (11% yield, entry 4) because it has the least acidic sites. The yield of ML with the n-H-MMT was higher than the yield of ML when raw MMT was involved, which is caused by more acidic sites in the n-H-MMT than those in the raw MMT. In n-H-MMT, acidic sites increased with the increase of the concentration of sulfuric acid via an ion-exchange reaction between interlayer cations in MMT and H⁺ of sulfuric acid [22]. However, the yield of ML was higher when the catalyst was the $n-SO_4^2$ /MMT rather than the n-H-MMT under the same concentration of sulfuric acid, which can be due to the lower Brønsted acidic sites in the n-H-MMT than those in the $n-SO_4^2$ /MMT. Based on the reaction mechanism, the Lewis acidic sites could be responsible for the isomerisation of methyl glucoside intermediates to methyl fructosides, and the Brønsted acidic sites subsequently catalyzed dehydration to produce 5-methoxymethylfurfural and esterification to form ML and methyl formate (Scheme 1). The $n-SO_4^2$ -/MMT contained a certain amount of sulfate groups which promoted the number of Brønsted acidic sites [25]. Therefore, the higher catalytic activity of $n-SO_4^2$ -/MMT is attributed to in situ sulfation on the MMT surface [2]. Moreover, it's also worth noting that when the concentration of sulfuric acid increased to 30 wt.%, the catalytic activity of these catalysts (30-H-MMT and $30-SO_4^2$ -/MMT) both declined (entries 8, 12), which was due to the damage to the clay layers in the acid treatment process, and the damage hindered the formation of the acid sites. During all the experiments, the main by-product was humin, which was a dark-brown insoluble substance. And there were some amounts of dehydrated intermediates (methyl glucosides and 5-methoxymethylfurfural) in the liquid phase.

The recyclability of $20-SO_4^{2-}/MMT$ was investigated. The yield of ML dropped from 48% to 12% (entry 13) after the third run using the $20-SO_4^{2-}/MMT$ without further treatment as catalyst. The adsorption of humin on the catalyst surface may explain the catalyst deactivation. Therefore, the catalyst was calcined at 500 °C for 5 h after each run. The result demonstrated that the catalytic activity of the catalyst had not completely recovered after calcination, and only 21% yield of ML (entry 14) was obtained in the third run, which can be attributed to partial loss of sulfur in the catalyst by solvation. The main problem of sulfated catalyst was unstability, since they were easy to lose sulfur. Accordingly, how to improve the stability remains as one of the topics for future exploration.

3.2. Effects of the reaction conditions

Fig. 1 shows a variation of the conversion of glucose and the yield of ML with reaction temperature. The experiments were carried out at 140, 160, 180, 200, and 220 °C. The conversion increased from 90% (140 °C) to 99% (180 °C) and then remained constant at nearly 100%. As expected, the yield of ML increased from 5% to 48% with the temperature rising from 140 °C to 200 °C, and then decreased. It is assumed that the existence of partial dehydrated intermediates led to the low yield at lower temperatures (<180 °C). Although elevated temperature could accelerate the rate of chemical reaction, the yield of ML began to fall when the reaction temperature was higher than 200 °C. This is probably due to decomposition of ML and production of byproducts. After the reaction, the color of the catalyst changed to deep brown from white, indicating an accumulation of humin on the surface of catalyst.

The experiments were conducted to find out the effect of catalyst loading on ML yield over reaction time using $20-SO_4^{2-}/MMT$ as catalyst,



Scheme 1. Proposed reaction pathway for the acid-catalyzed conversion of glucose to methyl levulinate in methanol.



Fig. 1. Influence of temperature on the conversion of glucose and the yield of ML. Reaction conditions: 20 mL of methanol, 1 mmol of glucose, catalyst: $0.15 \text{ g of } 20\text{-}SO_4^2\text{-}/MMT$, reaction time: 4 h.

and the results were given in the Supplementary information (Fig. S1). Taking the cost and the efficiency into consideration, the optimal condition is 0.15 g catalyst loading and 4 h.

3.3. Conversion of various carbohydrates

Other carbohydrates including monosaccharide (fructose), disaccharide (sucrose) and polysaccharide (starch and cellulose) were also investigated under similar reaction conditions, as shown in Table 2. With monosaccharide as the substrates, it could be clearly seen that the yield of ML from fructose was higher than from glucose (65% and 48%, respectively) because the reaction pathway of glucose involved an initial isomerization of methyl glucoside to methyl fructosides. For sucrose (a disaccharide of glucose and fructose), the yield of ML was between those from fructose and glucose, which was in accordance with its structure. As for polysaccharide (starch and cellulose), two different kinds of results were achieved. On the one hand, the yield of ML from starch was similar to that from glucose. A possible explanation is that starch is easy to convert into glucose as the intermediates [14]. On the other hand, the conversion of cellulose and the yield of ML from cellulose were appreciably lower than those of other carbohydrates (72% conversion and 24% ML yield), which could be concluded that the sugar units of the cellulose molecules are relatively difficult to decompose than other carbohydrates due to stronger binding force in the sugar units.

3.4. Catalyst characterization

As shown in Fig. 2, the sulfated MMT catalysts had similar XRD pattern to the MMT. When the concentration of sulfuric acid was higher than 20 wt.%, the 001 reflection of the sulfated MMT catalysts gradually weakened, indicating that the layers of MMT were damaged because sulfuric acid reacted with Al^{3+} in MMT, and some new reflections

Table 2

ML yields from different carbohydrates catalyzed by 20-SO₄²⁻/MMT.^a

Substrate	Conversion (%)	Yield (mol %)
Glucose	>99	48
Fructose	>99	65
Sucrose	98	60
Starch	85	41
Cellulose	72	24

 $^{\rm a}\,$ Reaction conditions: 20 mL of methanol, catalyst (0.15 g), reaction temperature: 200 $^{\circ}{\rm C},$ reaction time: 4 h.



Fig. 2. X-ray diffraction (XRD) patterns of the catalysts: (a) the MMT-K10; (b) $5\text{-}SO_4^{2-}/MMT$; (c) $10\text{-}SO_4^{2-}/MMT$; (d) $20\text{-}SO_4^{2-}/MMT$; (e) $30\text{-}SO_4^{2-}/MMT$.

emerged at 15 and 27 (denoted as *), which might be a characteristic of aluminum sulfate [26].

Table 3 lists the characterization results of the catalysts. From Table 3, the surface S content increases (0 to 5.5 wt.%) and Al content falls (13.5 to 5.7 wt.%) with the increase of the concentration of the sulfuric acid solution from XPS, showing that the sulfuric acid has a certain modification effect on MMT. The XPS survey spectrum and the survey scan of the S $2p_{3/2}$ region were obtained from the $20-SO_4^{2-/}$ MMT (Fig. S2). It shows S $2p_{3/2}$ lines at 170.2 eV, which is a characteristic of sulfur in the + 6 oxidation state [25]. All the discussion above suggests the successful adsorption of SO₄²⁻ on the surface of the MMT, which was also proved from FTIR (Fig. S3). The band at 925 cm⁻¹ gradually disappears owing to the damage of Al – OH – Al bond, which suggests that MMT was modified by sulfuric acid. A band at 1180 cm⁻¹ is ascribed to the symmetrical stretching vibration of O—S—O from (Fig. S3d-e) [27]. This result verifies the presence of super acid sites through acid treatment to the MMT.

 N_2 adsorption–desorption isotherm of MMT-K10 and the sulfated MMT catalysts are shown in Fig. S4. According to the BDDT classification, all of the samples show type IV isotherms with type H3 hysteresis loop, indicating the presence of mesopores. However, the N_2 adsorption capacity of the sulfated MMT catalysts has decreased compared to the MMT. It is speculated that the sulfate group partially blocked the pores of the MMT. A decrease in surface area (229 to 126 cm³/g) and in pore volume (0.40 to 0.21 cm³/g) can be observed (Table 3) with the increase concentration of sulfuric acid. This suggests that the layers of MMT were damaged and sulfate group not only deposited on the

Table 3

Characterization results of the catalysts.

Catalysts	Al ^a	S ^a	S _{BET} ^b	$\Sigma V p^c$	Acidity ^d	Acidic sites _{distribution} ^e	
	wt.%	wt.%	(m^2/g)	(cm ³ /g)	(mmol/g)	LT-peak ^f	HT-peak ^f
MMT-K10	13.5	0	229	0.40	0.49	79	21
$5-SO_4^2$ /MMT	13.1	1.4	210	0.37	0.51	72	28
10-SO ₄ ²⁻ /MMT	12.2	2.7	174	0.31	0.57	54	46
20-SO ₄ ²⁻ /MMT	8.4	3.9	137	0.24	0.58	50	50
30-SO ₄ ²⁻ /MMT	5.7	5.5	126	0.21	0.52	51	49

^a Al content, S content, determined by XPS analysis.

^b BET surface area, measured by N₂-TPD.

^c $\Sigma Vp =$ total pore volume, measured by N₂-TPD.

^d Total acidity amount, determined by NH₃-TPD.

^e The NH₃-TPD (%) distribution of acidic sites.

 $^{\rm f}\,$ LT-peak represents weak acid sites (less than 350 °C), HT-peak represents strong acid sites (greater than 350 °C).

external surface of MMT but also filled the pores making N_2 inaccessible to them.

The TPD profiles of desorbed ammonia (NH₃) on various catalysts are presented in Fig. S5 and the corresponding results of total acidity are listed in Table 3. As can be seen from Table 3, the total acidity and the proportion of strong acid sites increased with increasing sulfuric acid content in the sulfated MMT (5–20 wt%), implying that the sulfate groups can promote the acidic amount on the MMT. However, when the concentration of sulfuric acid increased to 30 wt.%, the total acidic amount and the proportion of strong acid sites declined, indicating that the acidic sites were damaged. The MMT also has acidity as confirmed from the HT-peak between 450 °C and 550 °C, and LT-peaks at around 200 °C. The HT-peak of the sulfated MMT catalysts becomes wider (Fig. S5), which suggests the increase in the total amount of the strong surface acidic sites.

4. Conclusions

In summary, under mild conditions, a series of sulfated MMT catalysts with tunable surface acid strength and site density were synthesized through a simple impregnation method. Among these catalysts, the $20-SO_4^2$ /MTT exhibits the best performance. Under the optimal conditions, the conversion of glucose and fructose was up to 100%, and the ML yield obtained were 48% and 65%, respectively. The sulfate groups on the MMT can promote the amount of strong acidic sites and the acidic amount, which is beneficial to the reaction. Hence, the sulfate d MMT catalyst, due to its low cost, simple preparation and high activity, has excellent potential for the conversion of biomass into biofuels and platform chemicals.

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Appendix A. Supplementary data

Experimental details, XPS, FTIR, N₂-TPD, NH₃-TPD and additional reaction data are available in the Supplementary information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.catcom.2015.01.011.

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