



Short communication

Conversion of carbohydrates to methyl levulinate catalyzed by sulfated montmorillonite



Xingliang Xu, Xianlong Zhang, Weijian Zou, Huijuan Yue, Ge Tian*, Shouhua Feng

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, PR China

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ABSTRACT

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

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 well-established 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.

* Corresponding author.

E-mail address: tiange@jlu.edu.cn (G. Tian).

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

Entry	Catalyst	Conversion (%)	Yield (mol%)
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 Al₂(SO₄)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-SO₄²⁻/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-SO₄²⁻/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

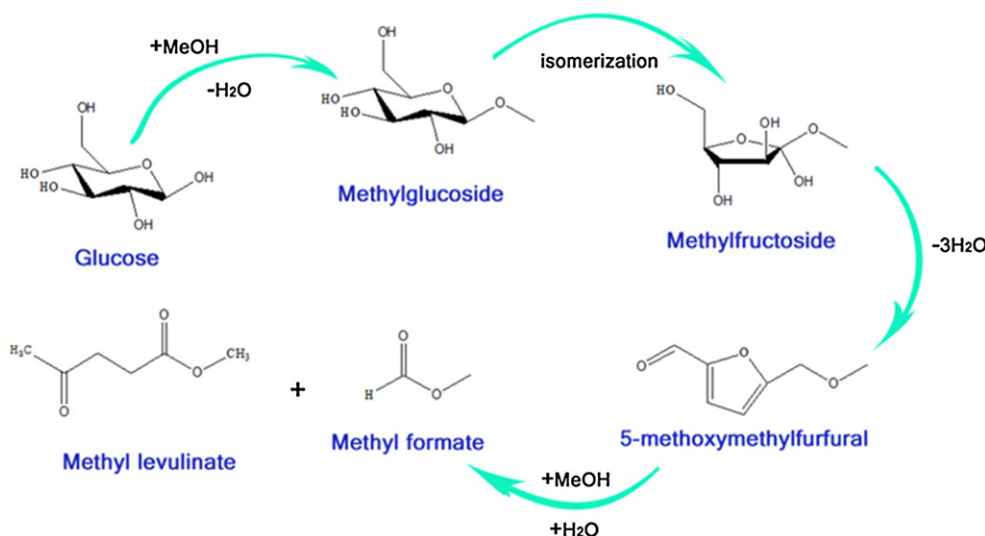
dehydration to produce 5-methoxymethylfurfural and esterification to form ML and methyl formate (Scheme 1). The n-SO₄²⁻/MMT contained a certain amount of sulfate groups which promoted the number of Brønsted acidic sites [25]. Therefore, the higher catalytic activity of n-SO₄²⁻/MMT is attributed to in 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-SO₄²⁻/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-SO₄²⁻/MMT was investigated. The yield of ML dropped from 48% to 12% (entry 13) after the third run using the 20-SO₄²⁻/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 instability, 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-SO₄²⁻/MMT as catalyst,



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

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