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Efficient production of ethyl levulinate from cassava over $\text{Al}_2(\text{SO}_4)_3$ catalyst in ethanol–water system

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ABSTRACT

One-pot achievement of ethyl levulinate from cassava was conducted in ethanol–water system over several simple sulfate salt catalysts. $\text{Al}_2(\text{SO}_4)_3$ catalyst had the best performance in synthesizing ethyl levulinate comparing with those of a series of sulfate salts. The highest yields of ethyl levulinate was up to 39.27% as well as 7.78% levulinic acid when cassava was catalyzed in ethanol medium by adding 10 wt% water. ^{13}C and ^1H NMR spectroscopic investigations confirmed that isomerization of glucose to fructose over $\text{Al}_2(\text{SO}_4)_3$ catalyst is an important step in producing ethyl levulinate and levulinic acid. Due to aggregations of Al^{3+} under hydrothermal conditions, tiny amount of Al^{3+} were detected in filtrate at the percentage of 0.32% even if in absolute water. Brønsted and Lewis acids could improve the yield of ethyl levulinate and levulinic acid by synergistic effect. All results suggested that $\text{Al}_2(\text{SO}_4)_3$ was a simple and efficient catalyst for ethyl levulinate and levulinic acid production.

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1. Introduction

Conventional fossil fuel depleting and carbon dioxide emission cause much compositional changes in environment disequilibrium [1]. Plenty of attentions have been paid on the exploitation of renewable green energy which could substitute those originated from fossil fuels. As an important kind of platform chemicals derived from biomass, ethyl levulinate (EL) and levulinic acid (LA) have extensive advantages in potential industrial applications either in flavoring and fragrance industry or as blending component in biodiesel [2]. Moreover, EL and LA are the perfect renewable green substrates in synthesis of long carbon biofuels with straight or branched chains [3]. Further investigation shows that EL could be transformed into angelica lactones which also give the carbon chain prolonged products at mild conditions without using noble catalyst and solvent [4].

In fact, LA is one product of acid-catalyzed hydrolysis of cellulose in aqueous phase [5]. Cellulose is firstly depolymerized to glucose over protonic acid, and then further isomerized to fructose by Lewis acid. LA could be finally produced after dehydration of fructose catalyzed through Brønsted acid, going through an important intermediate compound named hydroxymethylfurfural (HMF) [6].

When an alcohol medium is used to instead of water, the newly produced LA is esterified to levulinate ester at once in the presence of Brønsted acid until esterification reaction strikes a balance. In essence, a series of carbohydrates, like fructose, glucose and cellulose, are usually adopted to gain high yield of EL over different acid catalysts in ethanol [7–9]. In order to abbreviate the process of lignocellulose to EL, those raw materials which mainly consist of abundant cellulose are alcoholized directly over protonic acid catalysts. Several investigations have been reported on EL production by converting cellulosic biomass. Because of undesired humins and byproducts production during depolymerizing lignocellulose to EL using single Brønsted acid, most yields reported are lower than 50% (based on theoretical yield) [10]. For example, the yields of EL are achieved only at 23.0%, 37.3% and 44.4% respectively when wood powder, paper pulp and wood chips are adopted as raw feedstock [9,11].

According to the mechanism of raw carbohydrates to EL, hydrolysis, isomerization and dehydration are still inevitable in the ethanolysis process. Especially, isomerization of glucose to fructose over Lewis acid is the most important step in EL and LA production. Herein, it is meaningful to use an efficient and simple catalyst with Brønsted and Lewis acid for transformation of lignocellulose to levulinate esters with higher yields, attributing to the synergistic effect of both acids [12]. Therefore, several combinatorial catalysts, like hybrid catalysts [13,14], metal salts mixed with acid ionic liquid [15], metal salts combining Brønsted acid [16] are

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Table 1. Comparison of different catalysts for cassava decomposition.

Entry	System	Catalysts	Conversion (%)	Mass yield (%)					pH	
				FFA	EL	EMF	LA	HMF	pH ^c	pH ^d
1 ^a	Water	Al ₂ (SO ₄) ₃	65.97	0.07	–	–	14.53	0.57	3.5	2.5
2 ^a		Fe ₂ (SO ₄) ₃	66.43	0.04	–	–	1.22	–	2.0	3.0
3 ^a		H ₂ SO ₄	73.27	–	–	–	13.98	–	2.3	2.4
4 ^a		NaHSO ₄	64.90	0.20	–	–	1.64	0.03	2.5	2.6
5 ^a		MgSO ₄	90.00	0.35	–	–	2.91	0.86	5.9	3.7
6 ^a		ZnSO ₄	75.89	0.06	–	–	0.92	–	5.8	3.6
7 ^a		NiSO ₄	80.47	0.21	–	–	4.54	0.04	5.7	2.6
8 ^b	Ethanol	Al ₂ (SO ₄) ₃	97.8	0.26	36.47	0.36	6.35	0.85	6.0	4.0
9 ^b		Fe ₂ (SO ₄) ₃	87.5	0.30	9.28	3.01	4.01	1.51	6.0	6.0
10 ^b		H ₂ SO ₄	97.3	0.08	30.63	2.05	5.63	1.52	3.0	4.0
11 ^b		NaHSO ₄	64.23	0.45	15.14	4.43	3.79	0.86	4.5	5.5
12 ^b		MgSO ₄	23.25	0.03	0.42	0.09	0.41	0.06	6.5	5.8
13 ^b		ZnSO ₄	81.50	0.16	0.38	3.25	0.25	2.22	6.4	5.0
14 ^b		NiSO ₄	80.99	0.30	1.38	11.04	0.42	2.54	6.5	5.3

Reaction conditions: 2.0 g cassava, 38 g solvent, 473 K, 0.2 g catalyst, 6.0 h. Entries 1–7 meant that the reactions were conducted in water, while Entries 8–14 showed that the reaction happened in ethanol, and pH^c and pH^d represented the pH value of solution before and after reaction. FFA: furfural; EL: ethyl levulinate; EMF: 5-ethoxymethylfurfural; LA: levulinate acid; HMF: 5-hydroxymethylfurfural.

employed to catalyze carbohydrates such as cellulose, sucrose, glucose to LA or levulinate esters. In this work, single component Al₂(SO₄)₃ was developed as catalyst for conversion of cassava to EL in ethanol–water without any co-catalyst. The catalytic performance of Al₂(SO₄)₃ in the conversion of cassava to EL was investigated.

2. Experimental

2.1. Materials

Cassava was provided by South China Agricultural University; Fructose (purity > 99%) was purchased from MYM Biological Technology Company Limited; glucose, H₂SO₄, Al₂(SO₄)₃·18H₂O, NaHSO₄·H₂O, Fe₂(SO₄)₃, ZnSO₄·7H₂O, MgSO₄ and NiSO₄·6H₂O (purity > 99%) were all bought from Damao chemical reagents company, China; C₂H₅OH was bought from Guangdong Guanghua Sci-Tech Co. Ltd. China.

2.2. Experimental setups and procedures

Cassava was laid in an oven at 353 K for enough time to dehydration until constant weight. Fine powders were obtained by a grinder following mesh screening with 40–60 mesh sieves. 2.0 g cassava powders, 0.2 g catalyst (converted to sulfate salts with no crystalliferous water) and 40 g solvent were put into a batch reactor successively. In order to avoid oxidation, the air in reactor was displaced with nitrogen for three times. After preparation, reaction system was heated to expectant temperature for a certain time. And then, the system was halted and cooled down to room temperature by cold water. The liquid after reaction was filtered and the filter residue was washed with ethanol (containing 10 wt% water) for three times.

The pH values of ethanol–water solution before and after reaction were measured at room temperature through pH meter. The liquid products were analyzed on an Agilent GC-7890A gas chromatograph (HP innowax capillary column 19091N-133 N, 30 m × 250 μm × 0.25 μm) with external standard method. The column temperature was held at 323 K for 2 min and then heated via temperature programming at a rate of 10 K/min to 523 K, holding for 3 min. The identification and quantification of the isomerized products were performed by HPLC (Waters 2695) equipped with Aminex HPX-87C column (300 × 7.8 mm, H₂O, 0.6 mL/min, 358 K). The detection of Al³⁺ and SO₄²⁻ in filtrate and residue was measured through ICP-OES 8000 and turbidimetry, respectively. ¹H and

¹³C chemical shifts of glucose, fructose and liquid products were tested using a nuclear magnetic resonance scanner (Bruker Advance 400 III) with H₂O and D₂O as solvent (100 MHz), in order to test the activity of catalyst for recyclability and obtain pure EL and LA from the mixed medium. According to the literatures [17,18], filtrate was dealt with a rotary evaporation to remove the surplus ethanol and partial water until a dense mixture was formed. Then exaction was conducted with dichloromethane (CH₂Cl₂) for five times to get EL and LA. After removing CH₂Cl₂ solution, Al₂(SO₄)₃ in the filtrate was nearly completely retained and dried at room temperature for the next use. Residues and dried Al₂(SO₄)₃ were put together followed another batch of cassava and ethanol–water solvent were added. The relevant calculations were conducted as the following formulas:

$$\text{Mass yield (\%)} = m_i/m_0 \times 100\% \quad (1)$$

$$\text{Mole yield (\%)} = n_i/n_0 \times 100\% \quad (2)$$

$$\text{Mole percentage (Al}^{3+}\text{)(\%)} = n_i/n_j \times 100\% \quad (3)$$

$$\text{Mole percentage (SO}_4^{2-}\text{)(\%)} = n_k/n_l \times 100\% \quad (4)$$

where m_i is the weight of one product and m_0 is the weight of cassava powder. For the yields of EL and 5-ethoxymethylfurfural (EMF) calculation, the increased –CH₂CH₃ group was subtracted from molecular weight. n_i is the mole content of substrate (i = fructose, mannose, HMF and LA, respectively) and n_0 is the mole content of glucose. n_i and n_k are the mole content of Al³⁺ and SO₄²⁻ in filter liquid. While n_j and n_l are the initial content of Al³⁺ and SO₄²⁻ in Al₂(SO₄)₃.

3. Results and discussion

3.1. Comparison of catalysts performance in water/ethanol system

Because of unique components (Table S1), common acid catalysts were adopted to depolymerize cassava in water or ethanol medium and the results were exhibited in Table 1. The catalysts used in this work were divided into two types, one was classic Brønsted acid (NaHSO₄ and H₂SO₄) and another was Brønsted acid combined with Lewis acid after hydrolysis/ethanolysis (other sulfate salts). The results obvious showed that higher total yields of EL and LA were achieved by the ethanolysis of cassava over Al₂(SO₄)₃, and the highest value of total yield reached 42.82%. However, only

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