

# Conversion of Biomass-Derived Furfuryl Alcohol into Ethyl Levulinate Catalyzed by Solid Acid in Ethanol

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A green and efficient process was developed for the conversion of biomass-derived furfuryl alcohol to ethyl levulinate using eco-friendly solid acid catalysts (zeolites and sulfated oxides) in ethanol. Studies for optimizing the reaction conditions such as the substrate concentration, the reaction time, the temperature, and the catalyst loading dosage were performed. With  $\text{SO}_4^{2-}/\text{TiO}_2$  as the catalyst, a high ethyl levulinate yield of 74.6 mol% was achieved using a catalyst load of 5 wt% at 398 K for 2.0 h. The catalyst recovered through calcination was found to maintain good catalytic activity (47.8 mol%) after three cycles, and it was easily reactivated by re-soaking in  $\text{H}_2\text{SO}_4$  solution. Catalyst characterization was based on BET surface area,  $\text{NH}_3$ -TPD, and elemental analysis techniques.

*Keywords:* Furfuryl alcohol; Ethanol; Ethyl levulinate; Solid acid catalyst

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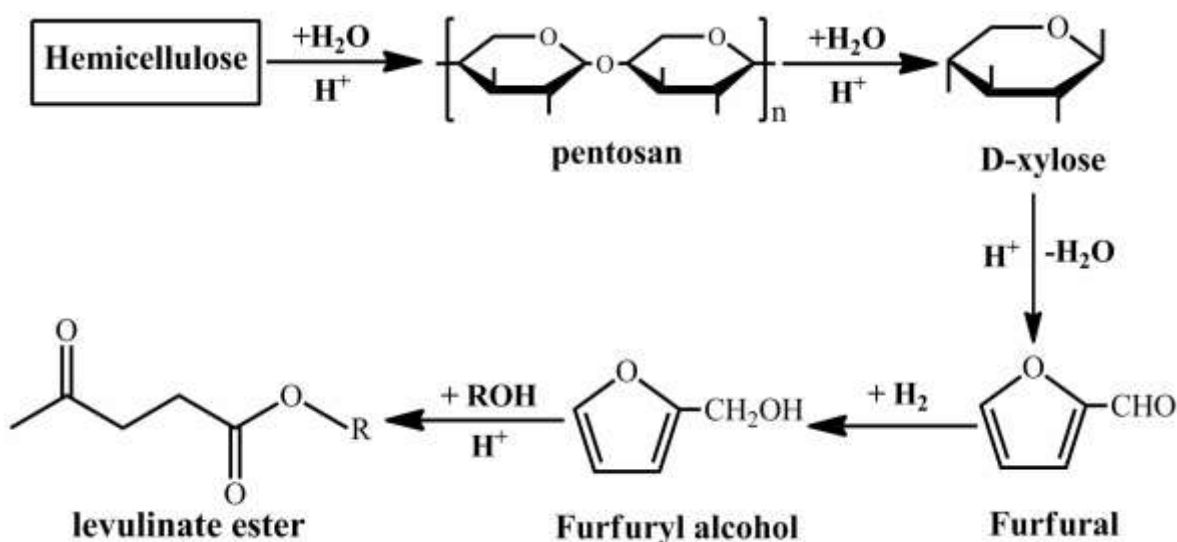
## INTRODUCTION

With diminishing fossil resources and rising concerns about global warming caused by greenhouse gas emissions, biomass is regarded as a promising alternative to non-renewable fossil resources for the sustainable supply of fuels and chemicals (Dodds and Gross 2007; Bozell 2010). One attractive option is the conversion of biomass to ethyl levulinate, a value-added chemical with numerous potential applications either in the flavoring and fragrance industry or as an additive for transportation fuels (Hayes 2009; Joshi *et al.* 2011; Wang *et al.* 2012). Additionally, ethyl levulinate is the preferred substrate for conversion into other viable biofuels, such as  $\gamma$ -valerolactone (Maldonado *et al.* 2012).

In the past few years, many researchers have obtained levulinate esters through esterification of levulinic acid with ethanol in the presence of sulfuric acid, solid acid, or immobilized lipases, and good yields have been achieved (Bart *et al.* 1994; Fernandes *et al.* 2012; Pasquale *et al.* 2012; Lee *et al.* 2010). However, as raw material for this purpose, levulinic acid is of high cost with its present uneconomic production from the acid hydrolysis of lignocellulosic biomass due to its high boiling point and activity (Ya'aini *et al.* 2012; Galletti *et al.* 2012; Chang *et al.* 2007). Increasing studies have reported the direct production of ethyl levulinate from biomass such as carbohydrates, cellulose, wood, bagasse, and wheat straw (Peng *et al.* 2011a, 2011b, 2012; Saravanamurugan *et al.* 2011; Garves 1988; Mao *et al.* 2011; Chang *et al.* 2012). In the aforementioned studies, sulfuric acid was the most commonly employed catalyst. Although it is inexpensive and highly active, the homogeneous acid has serious drawbacks in terms of separation and recycling, as well as equipment corrosion. However, solid acid catalysts can overcome these disadvantages. Among various solid acid

catalysts, zeolites and sulfated oxides have attracted considerable interests because of their strong acidity and excellent thermal stability (Peng *et al.* 2011a).

As can be seen from Scheme 1, furfuryl alcohol is easily obtained from the hydrogenation of furfural (Nagaraja *et al.* 2007; Merlo *et al.* 2009), and furfural is also a biomass derivative that can be produced from hemicellulose-rich biomass including corncob, corn stock, rice hull, and olive stones. Up to now, there are more than 400 furfural production plants in China, and the current output of furfural is about 700,000 tons per year worldwide (Mao *et al.* 2012; Zhang *et al.* 2012; Yemis and Mazza 2011). The conversion of furfuryl alcohol into levulinate esters has been regarded as an atom-economic and convenient method (Zhang *et al.* 2011) that has numerous advantages, such as mild reaction conditions, relatively inexpensive raw materials, and high product yield. However, less attention has been paid to this approach. Only a few researchers have obtained ethyl levulinate from furfuryl alcohol catalyzed by sulfuric acid, acidic ion-exchange resins, sulfonic acid functionalized ILs, aluminosilicates, and benzenesulfonic acid (Lange *et al.* 2009; Maldonado *et al.* 2012; Patrícia *et al.* 2013; Hengne *et al.* 2013). It should be pointed out that acidic ion-exchange resins, sulfonic acid functionalized ILs, and porous aluminosilicates are expensive due to their complex preparation processes, and sulfuric acid and benzenesulfonic are homogeneous acids. Furthermore, in these related studies, good ethyl levulinate yields (80 to 92.5%) have been achieved but under longer reaction time (24 h) or lower substrate concentration (1.0 wt%), which may be the hurdles to commercialization of ethyl levulinate.



**Scheme 1.** Reaction pathway for the conversion of hemicellulose into levulinate ester

In this work, a series of low-cost and environmentally benign zeolites (HY, HZSM-5, and H-mordenite) and sulfated oxides ( $\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{SnO}_2$ , and  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$ ) were selected as solid acid catalysts for the conversion of furfuryl alcohol into ethyl levulinate in ethanol. The effects of different reaction parameters and catalyst reuse on the reaction performance were studied.

## EXPERIMENTAL

### Materials

Ethyl levulinate (99%) and furfuryl alcohol (98%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). The manufacturer of the furfuryl alcohol (Sheng Quan Group, Jinan, China) used corncob as the biomass feedstock. All other reagents and chemicals (chemical pure) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification or treatment.

### Catalyst Preparation and Characterization

$\text{SO}_4^{2-}/\text{TiO}_2$ ,  $\text{SO}_4^{2-}/\text{ZrO}_2$ ,  $\text{SO}_4^{2-}/\text{SnO}_2$ , and  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$  were prepared according to the precipitation and impregnation method (Peng *et al.* 2011a). Additionally, sulfated oxides catalysts were obtained and labeled ST, SZ, SS, and SA, respectively. The H-form zeolites HY (Si/Al=5), H-mordenite (Si/Al=10), and HZSM-5 (Si/Al=25) were supplied by Nankai University Catalyst Co. Ltd. (Tianjin, China).

Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) and BET surface area measurement was performed on a Micromeritics Autochem II 2920 instrument. The surface area was determined by BET adsorption–desorption isotherms of  $\text{N}_2$  adsorption at 77 K.

The amount of acid in the catalysts was measured by  $\text{NH}_3$ -TPD. About 0.1 g of sample was pre-treated at 873 K for 0.5 h to eliminate all physisorbed and chemisorbed species, and then  $\text{NH}_3$  was adsorbed onto the catalyst for 1 h at 373 K. Finally, the TPD data was recorded when the sample was heated from 373 K to 873 K with a ramp of 15 K/min.

The element content of ST was determined by elemental analysis with an Elementar Vario EL.

### Catalytic Reaction Procedure

Catalytic reaction tests were performed in a 50 mL cylindrical stainless steel pressurized reactor made by PARR Instrument Company, USA. The reactor was heated in an adjustable electric stove. In a typical cycle, furfuryl alcohol (1 mL), ethanol (20 mL), and a given amount of solid acid catalyst were mixed in the reactor. The reactor was then heated to the desired temperature and stirred magnetically at 500 rpm. At the end of the reaction, the reaction mixture was cooled to room temperature. The liquid products and solid acid catalyst were separated by centrifugation at 10000 rpm for 3 min and analyzed.

In the reuse of ST catalyst experiments, at first the catalyst was recovered and reused without any treatment. On the other hand, the recovered catalyst was calcined for 3 h at 773 K in static air before every reuse. After being used three times, the reclaimed catalyst was regenerated by being re-soaked in 0.5 M  $\text{H}_2\text{SO}_4$  solution for 3 h and then filtered. The catalyst was dried for 12 h at 383 K and activated for 3 h at 773 K.

### Analysis of Products

The reaction products were analyzed by a GC (Agilent 7890A instrument) equipped with an HP-5 capillary column and a flame ionization detector (FID) at 543 K. The injection temperature was 523 K. The column temperature was maintained at 313 K for 4.0 min and then raised to 523 K at a ramp rate of 15 K/min.

The amount of ethyl levulinate was calculated using the external standard. The yield of ethyl levulinate on a molar basis was calculated as follows:

$$\text{Yield of ethyl levulinate (mol\%)} = \frac{\text{moles of ethyl levulinate produced}}{\text{moles of furfural alcohol converted}} \times 100 \quad (1)$$

## RESULTS AND DISCUSSION

### Comparison of Various Solid Acid Catalysts

A series of solid acid catalysts as well as a control treatment without catalyst were employed for the catalytic conversion of furfuryl alcohol into ethyl levulinate in ethanol at 473 K for 2.5 h with a catalyst load of 2.5 wt%. The catalytic activity results and characterization data of different catalysts are summarized in Table 1. In the absence of any catalyst, no ethyl levulinate was detected. All of the zeolites presented ethyl levulinate yields lower than 50 mol%, and the activities of the zeolites decreased in the order: HZSM-5, HY, and H-mordenite. Sulfated oxides presented high ethyl levulinate yields from 64.3 to 68.3 mol%. It is noteworthy that ST is the most active, presenting an ethyl levulinate yield of 68.3 mol%.

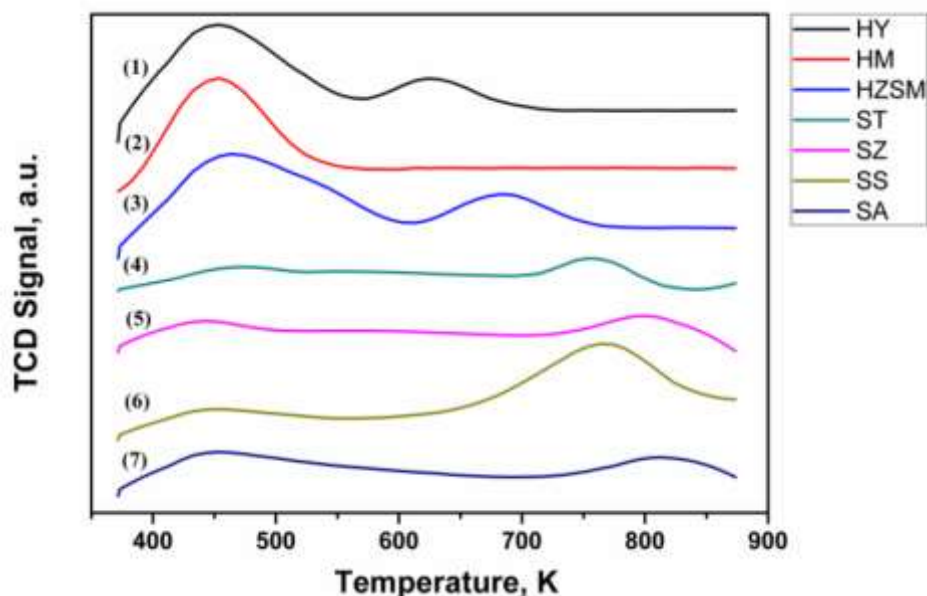
**Table 1.** Catalytic Activity Results and Characterization Data of Different Catalysts

Entry	Catalysts	EL yield <sup>a</sup> (mol%)	Surface area <sup>b</sup> (m <sup>2</sup> /g)	Acid amount <sup>c</sup> (mmol/g)	Peak temperature <sup>c</sup> (K)
1	HY	24.5	550.1	1.34	453, 626
2	H-mordenite	18.2	414.4	1.78	455
3	HZSM-5	48.7	335.3	1.42	466, 672
4	ST	68.3	129.9	0.54	476, 759
5	SZ	64.3	139.5	0.61	443, 803
6	SS	65.2	140.9	0.82	447, 773
7	SA	64.8	156.4	0.64	443, 825
8	No catalyst	0.0	-	-	-

<sup>a</sup> Reaction conditions: furfuryl alcohol, 1 mL; ethanol, 20 mL; catalyst, 0.5 g; temperature, 473 K; reaction time, 2.5 h; <sup>b</sup> determined by BET method; <sup>c</sup> obtained by NH<sub>3</sub>-TPD measurement

As can be seen in Table 1, the zeolites have a large surface area, which is characteristic of this type of material, and sulfated oxides have the smaller BET surface area from 129.9 to 154.6 m<sup>2</sup>/g. The NH<sub>3</sub>-TPD profiles of various catalyst samples are presented in Fig. 1. The acid content and peak temperature of various catalysts were determined according to the NH<sub>3</sub>-TPD profile. The acid content (corresponding to the amount of adsorbed NH<sub>3</sub>) was estimated by integrating the areas of NH<sub>3</sub>-TPD profiles. The desorption peak temperature indicated that the higher the peak temperature was, the stronger the acid was. The acid content of the zeolites was greater than 1 mM/g, and one or two NH<sub>3</sub> desorption peaks were observed. However, the highest peak temperature of

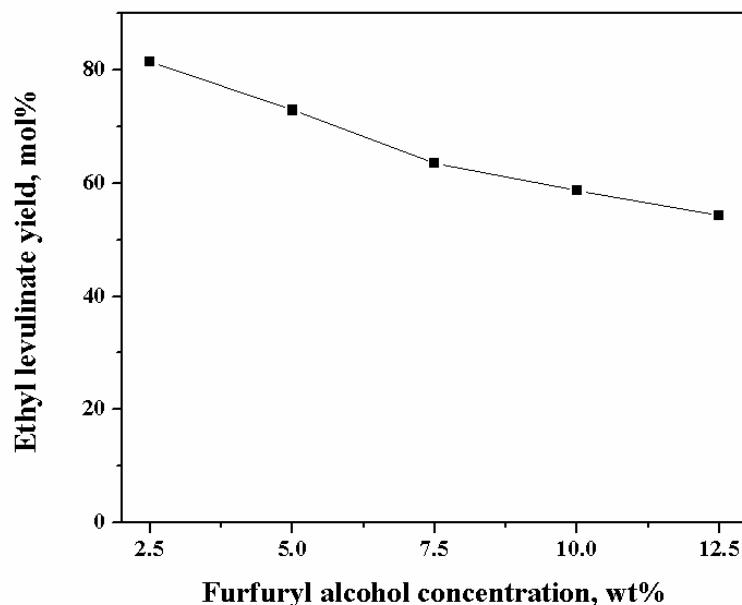
the zeolites was just 672 K, indicating that their acid sites had only weak acid strength. The acid content of the sulfated oxides ranged from 0.54 to 0.82 mM/g, and two  $\text{NH}_3$  desorption peaks were observed. The main peak temperature of the sulfated oxides was higher than 750 K. Hence, the sulfated oxides had mainly strong acid sites. The acid strength pattern for the peak temperature presented by these catalysts decreased in the order: SA, SZ, SS, ST, HZSM-5, HY, and H-mordenite. It is well known that the BET surface area, acid content, and acid strength are the important parameters of solid acid catalysts, which may greatly influence the reaction activity in acid-catalyzed alcoholysis. The comparison between the catalytic activity and the characterization data revealed that the activity had no correlation with BET surface area or acid content. Meanwhile these results suggested that the acid strength of the catalyst was a key factor for the formation of ethyl levulinate. That is to say, the strong acid site of the catalyst gives rise to high yield. However, furfuryl alcohol could be polymerized into a resin under the action of acid catalyst (Kim *et al.* 2011), so too strong acid site might be unfavorable for furfuryl alcohol alcoholysis. ST was the most active catalyst because of its moderately high acid strength. Thus, it was considered the suitable catalyst and was used in the subsequent exploration.



**Fig. 1.**  $\text{NH}_3$ -TPD profiles of different catalysts (1) HY; (2) H-mordenite; (3) HZSM-5; (4)  $\text{SO}_4^{2-}/\text{TiO}_2$ ; (5)  $\text{SO}_4^{2-}/\text{ZrO}_2$ ; (6)  $\text{SO}_4^{2-}/\text{SnO}_2$ ; (7)  $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$

### Influence of Initial Furfuryl Alcohol Concentration

In practical applications, it is desirable to use reactants at high concentrations, and so the initial furfuryl alcohol was investigated. As shown in Fig. 2, when the initial

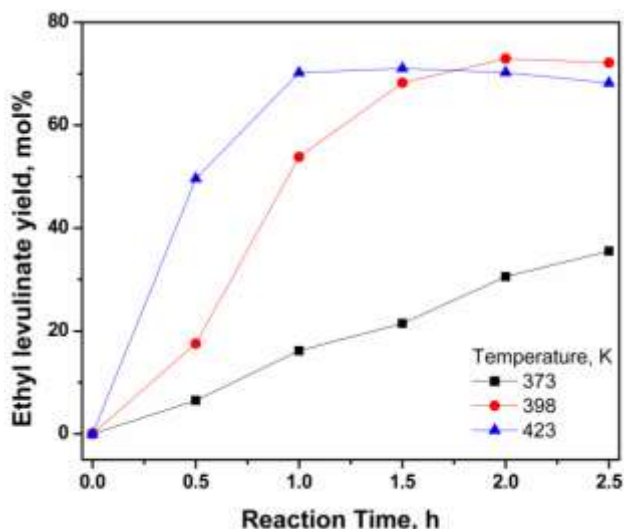


**Fig. 2.** Influence of reaction temperature on ethyl levulinate yield using ST as catalyst (Reaction conditions: temperature, 398 K; time, 2 h; catalyst loading, 2.5 wt%)

furfuryl alcohol concentration was 2.5 and 5 wt%, the yield of ethyl levulinate was 81.5 and 72.9 mol%, respectively. However, when the initial concentration of furfuryl alcohol was further increased from 7.5 to 12.5 wt%, ethyl levulinate yield began to decrease and reached down to 54.4 mol%. The losses in ethyl levulinate yield with increasing the initial furfuryl alcohol concentration were most likely due to self-polymerization of furfuryl alcohol and formation of other by-products (Maldonado *et al.* 2012; Patrícia *et al.* 2013). Taking the cost and the efficiency into consideration, 5 wt% initial concentration should be suitable for the production of ethyl levulinate from furfuryl alcohol.

### Influence of Reaction Temperature

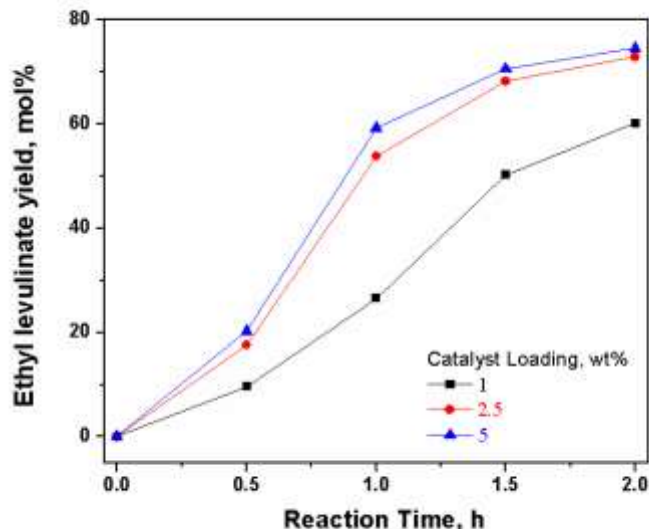
It is well known that temperature has a tremendous effect on both reaction rate and yield. The experiments were conducted at 373, 398, and 423 K with different residence times to discover the optimum conditions for increasing the ethyl levulinate yield. As shown in Fig. 3, when the reaction was performed at 373 K, only 35.5% ethyl levulinate yield was achieved in 2.5 h. When the reaction temperature was elevated to 398 K, the maximum yield of ethyl levulinate was increased to 72.9 mol% in 2 h. Moreover, at 398 K and 423 K, when ethyl levulinate yields reached their peak values, longer reaction time resulted in lower yield of ethyl levulinate, which indicated that ethyl levulinate might be decomposed to some extent and more undesired byproducts such as soluble polymers and insoluble humins were formed under higher temperature (Milan *et al.* 2014). Therefore, 398 K was used as an appropriate reaction temperature.



**Fig. 3.** Influence of reaction temperature on ethyl levulinate yield using ST as catalyst (Reaction conditions: catalyst loading, 2.5 wt%)

### Influence of Catalyst Loading

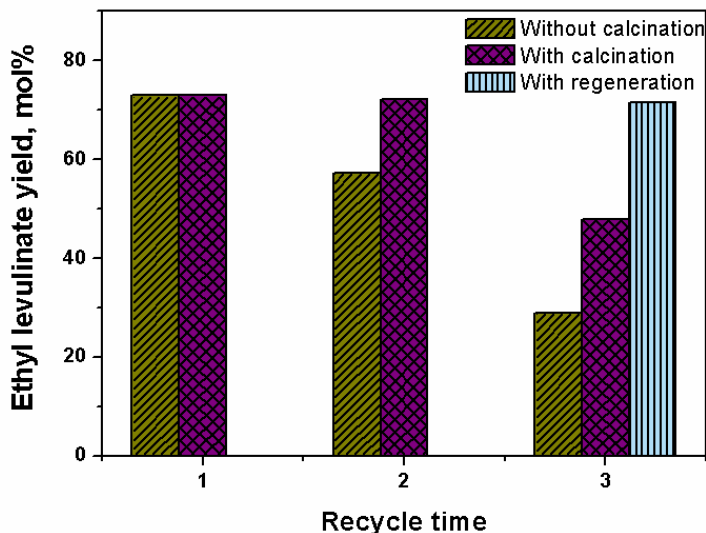
As an important parameter, the catalyst loading must be optimized to increase the ethyl levulinate yield. The experiments were conducted at three different catalyst loadings (1.0, 2.5, and 5.0 wt%), and the results are presented in Fig. 4. When the reaction time was 2.0 h, ethyl levulinate yield was only 60.1 mol% when 1 wt% ST was used. Increasing the amount of ST to 2.5 wt% resulted in an increase in ethyl levulinate yield to 72.9 mol%. But when the catalyst loading dosage doubled to 5.0 wt%, the yield of ethyl levulinate increased only 1.7 mol%. The final yield of ethyl levulinate did not change significantly between the catalyst loadings of 2.5 and 5 wt%, which could be ascribed to the fact that the equilibrium conversions for the formation of ethyl levulinate were almost reached by 2 h (Peng *et al.* 2011b). Thus, 2.5 wt% catalyst loading dosage was judged to be optimal.



**Fig. 4.** Influence of catalyst load on ethyl levulinate yield using ST as catalyst (Reaction conditions: temperature, 398 K)

### Catalyst Reuse Cycle

The stability and reusability of the catalyst are extremely important considerations to reduce production costs in practical biomass transformation. After the reaction was completed, the ST was separated from the liquid mixture and used in the next reaction experiment. The results of ethyl levulinate yield are presented in Fig. 5.



**Fig. 5.** The reuse of ST catalyst (Reaction conditions: temperature, 398 K; time, 2 h; catalyst loading, 2.5 wt%)

When the catalyst was reused without calcination, an obvious decrease of the ethyl levulinate yield from 72.9 to 28.9 mol% was observed after the third cycle. However, when the catalyst was reused after calcination, the yield of ethyl levulinate in the second cycle was almost the same as that in the first cycle, but it decreased to 47.8 mol% in the third cycle. After being used three times, the reclaimed catalyst was regenerated by re-soaking in  $\text{H}_2\text{SO}_4$  solution, and the yield of ethyl levulinate was restored to 71.5 mol%, which was close to that of the fresh catalyst (72.9 mol%).

The amounts of carbon and sulfur in the reclaimed catalysts are summarized in Table 2. It can be observed that the carbon content of ST without calcination increased from 0.11 to 2.37 wt% after three cycles, which indicated that ST adsorbed the humins formed during the reaction. On the other hand, the sulfur content of calcined ST reduced from 2.79 to 0.64 wt% after three cycles, and the sulfur loss might be caused by solvation during the alcoholysis reaction. The comparison between the catalytic activity and the element content of ST indicated that carbon deposition and sulfur loss was the predominant reason for the reduction of ethyl levulinate yield. Therefore, the deactivated catalyst could be regenerated by calcination to remove deposited carbon and by re-soaking in  $\text{H}_2\text{SO}_4$  solution to increase the sulfur ( $\text{SO}_4^{2-}$ ) content.



**Table 2.** Carbon and Sulfur Contents of the Reclaimed ST Catalysts

Recycle time	Carbon Content <sup>a</sup> (wt%)			Sulfur Content <sup>a</sup> (wt%)		
	Without calcination	With calcination	With regeneration	Without calcination	With calcination	With regeneration
1	0.11	0.11	-	2.79	2.79	-
2	1.14	0.04	-	2.18	1.91	-
3	2.37	0.06	0.09	1.71	0.64	2.44

<sup>a</sup> Determined by elemental analysis.

## CONCLUSIONS

1. A catalytic process for converting biomass-derived furfuryl alcohol into ethyl levulinate using eco-friendly heterogeneous catalysts was developed.
2. Among all the solid acid catalysts, sulfated metal oxides (especially ST) were found to be potential catalysts. The yield of ethyl levulinate could reach 74.6 mol% under the optimal experimental conditions.
3. The catalyst reclaimed through calcination was found to retain good catalytic activity (47.8 mol%) after three cycles, and it was easily reactivated by calcination and re-soaking in H<sub>2</sub>SO<sub>4</sub> solution.
4. Ethyl levulinate is attracting more and more attention recently, which can be attributed to its potential applications as biofuel or biorefinery feedstock. The assembling pathway of ethyl levulinate converted from furfuryl alcohol over ST, which is employed in this study, may break through the bottleneck and promote its applications.

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