

# Esterification of Levulinic Acid into Ethyl Levulinate Catalyzed by Sulfonated Bagasse-carbonized Solid Acid

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A sulfonic carbon-based catalyst (C-SO<sub>3</sub>H) was successfully prepared by sulfonating incompletely carbonized sugarcane bagasse. The optimized catalyst of high activity in the esterification of levulinic acid (LA) with ethanol was produced under sulfonation at 150 °C for 15 h with a 75 mL/g sulfonation ratio. The prepared catalysts were characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) analysis, scanning electron microscopy (SEM), and elemental analysis (EA). The bagasse-carbonized catalyst was porous, and the porous structure remained unchanged after sulfonation treatment. Moreover, the introduced acidic group was the catalytic center. A high yield of ethyl levulinate (ELA) of 88.2% was obtained at 120 °C for 9 h. The sulfonic carbon-based catalyst could be reused at least five times and still exhibited great stability. The application of the sulfonic carbon-based catalyst was not only the effective use of biomass resources but also promoted the production of various high value chemicals.

*Keywords:* Sugarcane bagasse; Sulfonation; Levulinic acid; Esterification

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## INTRODUCTION

With increasing world energy consumption, non-renewable energy resources are inevitably exhausted. Therefore, research on biomass fuels or high-grade chemicals is accelerating (Zhou *et al.* 2011; Jadhav *et al.* 2013; Polykarpos *et al.* 2015). As a chemical with industrial application value, alkyl levulinate is used in many fields such as coating, plasticizer, and medicine (Corma *et al.* 2007; Zhang *et al.* 2012). Especially, ethyl levulinate is considered to be one of the most valuable fuel additives due to their high lubricity, flow properties, and flash point stability (Démolis *et al.* 2014; Bohre *et al.* 2015). In addition, as a potential biomass-derived platform molecule, ethyl levulinate can be used as a substrate in a variety of reactions generating numerous industrial chemicals such as valerolactone, bisphenol ester, and vinyl levulinate, *etc.*

The catalysts employed in the esterification of levulinic acid (LA) have evolved from the traditional mineral acids (Peng *et al.* 2012; Xu *et al.* 2013) to solid acid catalysts. Solid acid catalysts are very popular due to their environmental protection and renewability, such as zeolite molecular sieve (Zhou *et al.* 2015; Sankar *et al.* 2016) and solid super acid (Peng *et al.* 2011). In fact, the solid acid catalysts either contained acidic sites itself or was pretreated to enhance the acidity, for example, many porous carriers were modified into solid acid catalyst by loading acidic material or sulfonation treatment. A sulfated Si-doped ZrO<sub>2</sub> solid acid catalyst has been reported to investigate the relationships between the structural properties and catalytic performances (Kuwahara *et al.* 2014). The catalysts prepared by sulfonating pyrolysis char with concentrated or fuming

sulfuric acids have been compared by the result of transesterification of vegetable oils and esterification of free fatty acids (Dehkhoda *et al.* 2010.) Sulfonation treatment is one of the effective means to improve the catalytic performance of solid acid catalysts (Melero *et al.* 2013; Chang *et al.* 2015; Unlu *et al.* 2017). Considering the expensive price or complicated preparation process of popular catalysts such as molecular sieves, a sulfonated carbon catalyst showing cheapness and high performance is more widely used in the esterification of free fatty acids (Wang *et al.* 2014), caprylic acid (Mo *et al.* 2008) and LA (Oliveira and Silva 2014; Pileidis *et al.* 2014).

Sugarcane bagasse is an agricultural residue that is usually disposed of by burning, which is a waste of resources and pollutes the environment. A highly active bagasse-derived solid acid catalyst has been successfully prepared from this material, with the result of a high yield of around 95% in esterification of oleic acid with methanol (Lou *et al.* 2012). It has been found that the synthesized sugarcane bagasse catalyst can be highly active for hydrolysis of cellulose, delignified sugarcane bagasse, and cassava starch (Namchot *et al.* 2014). For this paper, a promising carbon-based solid acid catalyst was prepared by sulfonating incompletely carbonized sugarcane bagasse and was applied in the esterification reaction of LA with ethanol. Sugarcane bagasse was prepared as the solid acid catalyst and used in the esterification of LA with ethanol. The goals of this research were to alleviate environmental problems and resource waste caused by sugarcane bagasse and to generate new research ideas for the synthesis of biomass energy chemicals.

## EXPERIMENTAL

### Raw Materials

Levulinic acid and ethyl levulinate were purchased from Aladdin Reagent (Shanghai, China). Ethanol, methylbenzene, and sulfuric acid were purchased from Guangdong Guanghua Reagent (Guangzhou, China). All the chemicals were of analytical grade. Sugarcane bagasse raw materials were taken from local factories in Guangzhou.

### Catalyst Preparation

#### *Carbonization of sugarcane bagasse*

Prior to carbonization, sugarcane bagasse was milled to 150 to 180  $\mu\text{m}$  particles and dried overnight. The milled sugarcane bagasse was extracted using methylbenzene-ethanol (2:1 v/v) for 6 h at 140  $^{\circ}\text{C}$ . The dry extractives were placed in a tubular furnace and carbonized at 450  $^{\circ}\text{C}$  under a nitrogen flow of 70 to 80 mL/min. The product was incompletely carbonized black sugarcane bagasse powder (CSB).

#### *Sulfonation of carbonized sugarcane bagasse powder*

For the sulfonation determination, a certain volume of concentrated sulfuric acid (98%) was added to 1 g of CSB in a round bottom flask for a desired sulfonation ratio (mL/g). The mixture was heated at 150  $^{\circ}\text{C}$  for a given sulfonation time (h). Following the reaction, the mixture was added to cool distilled water and then washed repeatedly with hot distilled water until the wash water was free from sulfate ions (Dehkhoda *et al.* 2010). The samples were vacuum-dried at 60  $^{\circ}\text{C}$  for 16 to 20 h and denoted as C-SO<sub>3</sub>H(x, y) (x: sulfonation ratio, y: sulfonation time).

## Catalytic Reaction

The esterification reaction of 0.05 mol levulinic acid with 0.25 mol ethanol was accomplished in a round bottom flask fitted with a reflux condenser. The single-factor experiment was optimized for sulfonation ratio, sulfonation time, the molar ratio of EtOH/LA, the dosage of the catalyst, the reaction temperature, and the reaction time. When the reaction was over, the products of the reaction were analyzed by a gas chromatograph (Agilent 6890) equipped with a HP-INNOWAX capillary column (30 m × 0.25 mm × 0.25 μm) and a FID detector. The column temperature was held at 100 °C for 2 min, raised to 230 °C at 15 °C/min, and then kept at 230 °C for 1 min. To investigate the reusability of the catalyst, the esterification reaction was performed under the optimized reaction conditions in five consecutive catalytic runs. After each catalytic cycle, the catalyst was recovered by filtration, washed with water, and dried overnight.

## Catalyst Characterization

The X-ray diffraction (XRD) patterns of samples were examined in a Bruker D8 Advance diffractometer (Karlsruhe, Germany) using Cu K $\alpha$  radiation. The Fourier transform infrared (FTIR) measurements were carried out on a Tensor-27 FTIR spectrometer (Bruker, Germany) with the spectral resolution of 4 cm<sup>-1</sup>. The elemental analysis (EA) of the catalysts was determined by the use of a Vario EL cube element analysis instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany). The scanning electron microscopy (SEM) images were recorded in an EVO 18 (CARL ZEISS, Germany) microscope.

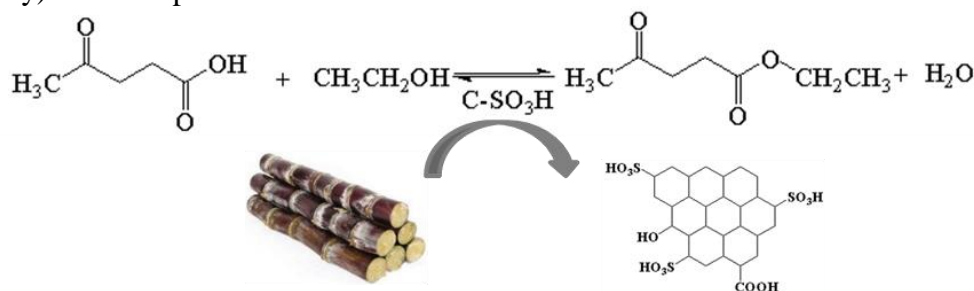


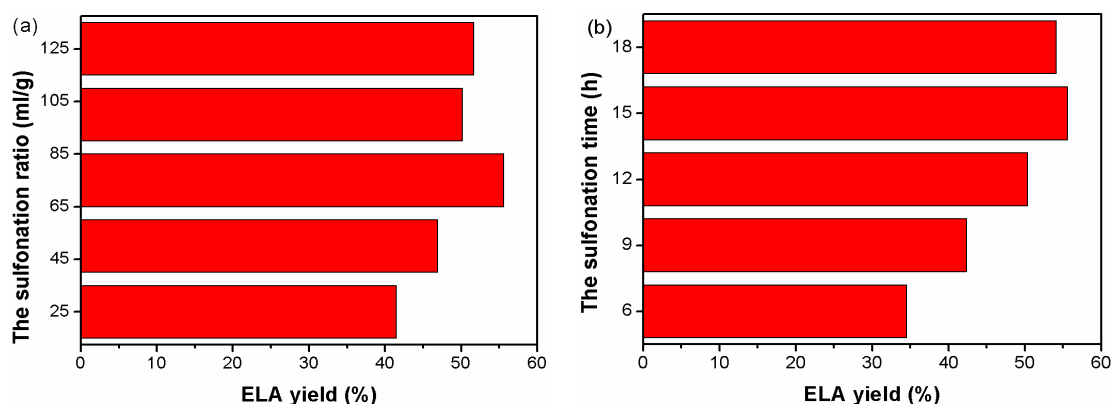
Fig. 1. The esterification reaction of levulinic acid with ethanol catalyzed by C-SO<sub>3</sub>H

## RESULTS AND DISCUSSION

### Effect of Catalyst Preparation Conditions on Esterification of LA with Ethanol

The catalyst preparation conditions influence the activity of the carbon-based solid acid catalyst, which is simultaneously associated with the esterification effect of LA. The two parameters of sulfonation ratio and sulfonation time were studied for preparing the optimal catalyst.

As shown in Fig. 2(a), the ELA yield increased with the increasing sulfonation ratio from 25 mL/g to 75 mL/g. When the sulfonation ratio was 75 mL/g, the ELA yield was the highest at 55.6%; when the sulfonation ratio was above 75 mL/g, the ELA yield began to decrease. Figure 2(b) shows that the ELA yield was positively affected by the sulfonation time to some extent. Compared with the ELA yield from 12 h to 15 h, it increased more evidently from 34.5% at 6 h to 50.3% at 12 h. The best sulfonation time was 15 h because of the decline of the ELA yield at 18 h. The optimal catalyst with the highest activity was sulfonated at 15 h with a 75 mL/g sulfonation ratio.



**Fig. 2.** The effect of the sulfonation ratio (a) and sulfonation time (b) on the esterification of LA with ethanol. Reaction conditions: 5:1 molar ratio of EtOH/LA, 0.3 g catalyst, 120 °C, 3 h

According to the contrast experiment, sulfonation and carbonization treatments were the root causes of the effectiveness of catalyst (Table 1). The SB-SO<sub>3</sub>H and the AC-SO<sub>3</sub>H was prepared by the same sulfonation method with C-SO<sub>3</sub>H. No sulfonation resulted in the absence of product formation, and the carbonization treatment improved the product selectivity. Moreover, the bagasse-based catalyst worked better than that of purchased activated carbon in such conditions.

**Table 1.** Yield of ELA Over Various Catalysts

Entry	Sample	LA Conversion <sup>a</sup> (%)	ELA Yield <sup>a</sup> (%)
1	CSB	3.1%	0
2	SB-SO <sub>3</sub> H <sup>b</sup>	97.3%	67.7%
3	C-SO <sub>3</sub> H	92.5%	88.2%
4	AC-SO <sub>3</sub> H <sup>c</sup>	100%	47.7%

<sup>a</sup> Reaction conditions: 5:1 molar ratio of EtOH/LA, 0.3 g catalyst, 120 °C, 9 h

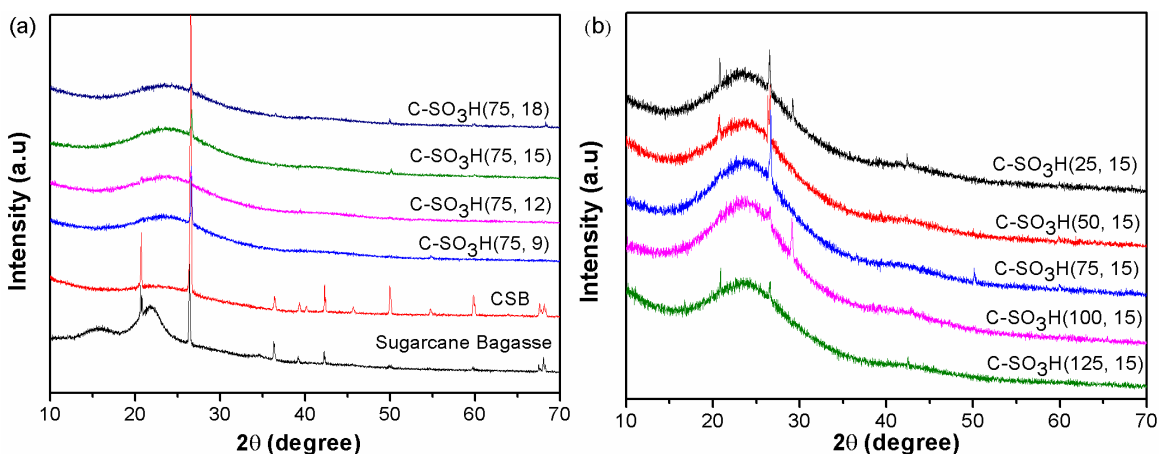
<sup>b</sup> The catalyst prepared by sulfonating sugarcane bagasse directly

<sup>c</sup> The catalyst prepared by sulfonating purchased activated carbon

## Catalyst Characterization

### XRD analysis

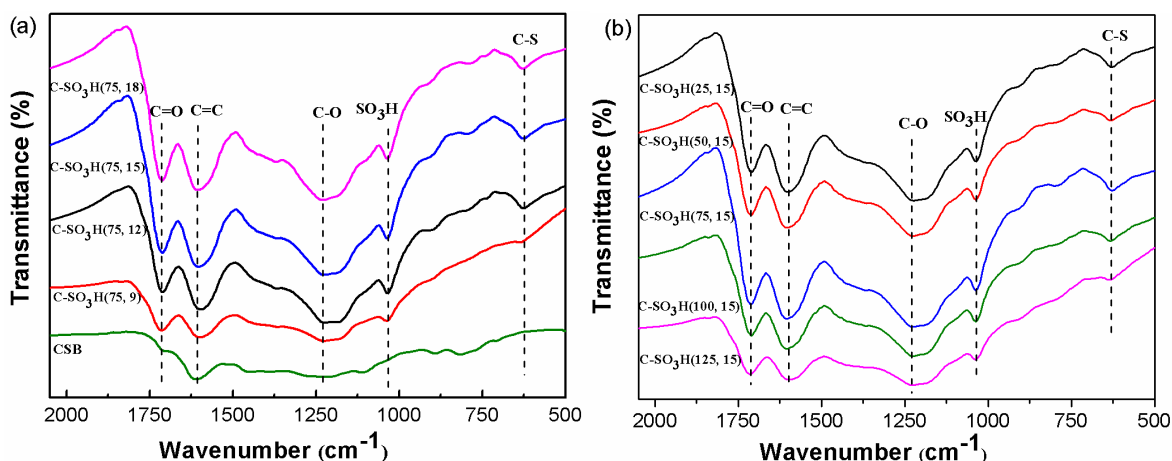
Figure 3(a) shows the XRD patterns of sugarcane bagasse, CSB, and C-SO<sub>3</sub>H prepared at different sulfonation times. A characteristic and strong peak at  $2\theta = 22.5^\circ$  was found in sugarcane bagasse, but it formed a broad diffraction peak ( $2\theta = 15$  to  $35^\circ$ ) in CSB after carbonization, indicating that carbonization can reduce the crystallinity of cellulose in sugarcane bagasse (Li *et al.* 2018). Observing the XRD pattern of the sulfonated catalyst, the broad diffraction peak which was attributable to amorphous carbon remained after sulfonation (Lou *et al.* 2012). The sulfonation time had no obvious effect on the structure of the catalyst. Figure 3(b) shows the XRD patterns of C-SO<sub>3</sub>H prepared at different sulfonation ratios. The five samples had a wide diffraction peak ( $2\theta = 15$  to  $35^\circ$ ), which was consistent with the results of Fig. 3(a). However, a weak diffraction peak at  $2\theta = 35$  to  $50^\circ$  was visible because of the generation of a new carbonized structure.



**Fig. 3.** XRD patterns of (a) sugarcane bagasse, CSB, and C-SO<sub>3</sub>H prepared under different sulfonation time; (b) C-SO<sub>3</sub>H prepared under different sulfonation ratio

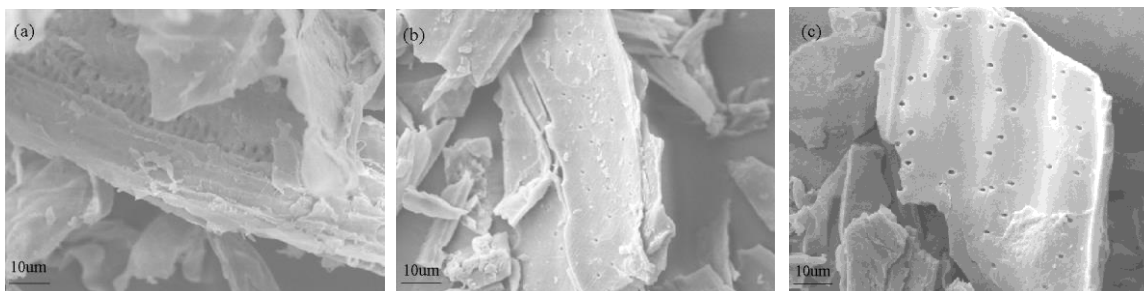
The FTIR spectra of CSB and C-SO<sub>3</sub>H prepared at different sulfonation times were displayed in Fig. 4(a). At first, the peak at around 1605 cm<sup>-1</sup> was obvious in five samples due to the stretching of C=C groups. As the sulfonation time increased, the intensity of the peak assigned to C=O groups at around 1709 cm<sup>-1</sup> was raised. In addition, because of the sulfonation treatment, three new peaks at around 1226 cm<sup>-1</sup>, 1038 cm<sup>-1</sup>, and 628 cm<sup>-1</sup> were generated, corresponding to the stretching vibration of C-O, SO<sub>3</sub>H, and C-S, respectively. These results fully demonstrated that the sulfonic acid groups were successfully grafted into CSB which itself had no catalytic effect. Compared with intensity of the characteristic peaks in the C-SO<sub>3</sub>H (75, 9) catalyst, it was significantly enhanced in the C-SO<sub>3</sub>H (75, 15), which may be responsible for the high activity of the C-SO<sub>3</sub>H (75, 15) catalyst. Finally, it was clearly observed that the sulfonation time influenced the peaks intensity, explaining the effect of sulfonation time on the yield of ELA. The FTIR spectra of C-SO<sub>3</sub>H prepared at different sulfonation ratios are displayed in Fig. 4 (b).

#### FTIR analysis



**Fig. 4.** FT-IR spectra of various samples. (a) CSB and C-SO<sub>3</sub>H prepared under different sulfonation times; (b) C-SO<sub>3</sub>H prepared under different sulfonation ratios

By the analysis methods and results discussed above, it can be concluded that the sulfonation treatment introduced the sulfonic acid groups into CSB and the sulfonation ratio had an effect on the yield of ELA. The peak intensity owing to C-S exhibited a big change because of increasing sulfonation ratio. When the sulfonation ratio exceeded 75 mL/g, the peak intensity went down resulting in low yield of ELA.



**Fig. 5.** SEM images of (a) and (b) CSB, (c) C-SO<sub>3</sub>H (75, 15), and (d) C-SO<sub>3</sub>H (75, 15) (used 5th)

#### SEM analysis

According to the SEM images shown in the Fig. 5, the three samples of CSB, C-SO<sub>3</sub>H (75, 15), and C-SO<sub>3</sub>H (75, 15) of recycling five times were porous material. Compared with CSB, the C-SO<sub>3</sub>H (75, 15) catalyst had no great change in topography, even if it was recycled five times.

#### EA analysis

To determine the change of the element composition of the catalyst during the preparation process, EA was carried out on sugarcane bagasse, CSB, and C-SO<sub>3</sub>H (75, 15), as shown in Table 2. The main loss of elements were H and O during the carbonization process, and there was no sulfur in sugarcane bagasse and CSB. However, the sulfur content increased after sulfonation, which was the most direct evidence of the success of the sulfonate group introduction.

**Table 2.** Element Composition of Three Different Samples

Entry	Sample	Content (wt %)				
		C	H	O <sup>a</sup>	N	S
1	Sugarcane Bagasse	47.18	6.25	46.30	0.27	0
2	CSB	75.33	4.80	19.49	0.38	0
3	C-SO <sub>3</sub> H(75, 15)	53.18	3.65	41.06	0.36	1.75

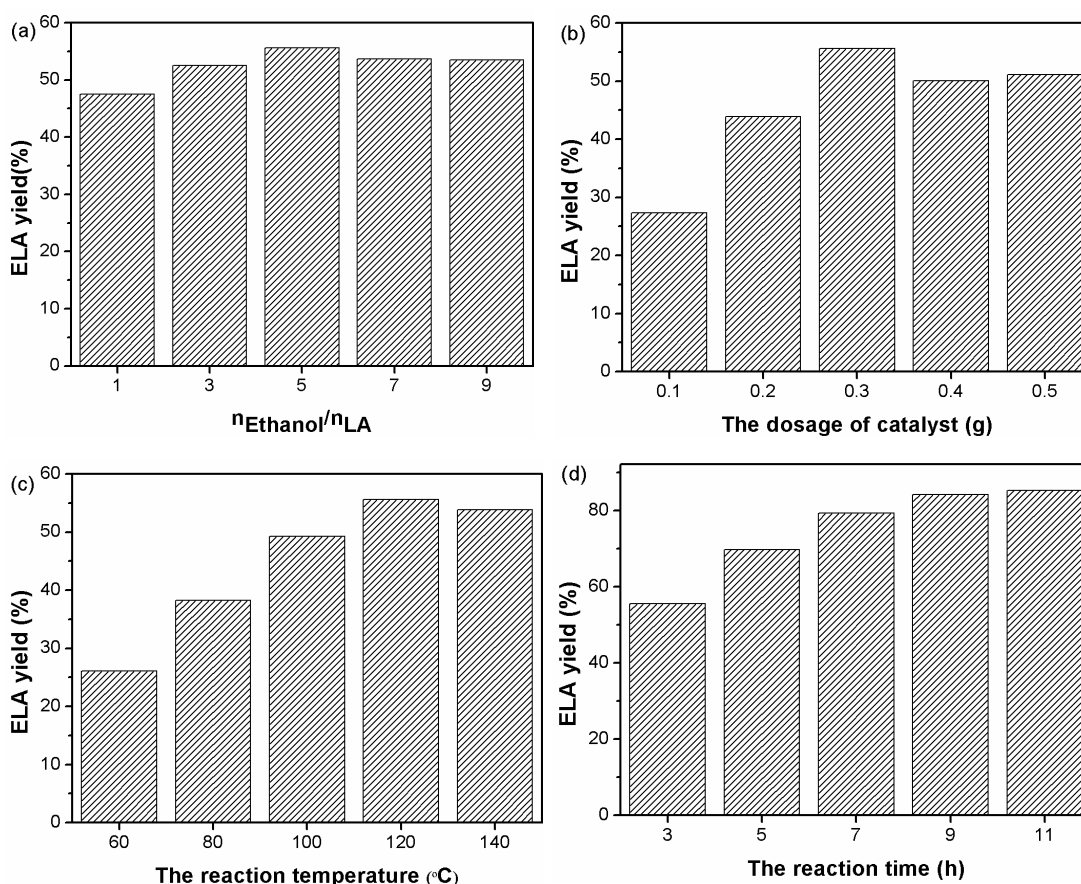
$$^a\text{O} = 100 - \text{C} - \text{H} - \text{N} - \text{S}$$

In addition, the sulfur content of the different catalysts was determined by EA (Table 3). Acid-base titration was conducted to estimate the surface acid amount of different catalysts (Table 3). Obviously, the catalyst preparation conditions directly affected the sulfur content and acid amount which in turn affected the ELA yield. No acid amount was detected on the CSB catalyst consistent with the result in the Table 1 (entry 1). At the same time, there were just two obvious absorption peaks assigned to C=C and C=O of the CSB in the Fig. 4(a). The sulfur content and acid amount rose with the increasing sulfonation ratio and sulfonation time. Considerable acid amount was obtained at the C-SO<sub>3</sub>H (75, 15) catalyst, meanwhile, the ELA yield reached the maximum. As shown in Table 3 (entry 9 to entry 10), the sulfur content was high along with a drop in

acidity, which may be because excess sulfuric acid was not conducive to the introduction of the sulfonic acid group. It explained why the yield of ELA started to decrease when the sulfonation ratio was above 75 mL/g.

**Table 3.** Surface Acid Amount of Catalysts Prepared Under Different Conditions

Entry	Sample	S Content (wt %)	Surface Acid Amount (mmol g <sup>-1</sup> )
1	CSB	0	0
2	C-SO <sub>3</sub> H (75, 6)	1.51	0.84
3	C-SO <sub>3</sub> H (75, 9)	1.53	0.92
4	C-SO <sub>3</sub> H (75, 12)	1.61	1.04
5	C-SO <sub>3</sub> H (75, 15)	1.75	1.20
6	C-SO <sub>3</sub> H (75, 18)	1.76	1.24
7	C-SO <sub>3</sub> H (25, 15)	1.59	0.96
8	C-SO <sub>3</sub> H (50, 15)	1.62	1.02
9	C-SO <sub>3</sub> H (100, 15)	1.83	1.08
10	C-SO <sub>3</sub> H (125, 15)	1.80	1.12
11	C-SO <sub>3</sub> H (75, 15) <sup>1st</sup>	1.70	1.12
12	C-SO <sub>3</sub> H (75, 15) <sup>5th</sup>	1.67	1.10



**Fig. 6.** The influences of (a) the molar ratio of EtOH/LA (with catalyst dosage 0.3 g, reaction temperature 120 °C, and reaction time 3 h), (b) the dosage of catalyst (with molar ratio of EtOH/LA 5:1, reaction temperature 120 °C, and reaction time 3 h), (c) the reaction temperature (with molar ratio of EtOH/LA 5:1, catalyst dosage 0.3 g, and reaction time 3 h), and (d) the reaction time (with molar ratio of EtOH/LA 5:1, catalyst dosage 0.3 g, and reaction temperature 120 °C) on the esterification of LA with ethanol

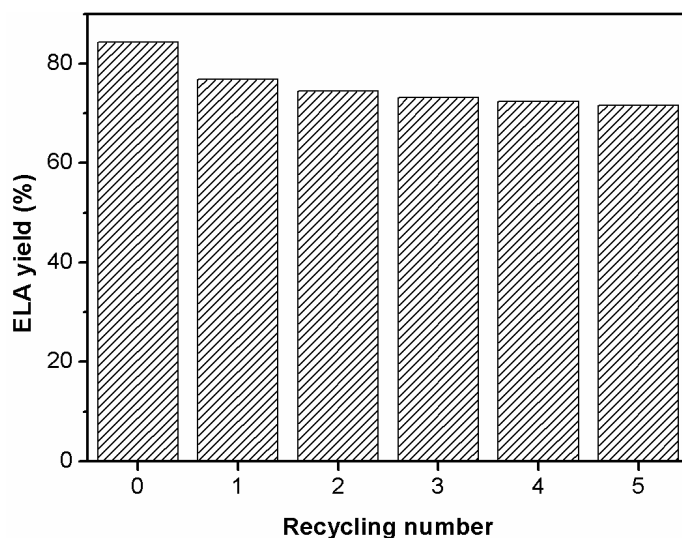
### Catalyst Performance in the Single-factor Experiment

The esterification reaction is a reversible process that is promoted by adding more reactant. Therefore, the parameter of EtOH/LA molar ratio was explored. The maximum yield of ELA was 55.6% at 5:1 EtOH/LA molar ratio; the yield of ELA was slightly influenced with rising EtOH/LA molar ratio in these reaction conditions (Fig. 6 (a)). Excess ethanol reduced contact of the reactant with the catalyst and resulted in the formation of ether by-products. As clearly displayed in Fig. 6 (b), there was an increased ELA yield from 27.4% at 0.1 g to 55.6% at 0.3 g, which is explained by an increase in the acidity of the reaction system. Potentially, the ELA yield dropped because of the reduction of the contact between reactant molecules. Therefore, it should be noted that 0.3 g (2 wt% of the reactant mass) was the optimum dosage of the catalyst.

The reaction temperature played an important role in the generation of ELA, and the best reaction temperature was 120 °C (Fig. 6 (c)). High temperature promoted the movement of reactant molecules, and water vaporization accelerated the reaction. But the higher temperature caused the ethanol evaporation rate to be significantly higher than the water evaporation rate, which reduced the intermolecular contact and was not conducive to the reaction. The effect of the reaction time on the esterification of LA with ethanol was investigated at 3, 5, 7, 9, and 11 h (Fig. 6 (d)). Increased time led to greater production of ELA. When the reaction time reached 9 h, the yield of ELA was 84.2%. The ELA yield increased by only 1.1% after 11 h, and the reaction was basically balanced. Consequently, the optimum reaction time was 9 h under above reaction conditions.

### Catalyst Recycling

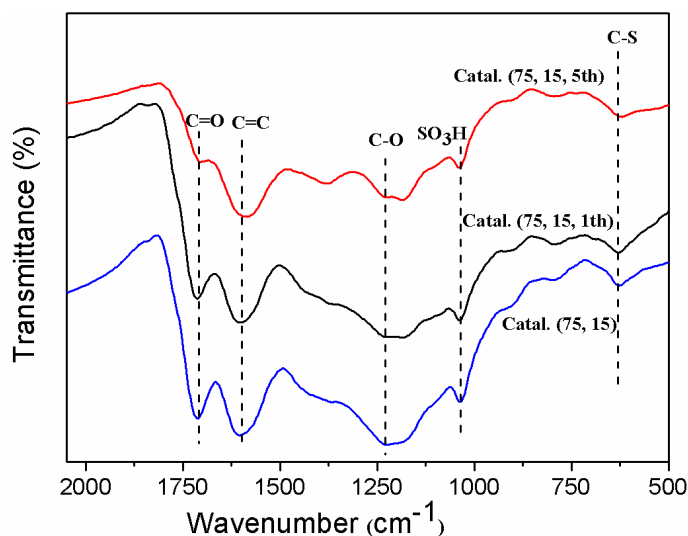
The recycling performance of a catalyst is an important indicator of its quality. As shown in Fig. 7, the yield of ELA dropped almost 8%, from 84.2% to 76.8%, in the first cycle. A possible reason was that some unstable acidic sites remained on the catalyst surface after the catalyst was repeatedly washed with deionized water, and most of the unstable acidic sites were lost during the first cycle reaction, corresponding to decreased acidity in Table 3 (entry 5 and entry 11). The yield of ELA decreased slightly in the next four recycling processes.



**Fig. 7.** Recyclability of C-SO<sub>3</sub>H catalyst on LA esterification. Reaction conditions: 5:1 molar ratio of EtOH/LA, 0.3 g C-SO<sub>3</sub>H (75, 15) catalyst, 120 °C, 9 h



The peaks produced by sulfonation treatment of the C-SO<sub>3</sub>H (75, 15) catalyst recycled five times are observed in Fig. 8. Furthermore, the total acid strength of the catalyst recycled five times was outstanding, as shown in Table 3 (entry 12). The results above suggested that the sulfonic acid groups were retained after the reaction. The value was 71.5% in the fifth cycle, which indicated that the catalyst had a good recycling performance.



**Fig. 8.** FT-IR spectra of C-SO<sub>3</sub>H (75, 15) (fresh), C-SO<sub>3</sub>H (75, 15) (used 1st) and C-SO<sub>3</sub>H (75, 15) (used 5th)

## CONCLUSIONS

1. A sulfonic carbon-based catalyst was prepared by the carbonization-sulfonation method along with the optimization of preparation conditions including sulfonation ratio and sulfonation time. The optimal catalyst was prepared at a sulfonation ratio of 75 mL/g and a sulfonation time of 15 h.
2. The introduction of sulfonic acid groups played a crucial role in the effectiveness of the catalysts, and the yield of ELA reached 88.2% under the conditions of 120 °C, 9 h, 0.3 g catalyst dosage, and 5:1 molar ratio of EtOH/LA.
3. The recycling performance of C-SO<sub>3</sub>H was outstanding, reflecting the considerable yield of ELA after five successive cycles of reuse.

## ACKNOWLEDGMENTS

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