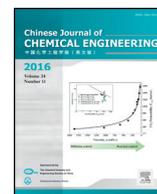




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Article

Glucose-derived solid acids and their stability enhancement for upgrading biodiesel *via* esterification☆

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ABSTRACT

Utilization of biomass-derived materials or chemicals plays a significant role in reducing the dependence of unsustainable resources of petroleum and coal. A series of sulfonated glucose-derived solid acids (SGSAs) were developed in this study through a one-step method. These catalysts were characterized by XRD, FT-IR, SEM, and BET to determine their physicochemical properties, and their acid content was measured by acid–base titration. The catalytic performances of SGSA catalysts were evaluated in two esterification reactions: propionic acid or oleic acid with methanol (a typical reaction to upgrade biodiesel). Conversion of oleic acid and selectivity of methyl oleate can reach as high as 93.3% and 94.7% respectively over SGSA-6, which has the highest $-\text{SO}_3\text{H}$ density. Moreover, regeneration of spent catalysts by sulfuric acid solution can significantly enhance their stability and reusability.

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1. Introduction

The phenomenal development of society, economy and industries has led to significant increase in material exploitation and energy consumption. Nowadays, a large proportion of raw materials and fuels derive from petroleum and coal resources; besides the dependence of unsustainable natural resources, the production and utilization of the aforementioned materials and fuels concomitantly cause severe environmental issues such as global warming due to the emission of greenhouse gases [1] or acid rain by releasing harmful gases [2]. In view of these urgent issues in materials, energy and environment, many countries are taking substantial measures to promote a greener use of renewable energy resources to reduce the heavy dependence on fossil fuels [3,4]. Among existent renewable resources, biomass has fascinated researchers' attention for its abundance, accessibility and biodegradability, and it can be exploited to produce biofuels, heat or chemicals *via* different conversion technologies [5,6].

Traditionally, biodiesel is obtained from transesterification or esterification of vegetable oil and animal fats with short-chain alcohols catalyzed by homogeneous bases or acids as catalysts [7]. However, saponification occurs between reactants and alkali catalysts [8] and homogeneous acids also have some drawbacks in terms of separation,

recycling and corrosion, thus necessitating novel and efficient catalysts for the preparation of biodiesel. For these purposes, various solid acids are developed, such as heteropoly acids, ion exchange resins, zeolites, and sulfated metal oxides [9]. In addition to applications in esterification, solid acid catalysts also have popular applications in hydrogenation [10,11] transesterification [12,13] hydrolysis [14,15] dehydration and the like [16,17].

Recent years have seen the development of biomass-derived carbon materials [18,19] and carbon-based solid acids as promising acidic catalysts, owing to their high acid density, chemical inertness, mechanical stability, structural diversity and surface hydrophobicity [10]. The synthesis of carbon-based solid acids generally involves both carbonation and sulfonation steps: in the carbonation process, some carbon precursors such as cellulose, starch, sucrose, glucose or other household waste were heated to high temperature ($>400\text{ }^\circ\text{C}$) under N_2 atmosphere to generate black powder, followed by sulfonation process, the black powder also needs to be heated to $100\text{ }^\circ\text{C}$ – $150\text{ }^\circ\text{C}$ in concentrated sulfuric acid or fuming sulfuric acid at $150\text{ }^\circ\text{C}$ – $200\text{ }^\circ\text{C}$ under N_2 flow to introduce $-\text{SO}_3\text{H}$ [20–22]. Although a decent conversion and product yield have been achieved, the preparation of these catalysts is complicated and produces a large amount of waste gas and liquid. More recently, the preparation of solid acid catalysts through the one-step method using *p*-toluenesulfonic acid as a sulfonating agent is widely reported in literature. Xu and co-workers prepared a novel solid acid catalyst by the copolymerization of *p*-toluenesulfonic acid and paraformaldehyde [23] and this solid catalyst displayed a high activity for furfural production. Wang and co-workers carbonized glucose with *p*-toluenesulfonic acid at $180\text{ }^\circ\text{C}$ in a sealed autoclave [24,25] and it exhibited excellent catalytic performance in the dehydration of fructose to 5-hydroxymethylfurfural

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(5-HMF) and the esterification of succinic acid with ethanol. Although simple and environmentally-friendly, this preparation method needs *p*-toluenesulfonic acid that is very expensive.

To tackle the existing problems in catalyst preparation and applications, cheap raw materials and stable catalytic performances are required. In this work, a series of carbon-based solid acid catalysts have been synthesized by a simple and effective one-step method and examined in two esterification reactions: propionic acid or oleic acid with methanol, and the esterification of oleic acid with methanol is a typical reaction for biodiesel production. Glucose that can be derived from biomass is treated with aqueous sulfuric acid solution with a gradient concentration under hydrothermal conditions to give solid products. The concentration of sulfuric acid substantially affects the catalytic performances of the catalysts, and this can be reflected by the esterification reaction. It is anticipated that our findings will inspire peer researchers in catalyst design for the exploitation of biomass or its derived platform chemicals to produce value added chemicals and fuels.

2. Experimental

2.1. Raw materials

Sulfuric acid (H₂SO₄, 95 wt%–98 wt%) and hydrochloric acid (HCl, 36–38 wt%) were purchased from the Nanjing Chemical Reagent Co., China. Propionic acid was obtained from the Shanghai Ling Feng Chemical Reagent Co., China. D-(+)-Glucose, methanol and naphthalene were supplied by the Sinopharm Chemical Reagent Co., Ltd., China. Oleic acid, methyl propionate and methyl oleate (85%) were purchased from the Aladdin Industrial Co., China. Phenolphthalein used for acid–base titration was obtained from the Tianjin Institute of Chemical Reagents. Sodium hydroxide (NaOH) was supplied from the West Long Science Co., Ltd. Other chemicals that were not marked with brackets were of analytical grade. These chemicals were used as received without further treatment.

2.2. Preparation of SGSA catalysts

The catalysts were prepared by hydrothermal treatment of glucose in the aqueous solution of sulfuric acid with a series of different concentrations. For the sulfuric acid solution, the volumetric ratios of sulfuric acid and water were 1:2, 1:1.25, 1:1, 1:0.5 and 1:0, and all experiments were performed, keeping the acid solution volume:glucose mass ratio of 6:1. The final acid–glucose solution was sealed in an autoclave with the Teflon inner container at 180 °C for 4 h. The catalysts were denoted as SGSA-1, SGSA-2, SGSA-3, SGSA-4 and SGSA-5, corresponding to the above-mentioned five different concentrations. For comparison, the solution with the initial 1:0 ratio was also treated in the three-necked flask equipped with a reflux condenser at 80 °C for 4 h, and the sample was denoted as SGSA-6. After treatment, the resulting solid products were filtered and washed with deionized water to remove residue acids, until the pH reached 7, and then were dried at 80 °C overnight.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) was conducted by a FTIR spectrophotometer (Thermo Electron Nicolet-360, USA) using the KBr wafer technique. The phase structure of the SGSA catalysts was examined by X-ray diffraction (XRD) using Rigaku MiniFlex II with Cu K α radiation. Nitrogen adsorption–desorption analysis was recorded using a Micromeritics ASAP 2020 at 77 K. Each sample was degassed at 180 °C for 720 min prior to analysis. The morphology of the samples was observed by scanning electron microscopy (SEM) utilizing a JSM-7600F (JEOL Ltd., Japan) with an operating voltage of 30 kV. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method.

2.4. Acid density analysis

The total acid density of SGSAs was determined by an acid–base back neutralization titration method. 0.05 g of the catalyst was placed in a beaker, mixed with 15 ml of 0.1 mol·L⁻¹ NaOH solution [26]. The mixed solution was stirred for 4 h and sonicated for 1 h, and then was filtered. The concentration of OH⁻ in the filtrate was titrated with hydrochloric acid solution. The acid density of —SO₃H was determined as follows, 0.05 g of SGSA was mixed with 15 ml of 2 mol·L⁻¹ NaCl solution. After stirring for 4 h and ultrasound for 1 h, the solution was filtered and the filtrate was titrated with a sodium hydroxide solution.

2.5. Catalytic tests

The reactions were carried out in the conventional reflux system. A three-necked round flask was immersed in an oil bath placed on a hot plate stirred with a temperature controller. In a typical procedure for the esterification of propionic acid and methanol, 2 ml of propionic acid, 30 ml of methanol and 0.1 g of the SGSA were mixed in the reactor at 60 °C for 6 h. For the esterification of oleic acid and methanol, 9.5 ml of oleic acid, 24.3 ml of methanol and 0.1 g of the SGSA were added to the reactor at 80 °C for 8 h. Both experiments used naphthalene as an internal standard and the reaction samples were removed periodically then analyzed by the gas chromatograph (Agilent 7820A). Conversion, yield and selectivity were defined as follows:

$$\text{Conversion} = \frac{\text{moles of acid reacted}}{\text{moles of initial acid}} \times 100\%$$

$$\text{Yield} = \frac{\text{moles of ester produced}}{\text{moles of initial acid}} \times 100\%$$

$$\text{Selectivity} = \frac{\text{moles of ester produced}}{\text{moles of acid reacted}} \times 100\%$$

2.6. Reusability and regeneration of SGSA catalysts

In order to study the stability of the SGSAs and the approaches to enhance their reusability, SGSA-5 and SGSA-6 were collected from the spent reaction solution by a suction filter after each run and then washed with acetone to remove the adsorbed species. After drying at 80 °C overnight, the spent catalyst was mixed with oleic acid and methanol, maintaining identical weight ratio of naphthalene/catalyst/methanol/oleic acid. Considering the fact of catalyst deactivation, regeneration was necessary to conduct. The spent catalyst was dipped into the aqueous solution of H₂SO₄ (20 wt%) stirring for 4 h, filtered and washed with deionized water, dried and then used for the next run in the same weight ratio of naphthalene/catalyst/methanol/oleic acid with the first run of fresh catalysts.

3. Results and Discussion

3.1. Characterization of SGSAs

The FT-IR spectroscopy was conducted and the results are shown in Fig. 1(a). The absorption peak at the 1181 cm⁻¹ wavenumber can be ascribed to the O=S=O stretching vibration in —SO₃H groups, demonstrating that the —SO₃H has been successfully incorporated into amorphous carbonaceous structure [22]. The XRD patterns of SGSAs are displayed in Fig. 1(b). The crystal structure of glucose was destroyed after treatment by sulfuric acid solution. The broad peaks at 2 θ angles of 10°–30° could be attributed to (002) planes of amorphous carbon, indicating that glucose has been carbonized [27,28]. SGSA-4, SGSA-5 and SGSA-6 (SGSA4–6) show a higher intensity of acidity than that of SGSA-1, SGSA-2 and SGSA-3 (SGSA1–3), demonstrating that they

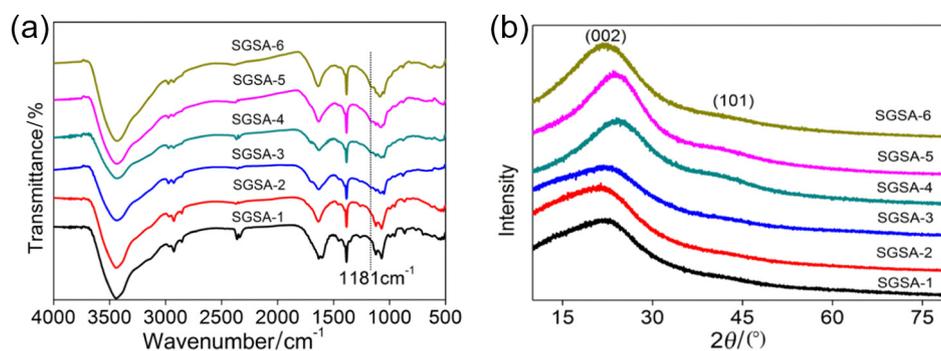


Fig. 1. FT-IR spectra (a) and XRD patterns (b) of SGSAs.

(SGSA4–6) have a relatively better carbon framework [25]. In addition, an identifiable C(101) diffraction peak ($2\theta = 35^{\circ}$ – 50°) can be observed in the SGSA-4 and -5, indicating that they consist of larger carbon sheets and are more deeply carbonized than SGSA1–3 and SGSA-6 [28]. The aforementioned experimental results and associated reports show that high sulfuric acid concentration results in relatively better carbon frame structures.

The morphologies of SGSAs were examined by SEM, and the images are given in Fig. 2, showing that the morphologies of SGSAs were essentially affected by the concentration of sulfuric acid. In detail, SGSA-1 (Fig. 2(a)) is composed of carbonaceous microspheres with a size range of 1–3 μm ; SGSA-2 (Fig. 2(b)) and SGSA-3 (Fig. 2(c)) are spherical but obviously agglomerate with the increase of sulfuric acid concentration. The other SGSAs (Fig. 2(d)–(f)) are non-spherical particles with various shapes and sizes regardless of whether they are prepared in the autoclave at 180 $^{\circ}\text{C}$ or in the three-necked flask at 80 $^{\circ}\text{C}$.

The density and strength of acid sites of carbon-based solid acid are important factors that affect the catalytic activity [29]. The acid density of the SGSA catalysts is also measured, as shown in Table 1. SGSA 1–5 have a $-\text{SO}_3\text{H}$ amount from 0.12 $\text{mmol}\cdot\text{g}^{-1}$ to 1.45 $\text{mmol}\cdot\text{g}^{-1}$ as the increase of sulfuric acid concentration. SGSA-5 and SGSA-6 have a similar content of sulfonic acid although they differ in the preparation conditions. However, the total acid density changes little, because the total acidity includes some weak acids existing on the surface of SGSAs in addition to $-\text{SO}_3\text{H}$, and the weak acids are Ph-OH and $-\text{COOH}$, as reported in literature [30]. The BET surface area of the SGSAs is also affected by the concentration of sulfuric acid, it is interesting to find that the specific surface area of SGSA increases first and then decreases with the increase of sulfuric acid concentration, SGSA-3 and SGSA-4

Table 1

The BET surface areas, pore size, and acid density of SGSA catalysts

Catalysts	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	Mean pore size/nm	$-\text{SO}_3\text{H}/\text{mmol}\cdot\text{g}^{-1}$	Total acids/ $\text{mmol}\cdot\text{g}^{-1}$
SGSA-1	– ^①	– ^②	0.1	8.7
SGSA-2	–	–	0.2	8.8
SGSA-3	373	3.8	0.4	8.5
SGSA-4	610	2.2	0.9	8.9
SGSA-5	–	–	1.5	8.5
SGSA-6	–	–	1.5	8.4

^① The surface areas were quite low, around 1 to 7 $\text{m}^2\cdot\text{g}^{-1}$.

^② Unavailable.

reach as high as 373 and 620 $\text{m}^2\cdot\text{g}^{-1}$, and all the isothermal curves are provided in Fig. 3.

3.2. Catalytic performances of SGSAs

The catalytic performances of as-synthesized catalysts were tested in the esterification of propionic acid with methanol. As show in Table 2, reaction without catalysts (control experiment) was also performed to determine the reaction behaviors, and almost no product was detected after 6 h (not shown). As to SGSA-1, the conversion of propionic acid was only 6.1%, showing that SGSA-1 has little activity for the reaction under experimental conditions, but the conversion of propionic acid reached 55.8% and 74.3% over SGSA-2 and SGSA-3, respectively. It is noteworthy that the conversion of propionic acid was excellent and stable on SGSA 4–6. The $-\text{SO}_3\text{H}$ group is the key

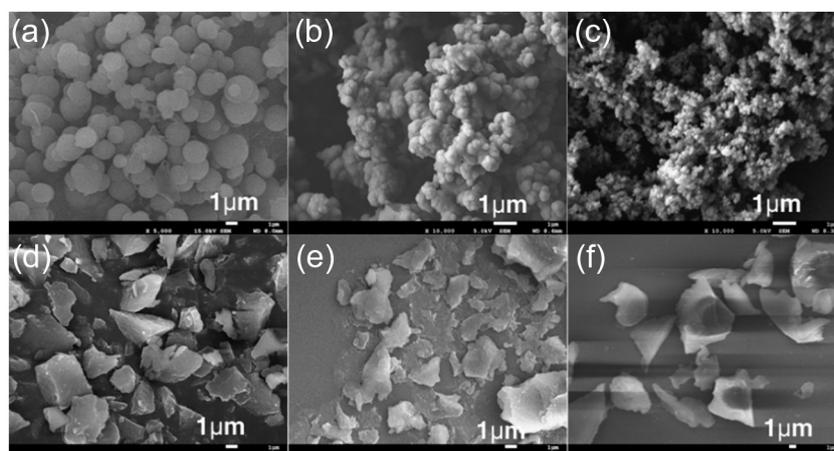


Fig. 2. SEM images of SGSAs: SGSA-1 to SGSA-6 (a–f).

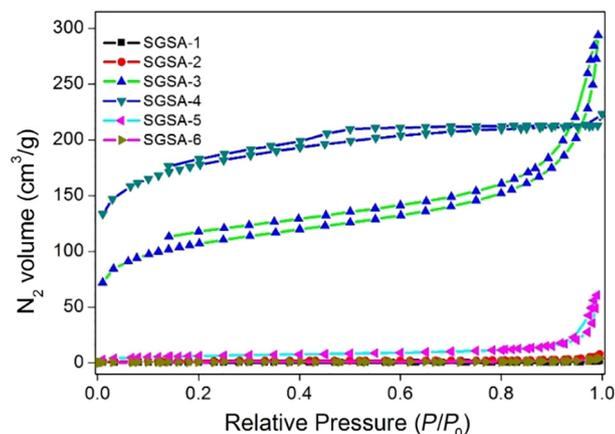


Fig. 3. Nitrogen adsorption-desorption isotherms of SGSAs.

Table 2
Esterification of propionic acid with methanol

Catalysts	Conversion/%	Selectivity/%	Normalized final reaction rate ^① /mol propionic acid · (g catalyst) ⁻¹
SGSA-1	6.1	68.0	0.3
SGSA-2	55.8	86.6	2.5
SGSA-3	74.2	88.1	3.3
SGSA-4	92.2	82.1	4.1
SGSA-5	92.3	81.4	4.1
SGSA-6	94.5	93.3	4.2

^① The normalized final reaction rate was calculated on the basis of the mass of catalysts. Reaction conditions: Catalyst (0.1 g), propionic acid (2 ml), methanol (30 ml), naphthalene (0.144 g), pressure (ambient), temperature (60 °C) time (6 h). Control experiments: No products were detectable without catalysts under identical experimental conditions.

contribution to the activity, thus propionic acid conversion has a linear relationship with the amount of sulfonic acid and then reaches a plateau owing to the final equilibrium [31]. The normalized reaction rate shows a similar trend with the conversions over these catalysts, namely, it rises and then reaches a plateau as the function of the acid concentration for treatment. Although fluctuating slightly, the selectivity of methyl propionate was between 80% and 90% (excluding SGSA-1 that has the lowest content of sulfonic acid and the quantification is difficult to be accurate). These results demonstrate that these as-made catalysts are potential candidates for esterification.

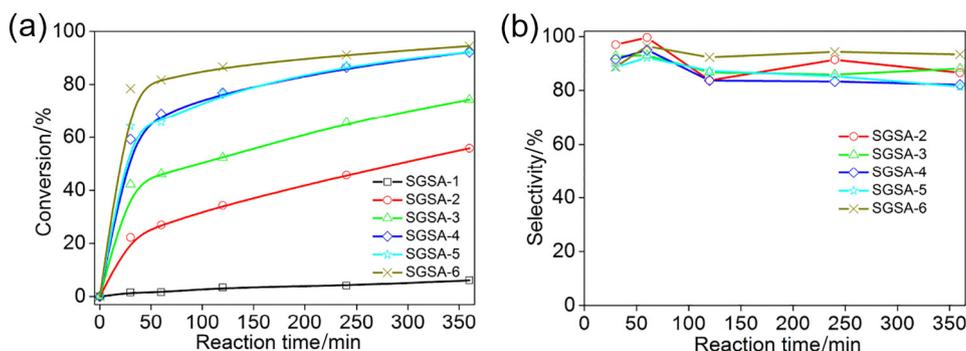


Fig. 4. Conversion of propionic acid in the presence of SGSAs (a) and selectivity of methyl propionate over SGSAs (b). Control experiments: no products were detectable without catalysts under identical experimental conditions.

Through the entire reaction time, the profiles of conversions and selectivities over these catalysts are provided in Fig. 4. Results in Fig. 4(a) show that SGSA-1 with the lowest density of acid exhibits a quite low conversion of propionic acid within 6 h, whereas SGSA2–3 present a gradually increasing trend of conversion and could achieve a high conversion if the reaction time was prolonged. SGSA4–6 displayed similar trends of conversion as the function of time, and achieve a high conversion within the first 1 h. Moreover, all the catalysts exhibited relatively high and stable selectivities (around 90%) through the whole reaction time (Fig. 4(b)).

In order to prove that the SGSAs have a wide range of applications, another valuable esterification reaction was also made at 80 °C for 8 h, Biodiesel synthesis from oleic acid and methanol. As can be seen from Table 3 (the activity of SGSA-1 was not given because it is extremely low), SGSA2–3 behave differently in terms of the conversion of propionic acid (25%–75%), and the conversion of oleic acid increased with the increase of sulfonic acid content, but the selectivities of methyl oleate are similar (45%–55%). SGSA4–6 that have a high content of sulfonic acid exhibit excellent conversion of oleic acid and selectivity of methyl oleate. These results demonstrate that SGSAs also have potential applications in the esterification of oleic acid with alcohols.

To understand the detailed catalytic performances, the profiles of conversion and selectivity of methyl oleate are conducted as the function of reaction time, as shown in Fig. 5. At the initial stage, results in Fig. 5(a) show that the catalytic conversion of SGSA2–4 shows an increasing trend at the same reaction time, whereas SGSA4–6 present a similar high conversion. Through the whole reaction time, SGSA-2 and -3 deactivate and are unable to reach high conversions. As to the selectivities, SGSA-5 and -6 perform best among these catalysts and are higher than 90% after 6 h.

The experimental results of the above-mentioned two selected reactions show that SGSA-5 and SGSA-6 outperform other catalysts in terms of catalytic activity and selectivity, probably because they almost have the same morphologies, specific surface areas, —SO₃H content, and total acid density. As to the preparation method, SGSA-5 was prepared in the autoclave at 180 °C and self-reaction pressure condition for 4 h, and SGSA-6 was obtained at a milder temperature of 80 °C for 4 h with no self-generated pressure. In this regard, glucose treated in the flask with concentration H₂SO₄ is a better choice to prepare sulfated carbon-based catalysts. Moreover, SGSA5–6 outlast other catalysts in terms of stability, showing no obvious deactivation under experimental conditions. Therefore, one may concern about their reusability of SGSAs5–6, and what measures can be taken to regenerate them if they deactivate after several runs.

3.3. Reusability of SGSAs

The stability and reusability of the catalyst are of great importance for practical applications. In this study, typical catalysts of SGSA-5 and

Table 3

Esterification of oleic acid with methanol

$\text{C}_{18}\text{H}_{33}\text{O}_2 + \text{CH}_3\text{OH} \xrightarrow[80^\circ\text{C}]{\text{H}^+} \text{C}_{18}\text{H}_{33}\text{O}_2 + \text{H}_2\text{O}$			
Catalysts	Conversion/%	Selectivity/%	Normalized final reaction rate ^① /mol·g ⁻¹ ·h ⁻¹
SGSA-2	25.7	54.2	1.0
SGSA-3	46.4	46.1	1.7
SGSA-4	74.8	57.1	2.8
SGSA-5	84.4	91.2	3.2
SGSA-6	93.3	94.7	3.5

^① The normalized final reaction rate was calculated on the basis of the mass of catalysts. Reaction conditions: Catalyst (0.1 g), oleic acid (9.5 ml), methanol (24.3 ml), naphthalene (0.152 g), pressure (no pressure), temperature (80 °C) time (8 h). Control experiments: no products were detectable using no catalysts or under identical experimental conditions.

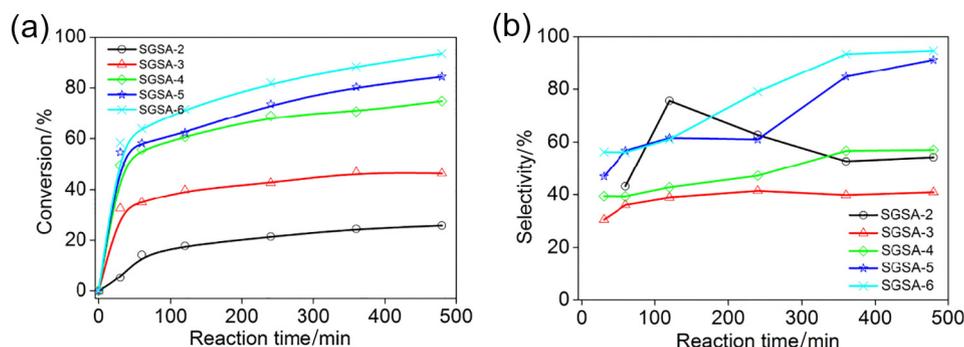


Fig. 5. Conversion of oleic acid and in the presence of SGSAs (a) and selectivity of methyl oleate over SGSAs (b). Control experiments: no products were detectable without catalysts under identical experimental conditions.

SGSA-6 were selected to examine their stability and reusability in the reaction of oleic acid and methanol. The catalytic results were presented in Table 4, and the change in the $-\text{SO}_3\text{H}$ density in each cycle was also provided, demonstrating that the $-\text{SO}_3\text{H}$ density of both SGSA-5 and SGSA-6 decreased from 1.5 $\text{mmol}\cdot\text{g}^{-1}$ to 0.1 $\text{mmol}\cdot\text{g}^{-1}$ after the third run. As a result, the catalytic performances decreased dramatically (e.g. the conversion of oleic acid was from 84.4% to 10% over SGSA-5 and from 93.3% to 10% over SGSA-6). However, after the regeneration with 20% H_2SO_4 treatment (details can be found in the Experimental part), the $-\text{SO}_3\text{H}$ density improved from 0.3 $\text{mmol}\cdot\text{g}^{-1}$ to 0.6 $\text{mmol}\cdot\text{g}^{-1}$ after the second run and from 0.1 $\text{mmol}\cdot\text{g}^{-1}$ to 0.6 $\text{mmol}\cdot\text{g}^{-1}$ after the third run as for the catalyst SGSA-5; and it was also improved from 0.4 $\text{mmol}\cdot\text{g}^{-1}$ to 0.7 $\text{mmol}\cdot\text{g}^{-1}$ after the second run and from 0.1 $\text{mmol}\cdot\text{g}^{-1}$ to 0.7 $\text{mmol}\cdot\text{g}^{-1}$ after the third run as for the catalyst SGSA-6.

According to the literature reports, catalyst deactivation was ubiquitous and unavoidable for sulfonated catalysts [32] owing to leaching of

Table 4

Reusability and stability tests of typical catalysts of SGSA-5 and SGSA-6 in the reaction of oleic acid and methanol

Catalysts	$-\text{SO}_3\text{H}$ density/ $\text{mmol}\cdot\text{g}^{-1}$	Conversion/%	Selectivity/%
SGSA-5-1 ^①	1.5	84.4	91.2
SGSA-5-2 ^①	0.3	35.3	37.1
SGSA-5-3 ^①	0.1	9.5	11.1
SGSA-5-2-R ^②	0.6	50.6	44.5
SGSA-5-3-R ^②	0.6	55.8	53.2
SGSA-6-1 ^①	1.5	93.3	94.7
SGSA-6-2 ^①	0.4	45.9	53.2
SGSA-6-3 ^①	0.1	10.0	16.8
SGSA-6-2-R ^②	0.7	64.6	82.4
SGSA-6-3-R ^②	0.7	62.3	80.6

^① The number of “1, 2 and 3” represents the cycle number.

^② “R” represents regeneration. The reaction conditions were provided in the footnotes of Table 3 for the first run and in the Experimental part for the reusability and stability tests.

the $-\text{SO}_3\text{H}$ [21,33,34] sites, the formation of sulfonate esters [35,36] and adsorbed species (e.g. humins, reactants, and products) [37,38]. In our work, conversion of oleic increased significantly after the regeneration of SGSA5–6 in the second and third runs, and this proved that the recovered catalytic activity significantly relied on the $-\text{SO}_3\text{H}$ groups, possibly from the hydrolysis of sulfonate esters by the aqueous solution of H_2SO_4 (20 wt%). Although the $-\text{SO}_3\text{H}$ density and the conversion of oleic acid remain unchanged after regeneration, they decreased remarkably after the first run. Therefore, strategies to improve the stability of sulfonate on the SGSAs by preventing the $-\text{SO}_3\text{H}$ groups from leaching would be the main objective in the future study.

4. Conclusions

To exploit biomass-derived materials/chemicals and to upgrade biodiesel, SGSA catalysts were prepared via the one-step method, using glucose as the raw materials together with sulfuric acid aqueous solution with different concentrations. Experimental results proved that the concentration of acid determined the final catalytic performances of these catalysts in terms of catalytic activity and selectivity. When concentrated sulfuric acid was used, the $-\text{SO}_3\text{H}$ density of the catalyst reached the maximum, and SGSA5–6 exhibited the best catalytic performances for both esterification reactions (conversion of propionic acid or oleic acid with methanol). The reusability test showed that retreatment of spent catalysts with sulfuric acid solution again could regenerate catalytic activity to a large extent (the release of $-\text{SO}_3\text{H}$ groups from the hydrolysis of sulfonate esters), and thus improvement of catalyst stability and the prevention of acid site leaching are our major targets in the future study.

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