Research article

Fabrication of sulfonated carbon catalyst from biomass waste and its use for glycerol esterification

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A B S T R A C T

Sulfonated carbon catalysts were prepared by sulfonation of carbonized catkins from willow under different sulfonated conditions. Such materials were characterized by SEM, EDS, FTIR and TGA. The results indicated that sulfonated conditions might influence the acid density of the sulfonated carbon catalysts, but did not influence the microtubular structure. These sulfonated carbon catalysts exhibited high acid capacity, good thermal stability and better catalytic activity for the glycerol esterification. With a molar ratio of acetic acid to glycerol of 5:1, a catalyst amount of 5 wt.% and a reaction temperature of 393 K for 2 h, glycerol was almost completely transformed into a mixture of glycerol esters including monoacetate, diacetate and triacetate. Controlling of acid density of the catalysts and reaction conditions could obtain highly desired products. Meanwhile, the hydrophobic property of these sulfonated carbon catalysts led to some tolerance to water. Moreover, excellent reusability of the catalyst was also confirmed by repeated experiments.

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1. Introduction

Biomass is the most abundant and renewable resource for the production of biofuel and valuable chemicals through a number of viable biorefining processes. To date, the utilization of biomass or industrial wastes to prepare the catalytic materials is becoming increasingly attractive from both academic and practical points of view due to its valuable advantages [1]. In view of "green chemistry", sulfonated carbon catalysts have recently emerged as promising solid acid catalysts for acidic catalysis [2,3], because carbon materials are widely available, considerably cheap and can be easily functionalized with —SO$_3$H group through simple treatment with concentrated sulfuric acid [4–6]. However, the preparation of sulfonated carbon catalysts is currently made mostly from pure carbohydrates such as cellulose, glucose, and starch [3,7–10], while these catalysts prepared from biomass waste or solid waste remain largely unexplored [11–15]. Carbon-based catalysts have been prepared from wood powder or bamboo, which are less stable compared with those from pure carbohydrates [16–18]. Zong's group chose the waste biomass as feedstock to prepare sulfonated carbon catalysts by treating bagasse with carbonization at 648 K for 0.5 h and then sulfonated it at 423 K for 15 h, which gave the —SO$_3$H density as high as 1.06 mmol g^{-1} [19]. Wang Yun's group prepared a solid acid catalyst using corn straw as feedstock under carbonization at 573 K for 1 h and then sulfonated it for 4 h at 353 K by fume H$_2$SO$_4$,

which was proved to be an efficient and environmental benign catalyst for the esterification of oleic acid and methanol [20] owing to its high acid density (2.64 mmol g^{-1}). Sulfonated carbon catalysts prepared from agroindustrial wastes (sugar cane bagasse, coconut husk, and coffee grounds) were reported by W. A. Carvalho and coworkers [21]. Their results presented the maximal acid density of 4.9 mmol g^{-1} or higher under carbonization at 673 K for 4 h followed by sulfonation at 453 K for 10 h by H$_2$SO$_4$. Therefore, it can be concluded that the catalytic performance of the carbon-derived catalysts highly dependent on the starting materials used and the treatment conditions. It is of great interest to prepare novel solid acid catalysts from new materials and investigate the relationship between catalyst structure, treatment conditions and catalytic performance. Willow catkins are a kind of biomass waste, which were widely used as template in preparation of carbon microtubes due to their natural microtubular structure applied in supercapacitors [22,23]. However, there is no report on the preparation of sulfonated carbon catalysts based on catkin and its associated performance in catalytic reactions. Meanwhile, microtubular structure of catkin might be available for providing a reactor for some reactions. Therefore, preparation of sulfonated carbon catalysts from catkin might not only give more value for this biomass waste, but also provide some information on microtube catalysis. Meanwhile, the benefits of such sulfonated carbon catalysts were low cost in preparation without any cost of feedstocks, and reusability as compared to the usual catalyst H$_2$SO$_4$.

As the major by-product in biodiesel production via the transesterification of natural oils with C$_1$–C$_4$ alcohols, glycerol is valued

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as promising low-cost feedstocks to produce value-added chemicals [24–28] through etherification [29], hydrogenolysis [30], oxidation [31] and esterification [32]. Among these processes, esterification of glycerol into acetins is quite attractive due to the versatile industrial applications ranging from cosmetic to fuel additives out of the final products including monoacetyl glyceride (MAG), diacetyl glyceride (DAG), and triacetyl glyceride (TAG) [24–33]. Now, special interest has been focused on DAG and TAG due to their potential for vast quantity utilization as valuable biodiesel and petro-fuel additives [34,35]. Glycerol acetylation has been carried out using different homogeneous acid catalysts such as H_2SO_4, or some heterogeneous catalysts including Amberlyst-15 [36], zirconia [37], SBA-15 [38], niobic acid [36] and heteropolyacids [39–41]. Nevertheless, it is still desirable to develop more environmentally friendly catalytic processes and the yield of the desired products can be improved at the same time by using more economic reaction conditions. Carbon based acid catalyst might meet this demand because of its easy preparation, being made from various feedstocks, strong acid sites, hydrophobic properties and regeneration.

At present, esterification of glycerol has been investigated by Sanchez et al. [32] using a carbon-based catalyst prepared by sulfonation of carbonized sucrose, which showed approximately 99% conversion and high selectivity to triacetyl glyceride (50%) at 378 K for 4 h. Khayoon and Hameed [42] reported a commercial sulfonated carbon catalyst with high catalytic activity in glycerol acetylation with a 91% glycerol conversion and selectivity of 38, 28 and 34% for MAG, DAG and TAG, respectively, at 393 K for 3 h. Carvalho et al. [21] also reported the conversion of glycerol with the aid of tert–butyl alcohol and 5 wt.% loading of sugar cane as bagasse-based acid catalyst to obtained the 80.9% conversion, and total 21.3% selectivity to diester and trimester at 393 K for 4 h. From the above results, the sulfonated carbon catalysts could be a viable alternative to improve the esterification reactions of glycerol [43]. Although there were some studies on carbon solid acid catalysts for glycerol acetylation, comparative studies of catalytic properties such as surface acidity, and structure of the carbon catalysts have been limited. Meanwhile, the commercial sulfonated carbon catalysts were prepared through sulfonation of activated carbon resulting in higher cost. The cheap sulfonated carbon catalysts being prepared from waste biomass are more desirable. In this study, sulfonated carbon catalysts were synthesized by using willow catkins as feedstock, which exhibited different acid strengths to evaluate the correlation between acidity and activity. In addition, this catalysts exhibited microtubular structure and could give some information on the relationship between structure and ester selectivity. The intrinsic catalytic properties based on glycerol conversion turnover rate and selectivity toward mono-, di-, and triacetin on these catalysts were extensively compared and characterized under the same reaction conditions, and the results were correlated with the physicochemical properties of the catalysts in details.

2. Experimental

2.1. Preparation of the sulfonated carbon catalysts

Willow catkins were collected in the autumn. The starting material (10 g) of catkins was initially carbonized at 723 K for 5 h under N_2 flowing to produce a black solid. The resultant black powder (1 g) was subsequently heated in 5 mL of concentrated sulfuric acid (95–98%) for 3 h at different temperatures at 343, 353, 363, and 373 K, respectively. Then the mixture was cooled down to room temperature. The suspension was carefully filtered to obtain a black precipitate, which was then dried at 353 K for 5 h. Such dried powder (1 g) was then treated in 14 mL of fuming sulfuric acid (15 wt.% SO_3) at 343, 353, 363, and 373 K, respectively, to introduce —SO_3H onto the surface of carbon for 2 h and then cooled to room temperature. A black precipitate was centrifuged from the suspension and then washed repeatedly with hot distilled water (>353 K) until impurities such as sulfate ions were

no longer detected in the wash water. The black solid was then dried at 353 K for 5 h with yield of 72%.

2.2. Catalytic tests

A 25 mL three-necked glass flask equipped with a water-cooled condenser was charged with glycerol (2.3 g, 25 mmol) with selecting different amounts of acetic acid and catalyst. The mixture was vigorously stirred and reacted at 393 K for a required reaction time. After the esterification reaction completed, the catalyst was separated by centrifugation and regenerated by washing with ethanol and then air dried at 373 K to recuperate its catalytic activity.

2.3. The measurement of acidic contents

The contents of acidic sites were evaluated by Boehm titration. For such a measurement, 0.1 g of carbon samples was added to 20 mL of $NaHCO_3$ solution (0.05 M) and stirred for 72 h at room temperature. Subsequently, the reacted powder was filtered and the obtained clear solution was used to determine the acidic contents by being titrated with HCl (0.1 M).

2.4. Physical measurement

The infrared spectra (4000–500 cm^{-1}) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. SEM micrographs were recorded on a scan electron microscope (XL30 ESEM FEG 25 kV). The concentrations of ester were determined periodically on Shimazu GC-14C instrument with a HP-INNO wax capillary column and the flame ionization detector. Qualitative analysis was performed by gas chromatography–mass spectrometry (GC–MS, Agilent 5970) with scan parameters set at low mass 20.0, high mass 700.0, and threshold 150.

3. Results and discussion

3.1. Characterization of catalysts

As shown in Fig. 1, by comparison, two new vibration bands at 1029 and 1500 cm^{-1} were observed after sulfonation, which were attributed to the indication of vibrational stretching mode of O═S═O bonds of —SO_3H group and vibration mode of C═O bonds of —COOH group, respectively. The peak at around 3420 cm^{-1} was typically assigned to the stretching modes of oxygen-containing —OH [44]. Therefore, the FTIR spectrum clearly demonstrated that sulfonation process has introduced —SO_3H, —OH and —COOH groups into the catkin-derived catalyst.

As shown in Fig. 2, peaks at 548 K and 722 K are due to the decomposition of the sulfonic and carboxylic groups, respectively. The peak at 820 K was associated with the decomposition of phenolic and carbonyl groups.

As shown in Fig. 3, the obtained sulfonated carbon catalysts consisted of mainly uniform carbon microtubes with diameters of 3–8 μm. Compared to the morphology of catkin (Fig. 3a), the tubular structure was not destroyed by carbonation and sulfonation. After chemical treatment, the catkin derived materials were broken into aggregates of short carbon microtubes (Fig. 3b–e). The EDAX measurement results (Fig. 4) indicate that the as-prepared catalysts contain S, C, and O. The sulfur content in materials was found to be 2.85 mmol/g.

It is known that the acidic capacity is an essential parameter for acidic catalysis. From the Boehm titration experiments, the acidic contents were listed in Table 1. The acidic contents of sulfonated carbon catalysts obviously varied upon different treatment conditions. The maximal acidic capacity (5.14 mmol/g) was obtained with 363 K treatment for 5 h. It showed that increasing sulfonated temperature to 363 K gave the maximal acidic capacity, and further increasing of the temperature did not enhance the acid density of the sulfonated carbon catalysts.
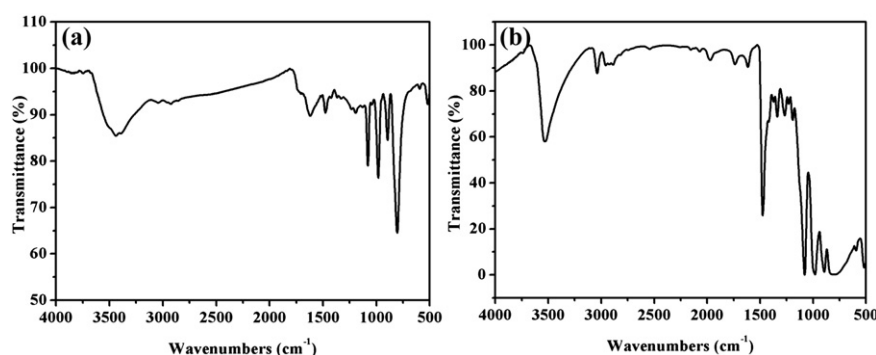
Fig. 1. FTIR spectra of (a) as-received catkins and (b) sulfonated carbon material.

This was attributed to that increasing sulfonated temperature could activate more H_2SO_4 molecules to link with carbon layer giving higher acidic capacity. Further increasing temperature did not enhance their acidity due to adsorption–desorption equilibrium for sulfonic acid groups from carbon surface.

Meanwhile, sulfonated carbon catalysts were made of waste biomass resulting in its lower cost of $ 5/kg than that of commercial products as $ 33/kg. This demonstrated that our catalysts were much more economic than previous products.

3.2. The catalytic activity of sulfonated carbon catalysts

3.2.1. Effect of sulfonated carbon materials

The acidic catalytic activity of as-prepared sulfonated carbon catalysts was evaluated by esterification of glycerol with acetic acid. It can be seen from Fig. 5 that without any acidic catalysts, the conversion of glycerol (32.0%) and the selectivities to MAG, DAG and TAG (95.7, 3.6, and 0.7%, respectively) were relatively at a low level. While the carbon material with higher acidic contents led to a higher glycerol conversion (98.4%), showing that an enhanced acid strength resulted in an increase of the intrinsic glycerol conversion. The order of the catalytic capacity based on different sulfonized temperatures turned out to be $C_{363\ K}$ (5.14 mmol/g) ~ $C_{353\ K}$ (5.12 mmol/g) > $C_{373\ K}$ (5.03 mmol/g) > $C_{343\ K}$ (4.85 mmol/g). The relationship between acidic contents and ester selectivity was displayed with the order of selectivity to MAG of $S_{343\ K}$ (93.3%) > $S_{373\ K}$ (80.2%) > $S_{353\ K}$ (72.4%) > $S_{363\ K}$ (32.8%); and the order of selectivity to DAG with $S_{363\ K}$ (54.5%) ~ $S_{353\ K}$ (14.2%) > $S_{373\ K}$ (12.5%) ~ $S_{343\ K}$ (5.7%); and finally the order of selectivity to TAG with $S_{353\ K}$ (13.4%) ~ $S_{363\ K}$ (12.7%) > $S_{373\ K}$ (7.3%) > $S_{343\ K}$ (1.0%), respectively. As the increasing of acid density of the sulfonated carbon catalysts, the glycerol conversion and the total yields to DAG and TAG significantly grow. Therefore, in order to obtain desired products (e.g. monoester yield), the carbon acid catalyst with lower acid density could be selected.

The difference of these activity and selectivity was attributed to the difference of acid density of the sulfonated carbon catalysts, because there was no difference in morphology and microtubular size between the different catalysts under different sulfurized temperatures. The large-pore size might result to litter difference on diffusion of glycerol or ester molecules.

3.2.2. Effect of reaction time

The reaction time played an important role on the conversion and selectivity (Fig. 6a), while the conversion of glycerol rapidly increased from 0.25 h to 2 h and reached almost 100% after 2 h using carbon catalyst being treated at 363 K. Further increasing the reaction time to 7 h led to a slight decrease of glycerol conversion. This might be contributed to the drop of glycerol concentration and the accumulation of by-product water [45]. The selectivity of glycerol ethers was also affected by the reaction time. In the mixture of glycerol ethers, the selectivity toward MAG obviously decreased from 0.25 h to 7 h, while the total selectivity toward DAG and TAG presented the opposite tendency and reached 95.3% after 7 h. It is known that glycerol esterification with acetic acid is a consecutive reaction including three continuous steps: glycerol + HOAc → MAG + H_2O; MAG + HOAc → DAG + H_2O; and DAG + HOAc → TAG + H_2O [42]. Prolonging the reaction time could increase the yields of DAG and TAG [42]. The highest selectivity to DAG and TAG was obtained and comparable to the best catalysts (Table S1) including $Ag_1H_2PW_{12}O_{40}$ [45], SO_3H-functionalized ionic liquids [46], Amberlyst-15 [47], TPA/Cs_x —ZrO_2 [26] and PW-silica [48]. The superior activity of these catalysts was attributed to the acid property and nature of the surface. After sulfonation, the carbonized willow catkin wall was decorated with —COOH and —SO_3H groups which could provide good access for hydrophilic glycerol to reach the active sites. For this reason, the carbon acid catalyst might more easily adsorb all of the reactants resulting in a higher catalytic activity. In addition, the cost of such process making of DTG and TAG was $1.6/kg much cheaper than those by other processes.

3.2.3. Effect of reaction temperature

The reaction temperature also influenced the conversion and selectivity due to the reversible reaction of glycerol esterification (Fig. 6b), while the conversion of glycerol increased with the increase of temperature from 363 to 393 K, and the almost complete conversion of glycerol
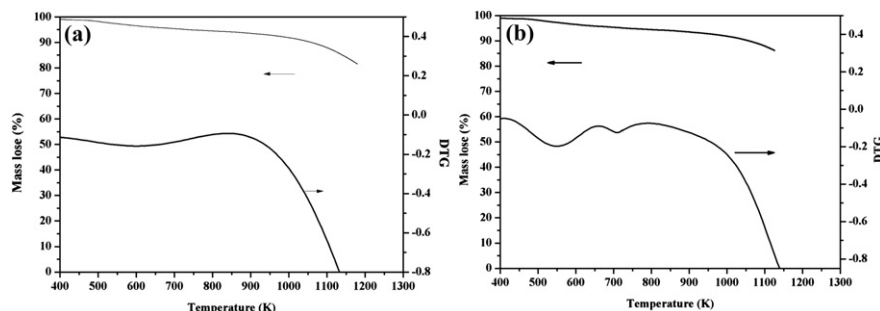

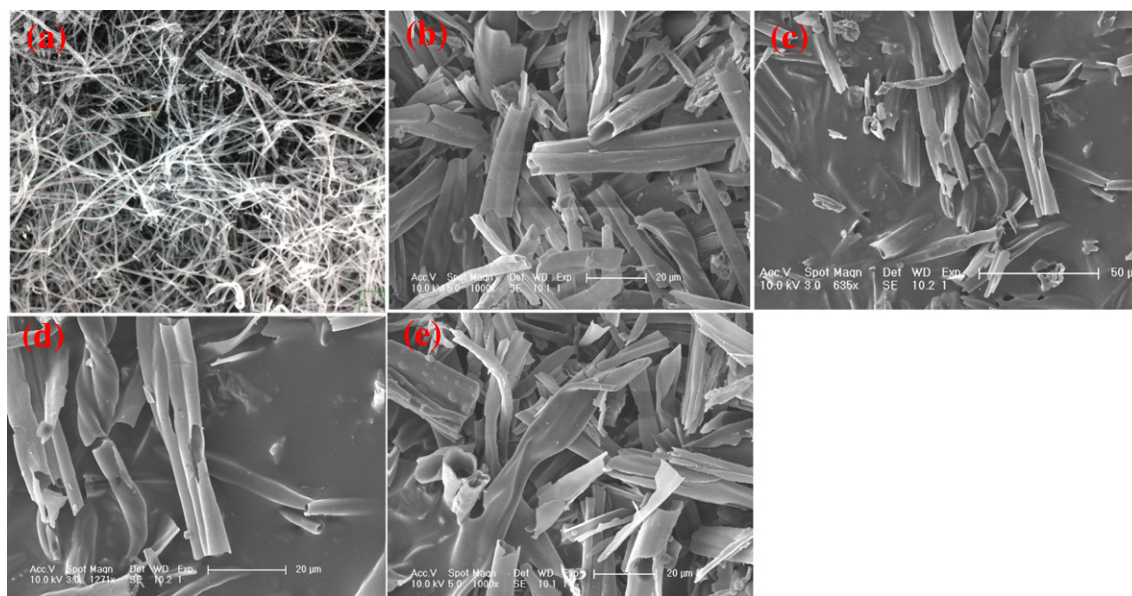**Fig. 2.** TG and DTG curves of catkin (a) and sulfonated carbon material (b).

Fig. 3. The SEM micrographs of aggregates of short micro-carbon tubes of (a) catkin and processed carbon material with sulfonated temperatures of 343 K (b), 353 K (c), 363 K (d), and 373 K (e).

was obtained at 393 K after 2 h. Then further increase of temperature to 403 K led to a sharp decrease of conversion. The selectivity toward the sum of DAG and TAG presented a similar tendency, which increased from 363 to 393 K and sharply reduced from 393 to 403 K. This result might be attributed to an increase in back-reaction when enhance with the reaction temperature.

3.2.4. Effect of molar ratio between glycerol and acid

If the DAG and TAG were desired products, at least three moles of acetic acid were required by stoichiometric equations. Because esterification is a reversible reaction, in the reaction mixture, the amount of acid must be in excess to drive the reaction toward the formation of DAG and TAG. Therefore, the influence of molar ratio between glycerol and acid was studied ranging from 1:3 to 1:5.5 (Fig. 6c). It could be seen that the glycerol conversion increased and the selectivity toward MAG decreased with an increase in the molar ratio from 3 to 5. Further increasing the molar ratio from 5 to 6, the selectivity to MAG increased while glycerol conversion decreased.

3.2.5. Effect of catalyst loading

In common sense, the usage of catalyst might be one of the important factors influencing the reaction rate. As shown in Fig. 6d,

the conversion of glycerol markedly climbed with increasing catalyst loading from 1 to 7 wt.%. The highest conversion was obtained when the catalyst loading was 5 wt.%. The glycerol conversion was insignificantly influenced by a further increase in catalyst loading from 6 to 7 wt.% because of the equilibrium limit.

As a result, the optimal processing parameters in our study for glycerol conversion included reaction temperature of 393 K, molar ratio of acetic acid and glycerol of 5:1 and reaction time of 2 h with catalyst loading of 5 wt.%.

Water is side-product of glycerol esterification reaction. Therefore, the solid acid catalyst was easily destroyed by water in the system. Water-tolerant solid acid catalyst is desirable. In Fig. 7, we can see that extra adding of some water to the reaction system could influence the catalytic activity on sulfonated carbon catalysts. The water content from 0 to 0.3 wt.% did not played significant role on the glycerol conversion, meaning this carbon acid catalyst exhibited some certain water-tolerant properties due to the hydrophobic properties of sulfonated carbon walls. With a further increase of the water content to 1 wt.%, the conversion of glycerol decreased sharply to 75.0%. The water content significantly influenced the selectivity to different esters. With the growth of water content, the selectivity to MAG increased and one to DAG decreased. The selectivity to TAG did not change significantly as increasing of water content.

The regeneration of the catalyst was studied by centrifuging the reaction mixture after reaction and the recovered catalyst was directly employed in the next reaction cycle without any further treatment. Fig. 8 illustrated a high conversion performance of glycerol in each cycle. Moreover, the activity of sulfonated carbon catalysts remained almost unchanged even after six cycles during the regeneration stage due to less loss of the —SO$_3$H group by hydrolysis during the reactions.
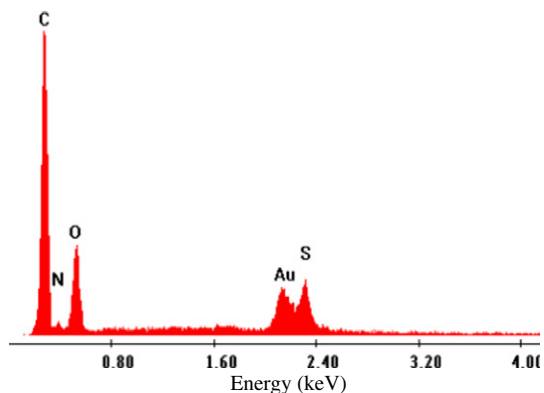

Fig. 4. EDAX diagram of carbon material with sulfonated temperatures of 363 K.

Table 1
Elemental analysis of carbon surface groups.

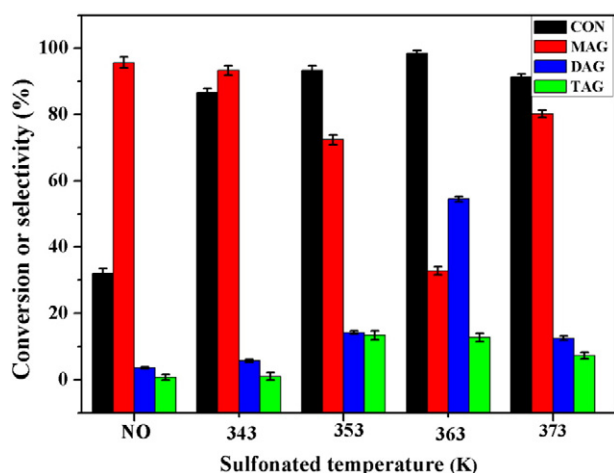| Temperature (K) for sulfonation	Content of S (wt%)	Content of —SO$_3$H (mmol/g)	Total acid content (mmol/g)
343	5.21	1.63	4.85
353	7.78	2.43	5.12
363	9.12	2.85	5.14
373	6.44	2.01	5.03

Fig. 5. The conversion and selectivity to MAG, DAG, and TAG catalyzed by carbon materials obtained through different sulfonated temperatures. Reaction conditions: molar ratio of glycerol to acetic acid = 1:5 and 5 wt.% of catalyst at 393 K for 2 h.
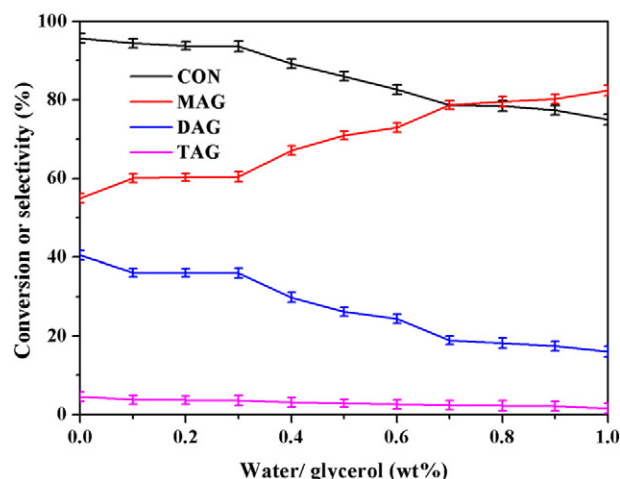

Fig. 7. The effect of water on the catalytic activity. Reaction conditions: molar ratio of acetic acid: glycerol = 5:1, 393 K, 5 wt.% of catalyst, 30 min.

4. Conclusions

Sulfonated carbon catalysts were prepared using native willow catkins as feedstocks through sulfonation. In the evaluation of their catalytic activity in esterification of glycerol with acetic acid, a strong correlation between acid strength and glycerol conversion was firmly justified by using the same structural materials. In addition, the ester selectivity can be easily controlled by using different catalysts with different acid density and reaction conditions. The highest conversion and selectivity to MAG, DAG and TAG was obtained to be 98.4, 32.8,

54.5 and 12.7%, respectively, at 393 K for 2 h. The sulfonated carbon catalysts were recycled and demonstrated to be rather chemically stable in subsequent reactions without significant deactivations. Moreover, our catalysts showed better heat stability and water-tolerance than some other solid acid catalysts, which is another appealing aspect in addition to its low cost.

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.fuproc.2015.06.021.
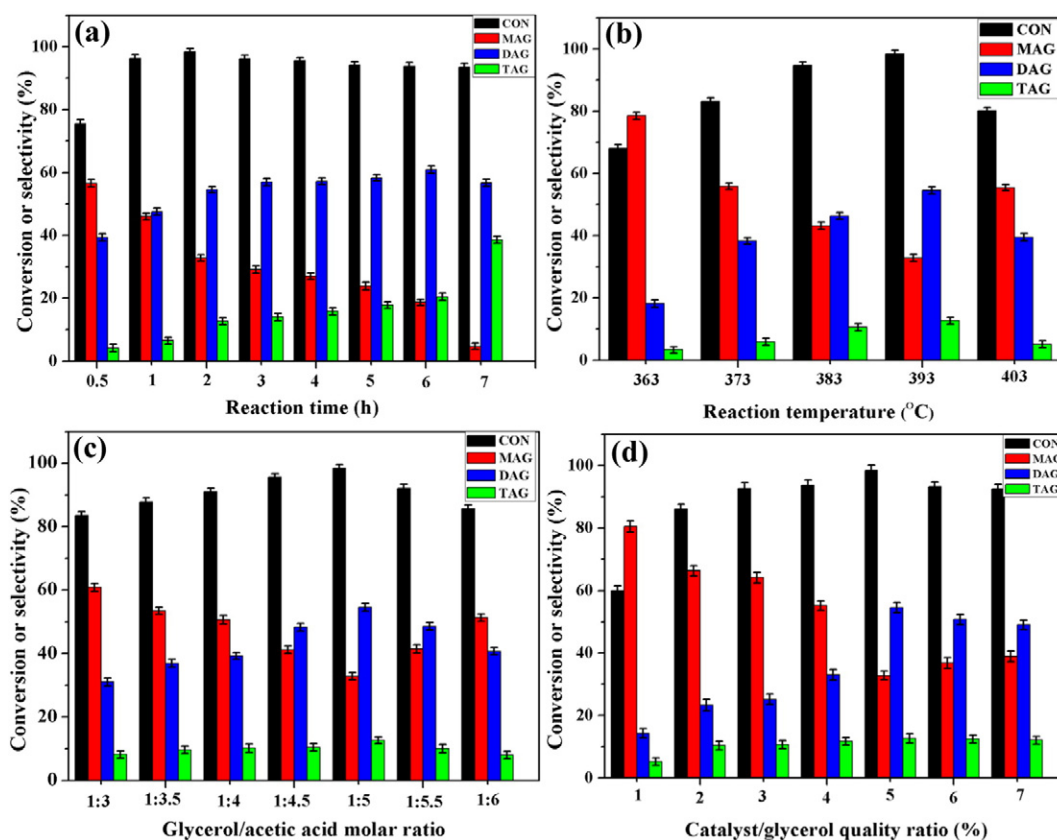

Fig. 6. The conversion and selectivity under conventional process at various process parameters of. (a) reaction time (molar ratio of acetic acid: glycerol = 5:1, 393 K, 5 wt.% catalyst); (b) reaction temperature (molar ratio of acetic acid: glycerol = 5:1, 5 wt.% catalyst, 2 h); (c) molar ratio of glycerol to acetic acid (393 K, 5 wt.% of catalyst, 2 h); (d) amount of catalyst (molar ratio of acetic acid: glycerol = 5:1, 393 K, 2 h).
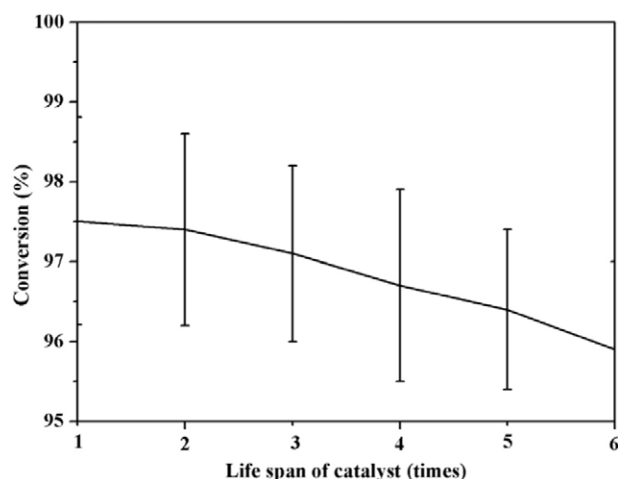
Fig. 8. The life span of regenerated catalyst for esterification. Reaction conditions: molar ratio of glycerol to acetic acid = 1:5 and 5 wt.% of catalyst at 393 K for 2 h.

Acknowledgements

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