

**Design and synthesis of sulfonated carbons with  
amphiphilic properties**

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## ARTICLE TYPE

## Design and synthesis of sulfonated carbons with amphiphilic properties

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A new kind of sulfonated carbon material with amphiphilic properties was synthesized by the hydrothermal carbonization of a mixture of furfural/ sodium dodecyl benzene sulfonate at 180°C in an autoclave. The addition of SDBS is necessary for the production of material with long carbon chains possibly used to improve the solubilization of long carbon-chain and steric compound, such as pivalic acid. The resulting material was characterized by means of N<sub>2</sub> adsorption, XPS, <sup>13</sup>C NMR, XRD, FT-IR and so on. Thus-synthesized material was proved to be the highly efficient solid-acid catalyst in the reactions such as esterification of pivalic acid with alcohols and much better catalytic performance was observed compared to conventional solid acid catalyst, e. g. Amberlyst-15 and Nafion resin.

## 1 Introduction

Homogeneous Brønsted acids such as H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> are essential catalysts for many reactions in chemical industry.<sup>1</sup> However, such liquid acid catalysts require energy-inefficient processing for separation and neutralization. Therefore, the principles of “green chemistry” and “green technology” have stimulated the research for reusable, insoluble and easily separable solid acids, such as zeolites,<sup>2-5</sup> heteropolyacid,<sup>6,7</sup> metal oxides or phosphates,<sup>8,9</sup> sulfonated resins<sup>10-12</sup> and sulfonated carbon.<sup>13-29</sup>

Sulfonated carbon is one kind of solid acid catalyst and well-studied because of its easy preparation and tunable surface properties, which have been reported to replace sulfuric acid in many reactions.<sup>22-29</sup> There are several methods to prepare sulfonated carbon, one is the sulfonation of active carbon, mesoporous carbon and pretreated char by using concentrated acid or oleum. However, the catalytic performance of sulfonated carbon materials by this method strongly depends on the property of the precursor materials employed,<sup>24,30,31</sup> among these precursors, an incompletely-carbonized ‘char’ was often used.<sup>1,13-15,25,32-34</sup> These chars were normally produced by carbonization of saccharides or polycyclic aromatic hydrocarbons at high temperature (e.g. 400°C) under an inert atmosphere for long time (>15 h) to form polycyclic aromatic carbon sheets. The structure or property of these ‘polycyclic aromatic carbon sheets’ is a key for the production of high efficient solid acid catalyst, which is dependent on the carbon precursor and carbonized temperature. Consequently, the properties of these sulfonated carbon materials, e. g. acid density, were not easy to tune due to the narrow acceptable temperature for the production of highly efficient solid-acids in spite of the drawback that high energy cost and a flow of inert gas were required for the carbonization.

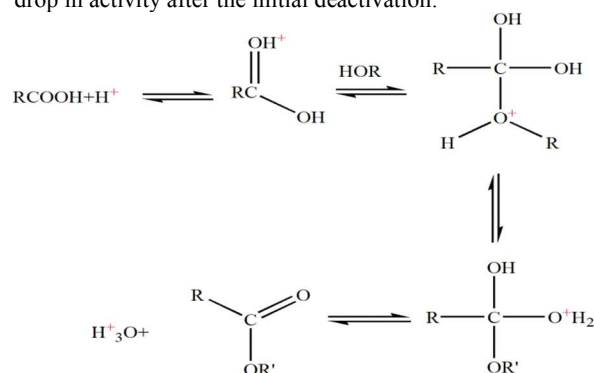
Another method for preparing sulfonated carbon is the direct hydrothermal carbonization (HTC) of sugars, such as glucose

with p-toluene sulfonic acid (TsOH).<sup>29</sup> Actually, HTC is a useful method and attracted much interest due to its simplicity, low operation temperature (433K–473K) and low cost.<sup>35, 36</sup> More importantly, HTC is a green method for generation of carbonaceous materials with tunable surface functionality such as with imidazole, sulfonic acid and carboxylic acid groups.<sup>29, 37, 38</sup>

Amorphous carbon bearing -SO<sub>3</sub>H groups can incorporate with other hydrophilic functional groups bonded to the flexible carbon sheets, such as carboxylic and hydroxyl groups. Such incorporation provides good access by reactants in solution to the -SO<sub>3</sub>H groups or has synergy effect, which gives rise to high catalytic performance for industrially important reactions, despite the small surface area of the material.<sup>1,13,26</sup> However, for many reactions, such as esterification and dehydration, the hydrophilic surface of carbon materials makes the sorption of bulky substrates non-effective and the removal of the byproduct water is difficult, thus leading to the deactivation of sulfonated carbon catalysts.<sup>14,24,34</sup> Very recently, Xiao’s group developed a mesoporous polymer-based solid acid catalyst with excellent hydrophobicity and extraordinary catalytic activity in esterification and dehydration of fructose.<sup>10,39</sup> In addition, in many bulky molecular involved reactions, the steric hindrance also hinders the application of solid acid, such as sulfonated resin and sulfonated carbon, thus the synthesis of sulfonated carbons with flexible long carbon chains and hydrophobic-hydrophilic properties, which can solubilize more substrates like surfactant are desirable for more applications.<sup>1,22,37</sup>

The esterification is a kind of typical acid-catalyzed reaction, and thus used here as a model reaction. The reaction mechanism is shown in Scheme 1. Accordingly, the organic acid is firstly adsorbed on the hydrophilic groups and activated by protons, and then reacts with alcohols, at the meanwhile, the in-situ generated water should be removed as soon as possible during the heterogeneous catalytic esterification. In addition, when bulky molecules involved in the esterification, which always happen for the production of cosmetic, a sulfonated carbon with amphiphilic

properties would be better to enhance the reactivity through solubilizing more starting materials, this kind of catalyst can be prepared by incorporating long carbon chains with the hydrophilic groups, such as  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$  and  $-\text{OH}$  in carbon framework. Previously, we reported the synthesis of carbon-based solid acid with glucose as the carbon source and p-toluenesulfonic acid as the sulfonating agent by hydrothermal method.<sup>23, 29</sup> Here we extended this method and used sodium dodecyl benzene sulfonated (SDBS), instead of p-toluenesulfonic acid as the source of sulfonic acid to get sulfonated carbon with flexible carbon chains and hydrophobicity. Its surface properties and catalytic activity in the esterification were investigated. This new type of sulfonated carbon catalyst exhibited remarkable catalytic performance for various acids involved reactions, especially for the esterification with long carbon chain or steric hindrance and can be reused for several times without significant drop in activity after the initial deactivation.



**Scheme 1** The mechanism of esterification under the conditions of acid catalysis

## 2 Experimental

### 2.1 Catalyst preparation

The carbon-derived solid-acid catalyst was prepared via thermal treatment of the mixture of furfural/ sodium dodecyl benzene sulfonate (SDBS)/ sulfuric acid at 453K. Typically, 8g of furfural, 8g of SDBS and a little amount of sulfuric acid were commixed in a 100mL Teflon-sealed autoclave and stirred for 30min. Then, the mixture was hydrothermally treated at 453K for 24h. The obtained black product was vacuum-oven dried at 423K for 8h to remove small molecules, then thoroughly washed with water and ethanol until the pH of the washing water closes to neutral and finally dried at 373K for 8h again. Thus-prepared sulfonated carbon was denoted as F-S. As a comparison, 8g of furfural and 10g of p-toluenesulfonic acid were also treated in the similar way and denoted as F-T.

### 2.2 Characterizations

The powder X-ray diffraction (XRD) patterns were collected in the  $\theta$ - $2\theta$  mode using a Bruker D8 Focus diffractometer ( $\text{Cu K}\alpha_1$  radiation,  $\lambda=1.5406\text{\AA}$ ), operated at 40 kV and 40 mA, respectively. The Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet Nexus 670 FT-IR spectrometer in the range of  $400\text{--}4000\text{ cm}^{-1}$ . The samples were ground along with

KBr and then pressed into thin wafers before analysis. X-ray photoelectron spectra (XPS) were measured using a Thermo ESCA LAB-250 spectrometer with monochromatic Al K $\alpha$  radiation and the XPS results were calibrated using C1s peak at 284.8 eV.  $^{13}\text{C}$  MAS NMR was tested on an apparatus BRUKER AV400 purchased from BRUKER Company. Nitrogen sorption isotherms were measured at 77K with a NOVA 4200e sorption analyzer. Before the measurements, the samples were degassed at 373K in vacuum for 8h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the apparent surface areas. Thermal gravimetric analysis (TG) and differential thermal gravimetry (DTA) were performed at a heating rate of 10 K/min from 40 to 800 °C in flowing air by using a WCT-2 thermal analyzer (PerkinElmer Diamond TG-DTA). The acidity of catalysts was measured by titration.<sup>40</sup> Typically, 0.1 g catalyst was put into 10 mL (0.05 mol/L) of an aqueous base solution (sodium hydroxide, sodium bicarbonate, or sodium chloride) and stirred for 1 h at room temperature. After washing with deionized water and filtration, the supernatant solution was titrated with an aqueous solution of hydrochloric acid or sodium hydroxide (0.05mol/L) by using phenolphthalein as an indicative. Sodium chloride, sodium bicarbonate and sodium hydroxide were used for the calculation of the  $-\text{SO}_3\text{H}$  density,  $-\text{SO}_3\text{H}$  plus  $-\text{COOH}$  density, and total acid site density ( $-\text{SO}_3\text{H}$  plus  $-\text{COOH}$ , lactic and phenolic groups), respectively.

### 2.3 Catalytic test

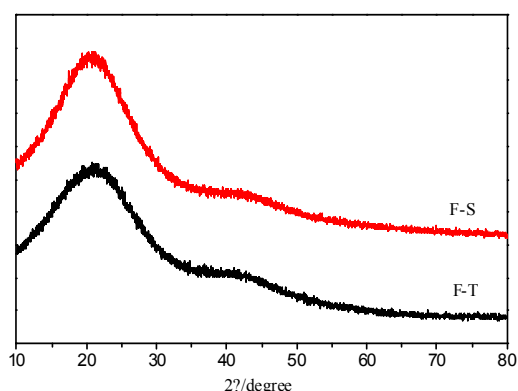
In a typical catalytic experiment, 10 mmol of pivalic acid (1.02g), 50 mmol of methanol (1.60g) and 0.25g of solid-acid catalyst were added to a 25 mL round-bottom flask with reflux condenser, and then heated to 343K under stirring. Few drops of reaction mixture were withdrawn periodically from the reaction mixture for GC analysis. Products were analyzed by GC-MS (Agilent 7890A-5975C) with a HP-5 column. Substrate was determined by titration with NaOH (0.05mol/L). Other reactions were carried out in the similar way except the reaction conditions.

## 3 Results and discussion

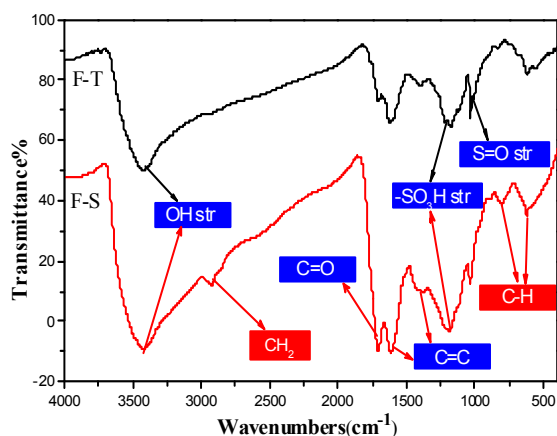
### 3.1 Structure and surface analysis of F-S and F-T samples

XRD, XPS, FT-IR and  $^{13}\text{C}$  MAS NMR techniques were used to characterize the structures and surface properties of these two samples. The XRD patterns of samples F-T and F-S (Fig.1) show that both samples all display amorphous carbon nature as indicated from the broad peaks of (002) at  $2\theta$  of  $10\text{--}30^\circ$ .

The FT-IR spectra of F-T and F-S samples are shown in Fig. 2. The bands attributed to  $-\text{SO}_3\text{H}$  groups stretching at 1032, 1007 and  $1118\text{ cm}^{-1}$  were observed for these two samples, indicating that the  $-\text{SO}_3\text{H}$  groups considered as the acid sites were successfully incorporated into the carbon framework. Compared to sample F-T, the stronger absorption band at  $2922\text{ cm}^{-1}$  attributed to C-H stretching on sample F-S would come from the long carbon chains from SDBS. In addition, the absorption bands at 698,  $730\text{ cm}^{-1}$  can be ascribed to C-H bending vibrations of the benzene and the band at 1495,  $1602\text{ cm}^{-1}$  can be assigned to C=C stretching vibration in benzene ring. According to the FT-IR spectra, the two samples have almost the same functional groups except the difference of  $-\text{CH}_2-$  amount.



**Fig. 1** XRD patterns of samples F-T and F-S.

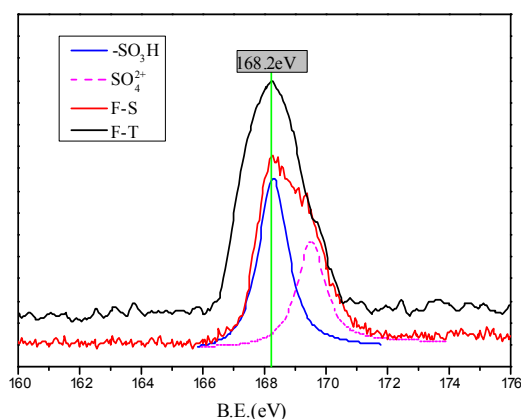


**Fig. 2** FT-IR spectra of samples F-S and F-T.

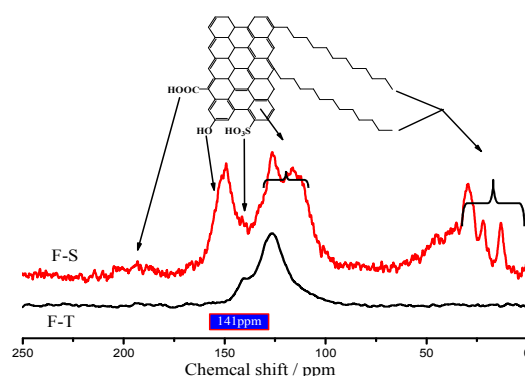
Besides FT-IR spectra, the X-ray photoelectron spectroscopy (XPS) of F-T sample reveals a single S 2p peak at 168.2 eV (Fig.3), which is attributed to sulfur in the  $\text{SO}_3\text{H}$  groups.<sup>29,30,41</sup> This result indicated that  $-\text{SO}_3\text{H}$  groups were successfully introduced into the carbon framework in sample F-T. For sample F-S, besides the peak at 168.2 eV, another S 2p peak at 169.5 eV was existed, which would be attributed to sodium sulfonate. It is reasonable, because during the synthesis, SDBS was used as the sulfonate source, instead of DBSA (dodecylbenzene sulfonic acid) and a small amount of sulfuric acid was added to generate sulfonic acid, thus, the by-product, sodium sulfonate was generated and may be tightly wrapped in carbon materials and presents a S 2p peak at 169.5 eV.

To confirm that the  $-\text{CH}_2-$  chains really linked on the F-S sample,  $^{13}\text{C}$  CP/MAS NMR was used and the spectra for these two samples are present in Fig. 4. It can be seen that sample F-T has the NMR resonance bands at 128 and 141 ppm, which were attributed to the aromatic carbons ( $\text{sp}^2$  carbon) and the polycyclic aromatic carbon coordinated with  $\text{SO}_3\text{H}$  groups ( $\text{Ar}-\text{SO}_3\text{H}$ ) in the framework.<sup>15,41</sup> For sample F-S, which used SDBS as the sulfonate source, a group of broad peaks appeared at 0~40 ppm, which can be assigned to methylene or other  $\text{CH}_x$  groups ( $\text{sp}^3$  carbon), beside the resonance bands at 128 and 141 ppm.<sup>14,41-43</sup> This confirmed the presence of few types of long carbon chains bonded onto the polycyclic carbon ring. In addition, the aromatic

carbon provided ample room to band lots of  $-\text{OH}$  groups.



**Fig. 3** S 2p XPS spectra of samples F-S and F-T.



**Fig. 4**  $^{13}\text{C}$  CP / MAS NMR spectra of samples F-S and F-T.

The acid site densities of the catalysts were determined by acid-base back titration<sup>44</sup> and summarized in Table 1. It shows that the F-S sample, which is rich in surface long carbon chains, contains almost the same acid density to F-T sample, according to the Boehm titration (Table 1). The abundant  $-\text{OH}$  and  $-\text{COOH}$  groups would be due to the partial oxidation by concentrated sulfonic acid ( $\text{H}_2\text{SO}_4$  and  $\text{TsOH}$ ).

**Table 1** Structural parameters and acid distribution of various solid acids.

Cata.	$\text{S}_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	Total acid ( $\text{mmolg}^{-1}$ ) <sup>a</sup>	Acid density( $\text{mmol/g}$ )		
			$-\text{SO}_3\text{H}^b$	$-\text{COOH}^c$	$-\text{OH}^d$
F-S	40	2.3	1.1	0.5	0.7
F-T	34	1.6	1.2	0.3	0.1
Amberlyst-15	53	4.7	3.8	-	-
Nafion-50	<1	0.9	0.9	-	-

Notes: <sup>a</sup>Determined by titration using NaOH

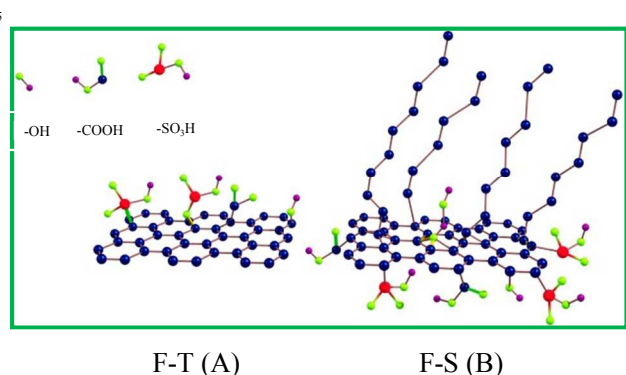
<sup>b</sup>Determined by titration using NaCl exchange and subsequent titration

<sup>c</sup>Obtained by subtracting the titration results of NaCl from the value of  $\text{NaHCO}_3$

<sup>d</sup>Obtained by subtracting the titration results of NaCl and  $\text{NaHCO}_3$

Combined all above characterizations, we can believe that SDBS really supplied long carbon chains to sample F-S. The long flexible carbon-chains is hydrophobic and can work together with the hydrophilic part ( $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ) to solubilize more

bulky organic acids (Scheme 2B) and therefore enhance the reactivity over F-S catalyst although the F-S sample has the similar functional groups, acid density and carbon framework as that of F-T synthesized by TsOH (Scheme 2A).



**Scheme 2** Possible structures of these two carbon-based solid acids.

### 3.2 Catalytic activity

The catalytic activities of thus-prepared solid acid (F-S) with amphiphilic properties were demonstrated through the esterification of various organic acids with methanol and the results are presented in Table 2. For comparison, the catalytic activities over sample F-T are also collected and summarized in Table 2. It shows that the two samples have similar yield for ethyl acetate, because of the small molecule of acetic acid. However, F-S has much higher catalytic activities than those of F-T for the bulky molecules, which proved the advantages of sulfonated carbon with long carbon chains, one would be come from the access of long-chain carboxylic acid by solubilization, and another may be due to the surface hydrophobicity to remove the in-situ generated water. Because of the bulky and steric structure, pivalic acid was selected as the substrate for further studies.

**Table 2** Comparison of various organic acid esterification over two catalysts.

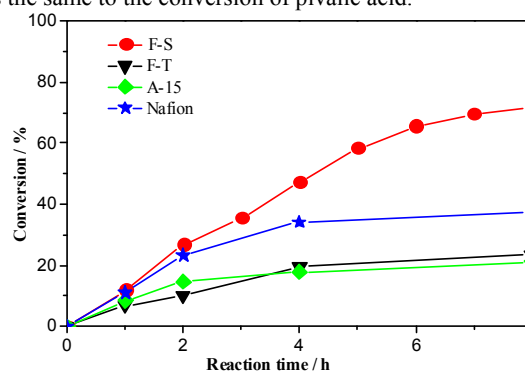
Substrate*	Conditions	Yield over F-S/%	Yield over F-T/%
Acetic acid	338K/5h	86.2	81.6
Oleic acid	338K/4h	87.3	63.8
Phenylacetic acid	338K/10h	95.7	58.3
Pivalic acid	338K/8h	73.6	23.5

Notes: \*Catalyst, 0.25g; molar ratio of organic acid and methanol: 1:5; methanol: 50 mmol

#### 3.2.1 Comparison of various carbon-based solid acids on the esterification of pivalic acid with methanol

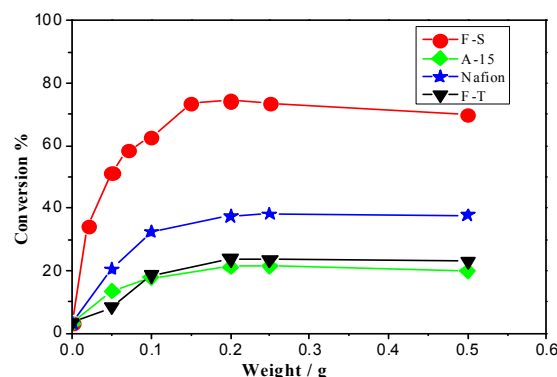
The influence of the molar ratio of methanol to pivalic acid on the conversion of pivalic acid was investigated firstly and found the maximum conversion was achieved at the ratio of 5:1, so this

ratio was used in the following study. Here, methanol was used not only as the reaction substrate, but also acted as solvent in this reaction. It should be noted that there was no any by-products being detected, so the yield of methyl trimethylacetate (MTMA) was the same to the conversion of pivalic acid.



**Fig. 5** Conversion of pivalic acid over various solid acid catalysts at 343K for different reaction times (catalyst, 0.5g; pivalic acid, 1.02g; methanol, 1.60g).

As a comparison, the commercial catalysts, Amberlyst-15 (A-15) and Nafion-50 were used in the esterification of pivalic acid and the results were present in Fig. 5. It shows that F-S was really an excellent solid acid catalyst, not only better than F-T, but also better than Amberlyst-15 and Nafion-50. The influence of the catalyst amount on the activity also confirmed the good performance of F-S (Fig. 6).



**Fig. 6** Conversion of pivalic acid in various solid acid catalysts at 343K for 8h (catalyst, different weights; pivalic acid, 1.02g; methanol, 1.60g).

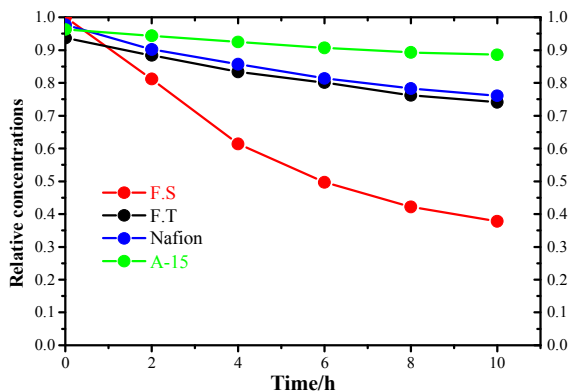
#### 3.2.2 Adsorption of pivalic acid and water on every solid acid

The solid acid Amberlyst-15 (3.8mmol/g) has a larger density of  $-SO_3H$  groups than F-S (1.1mmol/g), and Nafion has stronger acidity ( $H_0 = -11$  to  $-13$ ) than F-S. This indicates that the catalytic performance in the esterification reaction is not only related to the density and amount of acid sites although suitable acidity is necessary. One possible explanation for the excellent performance of F-S is that pivalic acid is much more easily adsorbed by sample F-S, which has both hydrophilic and hydrophobic properties to solubilize more pivalic acid; another possibility is that the hydrophobicity of F-S helps to remove the in-situ generated water from the active sites.

The adsorption of pivalic acid on every solid acid catalyst is



shown in Fig. 7, in terms of the decrease of pivalic acid concentration in methanol solution. In all experiments, 0.25g of the solid acid was added to 1.02g pivalic acid with 1.60g methanol solution, and the mixtures were stirred at room temperature (298K) for different times. The results revealed that pivalic acid can be absorbed by all solid acid, but the adsorption capacity is obviously different although the surface area of these solid acids is similar. It shows that F-S has the highest adsorption capacity and A-15 has the least, which is consistent with the catalytic reactivity in Fig. 5, indicating that the adsorption of pivalic acid really played a crucial role. The ability of F-S sample to adsorb pivalic acid was due to the presence of long carbon chains and the hydrophilic groups on its surface.



**Fig. 7** Concentrations of pivalic acid in methanol solution in the presence of various solid acids at room temperature (298K).

To confirm the hydrophobicity of F-S, which would prompt the reaction through removing the in-situ generated water, TG analysis was used to measure the amount of adsorbed water on F-S and F-T samples, respectively. During experiment, F-T and F-S samples were kept in the same two airtight containers with water in the bottom and lasted for 48h at room temperature, the data from TG analysis were summarized in Table 3. It should be noted that in the TG curve there is a weight loss from the adsorbed water, as well as a weight loss from the decomposition of  $\text{-SO}_3\text{H}$  groups. So the adsorbed amount of moisture was calculated according to the equation below by titrating the total acids of the two samples after treated at 473K:

$$M_C = M_{(\text{total weight loss})} - (M_{(\text{total acid})} - M_{(\text{acid weight rest})})$$

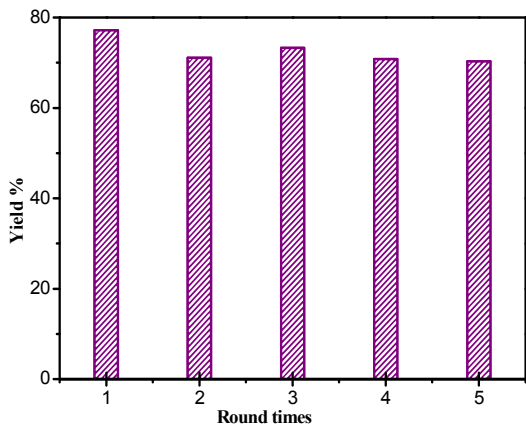
The results shown in Table 3 revealed that the long carbon chains from SDBS really prevent the adsorption of water (16.07% vs. 9.55%), which would be helpful for the removal of the in-situ generated water and prompted the reaction going to the right side.

**Table 3** TG and titration analysis results before and after 200 °C treatment.

Sample	Mass/mg				$M_C$ mg	Per. %
	Total weight	Total weight loss	Total acid	Acid weight rest		
F-S	2.806	0.352	0.346	0.262	0.268	9.55
F-T	2.527	0.435	0.284	0.255	0.406	16.07

### 3.2.3 Reusability of F-S catalyst in the esterification of pivalic acid

The stability of the catalyst is of great importance for practical usage, so the cycle usage of F-S was conducted and the results are shown in Fig. 8. After each reaction, the used catalyst was separated from the solution by centrifugation, washed with ethanol, dried at 363K overnight, and then put into a fresh mixture of pivalic acid/ methanol with keeping the same weight ratio of catalyst/ pivalic acid/ methanol. We can see from Fig.8 that the conversion of pivalic acid in five cycles was all above 70%, indicating a good stability after the initial deactivation.



**Fig. 8** Conversion of pivalic acid in the cycle usage.

### 3.2.4 Extension to other alcohols

To indicate that sample F-S is a wide-ranging catalyst in esterification, we chose four different alcohols: methanol (simple alcohol), cyclohexanol (cyclo alcohol), t-butanol (branch alcohol) and octanol (long chain alcohol). Table 4 shows the conversion of pivalic acid during esterification with four alcohols. We can see that high conversion of pivalic acid still can be obtained when using long chain and cyclo- alcohols though the temperature is relatively high, indicating F-S is really a good solid acid catalyst.

**Table 4** Conversion of pivalic acid between pivalic acid and different kinds of alcohol\*.

Substrate		Temperature	Yield %
Pivalic acid	Methanol	343K	73.8
	T-butanol	353K	48.8
	Cyclohexanol	413K	39.9
	Octanol	413K	59.8

Note: \* Reaction time: 8h, catalyst: 0.25g, pivalic acid: alcohol = 0.01mol: 0.05mol

## 4 Conclusions

Sulfonated carbon bearing long carbon chains was synthesized successfully by the hydrothermal carbonization of furfural, SDBS

and H<sub>2</sub>SO<sub>4</sub> and highly active in the esterification of bulky organic acids involved reactions. The long carbon chains from SDBS provide hydrophobic domain and play two roles in the esterification: one is working together with –SO<sub>3</sub>H, –COOH and –OH groups to solubilize more substrate like amphiphilic surfactant and enhance the touching of investigated organic acid with catalytic active sites; another is removing the in-situ generated water and prompts the reaction going further. The cycling usage indicated that the catalyst prepared by this method was relatively stable. Furthermore, thus-prepared catalyst can also be widely used in other kinds of esterification and this carbon-based solid acid can also be synthesized by using other cheaper carbon precursors, such as sugars, starch, cellulosic, polymers and anything that can be carbonized.

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## Notes and references

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## Design and synthesis of sulfonated carbons with amphiphilic properties

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