



# Impact of sulfonated hydrothermal carbon texture and surface chemistry on its catalytic performance in esterification reaction



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## ARTICLE INFO

### Article history:

Received 28 July 2014

Received in revised form

22 September 2014

Accepted 1 October 2014

Available online 25 October 2014

### Keywords:

Sulfonated hydrothermal carbon

Sulfonic solids

Esterification

Deactivation

Acid catalysts

## ABSTRACT

A carbon material consisting of interconnected spheres of around 350 nm diameter has been prepared by hydrothermal synthesis at 453 K. Subsequently, the hydrothermal carbon (HTC) has been treated in N<sub>2</sub> at different temperatures, 573, 673, 773, 973 K, giving rise to materials with similar spherical morphology but different microporous structure and oxygen content. Concerning porosity, the materials ranged from carbon formed exclusively by ultramicropores (<0.7 nm) to carbons with wider micropores. Concomitantly to the widening of micropores, the amount of oxygenated surface groups decrease as heat treatment temperature of HTC increases. Sulfonated carbon catalysts were prepared thereof and tested in the esterification of palmitic acid with methanol. The catalysts were benchmarked with a commercial activated carbon consisting of micro and mesopores that was sulfonated by the same method. The prepared materials showed significantly different catalytic activity and deactivation mechanisms, which have been explained on the basis of their different textural properties and oxygenated surface group content.

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## 1. Introduction

Esterification reactions has become a very essential reaction in the biorefinery industry for obtaining both biofuels such as biodiesel [1] and biomass derived chemicals such lubricants, surfactants etc. Biobased transportation fuels are increasingly considered as an alternative to traditional petroleum-based fuels due to the foreseen oil shortages and increasing volatility of oil-price. Additionally, the use of biodiesel is generally considered to be more environmentally benign than its petroleum–diesel counterpart due to strongly reduced sulfur and particulate emissions [2]. Current industrial biodiesel production is based on the (trans)esterification process, yielding fatty acid methyl esters (FAME) and glycerol from triglyceride feeds. This process can be catalyzed using either acid or base catalysts. Although the base-catalyzed reaction is faster, acid catalysts have a higher tolerance for free fatty acids and water present in triglyceride feeds, creating opportunities for the use of acid catalysts in biodiesel production [3]. Esterification reactions are usually catalyzed by Brønsted and Lewis liquid acid catalysts (H<sub>2</sub>SO<sub>4</sub>, HCl, BF<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>) but this poses problems of separation, corrosion and waste management. Solid acid catalyst

can circumvent these problems and therefore are preferred by industry. Acidic solids are among the most used heterogeneous catalyst both for bulk [4–6] and fine chemical synthesis [6,7]. Sulfonic acids supported on inert matrixes have been proposed as interesting alternatives to classical inorganic solids [8,9]. Among the sulfonic functionalized acid catalysts, sulfonated carbons have shown outstanding performance [10,11]. Moreover, carbon materials have some intrinsic advantages over other solid acid catalyst. Carbon materials have a tunable porosity and surface chemistry [12–14]. By changing the carbonization temperature, it is possible to prepare carbon materials with different degrees of graphitization and thus hydrophilic/hydrophobic character. Carbon materials have an inherently renewable origin and sometimes they are prepared using very mild conditions such as hydrothermal carbon [15]. In addition, sulfonated carbons are more stable and water-tolerant in hydrothermal conditions required for biomass conversion than other solid acid catalyst [16].

Hara et al. [10] prepared a strong and stable solid acid carbon catalyst by incomplete carbonization of sulfoaromatic hydrocarbons derived from naphthalene, which consisted of small polycyclic aromatic carbon sheets with attached SO<sub>3</sub>H groups. Using glucose as starting material, sulfonated carbon catalysts were prepared either by thermal carbonization at low temperature (673 K) [17] or by hydrothermal carbonization [18]. These carbonaceous materials showed higher turnover rates than other solid acid catalysts.

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However, a detailed study about the textural properties of these materials and the reasons of their superb activity is lacking.

Microporosity was created in sulfonated carbons prepared using cellulose as precursor and carbonized at several temperatures from 523 to 873 K [19]. The solid prepared at a carbonization temperature of 773 K showed the best turnover rate in esterification due to a compromise between high surface area and high density of sulfonic sites. Unfortunately, no result about reusability of these catalysts was shown. Mesoporous sulfonated carbons have been prepared using mesoporous silicas as sacrificial template [20–22]. The ordered mesoporous carbons with sulfonic groups exhibited larger initial reaction rates than other solid acid catalyst, which was attributed to the larger pore size and hydrophobic surface that can accommodate long chain fatty acids and reject water. Moreover, these catalysts showed excellent reusability in acid catalyzed reactions, which is attributed to their mesoporosity and good attachment of sulfonic groups to carbon. Sulfonated carbon nanotubes have also been used for esterification reactions showing deactivation, which is attributed to the adsorption of products [6]. On the contrary, carbon nanofibers functionalized with aryl sulfonic groups by diazonium chemistry were more stable and more active than other solid acids in esterification reaction. This was attributed to absence of microporosity, which facilitates the accessibility of reactants to sulfonic groups on CNF surface [23].

In a previous work [24], we tested sulfonated hydrothermal carbons in the esterification of palmitic acid with methanol. It was observed that the catalyst suffered some deactivation upon reuse which was demonstrated to be due to the formation of surface methyl sulfonyl esters. The textural properties of sulfonated hydrothermal carbons were characterized extensively in previous work [25]. The material showed ultramicropores, which became accessible to reactants under polar solvents due to breaking the hydrogen bonds between the high loading of acidic groups (sulfonic and carboxylic) present in the pore surface.

In all the above mentioned works, carbon materials of very different surface chemistry and texture have been used. Due to the scattering of the properties of these materials, withdrawing characterization–performance relationships is not a straightforward task. There is some consensus that a high density of acid sites is beneficial for activity. This could be one of the reasons why poorly graphitized materials with more defects, *i.e.* pyrolyzed at low temperatures, outperform highly graphitized materials [19]. It is not yet clear enough why some carbons exhibit deactivation upon reuse while others do not.

The need to shed some light into these aspects prompted us to prepare HTC materials heat-treated at different temperatures. This enabled the preparation of sulfonated HTC catalysts with a gradual variation of the porosity and surface chemistry. To the best of our knowledge, the effect of annealing temperature of HTC on its catalytic performance has not been studied systematically. The sulfonated HTC catalysts have been benchmarked against a sulfonated activated carbon with high surface area and high carbonization degree. The different textural properties and surface chemical composition of the materials can account for the different catalytic activity and deactivation behavior.

## 2. Experimental

### 2.1. Preparation of sulfonated hydrothermal carbons

D-glucose was purchased from Sigma–Aldrich. Norit SX Ultra Cat 8020-1 was a gift from CABOT. Hydrothermal carbon (HTC) synthesis was carried out from D-glucose (25 mL, 1 M in water) as described previously [24,26]. Subsequently, as-synthesized HTC carbon was heat treated under N<sub>2</sub> flow at different temperatures

from 573 to 973 K using a ramp of 5 K/min and a holding time of 2 h. The HTC carbon materials were named as HTC- followed by calcination temperature in K.

To prepare the sulfonated acid catalysts, the resulting material was then treated with concentrated (>96%) sulfuric acid (20 mL H<sub>2</sub>SO<sub>4</sub>/g solid) under argon atmosphere at 423 K during 15 h. The sulfonated samples were then washed thoroughly with hot distilled water until neutrality of the filtrate and dried overnight at 378 K. The sulfonated catalyst are denoted by adding –SO<sub>3</sub>H to the name of the carbon precursor.

### 2.2. Characterization

Surface areas were determined by N<sub>2</sub> adsorption at 77 K (BET) using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 423 K. Alternatively, it was also determined by CO<sub>2</sub> adsorption (Dubinin–Radushkevich) at 273 K up to 1 bar in the same apparatus, after outgassing under the same conditions.

C,H,S elemental analysis was carried out by combustion in a ThermoFlash 1112 elemental analyzer equipped with a TCD detector. Oxygen analysis was done by direct assay which involves pyrolysis of the sample at 1070 °C in a nickel/carbon bed under a known He flow. The outlet flow, after passing a separation column, ends in a TCD detector. The oxygen content of sample is quantified on the basis of CO analyzed.

SEM analysis was carried out with a SEM EDX Hitachi S-3400N microscope with variable pressure up to 270 Pa and with an EDX Röntec XFlash de Si(Li) analyzer. The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal.

Scanning transmission electron microscopy (STEM) of sulfonated hydrothermal carbon was carried out using a FEI TECNAI F30 electron microscope equipped with Gatan Energy Filter and cold field emission gun (FEG) operated at 300 kV with 1.5 Å lattice resolution. TEM specimens were prepared by ultrasonic dispersion in ethanol and a drop of the suspension was applied to a holey carbon support grid. The elemental S, C and O profiles along hydrothermal carbon sphere were collected using Energy Dispersive X-Ray Analysis (EDX).

The total amount of acid sites on each catalyst was determined by back titration. The solid (50 mg) was added to 25 mL of 0.01 M NaOH solution and allowed to equilibrate under stirring for 1 h. Thereafter, it was titrated with 0.05 M potassium hydrogen phthalate solution using a Crison pH Burette 24.

### 2.3. Esterification of palmitic acid with methanol

Palmitic acid (1.92 g, 7.5 mmol), methanol (3.04 mL, 75.0 mmol), sulfonated carbon (0.059 mmol SO<sub>3</sub>H), and 1-methylnaphthalene (0.30 g, 2.1 mmol) as internal standard were stirred (≈1000 rpm) in a round flask immersed into a silicone bath at 85 °C under reflux conditions. Reaction was monitored by gas chromatography (HP-5890-II).

## 3. Results and discussion

### 3.1. Characterization

HTC materials were prepared from diluted glucose solutions which gave rise to spheres of 350 nm average diameter (Fig. 1a). These spheres are not isolated but condensed to form aggregates. Upon calcination between 573 and 973 K the spherical morphology is retained but the diameter of the spherical basic units increases slightly. The average sphere diameters are 400, 450 and 520 nm for samples heat-treated at 673, 773 and 973 K, respectively (Fig. 1).

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