



## Tire-derived carbon for catalytic preparation of biofuels from feedstocks containing free fatty acids

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### ARTICLE INFO

#### Article history:

Received 10 May 2018

Revised 22 July 2018

Accepted 24 July 2018

Available online xxxxx

#### Keywords:

Biofuels

Solid acid catalyst

Recycled tires

Free fatty acids

Esterification

### ABSTRACT

The utilization of waste feedstocks rich in free fatty acids (FFAs) improves biofuel production on the basis of economics and sustainability. However, converting these feedstocks to usable biofuel poses inherent problems in terms of the FFA to biofuel conversion yield and the catalyst lifetime. Here, we report novel ferric sulfate impregnated carbon derived from waste tires as highly active catalysts for FFA to biofuel conversion. Our approach takes advantage of facile synthesis methods involving sonication and dehydration processes to create materials that are useful for the efficient catalytic conversion of FFAs to advanced biofuels. Esterification of FFAs to fatty acid methyl esters was achieved at 65 °C and atmospheric pressure with >98% yield even in the presence of triglycerides. These catalysts maintained similar activity after four successive uses, which indicates that the active catalytic sites are effectively supported by the three-dimensional meso/microporous architecture of the tire-derived carbon.

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### 1. Introduction

For biofuels to have a competitive edge in the market, catalytic processes in which inexpensive feedstocks are efficiently converted into advanced fuels must be investigated and developed. Waste oils, originating from plants or animal fats, represent ideal feedstocks for their overall cost. It is, however, difficult to obtain high conversion of the feedstock to useable biofuel when the free fatty acids (FFAs) content exceeds 10% [1–8]. FFAs undergo undesired saponification during the base-catalyzed transesterification

process typically used for the production of biofuel [9,10]. To alleviate this problem, a two-step treatment process is usually performed to maximize the yield of biofuels from FFA-rich feedstocks. In the first step, sulfuric acid is conventionally applied as a homogeneous acid catalyst to carry out the esterification of FFAs to fatty acid methyl esters (FAMES), and in the second step, a base-catalyzed transesterification process is used to convert the remaining triglycerides (TGs) to FAMES. The use of sulfuric acid as a homogeneous catalyst has obvious undesired problems such as environmental pollution, equipment corrosion, and the requirement of an extra neutralization step [2,6,11,12]. To alleviate this problem and improve the conversion of FFA to FAME, different sulfonated solid acid catalysts were studied using different precursors such as sugars [1,13], single-walled carbon nanotubes [14], polymers [15–18], silica [19,20], and biomass [21–24]. However, some of these catalysts have shown their tendency to leach catalytically active acid sites, which reduces their activity towards esterification [4]. Furthermore, surface functionalization of these carbon-based catalysts has largely utilized environmentally harmful chemicals,

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such as urea and chlorosulfonic acid. Therefore, new materials and functionalization processes are required to develop sustainable catalysts that efficiently convert FFAs to FAMES.

Ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) represents a catalyst with good activity towards the conversion of FFAs to FAMES, however ferric sulfate has poor solubility in oils and alcohols, limiting its use as a catalyst in mixtures of FFAs, TGs, and methanol [25–27]. To improve the catalytic conversion of FFAs to FAMES using ferric sulfate, it is critical to load this salt onto effective supports that allow for enhanced mass transfer in mixtures of FFAs, TGs, and methanol. Mesoporous carbon-based supports are ideal candidates since they can effectively support catalytically active materials and in some cases are miscible in FFAs, TGs, and alcohols; however many of these materials are expensive to produce in large quantities. Recently, we have shown that scrap tires could be processed into high-quality carbon with a well-controlled pore size [28–32]. Importantly, tire-derived carbon represents a sustainable carbon source that can be mass produced at a decreased cost while simultaneously decreasing the environmental and health impacts of waste tire rubber. Herein, we show that ferric sulfate impregnated waste-tire-derived carbon are effective catalysts for converting FFAs to FAMES. The hierarchical porous structure of waste tires not only allows for ferric sulfate impregnation but also provides necessary Lewis ( $\text{Fe}^{3+}$ ) and Brønsted acid sites for esterification reactions [33,34]. More notably, the unique meso/microporous morphology of waste-tire-derived carbon allows for the esterification of large molecules, such as FFAs, to take place on the surface of the catalysts without significantly losing its catalytic activity after several uses.

## 2. Materials and methods

### 2.1. Synthesis of ferric sulfate impregnated tire carbon catalysts

Waste-tire-derived carbons were prepared via pyrolysis as previously described in the literature [28,29,35]. Briefly, tire crumbs were heated in concentrated sulfuric acid at 110 °C for about 12 h and the resulting solid was washed with copious amounts of water; this step is critical in removing significant amount of steel and inorganic fillers (e.g. ZnO) [36,37] from the tire rubber while simultaneously allowing for higher yields of carbon. The resulting mass was then pyrolyzed at 1100 °C under  $\text{N}_2$  flow. The furnace was ramped from 25 °C to 400 °C at a ramp rate of 1 °C/min and further increased to 1100 °C at 2 °C/min; the furnace was then cooled to room temperature upon reaching 1100 °C. These pyrolysis conditions lead to tire-derived carbon with a unique hierarchical porous structure with a decreased concentration of inorganic fillers. The resulting carbon yield was about 50 wt.% (when comparing the starting mass of tire rubber to the resulting tire-derived carbon). To prepare the ferric sulfate impregnated tire carbon catalysts, 5, 10, 15, 20 and 50 wt.%  $\text{Fe}_2(\text{SO}_4)_3$  (Baker Analyzed Reagent, >90%) was mixed with tire carbon by grinding with a mortar and pestle for 5 min. The mixture was then added to deionized (D.I.) water (5.00 mL of D.I. water was added for every 1.0 g of tire carbon) and sonicated for 2 h (Branson 3800). After sonication, the mixture was then stirred overnight, and then the D.I. water was removed by thermal evaporation at 100 °C.

### 2.2. Structural characterizations

X-ray diffraction patterns were collected on a PANalytical X'Pert Pro equipped with a  $\text{Cu K}\alpha$  X-ray tube. All data were processed with HighScore Plus, a software package supplied by PANalytical. Brunauer-Emmett-Teller (BET) surface area measurements were

collected on a Micromeritics Gemini VI Surface Area and Pore Density Analyzer. Fourier transform infrared (FTIR) spectroscopy measurements were collected on a Varian 640 spectrometer (Agilent Technologies) with a spectral resolution of  $0.18 \text{ cm}^{-1}$ . All samples were dispersed in KBr (Sigma Aldrich) in a 1:200 weight ratio (sample: KBr), ground with a mortar and pestle, and pressed to form transparent pellets for FTIR analyses. Scanning electron microscopy (SEM) images were collected on a Zeiss Merlin with a gun acceleration of 10.0 kV. Energy-dispersive X-ray spectroscopy (EDS) elemental mappings and spectra were collected with an acceleration voltage of 15.0 kV using a Bruker EDS spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were collected for each powder sample on a Thermo K-Alpha XPS system with a spot size of 400  $\mu\text{m}$  at an energy resolution of 0.1 eV. Thermogravimetric analysis (TGA) was completed with a TA Instruments Q5000IR apparatus under a constant flow of air at 10 mL/min.

### 2.3. Evaluation of catalytic activities

The conversion of oleic acid (OA) to fatty acid methyl esters (FAMES) was completed by reacting OA with methanol in a round-bottom flask under reflux with vigorous stirring. The ferric sulfate impregnated tire carbon catalysts were dried at 100 °C before use. During the reaction study, a 10:1 M ratio of methanol to FFA was mixed with 10 wt.% of catalyst (in terms of the FFA content) and the reaction temperature was then maintained under reflux. To determine the Arrhenius activation energy of the catalyst, the esterification was performed at temperatures between 40–80 °C. To test the effect of water on the catalytic activity, the same procedure was followed where D.I. water (5, 10, 15, and 20 wt.% with respect to FFA content) was added to the reaction mixture. The catalytic activity tests varying methanol and the content of each catalyst follow the aforementioned procedure, where the amounts of methanol or catalyst were adjusted while the FFA volume remained constant. For mercury poisoning experiments, one or three drops of mercury were added to the reactions prior to heating the mixtures to reflux. To determine the content of FFAs and FAMES in the resulting reaction mixture, GC–MS spectra were collected using an Agilent 7890A GC with 5975C MSD coupled with an Agilent 30 m  $\times$  0.250 mm, 0.25  $\mu\text{m}$  HP-5MS column. The GC–MS samples were prepared by mixing 0.4  $\mu\text{L}$  of the reaction mixture in 1.0 mL HPLC grade hexane; 1  $\mu\text{L}$  of this sample was injected via the autosampler and split 50:1 (at a constant 1.2 mL/min He flow rate). The resulting GC–MS spectra were analyzed in MestReNova, where the total ion chromatograms were integrated to determine the percent conversion of OA to methyl oleate. For catalytic studies involving TGs, the FFA content was determined before and after the reactions using the standard titration method with KOH in isopropanol and phenolphthalein as the pH indicator.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the tire-derived carbon catalysts

Waste-tire-derived carbon was prepared by soaking tire crumbs (<3 cm in size) in concentrated sulfuric acid at 110 °C for ~12 h, washing the crumbs with  $\text{H}_2\text{O}$ , and pyrolyzing the mass at 1100 °C under a  $\text{N}_2$  flow in a tube furnace. Pre-treating tire rubber with concentrated sulfuric acid is critical to not only remove inorganic fillers (such as ZnO or steel) from the tire rubber, but also, increase the yield of high-value-added carbon. For pyrolysis, the furnace was heated from 25 °C to 400 °C at a ramp rate of 1 °C/min and then heated to 1100 °C at 2 °C/min before cooling to room temperature. These pyrolysis conditions yield a carbon with a unique hierarchical porous structure as seen by BET surface area analysis [29].

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