



## Synthesis of 4-aminobenzenesulfonic acid functionalized carbon catalyst through diazonium salt reduction for biodiesel production



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### ABSTRACT

A series of carbon catalysts are synthesized through the arylation diazonium salt reduction approach from coal to catalyze esterification of oleic acid with methanol for biodiesel production. Under the activated carbon preparation temperature of 900 °C, mass ratio of 4-aminobenzenesulfonic acid to activated carbon of 6 and arylation temperature of 45 °C, the synthesized carbon catalyst gains the surface area and pore volume of 629.3 m<sup>2</sup> g<sup>-1</sup> and 0.29 cm<sup>3</sup> g<sup>-1</sup>, respectively. Besides, the carbon catalyst possesses abundant and strong active sites with the 4-sulfophenyl group density of 0.97 mmol g<sup>-1</sup> and acid strength of 0.8 < pH < 3.3. Catalytic capability of the carbon catalyst, which is synthesized under the above optimized condition, in esterification is stronger than the commercial Amberlyst-15, where the maximum efficiency achieves 95.04% with the carbon catalyst added mass percentage of 12%, molar ratio of methanol to oleic acid of 10, esterification duration of 4 h and esterification temperature of 65 °C. Due to leaching of the 4-sulfophenyl groups, esterification efficiency declines to 77.63% for the fifth reused cycle of the carbon catalyst. Meanwhile, the regenerated carbon catalyst supplies the esterification efficiency of 86.05%. Chemical composition of the produced biodiesel is identical to pure methyl oleate and its fuel properties are in accordance with ASTM D 6751.

### 1. Introduction

Gradual depletion of petroleum fuels and aggravation of environmental pollution make the alternative energy urgent. Biodiesel, consisting of alkyl esters of C<sub>12</sub>-C<sub>22</sub> fatty acids, is normally produced through transesterification (Eq. (1)) of triglycerides (TGs) [1] or esterification (Eq. (2)) of free fatty acids (FFAs) [2] with methanol or ethanol, etc, under the effect of catalyst. Biodiesel is fuel of renewability, biodegradability and non-toxicity [3], and pollutant emissions, such as sulfur dioxide, unburned hydrocarbons and particulate matters are greatly reduced during biodiesel combustion [4]. Besides, no mechanical modifications of engines are required for the substituting of

diesel by biodiesel due to their similar physicochemical properties [5]. However, biodiesel production at commercial scale remains the major obstacle till now. To cut down the production cost, low-quality non-edible oils appear for biodiesel production [6], such as palm fatty acid distillate [7], waste cooking oil [8] or crude jatropha oil [9], where the free fatty acids (FFAs) in the non-edible oils restrict the alkali catalysts due to the undesirable saponification [10]. Liquid acid catalysts, like hydrochloric acid and sulfuric acid, etc, are also improper because of equipment corrosion, complicated separation and environmental pollution [11]. Subsequently, the solid acid catalysts, such as zeolites, resins and solid super acids, are used to catalyze esterification to avoid the above problems [12,13].

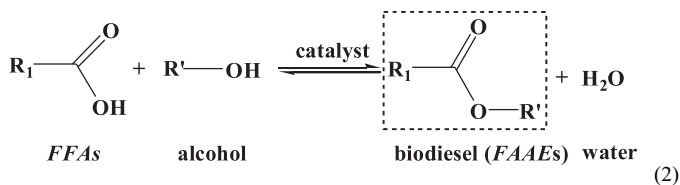
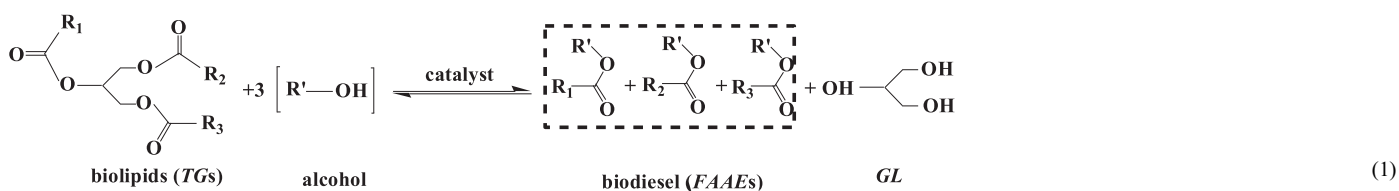
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Sulfonated carbons are proper candidates of the solid acid catalysts owing to the affinity of carbon support for the reactant molecules and the presence of strongly acidic sulfonic groups on the catalyst surface [14–16]. Traditionally, the carbon solid acids are synthesized through sulfonation of the partially carbonized carbon materials, where the catalytic performance is depressed by the limited microstructure [17–19]. Except for the sulfuric acid treatment method, sulfonation with 4-aminobenzenesulfonic acid to obtain solid acid catalyst has also been reported. Geng [20] grafted 4-sulfophenyl groups onto mesoporous carbon substrates to synthesize solid acids, which worked more efficiently than Amberlyst-15. Carbon catalyst with active sites density of 1.95 mmol H<sup>+</sup> g<sup>-1</sup> and specific surface area of 689 m<sup>2</sup> g<sup>-1</sup> was synthesized by Liu [21] through diazonium salt reduction and exhibited comparable catalytic activities with the commercial catalysts in esterification. For the above catalyst syntheses, hypophosphorous acid as reducing agent was employed and low temperature of 0–5 °C was required. Malins [22] altered the harsh condition for carbon catalyst synthesis from 4-aminobenzenesulfonic acid without reducing agent and operated higher than 5 °C, where esterification efficiency of rapeseed oil fatty acids with methanol achieved 95%. Also, Gao [23] sulfonated the ordered mesoporous carbons with 4-aminobenzenesulfonic acid at 80 °C and the maximum esterification efficiency of oleic acid with methanol achieved 96.25%. Coal mainly consists of carbonaceous organic compounds, where the aromatic rings connect with oxygen containing functional groups (carboxyl, hydroxyl and carbonyl groups) and alkyl side chains [24,25]. Except for the conventional applications of combustion, gasification and liquefaction, it is of great potential to be used as carbon precursor for catalyst synthesis. Nevertheless, researches about carbon solid acid catalyst synthesis from coal through arylation diazonium salt reduction using 4-aminobenzenesulfonic acid have never been reported.

In the present study, the coal activated carbon is firstly prepared and a series of coal carbon catalysts are then synthesized through the arylation diazonium salt reduction approach with 4-aminobenzenesulfonic acid. Conditions to synthesize carbon catalysts are optimized, including the activated carbon preparation temperature, mass ratio of 4-aminobenzenesulfonic acid to activated carbon and arylation temperature. In addition, carbon catalysts are characterized by different methods, such as elemental analysis, N<sub>2</sub> absorption-desorption analysis, acid-base titration method, Hammett indicator method, X-ray diffraction (XRD), Raman single grating spectrograph, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and X-ray photon spectroscopy (XPS). Influences of the carbon catalyst added mass percentage, molar ratio of methanol to oleic acid, esterification duration and esterification temperature on catalytic performances of the carbon catalysts are studied. The commercial cation exchange resin catalyst of Amberlyst-15 is also involved for comparison. Further, reusability and regenerability of the carbon catalyst are investigated. Finally, the chemical composition and fuel properties of the synthesized biodiesel are detected.

## 2. Materials and methods

### 2.1. Materials

Coal used for the activated carbon preparation is collected from Yulin, in Shaanxi province, China. Oleic acid, methanol, acetone, 4-aminobenzenesulfonic acid, sodium nitrite (NaNO<sub>2</sub>), sodium hydroxide (NaOH) and potassium hydroxide (KOH) are purchased from Kemiou Chemical Reagent Co., Ltd., Tianjin, China. Mineral acids of HCl (37.5%) and H<sub>2</sub>SO<sub>4</sub> (98%) are purchased from Laiyang Fine Chemical Plant, Shandong, China. All chemicals are analytical reagents (AR) and used without any further treatment.

### 2.2. Carbon catalyst synthesis

After dried at 105 °C, coal is grinded and filtered through a 200 μm metal sieve. Then, coal powder of 6 g and activation reagent KOH of 18 g are mixed and heated under N<sub>2</sub> stream at the designed temperature for 1.5 h to be carbonized. The carbonized coal is magnetically stirred in hydrochloric acid solution for 2 h and washed with hot de-ionized water, after which it is dried at 105 °C. Later, the coal activated carbon and 4-aminobenzenesulfonic acid are immersed in de-ionized water and heated at the arylation temperature with magnetic agitation, where the pH is adjusted between 7 and 8 through NaOH solution. Afterwards, NaNO<sub>2</sub> and HCl are dropwise added into the suspension for aryl diazotization to introduce active sites of the 4-aminobenzenesulfonic acid (namely, the 4-sulfophenyl groups) onto the coal activated carbon, which lasts for 10 min. The slurry is transferred into funnel and washed with hot de-ionized water for pH neutrality. Finally, the carbon catalyst is rinsed by acetone and dried at 105 °C for use. Syntheses of the carbon catalyst are optimized from the activated carbon preparation temperature (from 600 to 900 °C with an increment of 100 °C), mass ratio of 4-aminobenzenesulfonic acid to activated carbon (from 2 to 10% with an increment of 2%) and arylation temperature (from 30 to 90 °C with an increment of 15 °C). The synthesized carbon catalyst is defined as CT<sub>1</sub>-AT<sub>2</sub>, where C and A are for carbonization and arylation, T<sub>1</sub> and T<sub>2</sub> represent the temperature for carbonization and arylation.

### 2.3. Catalyst characterizations

Dry basis contents of carbon (C<sub>d</sub>), hydrogen (H<sub>d</sub>), nitrogen (N<sub>d</sub>) and sulfur (S<sub>d</sub>) for coal, coal activated carbon and coal carbon catalysts are determined by elemental analysis (EA) on a Vario El Cube Elementar, AR, Germany, with an accuracy of 0.3%. The oxygen content, O<sub>d</sub>, is calculated through 100-C<sub>d</sub>-H<sub>d</sub>-N<sub>d</sub>-S<sub>d</sub>-A<sub>d</sub>, where the ash content on dry basis, A<sub>d</sub>, is measured according to GB/T 212-2008. Microstructure parameters of the carbon catalysts are measured by N<sub>2</sub> absorption-desorption analysis on a TriStar II 3020 surface area and porosity analyzer, Micromeritics Co., Ltd, USA. The carbon catalyst is firstly degassed at 150 °C and the textural characterizations are then analyzed at -196 °C using N<sub>2</sub> as the isothermally adsorbed substance. The specific surface area and pore volume are calculated by Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model, respectively. The 4-sulfophenyl group density to label quantity of the active sites of the carbon catalyst is measured by the acid-base titration method. Carbon catalyst of 0.05 g is mixed with NaCl solution (2 mol L<sup>-1</sup>) of 30 mL and affected with ultrasonic oscillation for 30 min. Then, the carbon catalyst is filtered from the liquid-solid mixture and washed

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