A SYNTHESIS OF SOLID ACID CATALYSTS FOR USING IN HYDROLYSIS OF CELLULOSE FROM RICE STRAW INTO GLUCOSE

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ABSTRACT

In this study, a carbon–based solid acid catalyst was prepared via hydrothermal carbonization method (HTC) using glucose and pyrolysed waste tyre as carbon precursors and aqueous solution of H_2SO_4 as sulfonation agent. Prepared catalysts were characterized by X–ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared FT–IR and Brunauer–Emmett–Teller (BET). As the result, catalysts were manufactured with the appropriate physical and chemical characteristics and high acidity.

Keywords: glucose, cellulose, catalysis, hydrothermal carbonization (HTC).

1. INTRODUCTION

Biomass is one of the most promising renewable and sustainable alternative for energy and chemical production. As an energy source, biomass can be utilized without depleting the existing reserves. Current research interest is, therefore, to convert biomass to fuels and chemicals [1]. In recent years, many researchers have found alternative source material for the production of biofuel to replace fossil fuels urgently. The use of materials derived from biomass to produce biofuels and chemicals for plastics as well as pharmaceuticals not only enhances the value of the agricultural production but also contributes to solving environmental pollution issues and ensuring ecological balance. From the time being, efficient use of biomass is only 10% compared with that generated biomass energy. Meanwhile, resource-products are regarded as one of the potential sources of raw materials for energy production [2, 3].

For the effective consumption of cellulose, the primary and essential step is the hydrolysis of cellulose into glucose [1, 4]. Many studies have been concentrated on homogeneous acids and celluloses in a long period of time. With homogeneous acids, although they exhibit reasonable prices and good catalytic activities but practical applications are difficult due to a lot of problems

including reactor corrosion, waste treatment and poor recyclability [5–7]. In contrast to homogeneous acids, celluloses that can be derived from *aspergillus niger*, *trichoderma reesei* are more selective and competitive to hydrolyze cellulose into glucose at lower reaction temperature [8]. However, enzymatic hydrolyses of cellulose is a slow process, which will spend a long time to achieve a satisfactory yield of glucose [9]. In addition, prior to enzymatic hydrolysis of cellulose into glucose, an energy and cost–intensive pretreatment is necessary to remove the recalcitrance to celluloses. At this moment, celluloses are still very expensive [10]. From the viewpoint of green chemistry and industrialization, solid acid catalysts such as metal oxides, H–form zeolites, heteropoly acids, functionalized carbonaceous acids and magnetic functionalized carbon acids, which are separable, recoverable and reusable, should be the excellent choices for the hydrolysis of cellulose into glucose, because they have tremendous potentials to overcome the above–mentioned limitation [11]. In other words, solid acids catalysts case opens up opportunity to explore more efficient, economical, simple and greener processes for the hydrolysis of cellulose into glucose.

In this study, the solid acid catalysts (CS, CS1, CS2 and CP) were synthesized by hydrothermal carbonization (HTC) and characterized using analytical techniques such as XRD, SEM, EDS, FT–IR. Finally, their catalysts were high acidity and used for hydrolysis of cellulose from rice straw into glucose.

2.   MATERIALS AND METHODS

2.1. Materials

Glucose (> 99.5 % – Xilong, China), Ethanol (96 % – Xilong, China), H_2SO_4 (98 % – Xilong, China) and carbon from pyrolysed waste tyre. All the chemicals were used without further purification.

2.2. Synthesis of carbonaceous material from glucose (CS)

The glucose–derived carbonaceous material without in–situ functionalization was prepared by hydrothermal carbonization of glucose in the absence of any additive. Typically, 20 g of glucose was dissolved in 60 mL of water, and the mixture was then loaded into a 100 mL stainless steel autoclave. After that, it was heated up to 180 °C and kept for 10 h at the autogenous pressure. The resulting solid product was isolated by centrifugation, washed repeatedly with ethanol and water for several times, and oven–dried at 80 °C for 12 h. The obtained carbonaceous solid material is denoted as glucose–derived carbonaceous material

2.3. The synthesis of functional groups attached carbon catalyst

To realize *in–situ* functionalization of the carbonaceous material bearing with –SO_3H groups on surface, H_2SO_4 solution was used in the sulfonation processes. The as–synthesized 10 g CS was dispersed in a sulfuric acid solution under stirring. The suspension was placed in a 100 mL stainless steel auto clave and maintained at 180 °C for 4 h. The black products were filtered, washed and then dried following the same procedures in CS preparation. Sulfuric acid solutions with different concentrations were employed in the sulfonation processes. The sulfonated CS solid acid catalysts were labeled as CS1, CS2 according to the sulfuric acid and water volumetric ratios of 1:1 and 2:1, respectively. The sulfonation of CP (carbon from pyrolysed waste tyre) was prepared following the same procedures in CS2 sulfonation.

2.4. Physical characterization

In this work, X–ray diffraction (XRD) patterns of C–SO₃H catalysts were recorded with SIEMENS–D5000 diffractometer using monochromatic high intensity CuKα radiation (λ = 0.15418 nm) at the scanning rate of 0.03°/s and in the scanning range from 20 to 70°. Scanning Electron Microscope (SEM) was conducted using JSM–6500F, JEOL. Brunauer–Emmett–Teller (BET) specific surface area was obtained by nitrogen adsorption–desorption isotherms at 77 K after degassing the sample at 300 °C for 2 h under nitrogen gas, using Quantachrome NOVA 1000e. Sulfur content of the catalyst was measured with EDX (Model–9000, Thermo Jarrell–Ash Corp, USA), and elemental analysis was carried out using Elementar Vario EL cube (Germany). The FTIR spectrum for the carbon materials was obtained by using a KBr pellet containing the prepared biomass carbon powder.

Methods of analyses were conducted at Institute of Applied Materials Science, Viet Nam Academy of Science and Technology, 1 Mac Dinh Chi Street, Ben Nghe Ward, District 1, Ho Chi Minh City, Vietnam.

2.5. The process of determining the acid sites densities of catalyst

Acid density of solid acid catalysts as well as carbon background are essential elements for determining the catalytic activity. In terms of sulfonated carbon materials, there are two types of acidic sites: one is the strong acid sites (the introduced –SO₃H groups); and the other is the weak acid sites, including –COOH and –OH from incomplete carbonization of the carbon precursor. In general, the –SO₃H groups are the active sites. Therefore, the –SO₃H amount of carbon–based solid acid prepared in this study was calculated by cation exchange analysis [12].
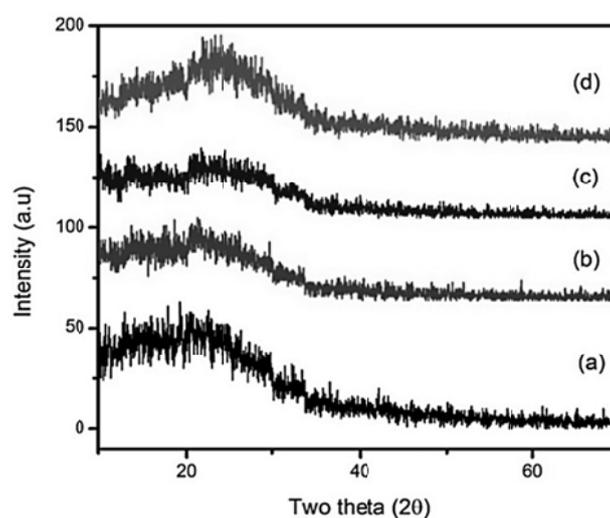
3. RESULTS AND DISCUSSION

Figure 1. XRD patterns of catalysts (a) CS; (b) CS1; (c) CP; (d) CS2.

Figure 1 illustrates the XRD patterns of the as–prepared CS, CS1, CP and CS2. In all samples, broad diffraction peaks at low diffraction angles (2θ) of 10–30° are observed [12], attributed to successful hydrothernal carbonization from glucose precusor and carbon derived

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from tyre pyrolysis. Compared to CS**1**, the higher the intensity of peak of CS2 and CP is, the better carbon structure of those is.
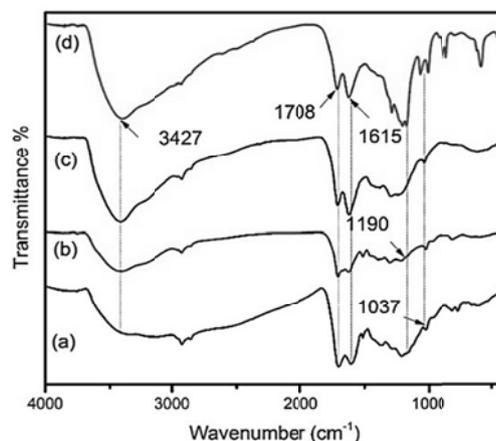

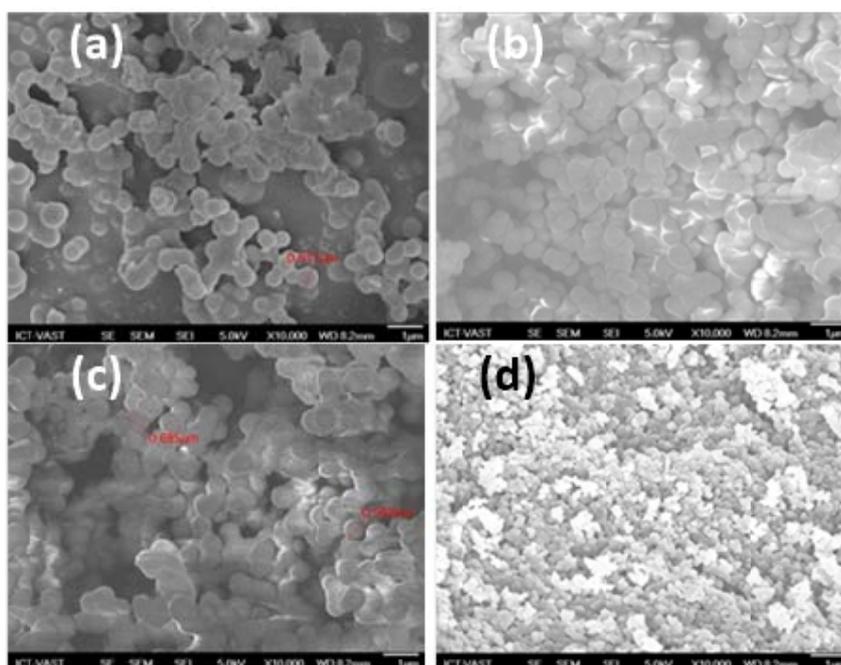*Figure 2.* FTIR (a) CS, (b) CS1, (c) CP and (d) CS2.

Figure 3. SEM image of (a) CS, (b) CS1, (c) CS2 and (d) CP.

Figure 2 is the FTIR image of CS, CS1, CP and CS2. The representative bands are summarized as follows. The bands at around 3500 and 3400 cm^{-1} are attributed to phenolic OH groups. The bands at about 3000 and 2800 cm^{-1} are assigned to –OH of carboxylic –COOH groups, while the C=C for condense aromatic appears at approximately 1650 and 1600 cm^{-1}; The bands at 1750 and 1700 cm^{-1} are corresponding to C=O groups (acid carboxylic); adsorption bands at 1118 and 1038 cm^{-1} [13] are ascribed to the S=O, implicating the appearance of SO$_3$H

in all samples (Figure 2). Peaks at 1618 and 1382 cm^{-1} are indicative of C=C group. C=O and C–O groups are located at 1707 and 1203 cm^{-1}, respectively, demonstrating the existence of –COOH group [14].

SEM micrographs of solid products are shown in Figure 3, the morphology of CS, CS1, CS2, and CP at 180 °C was separately spherical. The morphology and size of carbon particles are based on carbon sources and the increase in acid concentration from 49% to 65%. However, the size of particle trend to decrease from 0.67 μm to 68.6 nm when the acid concentration rises, attributable to pretty high pyrolysis temperature and long pyrolysis time (180 °C, 4 h).

Figure 4 and Table 1 show EDX results of CS, CS1, CS2 and CP. C and O elements are present at as–prepared carbon materials and corresponding sulfonated catalysts. S peaks due to sulfur in SO$_3$H groups were observed in all sulfonated samples, suggesting that all S atoms in the sulfonated material are contained in SO$_3$H groups. The decrease in S content of CS1 catalyst was assigned to mitigating acid sites of catalyst, which led to low catalytic activity.

Table 1. The EDX results of CS, CS1, CS2 and CP.

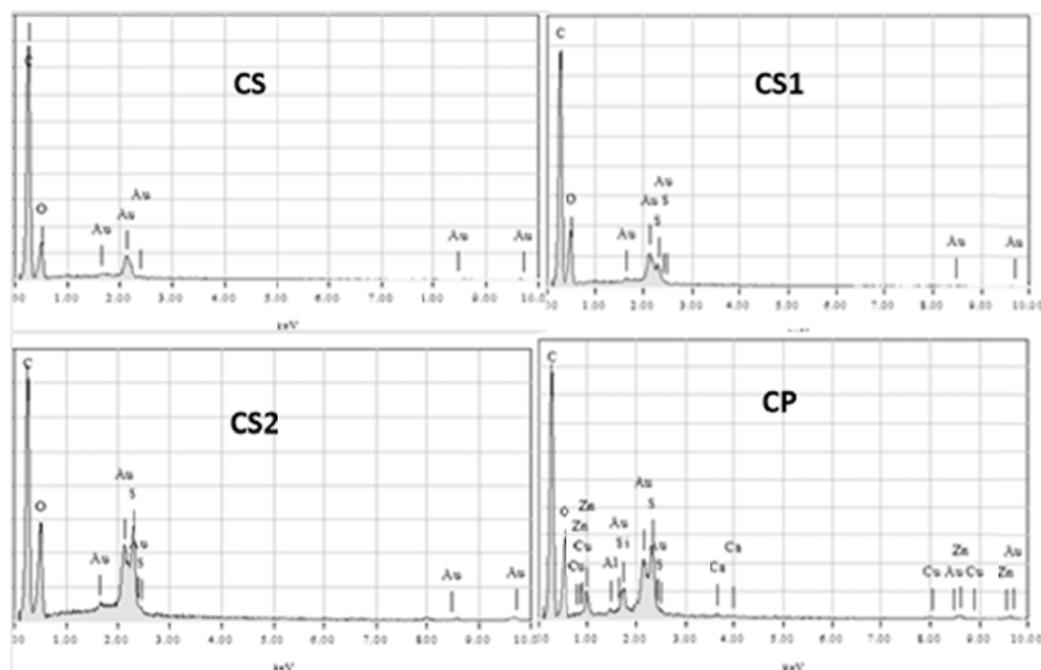| Element	CS	CS1	CS2	CP
C	96.61	93.8	86.05	84.23
O	3.39	5.2	8.27	6.86
S		1.00	5.68	4.69
Another	0	0	0	4.22
Total	100	100	100	100

Figure 4. The EDX results of CS, CS1, CS2 and CP.

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Table 2. Specific surface area and acid density.

Samples	SBET (m^2/g)	Acid density (mmol/g)
CS	38.55	0.24
CS1	43.95	0.42
CS2	55.37	1.08
CP	45.16	0.58

The acid site densities of catalysts were determined by EDX analytic method (Table 2) and acid–base back–titration. The acid titration experiments demonstrated that much higher acid site densities than the estimations based on sulfur elemental analysis. The higher estimated acid densities from titration are due to phenolic –OH and –COOH groups originating from incomplete carbonization of glucose. The strong sulfonation also may oxidize aliphatic CH$_3$/CH$_2$ groups to carboxylic acid groups, which may further explain the significant increase in total acid densit after sulfonation. The strength and density of acid sites of carbon–based solid acid is a vital factor closely related to the catalytic activity. The sulfonated CS have both strong and weak acid sites on the surfaces. As shown in Table 2, the total acid density on the surface increase from CS, CS1 and CS2 with increasing the concentration of the sulfuric acid solutions.

The preparation of catalysts includes two stages. Firstly, glucose is thermally treated by hydrothermal carbonization at 180 °C for 10 h to obtain a solid carbon material. Then, the obtained carbon material is sulfonated with different concentrations of sulfuric acid to introduce –SO$_3$H groups at 180 °C for 4 h. Specific surface area of CS2, CS1 and CP are 55.372 m^2/g, 43.949 m^2/g and 45.162 m^2/g, respectively. High acid density of CS1; CS2, CP are 0.417 mmol/g, 1.083 mmol/g, 0.58 mmol/g in turn. This indicated that catalytic activity mainly depends on total acid density regardless of its specific surface area. The carbon catalyst exhibits high catalytic performance in the presence of hydrophilic molecules despite its relatively low specific area, attributable to the incorporation of high densities of hydrophilic molecules into the carbon bulk binding with the flexible carbon sheets [15].

4. CONCLUSIONS

Rice straw treated with the two–stage process composed of separating hemicellulose with acid sulfuric and lignin by the aid of sulfomethylation agent for 7 h may be used as raw material for hydrolysis reaction of cellulose into glucose in support of the catalyst. Successful synthesized carbon catalyst containing –SO$_3$H functional groups via hydrothermal carbon chemistry (HTC) method from glucose precursors and pyrolysed tire. Synthesized catalyst has great activity in the hydrolysis reaction of cellulose from rice straw into glucose.

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