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# Carbon-based strong solid acid for cornstarch hydrolysis

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### Abstract

Highly sulfonated carbonaceous spheres with diameter of 100-500 nm can be generated by hydrothermal carbonization of glucose in the presence of hydroxyethylsulfonic acid and acrylic acid at 180 °C for 4 h. The acidity of the prepared carbonaceous sphere C4-SO<sub>3</sub>H can reach 2.10 mmol/g. It was used as a solid acid catalyst for the hydrolysis of cornstarch. Total reducing sugar (TRS) concentration of 19.91 mg/mL could be obtained by hydrolyzing 20 mg/mL cornstarch at 150 °C for 6 h using C4-SO<sub>3</sub>H as solid acid catalyst. The solid acid catalyst demonstrated good stability that only 9% decrease in TRS concentration was observed after 5 repeat uses. The as-prepared carbon-based solid acid catalyst.

**Keywords**: hydrothermal carbonization, solid acid catalyst, acidity, hydrolysis, total reducing sugar, corn starch.

#### 1. Introduction

In recent years, carbonaceous particle (CP) has been under intensive study because of its great chemical and physical properties such as monodisperse, stable particles, high surface functionalities and thermal stability. Carbonaceous particle has been used for a wide variety of applications, which include adsorbent [1], catalysts [2], electrode materials [3], stationary phases in liquid chromatography [4] as well as in the areas of energy generation and storage applications. A heterogeneous catalyst has stable and efficient functions for reactions would be very important to green chemistry application. Solid acid catalysis is one of the economically and ecologically important fields in catalysis. Solid acid catalysts have many advantages over liquid Brønsted acid catalysts. They are noncorrosive and environmentally benign, presenting fewer disposal problems, reusable and easy in separation. Therefore, the replacement of homogeneous catalysts with heterogeneous ones is becoming more important in chemical and life science industry [5]. Recently, a new class of sulfonated carbons derived through incomplete carbonization of simple sugars has been reported to have better catalytic performance for biodiesel synthesis and its catalytic performance compared with many other popular solid acids, including nation, sulfonated zirconia (SZ), and niobic acid [6-8]. Such sulfonated carbonaceous materials were synthesized via two steps. First, saccharides were incompletely carbonized at high temperature (>400 °C) under an inert atmosphere for long time (>15 h), which was not an environment-friendly process and numerous harmful wastes were formed. Second step, the sulfonation was carried out with large amount of sulfuric acid at high temperature. Furthermore, the separation of the final products from the concentrate sulfuric acid was also a tedious work.

Hydrothermal carbonization, which involves the hydrothermal decomposition of various carbohydrates in aqueous solutions at 180 °C has advantages of being very cheap, mild, "green" as it involves no organic solvents, and catalysts or surfactants. However, the carbonaceous materials obtained from the hydrothermal carbonization process possess few functional groups for specific application. Although the surface activation of carbon materials is now a well-established process, it is a rather harsh method because of the extremely low reactivity of the carbon. Recently, it is becoming increasing important to explore the feasibility of preparing solid acid catalyst with simple and high density of acid. However, far too little attention has been paid to the characterizations of carbonaceous materials as solid acid catalyst.

South Kalimantan of Indonesia is one of the largest corn producing regions in 2011 with production of 113,885 tons of dry shelled corn [9]. The cornstarch is one of main products that could be derived from shelled corn. In order to increase the value of cornstarch, starch can be hydrolyzed into values-added products such as monosaccharide or oligosaccharides (glucose, maltose, dextrin, and etc). In this work, the preparation of a highly sulfonated solid acid catalyst used for cornstarch hydrolysis was studied. The characterizations of as-prepared solid acid catalyst and its catalytic performance on starch hydrolysis reaction were also investigated.

### 2. Experimental

### 2.1 Material

D-glucose ( $C_6H_{12}O_6$ ), sulfuric acid ( $H_2SO_4$ ), citric acid ( $C_6H_5Na_3O_7.2H_2O$ ), hydroxyethylsulfonic acid ( $C_2H_6O_4S$ ), acrylic acid ( $CH_2CHCO_2H$ ), amberlyst-15, sodium hydroxide (NaOH), sodium chloride (NaCl), chloride acid (HCl), oxalic acid ( $H_2C_2O_4$ ), phenolphthalein, acetone (( $CH_3$ )<sub>2</sub>CO), 3,5-dinitrosalisic acid ( $C_7H_4N_2O_7$ ) were obtain from Sigma-Aldrich and Acros. All other chemicals were analytical grade used without further purification.

#### 2.2 Synthesis of Sulfonated Solid Acid Catalyst (C-SO<sub>3</sub>H)

Solid acid catalyst prepared by one-step hydrothermal carbonization was carried out according to the procedure developed by Xiao et.al [10] with slight modification. Briefly, a mixture of glucose (5 g), citric acid (2.5 g), hydroxyethylsulfonic acid (1.5 g), and deionized (DI) water (40 mL) was placed in a 50 mL teflon-lined stainless steel autoclave, which was then heated in an oven at 180 °C for 4 h. In order to reduce the particle size of material, acrylic acid (10% v/v) was added to the solution before heating [11]. Black brown carbonaceous materials were obtained by filtration and washed thoroughly with DI water followed by methanol. The solid acid catalyst (C-SO<sub>3</sub>H) was obtained after drying the washed carbonaceous materials at 80 °C for 8 h in an oven.

### 2.3 Catalytic Activity of Starch Hydrolysis

The performance of catalyst was investigated by cornstarch hydrolysis reaction. The hydrolysis was conducted in a sealed reactor (volume, 50 mL) containing solid acid catalyst (0.4 g), cornstarch (0.8 g) and distilled water (40 mL) at various temperatures and durations. After reaction, an aliquot of the supernatant solution obtained by centrifugation was analyzed using 3,5-dinitrosalicylic acid (DNS) method for detecting total reducing sugar concentration [12]. For comparison, concentrate sulfuric acid, zeolite, amberlyst-15, and carbonaceous materials prepared from glucose and hydroxyethylsulfonic acid with and without acrylic acid were also employed to carry out the similar catalytic hydrolysis reaction. All data presented were obtained from duplicated experiments.

#### 2.4 Characterization Method

The Brønsted acid sites on prepared carbonaceous material was determined by neutralization titration method [13]. Briefly, the solution of 1 M NaCl (40 mL) and carbonaceous material (80 mg) was added. The mixture was sonicated for 20 min and stirred for 24 h at room temperature. After centrifugation, the supernatant was titrated by 0.01 N NaOH and phenolphthalein was used as an indicator. Field emission scanning electron microscopy (FE-SEM) images of the samples were obtained by scanning electron microscope (JEOL, JSM-6500 LV). Brunauer-Emmet-Teller (BET) surface area was determined from nitrogen adsorption-desorption by a Quantachrome, Autosorb-1 instrument. Fourier transform infrared spectrometry (FTIR, Bio-rad, Digilab FTS-3500) was used for the identification of the functional groups on the particles surface. Thermal graphymetric analysis (TGA, Perkin Elmer, Diamond TG/DTA) was carried out from ambient temperature to 700 °C under nitrogen atmosphere at a heating rate of 10 °C/min. The carbon content in the particles was estimated by the percentage weight loss from the corresponding TGA curves. UV-Vis spectroscopy (V-550-JASCO) was used for measuring the absorbance for total reducing sugar measurement by DNS method.

# 3. Results and discussion

#### 3.1. Solid Acid Catalyst Preparation and Characterization

Four different types of carbonaceous particles were prepared separately by onepot hydrothermal carbonization. C1 and C2 particles used for control experiments were prepared from glucose solution and glucose solution containing acrylic acid, respectively. In order to generate strong acid functional groups on the surface of carbonaceous particles, hydroxyethylsulfonic acid was mixed in glucose solution

without and with addition of acrylic acid to prepare C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H particles, respectively. The schematic diagram for the carbonaceous solid acid preparation is shown in Fig. 1a. As shown in Fig. 1b, the color of these 4 types of particles obtained after 4 h hydrothermal reaction at 180 °C is very different. The addition of acrylic acid reduces the color intensity of particles. In contrast, the particles become darker when hydroxyethylsulfonic acid was employed.



**Fig. 1** (a) Preparation of solid acid catalyst by one step hydrothermal carbonization and (b) product of carbonaceous materials for C1, C2, C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H.

As observed by FE-SEM (Fig. 2a), C1 is spherical shape with micrometer diameter size about 5-8 µm. In comparison, the particle C2 produced in the presence of acrylic acid has a much smaller size (300-500 nm) but highly aggregated (Fig. 2b). Probably, the acrylic acid can stabilize the newly formed carbonaceous particles and prevents them from further growth in glucose hydrothermal carbonization process. It has been reported that addition of 10% w/v acrylic acid as co-monomer to the glucose solution for hydrothermal carbonization can obtain carbonaceous materials rich in surface carboxylic groups[1, 14].



**Fig. 2** FESEM micrograph of carbonaceous particle produced by hydrothermal carbonization of (a) glucose solution (C1) (b) glucose solution with acrylic acid (C2), (c) glucose solution and sulfonic acid (C3-SO<sub>3</sub>H), (d) glucose solution with sulfonic acid and acrylic acid (C4-SO<sub>3</sub>H).

The presence of acrylic acid may promote glucose dehydration and polymerization rate that leads to more particles to be formed but with a smaller size. Hydroxyethylsulfonic acid was employed in the glucose-based hydrothermal carbonization for generating solid acid particles. However, as shown in Fig.2c, the size as well as morphology of the obtained particles (C3-SO<sub>3</sub>H) were not affected much as compared with C1. In order to reduce the size and increase surface area of solid acid particles, acrylic 20 acid was employed to participate in the solid acid particles generation by using hydroxyethtylsulfonic acid. As shown in Fig. 2d, the obtained C4-SO<sub>3</sub>H has a significantly reduced size (100-500 nm) but highly aggregated morphology as observed for C2.

As shown in Table 1, hydrothermal carbonization significantly decreased the pH of glucose solution for C1 preparation from 6.0 to 3.11. The significant decrease of pH is mainly resulted from the 25 generation of carboxyl groups on the surface of particles [1, 10]. When acrylic acid was employed (C2), the initial pH of the glucose solution was lowered but the carbonaceous particles yield was enhanced significantly from 3.83 % to 15.71%. As observed in FE-SEM images, the addition of

acrylic acid reduced the particles size that also leads to double the BET surface area to  $11.17 \text{ m}^2/\text{g}$ . For the preparation of C4-SO<sub>3</sub>H, acrylic acids as well as hydroxyethylsulfonic acid were employed to participate the formation of solid acid particles. A significant increase of acidity to 2.10 mmol/g was observed for C4-SO<sub>3</sub>H.

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**Table 1** The pH before and after carbonization, yield and acidity of carbonaceous materials for C1, C2, C3–SO<sub>3</sub>H and C4–SO<sub>3</sub>H

Sample	Characterization				
	рН		Yield	Acidity (mmol/g)	
	Before	After	(%)		
C1	6.00	3.11	3.83	0.17	
C2	2.00	1.87	15.71	0.36	
C3–SO <sub>3</sub> H	2.10	1.75	20.10	1.99	
C4–SO <sub>3</sub> H	1.60	1.12	20.00	2.10	

As shown in FTIR spectrum of these particles (Fig. 3), the apparent sulfonate absorption bands at 10 1720 cm<sup>-1</sup> and 1207 cm<sup>-1</sup> were noticed for C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H. This indicates that the carbonaceous particles were successfully sulfonated by hydroxyethylsulfonic acid. The absorption bands of C=C double bonds at 1608 cm<sup>-1</sup>, C-OH stretching, and OH bending vibrations at 1000-1300 cm<sup>-1</sup> were also found for all the samples [8].

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Fig. 3 FTIR spectra of carbonaceous particle for C1, C2, C3-SO<sub>3</sub>H, and C4-SO<sub>3</sub>H



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Fig. 4 TGA curve for carbonaceous particle for C1, C2, C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H

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TGA was used to examine thermal stability of the prepared C1, C2, C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H. As shown in Fig. 4, the C1 displayed a slight weight loss (about 5%) over 25-150 °C, because of the loss of bonded water [8]. In contrast, the C3-SO<sub>3</sub>H particle shows a larger weight loss (15%) in the same temperature range. Evidently, the larger weight loss is due to a higher amount of water is associated 15 with the sulfonate groups. Interestingly, C4-SO<sub>3</sub>H prepared in the presence of acrylic acid shows a better thermal stability that up to 250 °C only 3% weight loss was resulted. With further increase in temperature above 600 °C, about 56%, 51%, 33%, and 50% of initial weight remained for C1, C2, C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H, respectively. When compared with carbon-based solid acids prepared by other investigators, our preparation C4–SO<sub>3</sub>H demonstrates a higher acid content as shown in Table 2.

**Table 2** Comparison of acid content on the as-prepared C-SO<sub>3</sub>H and other solid acid catalyst under different operation conditions.

Sample	<b>Operation condition</b>	Acid content (mmol/g)	Ref.
Carbon-based solid Catalyst (C4–SO <sub>3</sub> H)	One step: (carbonization 180 °C, 4 h)	2.1	This study
Carbon-based solid Catalyst (C– SO <sub>3</sub> H)	Two step: (carbonization 400 °C, 1 h and sulfonation 150 °C, 13 h)	2.0	[15]
Sugar catalyst	Two step: (carbonization 400 °C, 15 h and sulfonation 150 °C, 15 h)	0.66	[16]
Carbon-based	Two step: (carbonization 400 °C, 1	1.5	

solid Catalyst	h and sulfonation 120°C, 10, h) NUSCEI	ΡΤ	
Carbon-based	Two step: (carbonization 450 °C, 5	1.2	[17]
solid Catalyst	h and sulfonation 80 °C, 10 h)		
Carbon-based	Two step: (carbonization 550 °C,	1.3	[7]
solid Catalyst	15 h and sulfonation 80 °C, 15 h)		
Carbon-based	One step: (carbonization 180 °C, 4	1.7	[18]
solid Catalyst	h)		

#### 3.2 Corn Starch Hydrolysis

Sulfonated carbonaceous particles prepared by hydrothermal carbonization of glucose has been demonstrated to have a good catalytic activity for the synthesis of acetals and ketals [19]. The carbon-5 based solid acid not only can hydrolyze pure crystalline cellulose as well as mineral liquid acid but also lignocellulosic materials. Starch consists of amylose and amylopectin. C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H were employed for starch hydrolysis in a stainless autoclave at 90-150 °C for 6-12 h. The schematic diagram of starch hydrolysis by solid acid catalyst is shown in Fig. 5. The amount of glucose in the supernatant was considered as the hydrolysis product catalyzed by C-SO<sub>3</sub>H.



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Fig. 5 Schematic diagram for starch hydrolysis using C-SO<sub>3</sub>H as catalyst.

As shown in Fig. 6, total reducing sugar (TRS) concentration increased up to 4.271 g/mL and 7.252 g/mL at 150 °C for using C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H as catalyst, respectively. TRS produced by C4-SO<sub>3</sub>H at temperature 90-130 °C was lower than that produced by C3-SO<sub>3</sub>H. However, when temperature 20 increased to 150 °C, reactivity of C4-SO<sub>3</sub>H increased significantly that 76% higher amount of TRS was produced as compared with C3-SO<sub>3</sub>H. Hydrolysis reaction temperature higher than 150 °C was not performed because carbonaceous products will be generated from the hydrolysis products [20]. The increased color intensity developed by DNS assay indicates reducing sugars produced by carbon-based solid acid increased with reaction temperature (Fig. 6, inset). The highest TRS production yield

based on the amount of starch loaded was around 37.59%, this indicates some of the hydrolysis products may exist as oligomers.

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**Fig. 6** Total reducing sugar (TRS) for starch hydrolysis by C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H in the variation of temperature. Reaction condition: 0.8 g starch, 0.4 g C3-SO<sub>3</sub>H and 40 mL DI water for 3 h



**Fig. 7** Total reducing sugar (TRS) for starch thydrolysis by C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H in the variation of reaction time. Reaction condition: 0.8 g starch, 0.4 g C3-SO<sub>3</sub>H and 40 mL DI water at 150 °C.

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Fig. 7 shows the time course of TRS concentration at 150  $^{\circ}$ C using C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H solid acid catalyst. In the case of using C4-SO<sub>3</sub>H for starch hydrolysis, TRS increased to a peak value of

19.91 mg/mL with yield of 99.87% after 6 h reaction and oligomers are the primary products. It is apparent from Fig.7 that the time of reaction was affected to TRS production. The rate of hydrolysis increases linearly with the reaction time, after 6 h reaction the TRS start to decreased. In order to understand the reaction system in this case, it need to evaluate the selectivity of TRS. The selectivity 5 of TRS is described as moles of TRS in product divided by moles of starch reacted. Fig. 8 shows that after 6 h of hydrolysis reaction over C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H, the selectivity was dropped to 60.8% and 21.2 % at 7 h, respectively. By prolonging the reaction time, the selectivity started to decrease probably due to the degradation of sugar. It is known that at high temperature such as 150 °C sugar will dehydrate through an intermolecular condensation reaction that leads to the formation of furan-10 like molecules (furfural aldehyde and/or 5-(hydroxymethyl)-2-furaldehyde) [21].



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Fig. 8 Effects of reaction times on the glucose selectivity at 150 °C.

20 The recovered C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H were rinsed three times with 1000 mL of warm distilled water by vigorous stirring for 30 min and collected by centrifugation. The activity of the recovered catalyst was slightly lower than that observed in the original reaction. After 5 repeated uses, 9% TRS decrease was observed (Fig. 8). This indicates that starch can be effectively hydrolyzed into glucose by C4-SO<sub>3</sub>H and its catalytic performance is not significantly deteriorated after repeated use.



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**Fig. 8** The catalytic activity of C3-SO<sub>3</sub>H and C4-SO<sub>3</sub>H during 5 repeated used for starch hydrolysis. Reaction condition: 0.8 g starch, 0.2 g catalyst and 40 mL DI water at 150 °C for 3 h

It is of particular interesting to compare the catalytic activities of the carbon-based solid acid with 10 traditional concentrated H<sub>2</sub>SO<sub>4</sub> (>96%) and the two typical strong solid acid catalysts, zeolite and amberlyst-15 that are widely use in industrial process. As shown in Fig. 9, TRS about 4.08 mg/mL could be obtained without using any catalyst. It means starch can also be hydrolyzed in water under high temperature. In contrast, in the presence of C4-SO<sub>3</sub>H, the 0.8 g of starch loaded in the reactor was near completely hydrolyzed into TRS.





Fig. 9 Total reducing sugar (TRS) for starch hydrolysis by different type of catalyst. Reaction condition: 0.8 g starch, 0.4 g catalyst and 40 mL DI water for 3 h

The catalytic performance of C4-SO<sub>3</sub>H is comparable with that of concentrated  $H_2SO_4$  and amberlyt-15. This shows that this one-pot prepared carbon-based solid acid not only has the merit of non-toxic, eco-friendly, recyclable properties but also has excellent catalytic hydrolysis performance.

#### 54. Conclusions

Carbonaceous particle with rich content of strong acid can be easily synthesized in one-step hydrothermal carbonization reaction using glucose as starting material. Sulfonate and carboxyl groups are on the surface of carbonaceous nanoparticles. This carbonaceous particle can be used as solid acid catalyst with has good capability to hydrolyze cornstarch. It not only possesses good thermal stability 10 and high acidity content but also has the similar starch hydrolysis activity as concentrated H<sub>2</sub>SO<sub>4</sub> and amberlyt-15. The good chemical activity and thermal stability of this carbon-based solid acid may enable them for application in other potential acid dependent catalytic reactions.

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#### References

- 20 [1] R. Demir-Cakan, N. Baccile, M. Antonietti, M.-M. Titirici, Carboxylate-rich carbonaceous materials via one-step hydrothermal carbonization of glucose in the presence of acrylic acid, Chemistry of Materials, 21 (2009) 484-490.
  - [2] P. Makowski, R. Demir Cakan, M. Antonietti, F. Goettmann, M.-M. Titirici, Selective partial hydrogenation of hydroxy aromatic derivatives with palladium nanoparticles supported on
- 25 hydrophilic carbon, Chemical Communications, (2008) 999-1001.
  - [3] Y.-S. Hu, R. Demir-Cakan, M.-M. Titirici, J.-O. Müller, R. Schlögl, M. Antonietti, J. Maier, Superior storage performance of a Si@SiOx/C nanocomposite as anode material for lithium-ion batteries, Angewandte Chemie International Edition, 47 (2008) 1645-1649.

- [4] M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, H. Inomata, Catalytic glucose and fructose conversions with TiO2 and ZrO2 in water at 473 K: Relationship between reactivity and acid-base property determined by TPD measurement, Applied Catalysis A: General, 295 (2005) 150-156.
- [5] K. Tanabe, W.F. Hölderich, Industrial application of solid acid-base catalysts, Applied Catalysis A:
- 5 General, 181 (1999) 399-434.
  - [6] M. Okamura, A. Takagaki, M. Toda, J.N. Kondo, K. Domen, T. Tatsumi, M. Hara, S. Hayashi, Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon, Chemistry of Materials, 18 (2006) 3039-3045.
  - [7] K. Nakajima, M. Hara, S. Hayashi, Environmentally benign production of chemicals and energy
- using a carbon-based strong solid acid, Journal of the American Ceramic Society, 90 (2007) 3725-3734.
  - [8] M.-H. Zong, Z.-Q. Duan, W.-Y. Lou, T.J. Smith, H. Wu, Preparation of a sugar catalyst and its use for highly efficient production of biodiesel, Green Chemistry, 9 (2007) 434-437.
  - [9] B.K.P.M.D. (BKPMD), Kalimantan Selatan, (2012).
- 15 [10] H. Xiao, Y. Guo, X. Liang, C. Qi, One-step synthesis of novel biacidic carbon via hydrothermal carbonization, Journal of Solid State Chemistry, 183 (2010) 1721-1725.
  - [11] J.X. Yi, G. Weinberg, X. Liu, O. Timpe, R. Schlögl, D.S. Su, Nanoarchitecturing of Activated Carbon: Facile Strategy for Chemical Functionalization of the Surface of Activated Carbon, Advanced Functional Materials, 18 (2008) 3613-3619.
- 20 [12] G. Miller, Use of dinitrosalicylic acid reagent for determination of reducing sugar, Analyt Chem., 31 (1959) 426-428.
  - [13] A. Onda, T. Ochi, K. Yanagisawa, Selective hydrolysis of Cellulose into glucose over solid acid catalyst, Green Chemistry, 10 (2008) 1033-1037.
  - [14] I.F. Nata, C.K. Lee, Novel carbonaceous nanocomposite pellicle based on bacterial cellulose,
- 25 Green Chemistry, 12 (2010) 1454-1459.
  - [15] X. Mo, E. Lotero, C. Lu, Y. Liu, J. Goodwin, A novel sulfonated carbon composite solid acid catalyst for biodiesel synthesis, Catalysis Letters, 123 (2008) 1-6.
  - [16] M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, Adsorption-Enhanced Hydrolysis of β-1,4-Glucan on Graphene-Based Amorphous Carbon
- 30 Bearing SO3H, COOH, and OH Groups, Langmuir, 25 (2009) 5068-5075.
  - [17] M. Hara, Biomass conversion by a solid acid catalyst, Energy & Environmental Science, 3 (2010) 601-607.
  - [18] H. Xiao, Y. Guo, X. Liang, C. Qi, One-step synthesis of novel biacidic carbon via hydrothermal carbonization, Journal of Solid State Chemistry, 183 (2010) 1721-1725.

- [19] X. Liang, J. Yang, Synthesis of a novel-carbon based strong acid catalyst through hydrothermal carbonization, Catalysis Letters, 132 (2009) 460-463.
- [20] B.M. Kabyemela, T. Adschiri, R.M. Malaluan, K. Arai, Glucose and fructose decomposition in subcritical and supercritical water: detailed reaction pathway, mechanisms, and kinetics, Industrial
- 5 & Engineering Chemistry Research, 38 (1999) 2888-2895.
  - [21] M. Sevilla, Antonio B. Fuertes, Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides, Chemistry - A European Journal, 15 (2009) 4195-4203.

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# Highlights

- Carbon strong solid acid was succefully prepared by one-step mild hydrothermal carbonization.
- The acrylic acid as monomer was effectively reduce the diameter size of particle.
- The solid acid catalyst show good catalytic performance of starch hydrolysis.
  - The solid acid catalyst is not significantly deteriorated after repeated use.

Graphical abstract

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