



One-step synthesis of novel biacidic carbon via hydrothermal carbonization

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ABSTRACT

The novel biacidic carbon has been synthesized via one-step hydrothermal carbonization of glucose, citric acid, and hydroxyethylsulfonic acid at 180 °C for only 4 h. The novel carbon had an acidity of 1.7 mmol/g with the carbonyl to sulfonic acid groups molar ratio of 1:3, which was confirmed by IR, XPS, TPD, SEM, and BET analyses. The catalytic activities of the carbon were investigated through esterification and oxathioketalization. The results showed that the carbon owned the comparable activities to sulfuric acid, which indicated that the carbon holds great potential for the green processes.

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1. Introduction

Functional carbonaceous materials [1], e.g., fullerenes [2] and carbyne-like one-dimensional structures [3], have received more and more attention because of their wide variety of applications, which include adsorbents, catalysts [4], electrode materials [5], stationary phases in liquid chromatography [6], and others. Such carbonaceous materials are usually synthesized on harsh conditions, for example, electric-arc discharge techniques [7], catalytical chemical vapor deposition [8], catalytic pyrolysis of organic compounds [9], and high-temperature (800 °C) hydrothermal conversion from amorphous carbon [10]. Recently, much attention has been focussed on the sulfonated carbonaceous materials for their potential to replace the traditional homogeneous acid catalysts [11–15]. The sulfonated carbonaceous materials were synthesized via two steps. First, saccharides were incompletely carbonized at high temperature (> 400 °C) under inert atmosphere for long time. It was not the environment-friendly process with low yield and numerous harmful wastes were formed. The sulfonation was taken to introduce the sulfonic acid groups in the second step. The sulfonation procedure was also carried out on harsh conditions for the inactive surface. Hydrothermal carbonization, which involved the hydrothermal decomposition of various carbohydrates in aqueous solutions at low temperature, has the advantages of being very cheap, mild, and “green” as it involves no organic solvents, catalysts, or surfactants [16]. However, the carbonaceous materials obtained from the hydrothermal carbonization had little functional groups, and a subsequent chemical or steam activation has to be

applied for a certain purpose [17]. The sulfonated carbon has been synthesized in our previous work using hydrothermal carbonization [18]. However, sulfonation should be taken to introduce the sulfonic acid groups. Besides the harsh reaction conditions, the separation of the carbon material from concentrated sulfuric acid was a tedious work. Here a novel biacidic carbon has been synthesized via one-step hydrothermal carbonization of glucose, citric acid, and hydroxyethylsulfonic acid at 180 °C for only 4 h. The sulfonic acid groups were introduced to the carbon surface during the carbonization processes (Scheme 1). The catalytic activities of the novel carbon were investigated via esterification and oxathioketalization. The results showed that the carbon had the comparable activities to sulfuric acid.

2. Experimental

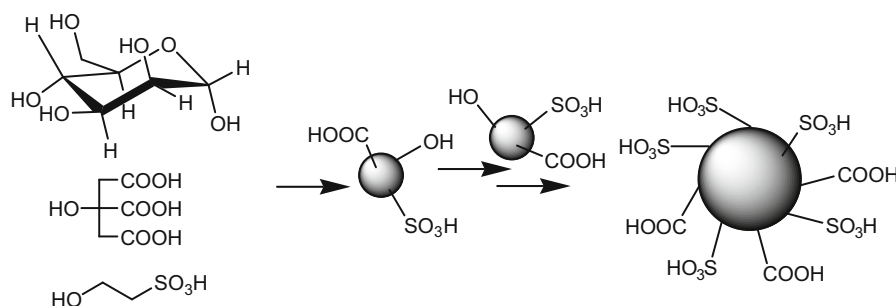
All organic reagents were commercial products of the highest purity available (> 98%) and used for the reactions without further purification. Cyclohexanone, acetic acid, *n*-butanol, 2-mercaptoethanol, and hydroxyethylsulfonic acid were purchased from Shanghai Chemicals Co. HY zeolite was purchased from Nankai University with the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ of 7 and the BET surface of 850 m²/g. Amberlyst-15 was purchased from Fluck with an acidity of 0.8 mmol/g and a BET surface of 35 m²/g.

2.1. Synthesis of the catalyst

The solution of the 10 g glucose, 5 g citric acid, 3 g hydroxyethylsulfonic acid, and 80 mL deionized water was placed in a 100 mL Teflon-lined stainless steel autoclave, which was heated in an oven at 180 °C for 4 h. The resulting products were filtered, washed

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Scheme 1. The synthetic route of the sulfonic acid groups functionalized carbonaceous material.

with water and methanol, and dried in a vacuum oven at 100 °C for 4 h and 2.3 g biacidic carbonaceous material was obtained.

2.2. The esterification of acetic acid and butanol

The mixture of acetic acid (24 mmol), butanol (20 mmol), and biacidic carbon (50 mg) was stirred at room temperature (25 °C). The process of the reaction was monitored by GC analysis of the small aliquots withdrawn. On completion, the catalyst was recovered by filtering and washing with acetone, and then dried in an oven at 80 °C for about 1 h.

2.3. The oxathioketalization of cyclohexanone and mercaptoethanol

Cyclohexanone (20 mmol), mercaptoethanol (24 mmol), and the acid carbon (50 mg) were mixed together. The mixture was stirred at room temperature (25 °C) for the specified period. The process of the reaction was monitored by GC analysis as mentioned above.

3. Results and discussion

3.1. Characterization of the novel catalyst

The formation for the novel biacidic carbon involves the dehydration of the glucose, citric acid, and hydroxyethylsulfonic acid as the first step. During the process, glucose transformed to various organic compounds such as furfural, 5-hydroxymethylfurfural, organic acids, aldehydes. These compounds could react with citric acid and hydroxyethylsulfonic acid to introduce carboxylic and sulfonic acid groups. Upon subsequent dehydration (polymerization), microscopic carbon-containing spheres with sulfonic acid, carboxylic acid, and hydroxyl groups were formed. Subsequent loss of water by these assemblies leads to further coalescence of microscopic spheres to larger spheres (Scheme 1) [19–21]. Here, hydroxyethylsulfonic acid was used to introduce the sulfonic acid groups, which owned the hydroxyl groups for intermolecular dehydration. Citric acid was quite useful here. The carbon with low acidity was obtained when hydrothermal carbonization was carried out in the absence of citric acid and the sulfonic acid groups also could transform to other groups such as sulfonate and sulfone. As a result, the amount of sulfonic acid and carboxylic acid groups of the carbon was quite different from the molar ratio of hydroxyethylsulfonic acid and citric acid. No solid product formed when the single citric acid was used as raw material. Also, the carbon with low acidity was obtained from glucose and citric acid. Furthermore, there were still many soluble acid materials in the filtrate, which could be reused for the next run. The carboxylic acid groups were much more active than sulfonic acid groups and participate in the reactions instead of sulfonic acid groups. Citric acid also acted as

the carbonyl acid groups supplier. The acidity of the novel sulfonic acid and carboxylic acid groups functionalized carbon was 1.7 mmol/g, which was determined through the neutralization titration. The titration was carried out as follows: carbonaceous material (40 mg) and 2 N aqueous NaCl (4 mL) were stirred at room temperature for 24 h. The solids were filtered off and washed with water (4 × 2 mL). The combined filtrate was titrated with 0.01 N NaOH using phenol red as indicator [22]. The carbon owned much higher acidity than that of the sulfonated carbonaceous materials, which were obtained via the sulfonation of the inactive carbon. The NH₃-TPD showed that the molar ratio of SO₃H/CO₂H was 3:1, which was determined by the acid strength. The SO₃H/CO₂H was quite different from the hydroxyethylsulfonic and citric acid. However, the amount of sulfonic acid groups could be increased by adding more hydroxyethylsulfonic acid.

The results of XPS analysis showed the S content of 7.4%, which indicated that the S existed in the forms of sulfonic acid groups and other groups. The S 2p XPS spectrum indicated that about 55% S existed in the forms of sulfonic acid groups (168 eV) (Fig. 1). The results indicated that the acidity from the sulfonic acid groups was 1.275 mmol/g, which matched well with the molar ratio of SO₃H/CO₂H. On the other hand, the O content was as high as 25%, which indicated that there were still many oxygen-containing groups besides the carboxylic acid groups. The BET surface of the novel carbon was 138 m²/g (Fig. 2). The results showed that there was some mesoporous structure in the carbon.

The IR spectrum of the novel carbon is shown in Fig. 3. Compared to the carbon from the single glucose, the absorbance at 1046 cm⁻¹ confirmed the existence of the sulfonic acid groups. Also, FT-IR spectra showed that the carbon materials contain resident functionalities including C=O (1704 cm⁻¹), Ar-H (3020 cm⁻¹), C-O (1204 cm⁻¹), which indicated the existence of phenol, ether, quinine, etc. oxygen containing groups. The strong absorbance at 1704 cm⁻¹ indicated the existence of carboxylic acid groups. Therefore, both the sulfonic acid and carboxylic acid groups existed in carbon.

The SEM images of the novel acid carbon showed that the resulting particles grow in size with the reaction time with a diameter of 2–5 μm as depicted in Fig. 4(a–c). Fig. 4 also shows the morphologies of the materials, micrometer sized, microporous carbon spheres with smooth surface, which was quite different from the amorphous structures of the sulfonated carbonaceous materials. The carbon spheres structure also made the recycle of the material very simple and the filtration was enough without suspension in the reaction mixture.

3.2. The catalytic activities for the esterification of acetic acid and butanol

The novel acid carbon (C–SO₃H) was applied to catalyze the esterification of acetic acid and butanol first (Fig. 5). For

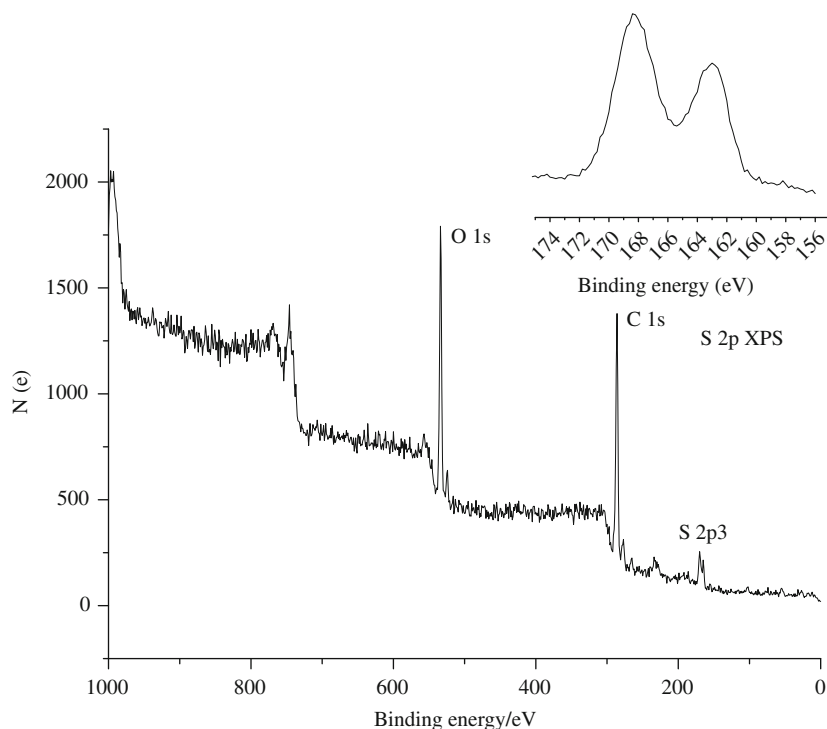


Fig. 1. The S 2p XPS spectrum of the carbonaceous material.

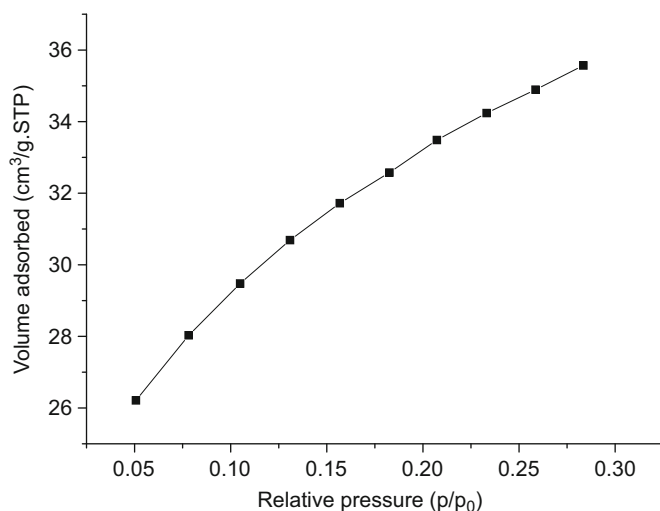


Fig. 2. The IR spectrum of the carbonaceous material.

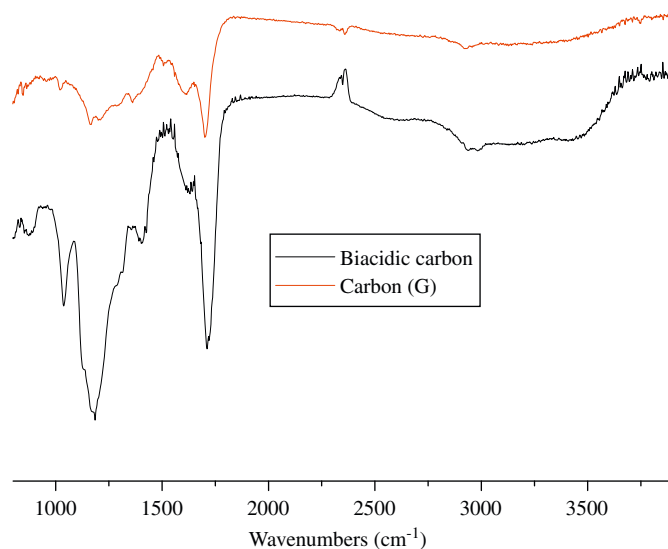


Fig. 3. The SEM images of the carbonaceous materials.

comparison, the results for concentrated sulfuric acid, zeolite (HY), Amberlyst-15, carbon from glucose, carbon from glucose and citric acid, carbon from glucose and hydroxyethylsulfonic acid and the sulfonated carbon are also shown. HY and Amberlyst-15 were industrial products and used without any treatment. Various carbon was synthesized from different raw materials under the same condition of the novel acid carbon. HY zeolite is an inorganic solid acid that exhibits only low activity, whereas Amberlyst-15 exhibits high activity for the reaction. The carbon (G) obtained via the single glucose showed almost no activity for little functionalities on the surface. The carbon (G+C) from glucose and citric acid showed a little higher activity than the carbon from glucose and carbon (G+HE), but the activity was still very low for low acidity. The sulfonated carbon also showed high activity for the reaction, which was higher than Amberlyst-15. The novel acid

carbon (C-SO₃H) exhibited a remarkably high activity for the formation of butyl acetate. The activity is much higher than those of conventional solid acids and the sulfonated carbon, which is comparable to sulfuric acid. After the reaction had reached equilibrium (9 h), the novel carbon was simply recovered by filtration and recycled for further reaction. It was confirmed that the activity remained unchanged, even after the carbon had been recycled for a fourth time.

3.3. The catalytic activities for the oxathioketalization of cyclohexanone and mercaptoethanol

Besides esterification, Fig. 6 also shows that the novel carbon rivals sulfuric acid in the oxathioketalization of cyclohexanone

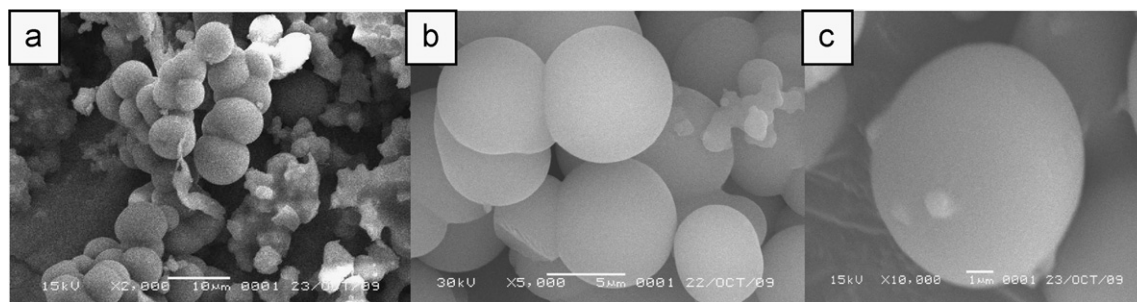


Fig. 4. The catalytic activities for esterification.

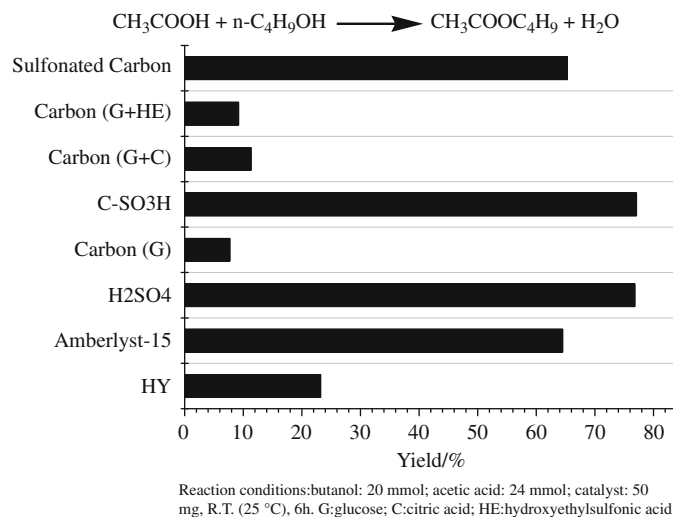


Fig. 5. The catalytic activities for oxathioketalization.

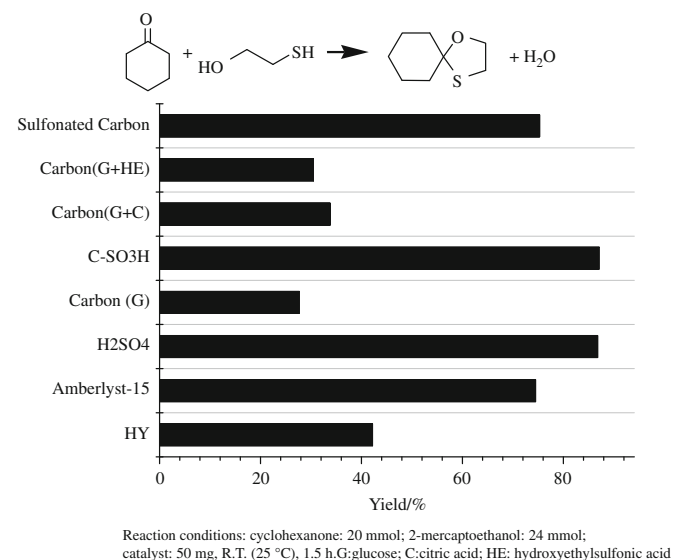


Fig. 6. The catalytic activities for oxathioketalization.

and mercaptoethanol. The obvious differences between various carbon and C-SO₃H also indicated the well-functioned surface of the novel acid carbon. Also, the activity remained unchanged, even after the sample had been recycled for a fourth time. These results indicated that the novel acid carbon material had high activity and good stability. Since many industrial important chemicals such as alcohols, esters, ethers, and acetals are produced by such reactions in the presence of sulfuric acid

catalyst, the comparable performance of the novel acid carbonaceous material as sulfuric acid indicated by the present results demonstrates that the acid carbon has great potential to replace the sulfuric acid catalyst for the green processes. Furthermore, the synthesis condition assured the high hydrothermal stability of the novel carbon material. The acidity remained even after the acid carbon was treated with boiling water for more than 15 h, which means that the novel carbon could be used in some special areas.

4. Conclusion

The novel biacidic carbon was synthesized via one-step hydrothermal carbonization of glucose, citrate acid, and hydroxyethylsulfonic acid under mild condition. The carbon had high acidity with both sulfonic and carboxylic acid groups and showed comparable activities to sulfuric acid for esterification and oxathioketalization. Operational simplicity, low cost of the catalyst used, high stability, high activity, and reusability are the key features of the novel acid carbon, which indicated that carbon holds great potential for green processes. Furthermore, the novel “copolymerization” methodology also provided an efficient procedure for the synthesis of various functionalized carbonaceous materials via one-step hydrothermal carbonization of selected compounds for a certain purpose.

Acknowledgments

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