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Acid functionalized, highly dispersed carbonaceous spheres: an effective solid acid for hydrolysis of polysaccharides

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Abstract Highly dispersed carbonaceous spheres with sulfonic acid groups were successfully prepared from glucose by hydrothermal method. Transmission electron microscopy (TEM) showed the as-synthesized carbonaceous materials were uniform, spherical in shape with an average diameter of about 450 nm. Fourier transform infrared (FT-IR) proved that $-\text{SO}_3\text{H}$, $-\text{COOH}$, OH groups were grafted on the surface of the carbonaceous spheres during the sulfonation. Interestingly, the functionalized carbonaceous spheres exhibited high dispersibility in the polar solvent due to the hydrophilic groups on the surface. The mechanism of the formation for the carbonaceous spheres was also discussed based on the analysis of structure and composition. At last, the functionalized carbonaceous spheres were employed as solid acid to hydrolyze starch and cellulose. By comparison, the as-synthesized catalyst showed considerable high yield of glucose.

Keywords Highly dispersed · Hydrothermal · Carbonaceous solid acid · Polysaccharide hydrolysis

Introduction

Solid acid has served as an important material in chemistry world due to its less corrosiveness, safety, less waste, ease of separation, and recovery. It has been widely used in esterification, hydration, and hydrolysis reactions (Okuhara 2002; Ye et al. 2009; Takagaki et al. 2003). More importantly, with declining petroleum resources, the solid acid has also been employed to realize the catalytic conversion of sustainable biomass to some value-added products, such as dehydration of polyols, esterification of fatty acid, hydrolysis of polysaccharides (Huber et al. 2006, 2004; Mo et al. 2008). It is well known that polysaccharide hydrolysis is a crucial process to produce glucose (an important building block for biochemistry). Recently, several solid acids have been developed to facilitate the hydrolysis of cellulose, starch, or other polysaccharides with moderate to good glucose yields (Takagaki et al. 2008; Shimizu et al. 2009; Bootsma et al. 2008; Onda et al. 2008). Among them, the SO_3H bearing carbonaceous solid acid (CSA), prepared via sulfonating the amorphous carbon or active carbon at high temperature, showed considerable catalytic activity for the hydrolysis of cellulose (Suganuma et al. 2008; Toda et al. 2005). While these CSAs were prepared with high temperature and exhibited relative low activity for the hydrolysis of polysaccharides due to the poor solid–solid contact between solid acids and substrates. Therefore, it is desirable to synthesize such solid acid

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through green and energy-efficient process and increase the activity for polysaccharides hydrolysis.

In this article, we report a novel fabrication method to prepare highly dispersive CSA catalyst for polysaccharide hydrolysis. The as-synthesized CSA is uniform, spherical in shape with the approximate size of 450 nm, which could be dispersed in the water homogeneously due to the specific structure. Compared with other solid acids, the obtained CSA exhibited a higher activity in the hydrolysis of starch and cellulose due to its excellent dispersibility in water.

Experimental

The synthesis of catalyst

In a typical preparation, 40 mL 10 wt% glucose solution was maintained at 453 K in a sealed Teflon-lined autoclave for 10 h. After cooling to room temperature, the red–brown precipitate was rinsed with pure water several times and oven-dried at 373 K for 12 h. Then, 1 g of the above powder was heated in 30 mL of fuming sulfuric acid (20% SO₃) at 393 K for 10 h to introduce SO₃H groups onto the surface of the obtained carbonaceous material. After cooling to room temperature, the suspension was filtered and washed repeatedly with hot distilled water (>358 K) to yield a brown–black precipitate. Finally, the as-synthesized carbon powder was dried in air at 373 K for 24 h.

Characterization

XRD patterns were collected on a Bruker iv8 Advance diffractometer using Cu K α radiation (wavelength $\lambda = 1.5147 \text{ \AA}$). FT-IR spectra were recorded on a Thermo Nicolet FT-IR spectrometer using the standard KBr disk method. TEM images were taken by a field emission H-7600 electron microscope at 120 kV. The amount of the sulfonic groups bonded to the CSA was estimated by elemental analysis (vario EL cube, ELEMENTAL).

Hydrolysis of polysaccharides

The hydrolysis reaction was carried out in a microwave reactor (Anton Paar, Synthos 3000 with the

temperature mode and CEM, Discovers). The catalysts tested were H-ZSM5 (Si/Al = 45, Zhengzhou Snowmountain Industrial Co, LTD), WO₃/ZrO₂ (homemade), Amberlyst-15 (polystyrene-based cation exchangeable resin with SO₃H, Aldrich), and the CSA prepared by our hydrothermal method (C-453) and the pyrolysis method (C-673), respectively. The C-673 was prepared according to the previous reported method (Okamura et al. 2006). In typical synthesis, 20 g D-glucose powder was heated at 673 K for 15 h under N₂ flow to produce a brown–black solid. The obtained solid was grounded into powder. 1 g of the powder was placed in 40 mL concentrated H₂SO₄ and heated at 423 K for 15 h. Subsequently, the black precipitate was washed thoroughly with hot water and dried at 373 K for 24 h.

For the hydrolysis of cellulose, cellulose powder was first pretreated by ball-milling for 24 h to reduce the size of crystalline cellulose. Then, 10 mg of milled cellulose, 100 mg of catalyst, and 0.8 mL of distilled water were added into the reaction tube. Lastly, the mixture was heated for 40 min at 423 K in a CEM microwave reactor with stirring; for starch hydrolysis, in a typical reaction, a mixture containing 180 mg of starch, 200 mg of catalyst, and 20 mL of distilled water was heated at 393 K for 4 h in an Anton Paar microwave reactor with stirring. The glucose was analyzed by high-performance liquid chromatography (HPLC with ECD detector, Dionex ICS-3000) using a Dionex P10 column and NaOH aqueous solution as mobile phase. The yield of glucose was calculated as follows:

$$\begin{aligned} \text{Glucose yield (\%)} \\ &= \text{weight of glucose} / \\ &\quad (\text{weight of charged polysaccharide}) \times 100 \end{aligned}$$

Results and discussion

Characterization of the CSA

In order to obtain the CSA structural information, TEM, XRD, and FT-IR were employed to characterize the as-synthesized carbonaceous material.

Figure 1 shows the pictures of the carbonaceous materials before (Fig. 1a) and after sulfonation (Fig. 1d). The color of the carbonaceous material prepared by hydrothermal method was red–brown

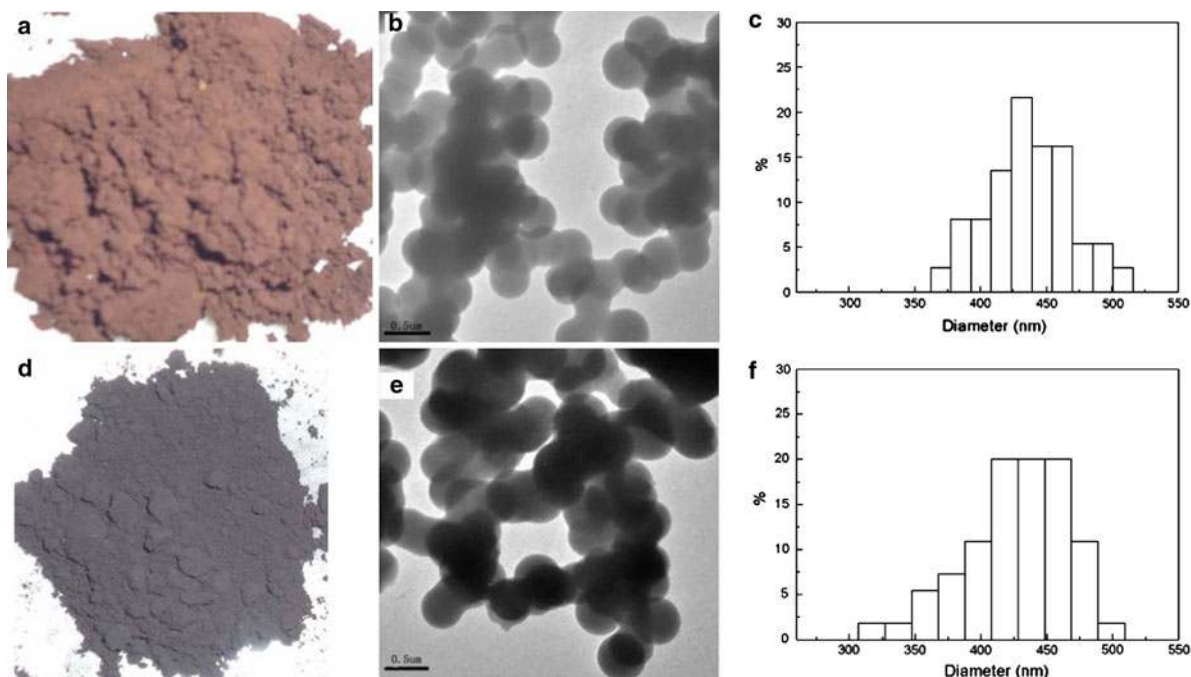


Fig. 1 Powders and TEM images of the carbon materials before **a, b** and after **d, e** sulfonation; the diameter distribution histogram based on the TEM images **c, f**

due to the incomplete carbonization. While, after sulfonation, the as-synthesized carbonaceous material became black, indicating the carbonaceous material was further carbonized during the sulfonation. It can be seen from TEM image (Fig. 1b), the carbonaceous materials prepared by hydrothermal method are uniform, spherical in shape with an average diameter of about 450 nm (Fig. 1c). After sulfonation, the sulfonated carbonaceous particles remained their same shape and size (Fig. 1e, f), which suggested the sulfonation did not result in obvious particle shrinkage under our experimental condition. While, the CSA prepared by a previous report observed irregular shape and size increasing of more than 1 μm after grinding due to the higher temperature. Also, the obtained carbon powders could only be temporarily dispersed in water under vigorous stirring, and precipitates formed rapidly when stirring was ceased (Okamura et al. 2006). Interestingly, our sulfonated CSA could be well dispersed in water after ultrasonic irradiation for several minutes, and no obvious precipitation in the aqueous dispersion could be observed even after several hours standing (see Fig. 2a). This might be due to the uniform submicron spherical structures and surface hydrophilic groups

such as SO_3H , OH , and COOH . In addition, the apparent volume of as-synthesized solid acid swelled distinctly (about 4.2 times) when soaking with water (Fig. 2b, c). The swelling can be attributed to some soft carbon material composed of flexible polycyclic aromatic carbon with functional groups. The volume change for the solid acid may improve the transfer of the substrates which enhances the catalytic activity.

Figure 3 shows the XRD patterns for the carbonaceous materials before and after sulfonation. XRD pattern for the carbon prepared by hydrothermal method exhibits a broad diffraction peaks at a 2θ angle of 10° – 30° with the center at about 20° , which can be typically attributed to the amorphous carbon. After sulfonation, it was found that the broad diffraction peak becomes more symmetrical and the center moves to a relative higher 2θ angle of about 25° , which corresponded to the (002) planes of the micrographites oriented in a random way (Okamura et al. 2006; Lin et al. 2010). At the same time, a new weak diffraction peak ($2\theta = 35^\circ$ – 45° , indicated in the rectangle of Fig. 3) appears, which is due to the (100) axis of the graphite structure (Lin et al. 2010). These changes of XRD pattern suggested that the crystallite growth of the graphite was underway due

Fig. 2 Stability of the CSA in the water solution (a), the cylinder of CSA powders before (b) and after water wetting (c)

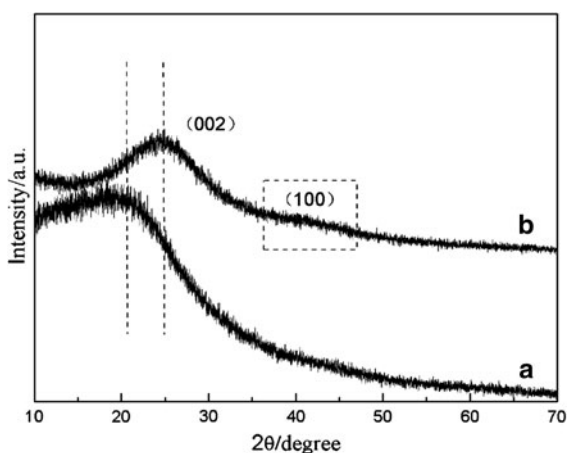
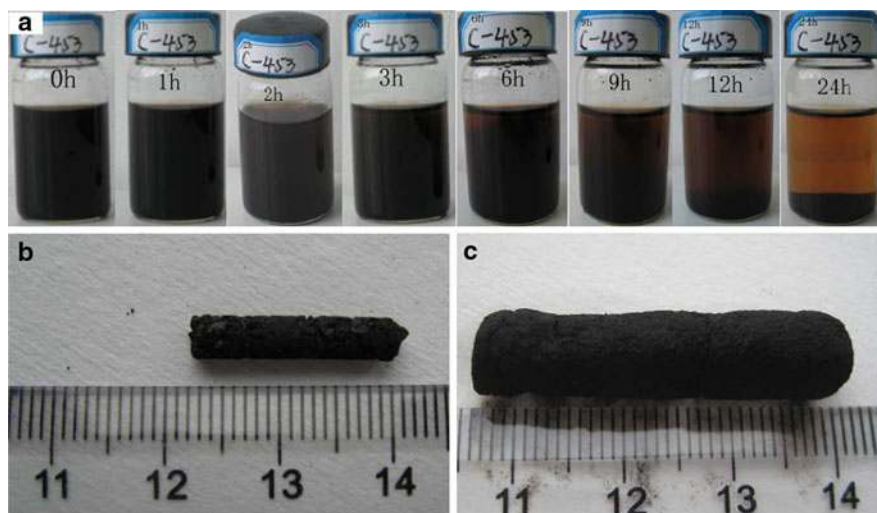


Fig. 3 XRD patterns for the carbon materials before (a) and after (b) sulfonation

to the further carbonization during the sulfonation, which introduced amorphous carbon composed of aromatic carbon sheets (Okamura et al. 2006). The fact that the color of carbon material transformed from red–brown (Fig. 1a) to black (Fig. 1d) during the sulfonation also suggested the change of the inner structure. To some extent, this color change was confirmed by XRD characterization.

Figure 4a shows the FT-IR spectrum of the carbon before sulfonation. The peaks at $2800\text{--}3000\text{ cm}^{-1}$ and broad band centered at about 1627 cm^{-1} are assigned to the C–H stretching and overlapping of C=O and O–H vibration, respectively. The bands in the range $1000\text{--}1300\text{ cm}^{-1}$ are attributed to C–OH stretching vibrations, implying the existence of a

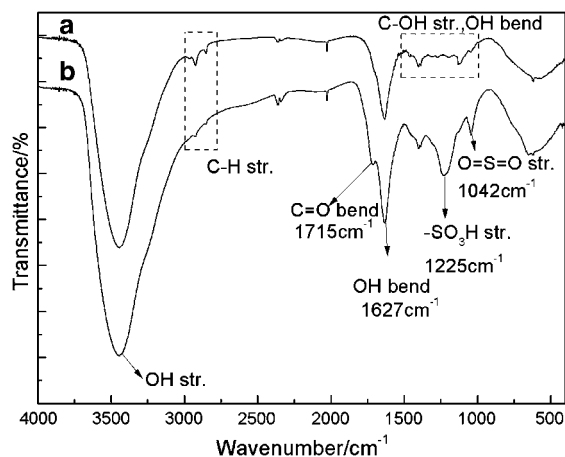
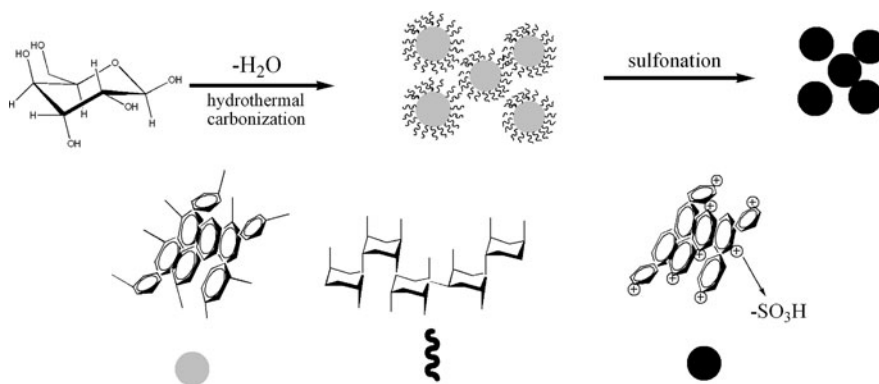


Fig. 4 FT-IR spectrum of as-synthesized carbon materials prepared by hydrothermal synthesis (a) and the CSA (b)

large number of residual hydroxyl groups (Sun and Li 2004). These observations all support the concept of incomplete carbonization of glucose during hydrothermal treatment. Interestingly, after sulfonation, the relative intensity of the C–H and C–OH vibration was reduced, and some new peaks appear simultaneously (Fig. 4b). The C=O bending vibration at 1725 cm^{-1} becomes more obvious after sulfonation (Fig. 4b), indicating the SO_3 oxidant has oxidized parts of the C–OH or HC=O groups to carboxylic groups during the sulfonation. The peaks at around 1225 and 1042 cm^{-1} are assigned to $-\text{SO}_3\text{H}$ and O=S=O stretching (Zong et al. 2007; Tian et al. 2008), respectively, suggesting the sulfonation has taken place.

Scheme 1 The formation of CSA from sugar by hydrothermal method



The formation of the CSA

According to the structural analysis and previous reports (Suganuma et al. 2008; Sun and Li 2004), the formation of our CSA is described in Scheme 1. First, under hydrothermal conditions, glucose is transformed into oligosaccharides by dehydration, and then the oligosaccharides are further cross-linked by intermolecular and intramolecular dehydration to form carbon spheres containing aromatic compounds. The C–OH stretching vibration in the range of 1000–1300 cm^{-1} (Fig. 4a) proved the carbon still had some incomplete carbonized oligosaccharides. So, the active groups $-\text{SO}_3\text{H}$ and $-\text{COOH}$ were introduced into the carbonaceous spheres during the sulfonation process, which was confirmed by the $-\text{SO}_3\text{H}$, $\text{O}=\text{S}=\text{O}$, and $\text{C}=\text{O}$ stretching in the FT-IR spectrum (Fig. 4b). These groups improve the dispersibility of the CSA in water.

In general, dehydration and aromatization are recognized to be a process of decreasing the number of groups, such as OH groups. So, elemental analysis can also provide helpful information for the formation of CSA. Table 1 shows the composition of products at different stages. Obviously, comparing with compositions of glucose, the content of hydrogen and oxygen both decreased after hydrothermal treatment, while the ratios of C/H, C/O, and O/H were enhanced greatly which indicated the dehydration occurred during hydrothermal treatment. After sulfonation, it was found the content of oxygen increased greatly in the CSA. In contrast, the content of hydrogen decreased. We believe the introduction of SO_3H and COOH groups led to the increase of the oxygen content during the sulfonation. In addition, dehydration reaction took place between parts of

Table 1 Elemental compositions of the glucose and carbon materials before and after sulfonation

Sample	C%	H%	O%	S%	C/H	C/O	O/H
Glucose	40	6.67	53.33	0	5.97	0.75	7.8
Before sulfonation	63.61	3.81	33.58	0	16.7	1.89	8.81
After sulfonation	46.51	2.52	45.01	5.96	18.46	1.03	17.86

residual OH groups under the sulfonation condition, which resulted in decreasing the hydrogen content and increasing the ratio of C/H, O/H in the solid acid. Thus, all evidence demonstrates the scheme of our CSA formation is acceptable.

Catalytic performance for polysaccharide hydrolysis

To estimate the catalytic performance for polysaccharide hydrolysis, our CSA (C-453) was applied to catalyze the hydrolysis of starch and cellulose. In comparison, results of other conventional solid acids, such as super solid acid (ZrO_2/WO_3), H-type zeolite (H-ZSM5), ion-exchange resins (Amberlyst-15), and CSA (C-673) obtained by pyrogenation (Okamura et al. 2006), were also shown (Fig. 5). The catalytic results are summarized in Fig. 5. For the hydrolysis of starch, ZrO_2/WO_3 almost had no activity; H-ZSM5, Amberlyst-15, and C-673 showed almost equal reactivity for starch hydrolysis. By contrast, our CSA prepared by hydrothermal method (C-453) showed the highest glucose yield of over 92%, which was more than four times higher than other catalysts. In the cellulose hydrolysis, ZrO_2/WO_3 and H-ZSM5 showed glucose yield of less than 1%; while

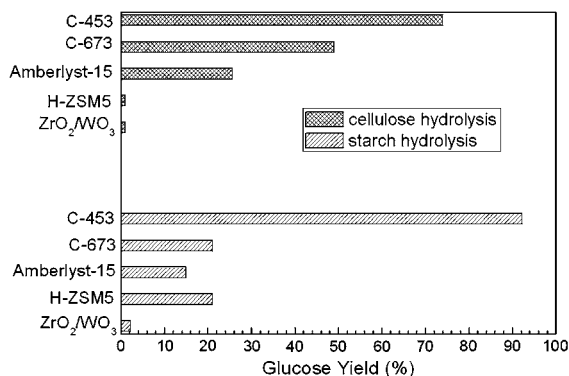


Fig. 5 Sugar yields of polysaccharides hydrolysis over various solid acids

Amberlyst-15 and C-673 gave glucose in 25.6, 49.0% yield, respectively. Similarly, our CSA C-453 gave the highest glucose yield of about 74.0%, which was much higher than the previous reported CSA (40.5%) (Onda et al. 2008), indicating our CSA exhibits considerably higher activity for cellulose hydrolysis.

From the above catalytic results, it is easy to find that the super solid acid ZrO_2/WO_3 has almost no catalytic activity for the hydrolysis of polysaccharide. While the protonic solid acids (H-ZSM-5, Amberlyst-5, CSA) show relative high performance for hydrolysis, indicating that the Brønsted acid (which can provide H^+) is more favorable for the hydrolysis of glycosidic bonds. In the previous study, it was proved that the CSA prepared by pyrolysis could adsorb β -1,4 glucan due to the hydrogen bonds between the OH groups bonded to the surface of the CSA and the oxygen atoms of glycosidic bonds in cellulose (Suganuma et al. 2008). Interestingly, under the same condition, the CSA C-453 always showed the higher catalytic performance compared with other solid acids (including the C-673). We believe this enhanced hydrolytic catalysis is associated with the intrinsic structure of the C-453. The presence of OH groups in the C-453 has been proved by the analysis of the FT-IR and the elemental analysis. It is known that the C-453 prepared by hydrothermal method has more OH groups than that of the C-673 prepared by pyrolysis due to the mild carbonization condition. Thus, the interaction between the C-453 and the substrate of polysaccharide is stronger than that of the C-673, which will enhance the catalytic performance in the hydrolysis of polysaccharide. At the same time, the particle of C-453 is uniformly spherical, highly

dispersive, and easily swells in water, which probably improves the effective contacts and increases the hydrolysis of polysaccharides. Contrarily, the CSA prepared through pyrolysis (C-673 or sulfonated activated carbon) could only be temporarily dispersed in water under vigorous stirring, and deposited rapidly when stirring was ceased. The poor aqueous dispersibility definitely hindered the interaction between the catalyst and the substrate in such a solid–solid reaction.

Conclusions

In summary, we have prepared a novel spherical CSA with a simple and energy-saving method. Under hydrothermal conditions, the sugar was first incompletely carbonized to carbon submicron spheres by dehydration. Then, the resulting carbonaceous spheres were sulfonated to form highly dispersive uniform CSA. More importantly, the uniform size and high aqueous dispersibility of the CSA improve the accessibility to the polysaccharides, and thus it exhibits excellent catalytic performance for polysaccharide hydrolysis.

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