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Effect of Solution pH on the Carbon Microsphere Synthesized by Hydrothermal Carbonization

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Abstract

Carbon microspheres(CMSs) in a diameter of 10 μ m were prepared by the hydrothermal carbonization of starch under different solution pH value. The structures and surface chemical properties of obtained CMSs before and after carbonization were characterized and compared by SEM images, nitrogen adsorption isotherms and FT-IR spectra. The results showed that the suitable solution pH value of hydrothermal carbonization ranged from 3 to 7, whereas starting pH of 1 only accelerated the hydrolysis of starch and the formation of microsphere in the early stage of the reaction. The surface chemical groups of the carbon microsphere determined its adsorption on acetic acid, while the porous structure took the role on adsorption after carbonization at 600°C for 2 h.

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Keywords: Starch, Carbon microsphere, Hydrothermal carbonization, Solution pH.

1. Introduction

Recently, synthesis of functional carbonaceous materials is a hot topic due to its potential applications in adsorbents, carbon fuel cell [1], catalyst supports [2], electrode [3], filters materials [4], etc. Carbon microspheres (CMSs) with low weight, thermal insulation and high compressive strength have attracted considerable attention. Many methods including chemical vapor deposition have been developed to prepare CMSs, however, from the viewpoints of economy and environment, hydrothermal carbonization(HTC) of carbohydrates has advantages on other complex, tedious, and highly cost methods. Xylose [5], glucose [6,7], fructose [8], sucrose [8], cyclodextrin [9], even starch [10] and cellulose [11] were used as carbon precursor to prepare CMSs by HTC. The obtained microspheres have a core-shell chemical structure consisting of a highly aromatic nucleus(hydrophobic)with oxygen forming stable groups(i.e. ether, quinine, pyrone)and a hydrophilic surface containing a high density of reactively hydrophilic oxygen functional groups(hydroxyl, phenolic, carbonyl, carboxylic, ester). The CMSs with rich surface functional groups can be used to load other functional groups, molecules, ions and nanoparticles [12-15], and to fabricate functional materials, which can be widely applied in the fields of

environmental protection and medicines.

In the process of hydrothermal carbonization of carbohydrates, many factors affect the morphology, yield and surface functional groups of resultant carbon microspheres. Sevilla [16] found that the diameter of the CMSs can be modulated by modifying the synthesis conditions. Mingtao Zheng [17] induced the self-assembly of colloidal carbon microspheres into spheroids by employing alcohol as a structure-directing agent. Jihye Ryu [18] added phloroglucinol to the raw material, and this led to a large increase (roughly 20%) of the carbon yield. Rezan Demir-Cakan [19] introduced carboxylic groups on the surface of CMSs in the presence of acrylic acid. Unfortunately, the effect of pH value on the preparation of CMSs by HTC has not been reported according to literature.

In this paper, CMSs were prepared by hydrothermal carbonization of starch under different solution pH values. The effect of solution pH value on the morphology, yield and surface property of the resultant CMSs was investigated. Moreover, the adsorption capacity for acetic acid before and after carbonization at 600°C was compared.

2. Experiment

2.1. Hydrothermal synthesis of carbon microspheres

A typical synthesis was carried out as follows: 15 g starch was added into 30 ml deion water with 1, 3, 5 and 7 of different pH values respectively and stirred to form a homogenous solution. The solution was then sealed into a 130 ml Teflon-lined autoclave and statistically treated at 210°C for different time. After thermal treatment, the autoclave was cooled to room temperature, and the obtained black powders were washed by water and ethanol to remove the soluble residues. Finally the obtained carbons were dried at 85°C for 12h, and designated as HTC-1, HTC-3, HTC-5 and HTC-7 according to different solution pH, respectively.

The as-prepared carbon microspheres were heated to 600°C with a rate of 1°C/min in nitrogen flow, then were kept at 600°C for 120 min. Finally, they were cooled to room temperature and denoted as HTC-1-C, HTC-3-C, HTC-5-C and HTC-7-C respectively.

2.2. Characterization

The nitrogen adsorption isotherms of prepared samples were measured on a Micromeritics ASAP 2000 (Micromeritics Ins. Corp.) at 77.4 K in the range of relative pressure from 10^{-6} to 1. All samples were out-gassed at 300°C for 2 h before the measurement. The specific surface area and pore structure were determined by BET equation and density functional theory, respectively.

The dried samples were observed through a scanning electron microscopy JEOL-JSEM (ESEM XL30 FEI, USA). Fourier-transform infrared (FT-IR) spectra of the samples were recorded on a NEXUS 670 FT-IR spectrophotometer, and KBr was used to prepare transparent and clean sample disks.

2.3. Acetic acid adsorption examination

The adsorption examination was performed in a sealed vessel (2000 mL) at 25°C. 10 g acetic acid was firstly placed into the vessel to reach its saturated vapor, then, 0.5 g carbons were transferred in. After certain adsorption time, the carbonaceous samples were weighted and the difference in weight was adsorbed acetic acid.

3. Results and discussion

3.1 Morphologies of carbon microspheres

The SEM images of carbon microspheres prepared by hydrothermal carbonization under different pH

values were shown in Fig.1. The panoramic SEM image in Fig.1a b revealed that the sample HTC-5 consisted of a large amount of uniform microspheres with a diameter of about 10 μ m, and they were smooth. However, the carbon microspheres of HTC-1 in Fig.1c d showed a double diameter of 5 μ m and 10 μ m, and they were piled together with many incompletely developed microspheres(indicated with a white arrow in Fig.1d). According to a nucleation-growth mechanism following the LaMer model, it was presumed that, the strong acid prohibited some species with reactive oxygen functionalities (hydroxyl, carbonyl, carboxylic, etc.) from diffusing and linking to the nuclei and stopped the growth of carbon microsphere. Hence, an incompletely developed microsphere was formed.

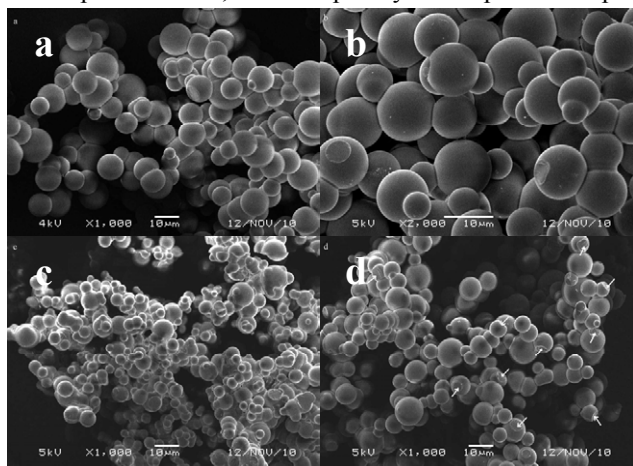


Fig.1 SEM images of carbon microspheres, HTC-5(a,b), HTC-1(c,d)

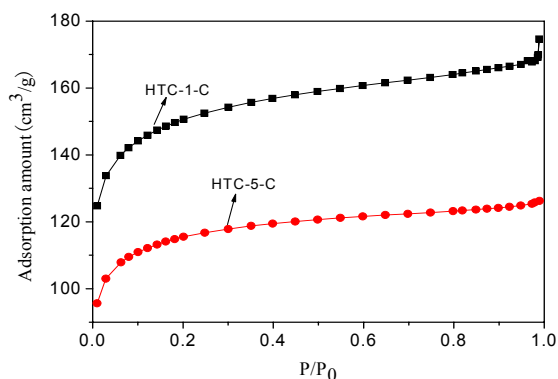


Fig.2 Nitrogen isotherms of HTC-1-C and HTC-5-C carbonized at 600°C

3.2 Pore structure of samples

The N₂ adsorption/desorption measurements showed that the BET surface area and pore volume of all hydrothermal carbons were smaller than 8 m²/g and 0.006 cm³/g, respectively, indicating they were nonporous materials. Fig. 2 showed the N₂ adsorption isotherms of HTC-1-C, HTC-5-C. The adsorption isotherms were planar at relative pressure above 0.1, which suggested that they were mainly comprised by micropores. It was obviously seen that the pH value of starting solution played important role on the amounts of adsorbed nitrogen. The BET surface area and pore volume of HTC-1-C, HTC-5-C were 512, 408 m²/g and 0.29, 0.22cm³/g, respectively.

3.3 Carbon yield

Fig. 3 showed the yields of CMSs prepared at 210°C for different time. The yields for all samples prepared under pH of 3, 5 and 7 increased with hydrothermal carbonization time, and reached their maximum after 3h. It should be noted that the curves for above mentioned pHs appeared very similar, and their maximum yields were very close, which were 43.69%, 43.57% and 44.6% for HTC-7, HTC-3 and HTC-5, respectively. The increased yields for all samples were less after 2 hours because the starch left was less and less during the hydrothermal process. In contrast, when the solution pH was 1, the yield of CMS was kept at 25% and changed very little with the reaction time increasing. A big difference should be pointed out that the yield for pH of 1 reached 25% while the yields of other 3 pHs were only 9% on average in 0.25 h. The pH of the soluble product were given in Fig.4, and it was believed that pHs played important roles on the yields of CMSs prepared by hydrothermal carbonization.

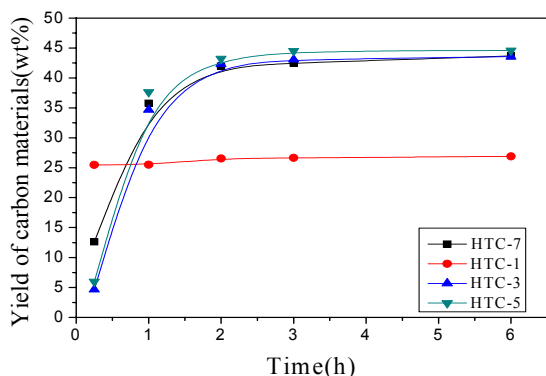


Fig.3 Yields of carbon microspheres prepared at 210°C

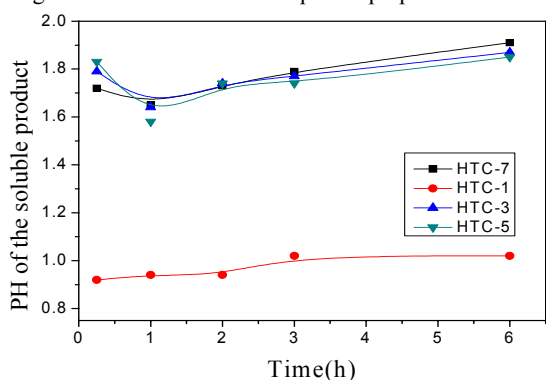


Fig.4 pH values of the soluble product obtained at 210°C

A simplified mechanism for the formation of carbons involves the dehydration of the starch into a furan-like compound (furfural aldehyde and/or 5 - (hydroxymethyl) - 2 -furaldehyde) as the first step and subsequent polymerization and carbonization as a second step. When the solution pH was 1, the strong acid promoted the starch hydrolyzed to low molecule monomers and hastened microsphere formation in the early stage of the reaction. On the other side, the sustaining strong acid inhibited the polymerization and carbonization of the produced molecule monomers, so the yield for pH of 1 reached maximum very quickly and kept unchanged.

Hydrothermal carbonizations under solution pH of 1.5, 2 and 2.5 were also carried out. It was also found that the maximum of yields increased as the solution pH increased. Hence, a conclusion can be drawn that the suitable solution pH value for hydrothermal carbonization ranged from 3 to 7, whereas solution pH of 1 can only accelerate the hydrolysis of carbohydrate and hasten the microsphere formation in the early stage of the reaction.

3.4 Surface properties

The surface functional groups of the carbon microspheres were characterized by FT-IR and were shown in Fig. 5(a). Two prominent features were found, assigning to the broad O-H adsorption in the region from 3700 to 3000 cm^{-1} and C=O stretching adsorption at 1699 cm^{-1} , respectively. The band at 2925 cm^{-1} was aliphatic hydrocarbon (-C-H), and the band at 1616 cm^{-1} could be attributed to the C=C stretching of aromatic and furanic rings. Besides, the bands at 1396 and 1157 cm^{-1} corresponded to C-O(hydroxyl, ester, or ether) stretching while the band at 786 cm^{-1} was assigned to aromatic C-H out-of-plane bending vibrations[20]. This suggested that these carbon spheres contained an aromatic core and resident functionalities in the shell.

When the carbons were heated at 600°C for 2 h, the surface functional groups were dramatically destroyed, and their FT-IR spectra was drawn in Fig. 5(b). There were complex and broad band between 1470 and 1380 cm^{-1} consisting of a series of overlapping adsorption bands that can be attributed to the carboxyl-carbonates structures.

3.5 The adsorption of acetic acid

Fig.6 showed the adsorption curves of acetic acid on CMSs before (a) and after (b) high temperature carbonization. It was found that the adsorption amount of acetic acid was relatively low (0.09 g/g) for CMSs before carbonization. Due to their low surface area and volume as mentioned above, the rich hydrophilic oxygen functional groups determined the adsorption of acetic acid. Hence, the external surface of these carbons directly determined the adsorption capacity and diffusion rate for the acetic acid.

When the CMSs were carbonized at 600°C for 2 h, most of the surface functional groups were destroyed and relatively rich micropores were produced meanwhile, therefore, the pore structure determined the main adsorption for acetic acid, and the adsorption capacity was as high as 0.25 g/g.

For CMSs before carbonization, it was proved that the adsorption of acetic acid was determined by the surface functional groups due to their interaction with the acetic acid, and the adsorption equilibrium reached in shorter time. While the pore structure of carbonized CMSs took important role on the adsorption which belonged to physical adsorption of pore filling process, and the adsorption velocity was relatively slow.

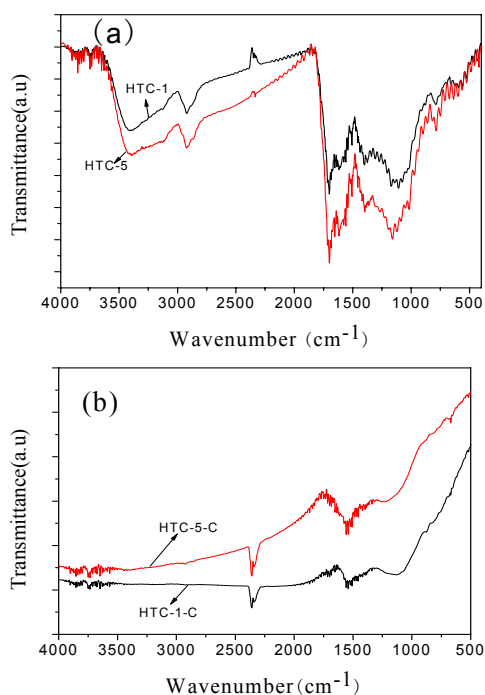


Fig.5 FT-IR spectra of carbon microspheres before (a) and after (b) carbonization

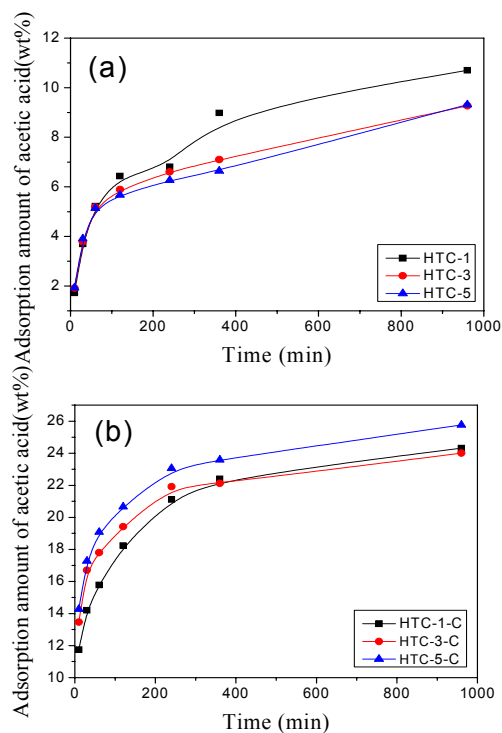


Fig.6 The adsorption curves of acetic acid on carbon microspheres before (a) and after (b) carbonization.

4. Conclusions

Carbon microspheres were prepared by the hydrothermal carbonization of starch under different starting pH value of solution. The results indicated that the suitable starting pH value for hydrothermal carbonization ranged from 3 to 7, whereas starting pH of 1 only accelerated the hydrolysis of carbohydrate and hastened microsphere formation in the early stage of the reaction. The surface functional groups of hydrothermal CMS before carbonization determined its adsorption of acetic acid, while the porous structure of carbon sample after carbonization took important role on the adsorption of acetic acid.

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