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Scientific paper
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Structural properties of carbon microspheres obtained by hydrothermal treatment of fructose

A carbon-rich solid product has been synthesized by hydrothermal treatment from fructose with HNO_3 at temperature of 140°C. The concentration of the precursor was changed in order to investigate how its change influences formation of carbon microspheres. pH value for every sample was the same, i.e. 1. The formation of the carbon rich solid through the hydrothermal carbonization of fructose is the consequence of dehydration reactions. Obtained carbon material is made of spherical micrometer-sized particles with the diameter in the 1-6 μm range, which can be modulated by modifying the concentration of fructose in solution. The best results are obtained with smaller concentrations of fructose. Spherical particles have more regular shape and they are less agglomerated. The structure and surface chemical properties of obtained material were characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectra and elemental analysis.

Keywords: *carbon microspheres; hydrothermal synthesis; fructose.*

1. AIMS AND BACKGROUND

Synthesis of functional and novel carbonaceous materials is a very interesting topic due to its variety of applications such as adsorbents, storage and production of electrodes, energy, nanocomposites, hydrogen storage, catalyst supports [1-4] drug delivery [5,6], filter materials [7] etc. Black solid residue contains mostly carbon microspheres (CMSs). Their properties like low weight, thermal isolation and high compressive strength have driven a considerable attention in the world of nanotechnology materials. When an aqueous solution/ /dispersion of a saccharide (e.g. fructose, glucose, sucrose, starch etc.) is heat-treated at a moderate temperature in the 170–250 °C range (under autogenous pressure), a carbon-rich black solid is obtained as insoluble product. The first research work on the hydrothermal carbonization of saccharides was carried out during the first decades of the 20th century with the aim of understanding the mechanism of coal formation. Renewed interest in the hydrothermal carbonization of carbohydrates has recently been established, and the objectives of these new investigations were completely different to those previously mentioned [8-13]. At this time, the main purpose is to use the process of the hydrothermal carbonization as a way to produce nanostructural carbonaceous materials with specific properties (such as shape, size, chemical functionalities etc.), depending on their application.

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There are many methods which have been developed to prepare microspheres of this nature. From the two main points of view, economy and conservation of environment, hydrothermal carbonization of carbohydrates has advantages on other complex and highly cost methods. Precursors such as xylose[8], glucose [14,15], fructose [9], sucrose [9], cellulose [10] and starch [11] were used as carbon sources to prepare this kind of microspheres by hydrothermal carbonization method. The obtained microspheres have characteristic chemical structure, and they can be widely applied in the fields of environmental protection and medicine. It has been reported that treatment by hydrothermal method of different carbohydrates in aqueous solution results in the formation of solid carbonaceous micro particles. In these works, obtained particles are regular spheres in the size range of 0.3-10 μm [8,9,12,13,15-18]. Some of these works widely explain dehydration process and formation of carbon microspheres using saccharides such as glucose, starch, sucrose and cellulose. Process is followed by aromatization under hydrothermal conditions and obtained carbonaceous spheres have highly aromatic nucleus and a hydrophilic shell [8, 12, 13, 15,16].

In the process of hydrothermal carbonization of carbohydrates, many factors affect the morphology, yield and surface functional groups of carbon. It has been found that the diameter of the obtained CMSs can be changed by modifying the synthesis conditions. In previous works it has been given that the diameter of CMSs widens with an increase in reaction temperature, saccharide concentration, or reaction time [13]. Also, researchers induced the self-assembly of colloidal carbon microspheres into spheroids by employing alcohol as a structure

directing agent [19]. The effect of the concentration change on the morphology, yield and surface property of the resultant CMSs were investigated. Most of the works recently published in this area have been mainly focused on the synthesis of carbonaceous products and hybrid carbon/inorganic materials.

The main aim of the present work was to investigate the effect of certain process parameters on the morphology of carbonaceous microspheres obtained by hydrothermal carbonization. Starting material in this case was a commercial fructose because it is cheap precursor and we assumed that hydrothermal carbonization could happen at lower temperature in comparison with other saccharide. The concentration of precursor was changed and the dimensions of obtained microspheres were compared.

2. EXPERIMENTAL

Hydrothermal synthesis of carbon microspheres was carried out in a glass reactor at 140 °C for 3 h. Hydrolysis was performed using HNO_3 water solution with pH value of 1 for all of the samples. Concentration of fructose used in the experiments was: 0.5 M, 1 M, and 3 M (CMS1, CMS2 and CMS3, respectively). Experiments were conducted in the following sequence: the required concentration of fructose solution was added in 40 ml of HNO_3 and the compound processed in this way was mixed with the magnetic stirrer for a period of 15 min. Then, the solution was placed in a glass reactor, put into the oven and heated under autogenously pressure at 140 °C for 3 h. The prepared samples were washed with distilled water several times. The next step was the filtration and washing with distilled water to pH=7. Finally, the samples were dried in an oven at 100 °C to obtain a final product.

The structure of dried samples was investigated by a scanning electron microscope (SEM) JEOL JSM-5800. Fourier-transform infrared (FTIR) spectra of samples were analyzed using BOMEM (Hartmann & Braun) spectrometer in transmission mode between 400 cm^{-1} and 4000 cm^{-1} with resolution 4 cm^{-1}. Elemental analysis (C, H and O) of samples was performed using a Vario EL III C, H, N, S/O Analyzer (Elementar). The sphere diameters were determined applying Image Pro Design program and histograms were given.

3. RESULTS AND DISCUSSION

In our investigation factors like pH value and concentration of precursor were changed to get the best results at 140 °C. In the case of changed pH value, only pH=1 gave solid black residue. Obtained carbon material was made of particles with a spherical morphology having the diameter in the 1.0 μm to 6.0 μm range, as shown by the SEM micrographs (Figure 1). The SEM image in Figure 1b revealed that the sample CMS2 consisted of a large amount of more uniform microspheres with average diameter of ~3.5 μm. CMS3 sample showed microspheres which were piled together with many incompletely developed microspheres.

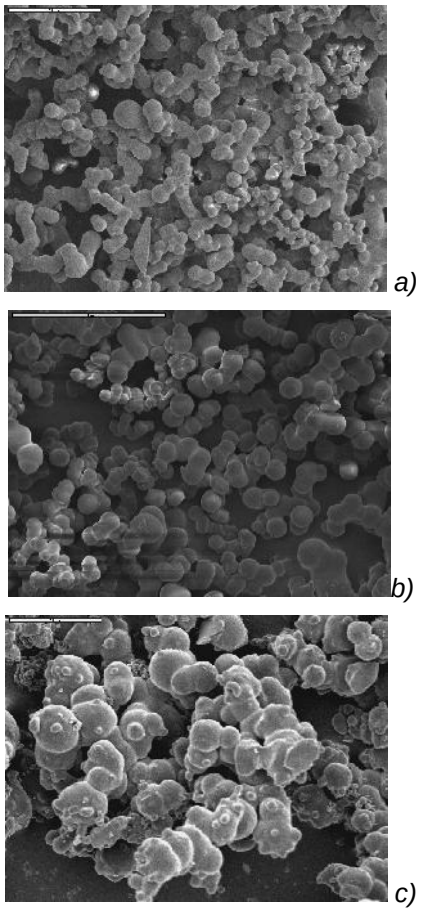

Figure 1 - SEM micrographs of the carbon microspheres obtained by hydrothermal treatment of fructose at 140°C for 3h: a) CMS1; bar length 20μm, b) CMS2; bar length 50μm and c) CMS3; bar length 20μm

Figure 2 includes the histogram of the diameter distribution of the microspheres. It may be seen from the histogram that distribution has a high degree of uniformity. It is clear that for the applied conditions (140 °C and short reaction time 3 h), with change of concentration of fructose, the microspheres fuse, and thereby giving rise to particles which have a peanut shape (Figure 1 b, c). The diameter of the carbon microspheres can be modulated by modifying the preparation conditions. In comparison with previous works where authors have been used water and higher temperatures, carbon microspheres obtained in this study are in the similar size range and they have the same morphology[12].

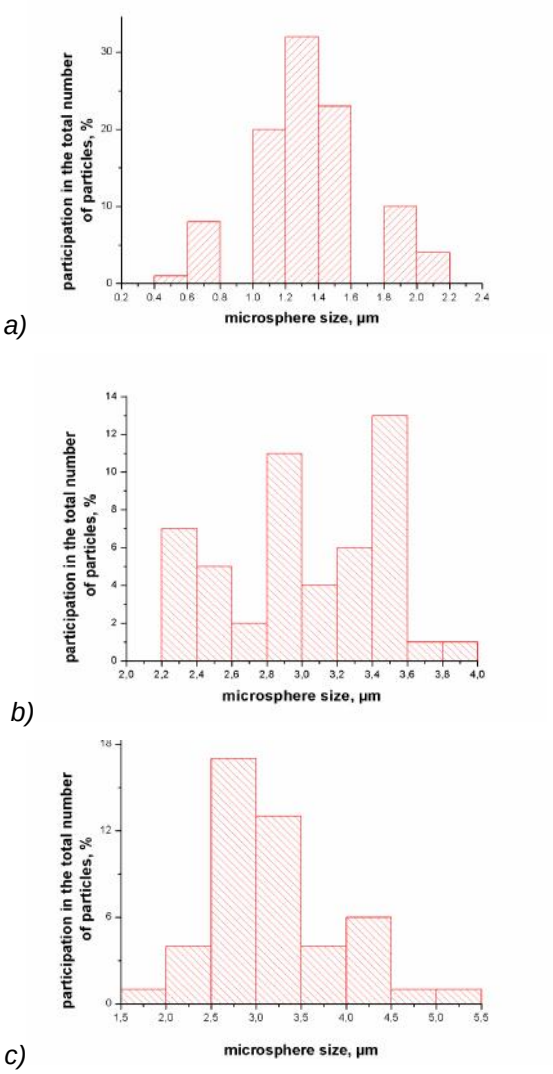

Figure 2 - Histograms of the carbon microspheres: a) CMS1, b) CMS2 and c) CMS3

Actually, we observed that increase the concentration of the reaction mixture, leads to an increase of the mean diameter of the micro particles decreasing the regularity of spherical shape of the particles (see Figure 1b). When the concentration of precursor is too high, particles lose their spherical structure, smoothness of the external surface and become more agglomerated (see Figure 1c). Adequate evidence to enable the identity and purity of all newly synthesized compounds should be provided.

The surface chemical functional groups of obtained carbon microspheres were characterized by FTIR spectroscopy and the resulting diagram is shown in Figure 3. The foremost bands were found, assigning to the broad O-H adsorption in the plan range from 3600 cm^{-1} to 3000 cm^{-1} and C=O stretching adsorption at 1700 cm^{-1}. Aliphatic hydrocarbon (-C-H) was at approximately 2900 cm^{-1} and the band at 1620 cm^{-1} could be attributed to the C=C stretching of aromatic and furanic rings. The characteristic bands due to C-O (hydroxyl, ester, or ether) stretching vibrations were observed in the range 1300 cm^{-1} to 1000 cm^{-1}, while the band at 790 cm^{-1} assigned to aromatic C-H out-of-plane bending vibrations[20]. These data reveal that these carbon spheres contained an aromatic core and resident functionalities in their shell.

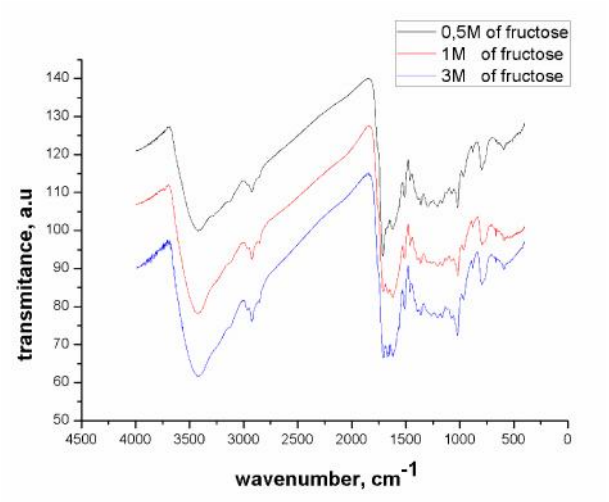

Figure 3 - FTIR spectra of the carbon microspheres obtained by hydrothermal treatment of fructose

The elemental chemical composition (C, O and H) of the carbon microspheres obtained by different concentration of fructose are listed in Table 1. It is shown that the carbon content increases from 40 % in raw fructose to approximately 60 % in obtained carbon material samples. Also, there is a reduction in the oxygen and hydrogen contents. It can be seen that there is no significant change of carbon content when the concentration of the precursor increases.

Table 1 - Chemical elemental analysis of carbon microspheres from the hydrothermal treatment of fructose

Sample	C (wt%)	H (wt%)	O (wt%)
raw fructose	40.00	6.72	53.28
CMS1	60.61	4.48	34.91
CMS2	60.64	4.50	34.86
CMS3	59.87	4.58	35.55

CONCLUSIONS

The treatment of fructose under hydrothermal conditions in HNO_3 solution at 140 °C and pH=1, leads to the formation of black solid carbonaceous residue consisting of micrometer sized spheres, with dimensions ranging from 1 μm to 6 μm. The diameter of obtained spheres can be modulated by change of precursor concentration. With increase of the concentration, spherical structure of particles and their smoothness diminish, agglomeration of particles is more expressed and the size of parti-

cles loses their uniformity. The change of carbon content is not significant when the concentration of the precursor increases.

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IZVOD

STRUKTURNE OSOBINE MIKROSFERA UGLJENIKA DOBIJENIH HIDROTERMIČKIM TRETMANOM FRUKTOZE

Čvrsti proizvod bogat ugljenikom je sintetizovan hidrotermičkim tretmanom fruktoze sa HNO3 na temperaturi od 140 °C. Koncentracija prekursora bila je menjana da bi se istražilo kako njegova promena utiče na formiranje mikrosfere atoma. pH vrednost za svaki uzorak bila je isti 1. Formiranje čvrstog proizvoda bogatog ugljenikom preko hidrotermičke karbonizacije fruktoze posledica je dehidracionih reakcija. Dobijeni ugljeni materijal izrađen je od sfernih čestica veličine prečnika od 1 do 6 μm, koji se može modulisati promenom koncentracije fruktoze u rastvoru. Najbolji rezultati se dobijaju sa manjim koncentracijama fruktoze. Sferne čestice imaju više pravilan oblik i oni su manje aglomerisane. Strukture i površinske hemijske osobine dobijenog materijala su sagledavane skeniranjem elektronskim mikroskopom (SEM) , FTIR-om i spektralnim i elementarnim analizama.

Ključne reči: *ugljene mikrosfere, hidrotermalna sinteza, fruktoza.*

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