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*in co-operation
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THERMAL TREATMENT INFLUENCE ON THE SURFACE CHARACTERISTICS OF THE BORON-DOPED HYDROTHERMAL CARBON

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ABSTRACT

Boron-doped carbons were produced using hydrothermal carbonization of glucose carbohydrates under mild temperature (180°C). Boric acid was introduced into glucose precursor solution in order to obtain boron concentration of 0.2% and 1%. Two types of samples were prepared: hydrothermal carbons (HTC) and hydrothermal carbons thermally treated to 1000°C (HTCc). Characterization of the samples obtained was performed by scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). SEM analysis showed that higher boron concentration in the precursor solution caused enlargement of particle size for both types of samples, while the thermal treatment induced decrease of particle size. FTIR spectra showed that the different amount of boron in the precursor solution induced quite diverse effects on the surface chemistry of hydrothermal carbons before and after the thermal treatment.

INTRODUCTION

In the past decade, the hydrothermal treatment of carbohydrate gained an increasing interest in the field of material science. Many studies already focus on both applications and fundamental aspects motivated by the interest in producing carbonaceous powders with tunable sizes and surface properties [1]. The important advantage of hydrothermal carbon (HTC) is undoubtedly the possibility of modifying the surface or the bulk of the carbonaceous network by introducing heteroatoms.

Boron is by far the most widely used doping element in carbon. It has been suggested that boron-doping can introduce boron atoms into the substitutional positions in the carbon lattice. Also, boron can be distributed in the bulk of the carbon materials and can act as an intrinsic inhibitor which

reduces both the number of active sites and the reactivity of these sites [2]. Our previously obtained results showed that the number and nature of active sites, and consequently, the formation of surface oxides, depend on the distribution of boron in the polymer precursors [3].

After additional carbonization, hydrothermal carbons with various shape, size and surface functional groups have shown novel and interesting intrinsic properties which allow widespread use of these materials [4]. The aim of this study was to investigate effect of the thermal treatment on the morphology and the surface properties of boron doped HTC.

EXPERIMENTAL

To produce HTC, 2M water solution of D(+)-Glucose was prepared. Boric acid was used as source of boron and it was mixed with starting solution to obtained boron concentration of 0.2% and 1%. After sealing, the autoclave was heated in programmable oven for 24 h at 180°C. Obtained samples were marked as HTC, HTC/B_{0.2} and HTC/B_{1.0}. Each type of HTC samples were additionally carbonized in nitrogen to 1000°C and these samples were marked as HTCc, HTCc/B_{0.2} and HTCc/B_{1.0} (thermally treated samples).

Surface structure and morphology were studied by scanning electron microscopy (Mira Tescan X3). The functional groups of examined samples were identified with Fourier transform infrared (FTIR) spectroscopy (Bomem MB-Series, Hartmann & Braun). The FTIR measurements were performed at wavelengths in the range 4000–400 cm⁻¹.

RESULTS AND DISCUSSION

The SEM photographs of the hydrothermally carbonized samples and thermally treated samples are shown in Figure 1. In general, the morphologies of all samples consisting of carbon spheres with smooth surface. For both type of samples presence of 1% of boron in precursor solution induced a significant increase in particle size. For thermally treated samples general trend is the decrease of average particle size compared to hydrothermally carbonized samples, caused by the mass loss and shrinkage which occurred during thermal treatment.

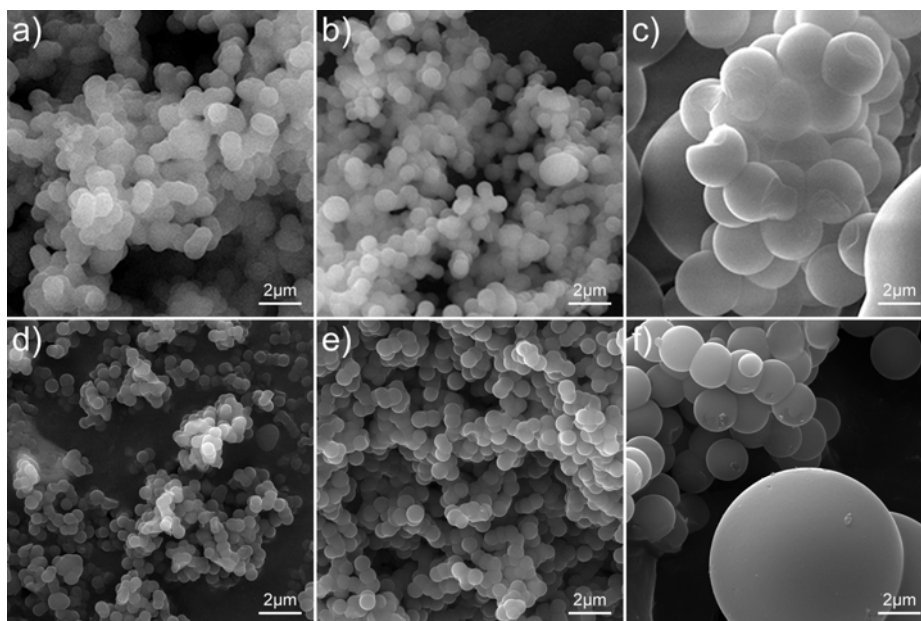


Figure 1. SEM photographs of all tested samples: a) HTC, b) HTC/B_{0.2}, c) HTC/B₁, d) HTCc, e) HTCc/B_{0.2} and f) HTCc/B₁

Figure 2 shows FTIR spectra of examined samples. The wide band between 3000 and 3700 cm^{-1} is assigned to the stretching vibrations of O-H (hydroxyl or carboxyl), and the bands around 2815–3000 cm^{-1} are the characteristic stretching vibrations of aliphatic C-H. The absorption bands near 1710 cm^{-1} is attribute to stretching vibration of -C=O from carbonyl and carboxyl groups. The out-of-plane bending vibration of aromatic C-H bands was observed in the region of 875–750 cm^{-1} , and the band at 1620 cm^{-1} are attributed to the C=C vibrations [5], suggesting the aromatization of the samples during the hydrothermal treatment. For hydrothermally carbonized samples boron addition of 0.2% in the precursor solution induced the formation of the highest number of the surface actives sites, while further increase of boron content reduced the number of surface actives sites. However, after thermal treatment FTIR spectra for sample HTCc/B_{0.2} shows the lowest intensity of the bands, indicating that incorporated boron acts as an inhibitor for formation of active sites. On the other hand, for the sample HTCc/B_{1.0} boron presence had catalytic effect on the formation of surface active sites.

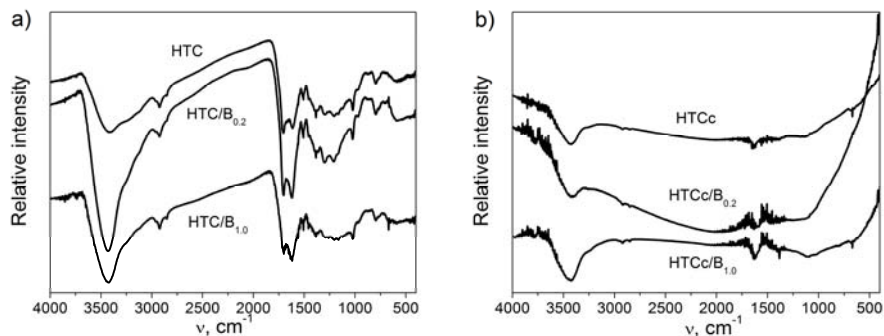


Figure 2. FTIR spectra of examined samples: a) before and b) after thermal treatment to 1000°C

CONCLUSION

It was established that boron addition of 1% into the precursor solution induces significant enhancement of the particles size for both hydrothermal carbon and thermally treated hydrothermal carbon. As it was expected, thermal treatment leads to decrease of particle size as a consequence of the mass loss and shrinkage processes. FTIR results show that thermal treatment induced reduction of the amount of surface oxygen groups. Nevertheless, for carbonized samples different amount of boron has quite a distinctive effect on the surface chemistry compared to untreated samples. Obtained results suggest that by applying boron addition and thermal treatment it is possible to create desired structural and surface properties of hydrothermal carbon.

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