

## Functionalization of carbon fibres with Br- and S-containing groups

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Bromination of Busofit carbon fiber with liquid bromine was carried out and chemical and thermal desorption properties of the samples obtained were studied. It was established that bromination resulted in grafting 1 mmol/g of bromine onto the superficial layer of the fiber. It was demonstrated that thermal desorption of bromine was observed as hydrogen bromide in the temperature range 150–650 °C with maxima at 390 °C and 470 °C. Treatment of the brominated samples with sulfur-containing compounds under heating led to grafting S-containing groups onto the superficial layer. The pre-bromination conditioned higher concentration of sulfo groups on the surface of Busofit as compared to the non-brominated samples. Oxidation of S-containing groups enabled obtaining fiber samples with concentration of sulfo groups up to 0.5 mmol/g. Desorption of sulfo groups from the fiber surface occurred in the temperature range 170–450 °C with maximum at 250±10 °C. The materials synthesized exhibit sufficient thermal stability for use in acid-base catalysis.

### Introduction

Carbon fibers (CFs) are known to have a very large surface area and a high thermal and mechanical stability. They can be used not only in adsorption processes, but also in catalysis as carriers and heterogeneous catalysts [1, 2]. Their properties can be varied considerably by means of functionalization of CFs surface with functional groups of different chemical nature [3, 4]. Unlike other methods of synthetic chemistry, bromination is a convenient procedure for further nucleophilic substitution of bromine for organic functional groups.

This paper is focused on the bromination of carbon fibers and explores the possibility to use Br-containing precursors for the synthesis of S-containing fibers.

### Experimental

Commercial Busofit carbon fibers with BET specific surface area 1380 m<sup>2</sup>/g and total pore volume 0.63 cm<sup>3</sup>/g were used as initial material. The source material for Busofit CFs manufacturing is viscose.

Bromination with liquid bromine was carried out as follows: a sample of fibers (5 g) was treated with 10 ml of liquid Br<sub>2</sub> at room temperature for 1 h and then with 10 % solution of potassium oxalate (200 ml) until carbon dioxide evolution ceased. The sample was filtered and washed with distilled water until no Br<sup>-</sup> ions were detected in the washing waters. The brominated sample was air-dried at 120 °C for 10 h. The sample was designated as CF/Br.

Substitution of bromine for a sulfo group: Samples of the initial and brominated CFs (1 g) were filled with a concentrated solution (5 ml) of sodium mercaptoacetate or sodium sulfide, and were allowed to remain at 120 °C for

15 h. CFs samples that has been treated with sodium mercaptoacetate were hydrolyzed by boiling with 15 % HCl for 2 h and were washed to remove the acid. All S-containing samples were oxidized by 30 % H<sub>2</sub>O<sub>2</sub> for 3 h, washed with distilled water and air-dried at 120 °C for 10 h. The samples obtained by treatment with sodium mercaptoacetate were designated as CF/S1 and CF/Br/S1 and those treated with sodium sulfide were designated as CF/S2 and CF/Br/S2.

All CFs samples were studied by chemical analysis (CA) [5], thermogravimetric analysis (TGA) and temperature-programmed desorption mass spectrometry (TPD-MS).

### Results and discussion

According to the CA data, the concentration of bromine in brominated CF/Br sample was 1 mmol/g. Analysis of the TPD-MS data revealed that desorption of bromine from the surface occurred as hydrogen bromide in the temperature range 150–650 °C, and two maxima – at 390 °C and 470 °C – were registered on the experimental curves. The fragments with m/z 80 and 82 (HBr) were observed in an equal amount that corresponded to the natural ratio of isotopes of bromine. Signals of the fragments with m/z 79 and 81 (Br) were significantly less intensive and completely synchronous to the temperature dependences of HBr evolution, indicating the formation of Br as a result of HBr dissociation in the mass-spectrometer but not as a result of decomposition of the Br-containing groups of the CFs surface.

As it was shown in [4], the treatment of brominated active carbon with S-containing compounds followed by oxidation with hydrogen peroxide enabled obtaining samples

with sulfo groups in the surface layer. Analysis of the TPD-MS data of carbon fibers CF/Br/S1 (CF/S1) and CF/Br/S2 (CF/S2) revealed that desorption of S-containing groups occurred as SO<sub>2</sub> (m/z 64) in the temperature range from 60 °C to 550 °C. That was due to the presence of sulfo groups in the surface layer. The signals m/z 48 that corresponded to SO desorption were also registered in TPD-MS spectra, but their intensity was much lower than that of SO<sub>2</sub>. Thermo desorption curves of SO evolution were completely synchronous to SO<sub>2</sub> evolution, indicating the formation of SO as a result of SO<sub>2</sub> dissociation in the mass spectrometer, but not as a result of decomposition of other S-containing surface groups.

The sulfo group concentration was calculated by TGA method according to the weight loss in the temperature range 170–450 °C (usually, the interval of SO<sub>2</sub> desorption registered by TGA is 50–100 degrees narrower than that obtained by TPD-MS due to different experimental conditions). According to the data obtained, the concentrations of sulfo groups for pre-brominated samples CF/Br/S1 and CF/Br/S2 were 0.37–0.53 mmol/g, and for the samples synthesized by S2 method those concentrations were higher. For all S-containing carbon fibers desorption of SO<sub>2</sub> occurred with a maximum at 250 ± 10 °C. The temperature dependences of mass loss for non-brominated samples CF/S1 and CF/S2 were similar to those described above but concentrations of sulfo groups for those samples were less and equaled 0.30–0.33 mmol/g.

Thus, bromination of carbon fibers Busofit with liquid Br<sub>2</sub> enabled obtaining active bromine-containing precursors,

in which bromine could be substituted by S-containing groups. It was demonstrated that pre-bromination led to synthesis of CFs samples with higher concentration of surface sulfo groups as compared to those obtained without such treatment. It was found that sodium sulfide was preferable in preparation of intermediate S-containing CFs samples compared to sodium mercaptoacetate. The synthesized samples with surface sulfo groups were much more thermally stable. They seem to be promising materials in selective adsorption and acid-base catalysis.

This work was carried out owing to support provided by the educational program of the Cabinet of Ministers of Ukraine "100 + 100 + 100" (according to the Resolution of the Cabinet of Ministers of Ukraine № 411 dd. 13.04.2011 and № 546 dd. 16.05.2011).

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Received to the editor 10.04.2015

## Функціоналізація вуглецевого волокна Br- та S- вмісними групами

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Проведено бромовання вуглецевого волокна Бусофіт рідким бромом та досліджено хімічні і термодесорбційні властивості отриманих зразків. Встановлено, що бромовання приводить до введення в поверхневий шар волокна до 1 ммоль/г бромом. Показано, що термодесорбція бромом спостерігається в температурному інтервалі 150–650 °C у вигляді бромоводню з максимумами при 390 та 470 °C. Обробка бромованих зразків сірковмісними сполуками при нагріванні приводить до введення в поверхневий шар S-вмісних груп. Попереднє бромовання приводить до отримання більшої кількості сульфогруп на поверхні Бусофіту порівняно з небромованими зразками. Окиснення S-вмісних груп дозволяє отримати зразки волокна з концентрацією сульфогруп до 0,5 ммоль/г. Десорбція сульфогруп з поверхні волокна відбувається у температурному інтервалі 170–450 °C з максимумом при 250±10 °C. Синтезовані матеріали характеризуються достатньою термічною стійкістю для використання їх у кислотно-основному каталізі.

## Функционализация углеродного волокна Br- и S- содержащими соединениями

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Проведено бромирование углеродного волокна Бусофит жидким бромом и исследованы химические и термодесорбционные свойства полученных образцов. Установлено, что бромирование приводит к введению в поверхностный слой волокна до 1 ммоль/г брома. Показано, что термодесорбция брома наблюдается в температурном интервале 150–650 °С в виде бромоводорода с максимумами при 390 и 470 °С. Обработка бромированных образцов серосодержащими соединениями при нагревании приводит к введению в поверхностный слой S-содержащих групп. Предварительное бромирование приводит к получению большего количества сульфогрупп на поверхности Бусофита по сравнению с небромированными образцами. Окисление S-содержащих групп позволяет получить образцы с концентрацией сульфогрупп до 0,5 ммоль/г. Десорбция сульфогрупп с поверхности волокна происходит в температурном интервале 170–450 °С с максимумом при 250±10 °С. Синтезированные материалы характеризуются достаточной термической стойкостью для использования их в кислотно-основном катализе.