

Decomposition of ethylene on iron catalyst to obtain carbon nanotubes and the way of their purification*

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This paper describes preparation and characterization of carbon nanotubes obtaining using ethylene as a carbon source and iron as catalyst. Additionally purification procedure of carbon nanomaterials is presented. Purification was conducted in two stages. In the first one hydrogen or air was used in order to gasify unwanted carbon forms. In the second one – various reactants (nitric, hydrochloric or nitro-hydrochloric acids) were applied to remove metal particles. Obtained materials were characterized using X-ray diffraction, transmission electron microscopy and thermogravimetry.

1. INTRODUCTION

Decomposition of hydrocarbons on transition metal catalysts leads to carbon material formation. This technique, called chemical vapor deposition (CVD) is one of the most effective to obtain carbon nanotubes [1-3]. This method is the most interesting one because of its low production costs and therefore it is very attractive for mass production. A yield and quality of obtained materials depend on many parameters, as a catalyst, temperature and also reaction time or addition of other gases (argon, hydrogen) to a hydrocarbon [4-6]. Depending on experimental conditions besides carbon nanotubes other forms of carbon (amorphous carbon, graphitic particles) are formed as well. Additionally, the

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material after synthesis is contaminated with catalyst particles. Then, this material after synthesis should be submitted to a purification procedure.

All purification methods can be divided into two groups [7]. The first group involves chemical methods (gas phase oxidation, gas phase reduction, liquid phase oxidation and electrochemical oxidation), the second one – physical (filtration, solubilization with functional groups or high temperature annealing). Chemical methods are based on the dissolution of metallic impurities by acids and on the idea of selective oxidation, because carbonaceous impurities (for example – amorphous carbon) are oxidized at a higher rate than CNTs [8-9]. Purification in the gas phase is applied to purify carbon nanotubes from carbon impurities. These impurities can be eliminated using air, steam, pure oxygen or hydrogen [10-13]. The gas phase oxidation or hydrogenation are effective in carbon impurities removal, but metal particles can not be directly removed and then a further acid treatment is needed. Liquid phase oxidation can simultaneously remove both amorphous carbon and metal catalyst. The oxidants used for liquid phase oxidation include: nitric, phosphoric, sulfuric or hydrochloric acids, sodium hydroxide [14-17].

Chemical methods always influence the structure of CNTs submitted to oxidation. The disadvantages of this method are that it often opens the end of CNTs, cuts CNTs, damages surface structure and introduces oxygenated functional group on CNTs [18-20]. Physical methods involve a separation of CNTs from impurities, based on differences in their physical size, aspect ratio, gravity, and magnetic properties. These methods are used to remove graphite sheets, carbon nanospheres, aggregates or to separate CNTs with different diameter/length ratios. They are complicated, time-consuming and less effective than chemical methods [7]. The best results were obtained using a combination of both kinds of methods, chemical and physical.

In this paper we present a synthesis method of multi walled carbon nanotubes based on decomposition of ethylene on nanocrystalline iron catalyst and their purification based on oxidation in gas phase and an acid treatment.

2. MATERIAL AND METHODS

The synthesis of carbon nanomaterials was carried out using ethylene as a carbon source and nanocrystalline iron as catalysts. Catalyst was obtained by a fusion of magnetite with a small amount of promoter oxides. The role of calcium and aluminum oxides was to stabilize the nanocrystalline structure at elevated temperatures. The obtained alloy was crushed and sieved in order to obtain a fraction of 1.2 to 1.5mm and next reduced under hydrogen. The catalyst chemical composition was determined using AES-ICP method (Yvon-Jobin) and the samples contained iron and ~2.9 wt.% Al_2O_3 and CaO. The mean crystallite

size determined using the X-ray diffraction method and calculated using Scherrer's equation amounted to ca. 17nm. The samples of catalysts were placed in ceramic boats inside a quartz tube (diameter 70mm, length 120mm) of high-temperature furnace (HST 12/400 Carbolite). Scheme of installation is presented in the Figure 1. The processes were performed under atmospheric pressure at 700°C for 60 min. After the synthesis the samples were cooled to the room temperature under argon atmosphere. The obtained samples were submitted to a purification procedure. In the first stage, gasification of unwanted carbon under hydrogen or air atmosphere was conducted and in the second one – an acid treatment was applied in order to remove catalyst particles.

The phase composition of the samples were determined using X-ray diffraction method. Transmission electron microscopy was applied to determine morphology of carbon materials and thermogravimetric method – to determine iron amount which remained in the sample after acid treatment.

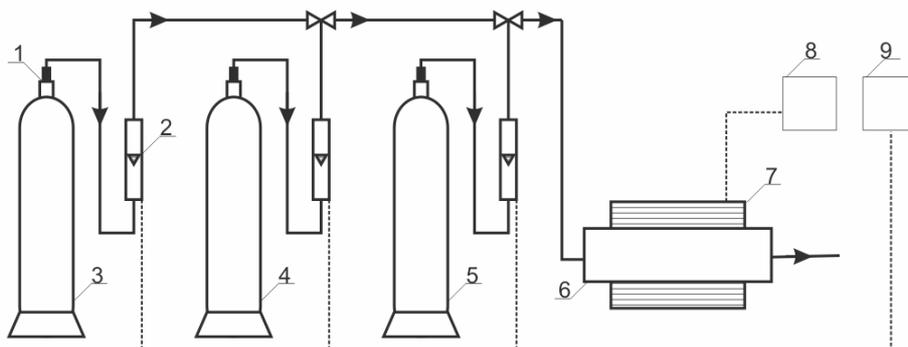


Fig. 1. Installation scheme for synthesis of carbon nanomaterials: 1-pressure reducing valve, 2-electronic flowmeter, 3-hydrogen, 4-argon, 5-ethylene, 6-quartz tube, 7-high temperature furnace, 8-temperature controller, 9-flow controller

3. RESULTS AND DISCUSSION

Carbon nanomaterials were obtained by ethylene decomposition on iron catalysts. Ethylene was diluted with argon, because it is known that an addition of an inactive gas (argon, nitrogen) or hydrogen [6] to hydrocarbons improve a quality of carbon nanotubes obtained using CVD method.

After the synthesis the samples were studied using X-ray diffraction method. On the diffraction pattern (not shown here) the peak corresponding to graphite phase and peaks corresponding to iron carbide in the form of cementite were visible [21].

The morphology of carbon materials was identified using high resolution transmission electron microscopy. TEM images are presented in the Figure 2. It was found that obtained carbon was mainly in the form of multi walled carbon nanotubes. Their external diameters were in the range from 10 to 50 nm. Larger particles were surrounded by several graphitic layers. This indicates that only small catalyst particles were suitable for the growth of carbon nanotubes. Inside the tubes catalyst particles can be seen. Similar structures were obtained by Ermakova et al. [22] and Zhao et al. [23].

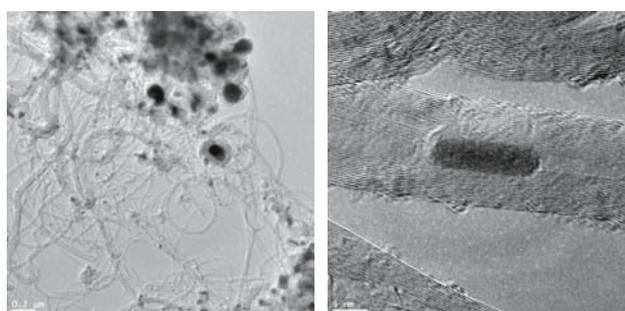


Fig. 2. TEM images of the sample after ethylene decomposition on the iron catalysts at 700°C.

So-obtained material was next treated under air atmosphere in order to eliminate unwanted carbon species, mainly amorphous carbon, which is less resistant to oxidation than nanotubes. The majority of researchers [8-9, 24] states that oxidation of carbon nanotubes starts at the tube ends, where the presence of pentagons produces both curvature and increased strain. Pang et al. [9] claimed that positive and negative curvatures are present along the length of tubes as well and these areas are also privileged in initial oxidation. However only sites on the outer walls of nanotubes are available to oxygen. Since these sites are relatively rare comparing to the bulk of carbon in inner layers and in unstrained structures, these materials are remarkably resistant to oxidation.

A morphology of the sample oxidized under air atmosphere at 500°C was studied using TEM techniques and the TEM images are presented in Figure 3. It was found that after oxidation carbon nanotubes were still present in the sample and majority of them had the open ends. This feature enables a better separation of catalyst particles from CNTs in the subsequent purification stage – an acid treatment. Under experimental conditions not whole amorphous carbon was removed and a little amount was still present on the external walls of CNTs. Some catalyst particles were also found inside the channels of CNTs.

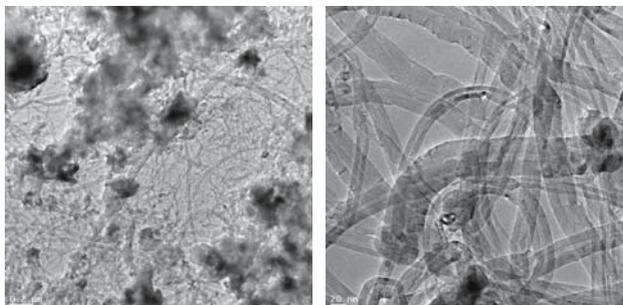


Fig. 3. TEM images of the sample after oxidation at 500°C.

The phase composition of sample after oxidation was analysed with X-ray diffraction method. The diffraction pattern is shown in Figure 4A. Two phases were identified: graphite and hematite. Under experimental conditions iron carbide – Fe_3C was decomposed and the whole amount of iron reacted with oxygen forming iron oxide. Therefore peaks derived from iron were not detected.

After purification in the gas phase, the samples were treated chemically in the liquid phase using different reactants. The nitric acid, hydrochloric acid as well as a mixture of these two acids was applied. After the treatment the amount of iron was measured using thermogravimetric method. The values of residual iron are shown in Table 1.

In the case of the samples treated using 1M hydrochloric acid, an acid concentration had any essential influence on the amount of iron remaining in the material. Generally, the percentage of iron in the samples equaled about 3%. In the case of the samples treated with nitric acid, very poor results were obtained when 1M HNO_3 was applied, only about 13% of iron was removed. For the same samples treated with 5M HNO_3 much higher degrees of metal removal were achieved and the amount of iron in the sample equaled about 7.3%. An increase of the reaction time to 24h led to a better elimination of metallic impurities and the amount of iron after the acid treatment equaled about 4.5%. The use of concentrated nitric acid instead of 5M HNO_3 did not have an essential influence on the percentage of iron in the sample when the reaction was conducted for 1 hour. Iron particles were better eliminated when the reaction time was longer. When the reaction time increased from 1 to 5h only about 1.8% of iron particles were detected. The best results were obtained when the sample was boiled in a mixture of nitric and hydrochloric acid. Only about 0.8% of iron after this purification was still found.

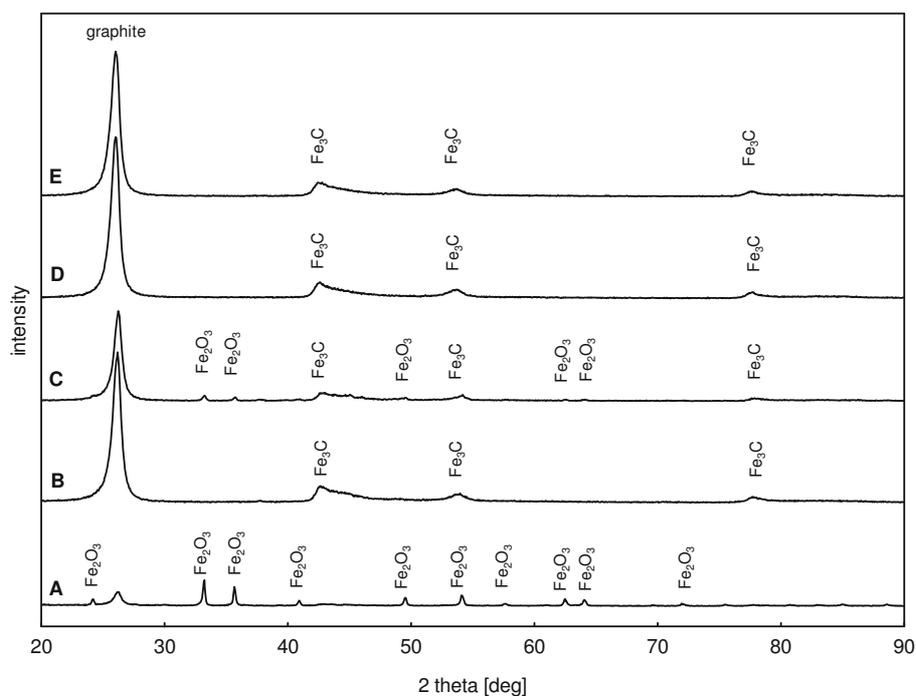


Fig. 4. X-ray diffraction pattern of the samples after oxidation (A) and after acid treatment using 5M HCl – 1h (B), 5M HNO₃ – 1h (C), concentrated HNO₃ – 5h (D) and HCl:HNO₃ 3:1 – 1h (E).

Tab. 1. The amount of iron (determined using TGA method) in the samples after treatment using different reagents.

sample	acid	concentration [M]	treatment time [h]	amount of iron [%]
1	hydrochloric	1	1	3.6
2	hydrochloric	5	1	3.1
3	Nitric	1	1	86.8
4	nitric	5	1	7.3
5	nitric	5	24	4.5
6	nitric	concentrated	1	5.7
7	nitric	concentrated	5	1.8
8	nitrohydrochloric	–	1	0.8

In the case of studies of carbon nanotubes purification, not only degree of metal particles removal is very important, but also the influence of chemical reactants on their structure and amount of unwanted carbon species (for example – amorphous carbon) in the sample. In the research papers concerning oxidation

of carbon nanotubes and their studies using thermogravimetric method, different combustion temperature of CNTs are given. Chen and co-workers [25] determined the burning temperature of MWNTs obtained by decomposition of acetylene using TGA analysis, and 510°C was chosen to be optimum temperature to eliminate non-nanotube carbon materials. Colomer and co-workers [26] reported that optimum temperature for burning of CNTs prepared also by decomposition of acetylene was 500°C. Shi and co-workers [27] studied SWNTs obtained by arc-discharge method and indicated 350°C as an optimum temperature for the burning of carbon impurities. Dillon and co-workers [28] determined 785°C as combustion temperature of SWNTs obtained by laser vaporization method. According to [6] a discrepancy between these data results from different techniques used for the preparation of carbon nanotubes and therefore differences in composition of the samples and their graphitization degree.

The TG curves of our samples after treatment in hydrochloric and nitric acids are presented in Figure 5. For comparison TG curve of the sample after oxidation only is shown in Figure 5 as well.

TG and DTG curves (not shown here) of the sample after purification in the gas phase reveal that a very slow decrease of the sample mass starts at 25°C and is observed to about 420°C. After this point the mass violently diminishes up to 690°C. At a further temperature increase the mass sample remains unchanged and the residual mass corresponds to iron oxide. The TG and DTG curves (not shown here) corresponding to the samples after treatment in hydrochloric and nitric acids were similar. For the samples treated in a concentrated nitric acid for 5h and 5M nitric acid for 24h the violent weight loss started at 25°C and lasted up to ~70°C. This stage corresponds to the loss of water. After this point the weight decreased more slowly up to ~370°C, which corresponded to the loss of some amorphous carbon. At the temperature of ~370°C the weight of the samples decreased sharply and the end of oxidation was achieved at ~670°C. For the samples treated in 5M HNO₃ and HCl for 1h, the mass decrease started at 25°C and lasted up to ~450°C, what corresponded to the loss of water and amorphous carbon. A further sample mass decrease was rapid and the end of oxidation was achieved at the temperature of ~680°C for the sample after treatment in nitric acid and at ~710°C for the sample after treatment in hydrochloric acid. Lower combustion temperature of the material after the treatment with 5M HNO₃ for 24h or with concentrated HNO₃ for 1h in comparison with combustion temperature of the material after the treatment in 5M HNO₃ and HCl for 1h indicates that the structure of tubes was more damaged in the two first cases. For all materials after the acid treatment, the

residual weight corresponds to catalyst particles, which were not removed from the sample.

The results of the XRD measurements confirmed that in the samples after acid treatment, some part of catalyst was still present in the sample (the amounts of residue calculated on the basis of TGA analysis are shown in Table 1 above.) Diffraction patterns of the selected samples are presented in Figure 4. In all the samples the small peaks derived from cementite phase were detected and for the sample treated with 5M nitric acid for 1h additionally the peaks corresponding to iron oxide were also observed. The presence of Fe_2O_3 peaks on the diffraction pattern C is connected with selected experimental conditions not sufficient for CNTs purification. A removal degree of iron for the sample treated with 5M HNO_3 for 1h was from ~2.5 to ~9 times lower than in the case of the samples treated under 5M HCl for 1h and HCl: HNO_3 3:1 for 1h, respectively. A small amount of cementite should be present (besides iron oxide phase) in the samples after an oxidation in the gas phase. However, the Fe_3C peaks were not detected, probably their intensity was very low in comparison with the high intensity of Fe_2O_3 peaks and they. It can be assumed that cementite particles remained inside the nanotubes channels or were encapsulated by graphitic layers during synthesis of CNTs.

In order to examine the CNTs structure after an acid treatment, a TEM analysis was performed. The TEM images of the samples are presented in Figure 6. In the samples treated under milder conditions (1M HCl, 1h – image A and 5M HNO_3 , 1h – image B) carbon nanotubes were noticed. Their tips were opened and inside of some nanotube channels darker spots corresponding to cementite phase were observed. In the sample after the treatment in 5M HNO_3 for 24h no nanotubes were discovered. These structures were destructed under the severe experimental conditions.

4. CONCLUSIONS

Multiwalled carbon nanotubes were obtained using nanocrystalline iron catalysts and ethylene as a carbon source. A two-stages procedure was applied for their purification. Amorphous carbon was removed in gas phase and catalyst particles in liquid phase, using hydrochloric, nitric or nitro-hydrochloric acids. Under the same conditions (acid concentration, reaction time) a better removal degree of metal particles was achieved with the use of hydrochloric acid instead of nitric one. The use of 5M HNO_3 for 24h resulted in a good removal degree of metal particles, however carbon nanotubes under these conditions were destroyed.

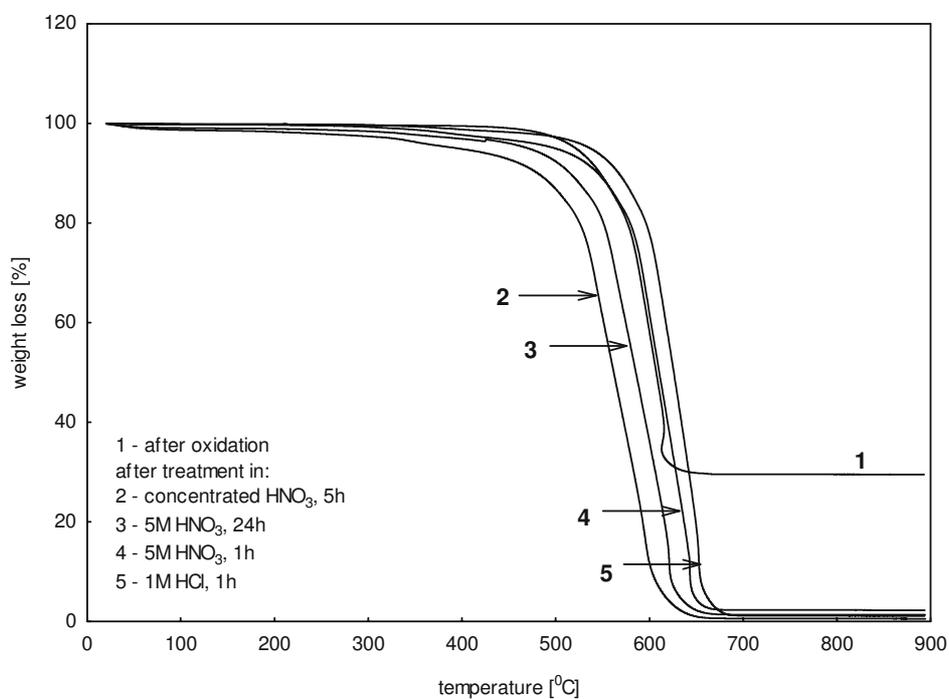


Fig. 5. TG curves of the samples after oxidation and treatment in different reagents.

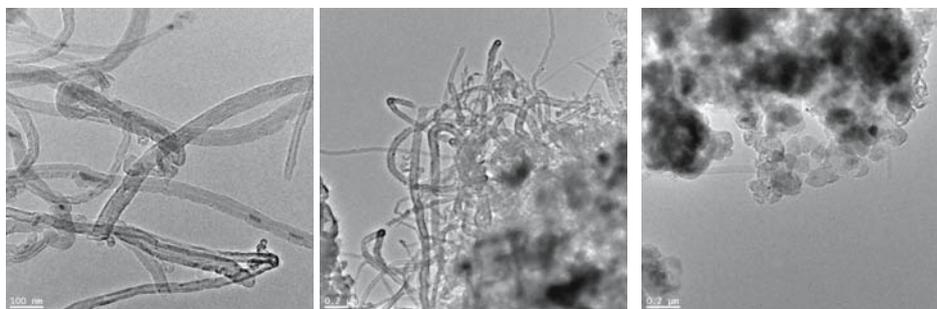


Fig. 6. TEM images of the sample after treatment in: 1M HCl by 1h (A), 5M HNO₃ by 1h (B) and 5M HNO₃ by 24h.

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