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Preparation and characterization of nanocarbons for hydrogen storage

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Carbon nanomaterials have been pronounced as the most prospective material family for nanoelectronic applications, as well as materials for hydrogen storage. The catalytic methods we used for preparing different carbon nanoforms have been presented. During the study, a catalyst system composed of alkaline support and supported iron has been used. The effect of synthesis conditions and the carbon source material have been emphasised. The properties of the materials across the synthesis route have been studied by various instrumental techniques (i.e., ICP, SEM, FT-IR, low temperature nitrogen adsorption). The role of the catalyst is shown. Synthesized materials before as well as after the purification processes have been found to be very promising for hydrogen storage.

Key words: *hydrogen storage; carbon nanomaterial; nanomaterial synthesis*

1. Introduction

Carbon nanotubes (discovered by Iijima in 1991 [1]) have become some of the most thoroughly studied materials for technical applications. They are considered a very promising material for many new products (e.g., composite materials, catalyst materials, field emission materials). Furthermore, they show a great promise as storage media for hydrogen [2–4] and as such are of great interest to hydrogen-based economy. The hydrogen storage process of carbon nanotubes by themselves as well as of other carbonaceous nanomaterials has been extensively studied. The success of hydrogen storage within nanotubes will depend on a variety of parameters, including storage capacity and nanotube purity. To this end, the optimisation of the process

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parameters for hydrogen storage and the quality of the prepared nanotube material are the key. To date, there are no methods [5–8] leading to the production of perfectly pure nanotubes. Most research has concentrated on the post-purification of the produced material from by-products like amorphous material, fullerenes, catalyst particles, and other carbon species [9–16]. Moreover, new methods enabling the mass production of storage materials should be studied. The carbon vapour deposition (CVD) method seems to be a solution (e.g. [17]), but in this case a suitable catalytic material is needed (mostly supported systems are used). The catalyst (the active agent as well as its support) should be removable after nanocarbons synthesis. In this work, an iron catalyst supported on calcium carbonate has been used.

2. Experimental

Carbon materials were synthesised by the decomposition of acetylene and methane in a tubular oven in the temperature range of 550–700 ºC. A monometallic salt of Fe(III) was applied as a catalyst. A calculated amount of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in distilled water, and $CaCO_3$ was suspended in the solution. pH of the solution was held at about 7 by injecting ammonia water. The mixture was stirred for 30 minutes and then filtered. Material from filtration was dried at 105 ºC for 5 hours and calcinated for 1.5 hours under argon at 700 ºC. So prepared material was used in carbonaceous materials synthesis. As a blind probe, a sample of $CaCO_3$ with the same history was used.

The catalyst sample or blind probe was placed in a quartz boat, which was inserted in a quartz tube under argon flow (400 cm^3/min) for 2 h. Keeping a constant flow, the temperature was raised to the value assumed for the synthesis. After that, the composition of the gaseous mixture was changed. In the case of acetylene, it was introduced to reach 2 vol. % of C_2H_2 in the mixture. In the case of methane, the atmosphere was changed from Ar to CH_4. After 1 h (in the case of C_2H_2) or 24–120 h (in the case of CH_4), the gas flow was switched from hydrocarbon to argon and the boat was cooled down to room temperature. Iron loading was controlled by the ICP method (1% Fe wt.).

A two-step procedure similar to those described by us in [18] was used for purification. In the first step, amorphous carbon was burned off in oxygen at 500 ºC. In the next step, the catalyst was dispersed in a solution of diluted nitric acid for 20 h at 80 ºC, washed with distilled water, and dried at 105 ºC overnight. The morphology of the samples was studied by scanning electron microscopy (SEM), specific surface and pore size distribution by low temperature nitrogen adsorption, surface properties by infrared spectroscopy (FT-IR), phase composition by powder X-ray diffraction (XRD), and, finally, hydrogen storage capacity by volumetric methods [19].

3. Results and discussion

Figure 1 shows a SEM micrograph of a catalyst sample after the calcination step. In Figure 2, the product of synthesis under C_2H_2 at 750°C is presented. At lower temperatures, the synthesis was ineffective. Figure 3 presents the surface of the samples after synthesis under methane for the syntheses lasting 27, 70, and 118 h. It can be observed that in the case of the shortest reaction time not all of the catalyst's surface is covered with a new material. On the other hand, there are no visible changes between the samples presented in Figs. 3b and c. No mass change was observed between the last two samples. The synthesis was probably concluded after 70 h.

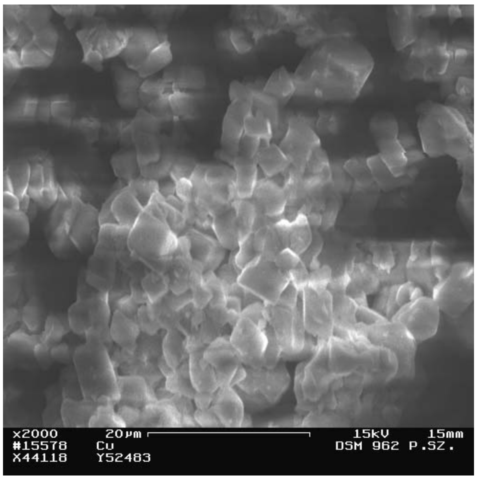

Fig. 1. The surface of the catalyst after calcination

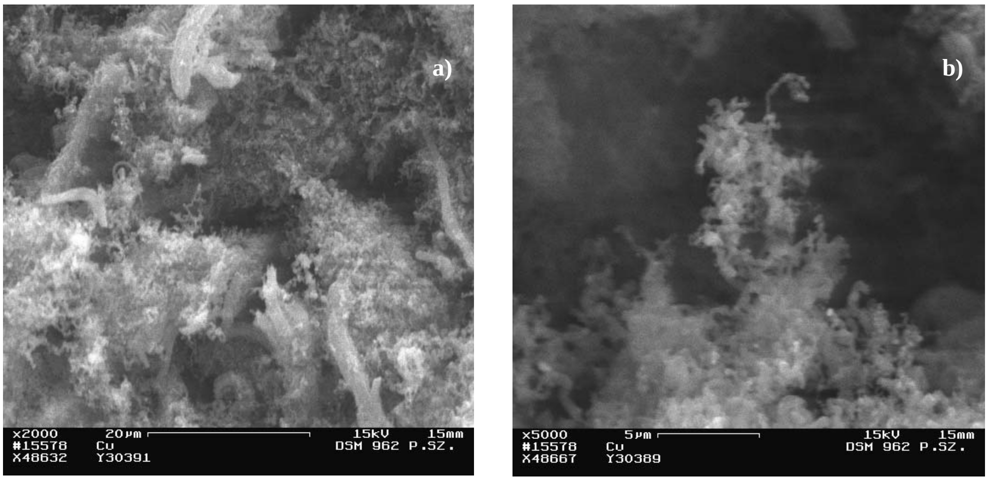

Fig. 2. The surface of the sample after synthesis
(acetylene) at 750 ºC under magnifications: a) 2000, b) 20 000

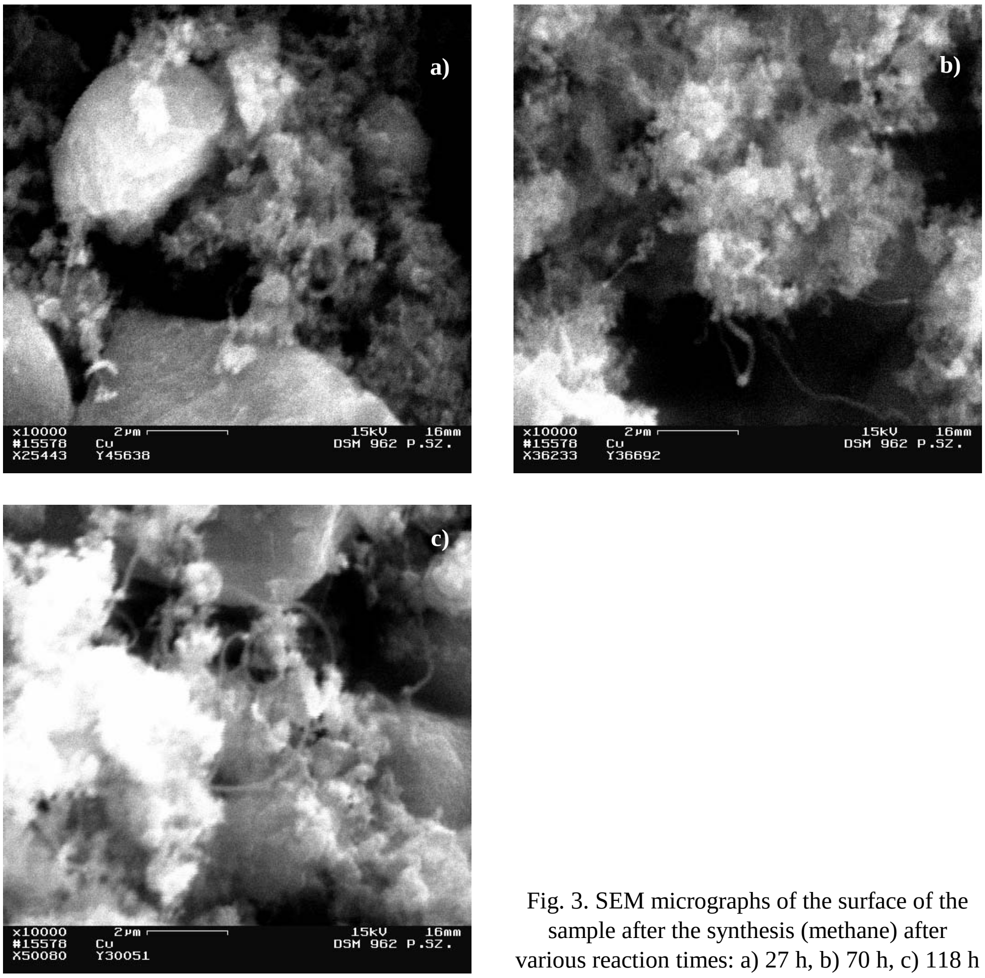

Fig. 3. SEM micrographs of the surface of the sample after the synthesis (methane) after various reaction times: a) 27 h, b) 70 h, c) 118 h

The forming of the nanomaterials was a catalytic process. In Figure 4, the pictures of the blind probe with no iron addition (support only, treated the same way as the catalyst) and of the catalyst surface are presented. It should be noted that in the case of the blind probe no new material occurs. Therefore it can be concluded that the process has a catalytic character. Now we will try to explain the phenomena following from Figure 3. Material synthesis was stopped because iron catalyst particles were blocked by new carbon materials.

In Figure 5, images of the synthesised materials after the purification procedure are presented. The material received with acetylene used as the carbon source (Fig. 5b) consists of fibres (tubes) with a larger diameter. Moreover, no catalyst material is observed. This was confirmed by ICP analysis: only traces of iron were found.

As follows from XRD measurements (not presented), the disintegration of $CaCO_3$ to CaO was concluded in the samples after synthesis at 750 ºC. The FT-IR method proved to be a very effective tool for studying the sample surface at different process steps. In Figure 6, spectra of a samples before synthesis (after catalyst calcination) and after synthesis and the purification procedure are presented. As is visible, the spectrum of the purified sample is sharper, with no additives.

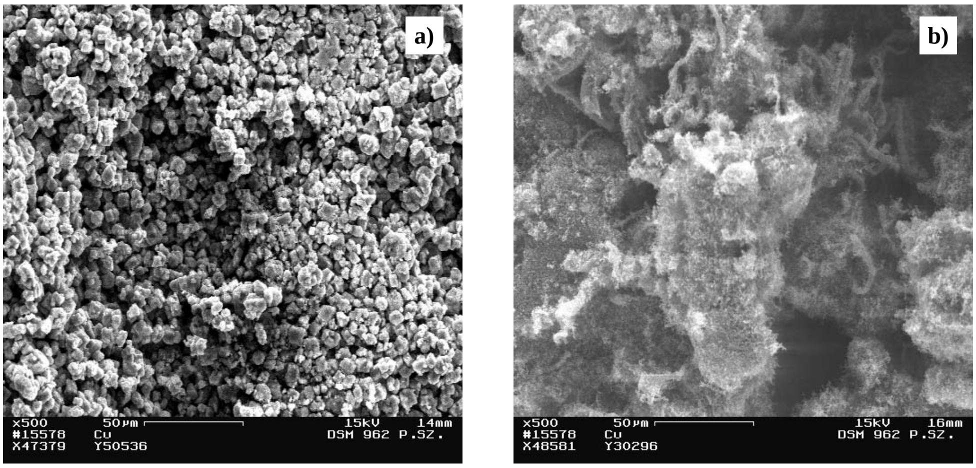

Fig. 4. Images of the surfaces of the sample after synthesis
on the blind probe (a) and on the catalyst (b), under the same magnification

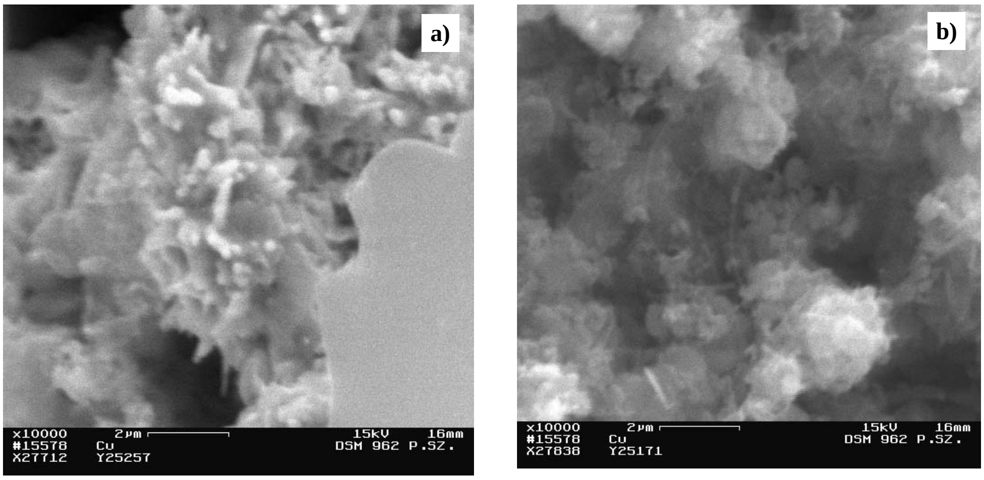

Fig. 5. Images of the surfaces of samples after the purification procedure: a) CH_4, b) C_2H_2)

The obtained samples, as follows from nitrogen adsorption measurements (not presented), differ in their specific surfaces, and pore size distributions. In samples after purification, a higher micropore content and a larger surface were found. This is due to the removal of amorphous carbon forms.

The prepared samples were used for studying hydrogen storage. Hydrogen loading ranges between 2 and 4 wt. %. When we compare these results to those already presented in previous studies, we see that hydrogen storage in carbon nanotubes is still questionable. Dillon et al. [20] concluded that pure single-walled carbon nanotubes (SWCNTs) are able to store 5–10 wt. % of H_2 (at 133 K and 0.04 MPa) that can be desorbed at room temperature. Chambers et al. [20] reported much higher storage capacities for carbon nanofibres – up to 67 wt. % at 25 ºC and 120 atm. Chen et al. [21] presented Li-doped multiCNTs (20 wt. % At 473–633 K and ambient pressure) and K-doped CNTs (14 wt. % at room temperature and ambient pressure). It is worth noting that Yang [22] pointed out that Chen’s results should be treated as unreliable due to the presence of H_2O, and highlighted the difficulties that can be encountered in such studies.

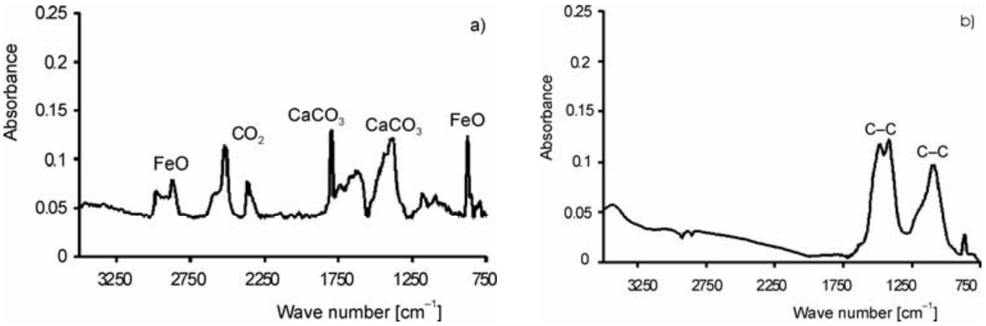

Fig. 6. FT-IR spectra for the studied samples:
a) the catalyst after calcination, b) the sample after synthesis and purification

4. Conclusions

The results presented here demonstrate that the described method can be used to prepare nanomaterials for the hydrogen storage but an optimisation of the synthesis parameters is needed.

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