The heat treatment duration effect on the efficiency of a catalyst for carbon nanotubes synthesis

E Burakova†, G Besperstova, A Tkachev, T Dyachkova, E Tugolukov, I Gutnik and N Orlova

Department “Technology and Methods of Nanoproducts Manufacturing”, Tambov State Technical University, 106 Sovetskaya Street, 392000, Tambov, Russian Federation

†E-mail: elenburakova@yandex.ru

Abstract. The present paper shows that the duration of the pre-catalyst heat treatment stage implementation for obtaining a metal oxide Co-Mo/Al₂O₃ catalyst through thermal decomposition has a significant impact on its effectiveness in the synthesis of carbon nanotubes (CNTs) via chemical vapor deposition (CVD). The size of active sites formed and the specific surface area of the Co-Mo/Al₂O₃ catalyst were found to depend on the pre-catalyst heat treatment conditions. It was experimentally proved that the characteristics of both the catalyst (specific surface area and efficiency) and the CNTs (diameter and degree of defectiveness) can be controlled by the mode parameters of the thermal decomposition stage. The research results confirm the possibility of obtaining an effective catalyst system without implementing the secondary heat treatment stage - calcination. Moreover, the use of the Co-Mo/Al₂O₃ catalyst, obtained according to this procedure, in the CVD process allows to reduce the cost of CNTs synthesized.

1. Introduction

Carbon nanotubes (CNTs) are widely used as modifiers of many construction and functional materials. Various composites possessing improved performance characteristics [1, 2], as well as materials absorbing electromagnetic waves [3, 4], accumulating electrochemical energy [5] and hydrogen, and carrying out targeted drug delivery, have been developed on the basis of these nanostructures. There exist research works, in which CNTs are involved in recent neurocomputer developments to create connections between biological neurons and electronic devices. CNTs are employed in many areas due to their unique properties. They are being produced on a commercial scale; however, for each application area, nanostructures with a specific morphology are required, so it is very important to be able to manage their characteristics (diameter, degree of defectiveness, length, etc) at the synthesis stage.

There are various methods for synthesizing CNTs, but chemical vapour deposition (CVD) is the most preferable option for their industrial manufacturing [6-8]. To implement this method a catalyst is needed since the formation and growth of nanotubes occurs at its active sites. Therefore, the structure and morphology of CNTs are affected not only by the mode parameters of the synthesis procedure (temperature and pressure), nature [7] and consumption of carbon-containing raw materials [9, 10], but also by the characteristics of the catalyst [11-13]. According to the paper [14], the CNTs diameter depends on the size of the active catalyst particles; therefore, properly selected catalysts and synthesis
conditions make it possible to obtain nanoproducts with specified characteristics. In recent years, many catalyst compositions have been developed for CNTs synthesis, but obtaining an effective catalytic system to directly create nanostructures (by length, diameter, structure, degree of defectiveness, etc) still remains an urgent issue.

There exist several methods for producing catalysts, but thermal decomposition is the most popular one. Its widespread use in obtaining catalysts for synthesizing CNTs can be explained by the simplicity of its implementation, as well as by the ability to control the formation of active sites of the catalyst system at the stage of its manufacturing [15].

The main stages of obtaining the catalyst through the thermal decomposition are as follows: 1) selection of reagents and preparation of a solution from them, 2) heat treatment of a pre-catalyst (decomposition and/or calcination), and 3) mechanical activation. In the work [16], it is shown that the quality of the initial reagents and the heat treatment conditions for the solution on the basis thereof significantly affect the stability and efficiency of the catalyst synthesized. The methods of initial components validation proposed by the authors have made it possible to exclude the use of low-quality reagents at the initial stage of catalyst preparation, thereby contributing to the improvement of the quality of the nanoproduce obtained.

Since the structure of the catalyst and its active grains are formed as a result of the thermal decomposition, special attention should be paid to studying the heat treatment stage. Therefore, in the present work, the effect of the mode parameters of the heat treatment (thermal decomposition) of an initial components solution on the characteristics of Co-Mo/Al₂O₃ catalyst systems and the morphology of CNTs synthesized was experimentally investigated.

2. Materials and methods

A cobalt-containing catalyst system (Co-Mo/Al₂O₃) was chosen for studies. The catalyst was obtained by thermal decomposition. In order to increase its efficiency, it was chemically activated (promotion); molybdenum was used as a promoter, since its introduction to the catalyst in small amounts contributed to an increase in the efficiency of the metal oxide system considered. Co(NO₃)₂·6H₂O (chemically pure), Al(NO₃)₃·9H₂O (chemically pure), (NH₄)₆Mo₇O₂₄·4H₂O (pure), and tribasic carboxylic acid served as initial reagents to prepare a solution of catalyst initial components (a so-called pre-catalyst).

The catalyst, obtained from the pre-catalyst solution after heat treatment (thermal decomposition), was employed to synthesize CNTs through the CVD method, and ethylene was used as a carbon-containing raw material. The synthesis of nanostructures was carried out in a laboratory batch reactor at 650 °C.

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The X-ray phase analysis of the obtained Co-Mo/Al₂O₃ catalyst samples was carried out using a Difrey-401 X-ray diffractometer (Scientific Instruments, St. Petersburg, Russia) with a Bragg-Bretano focus.

The specific CNTs yield (gC/gcat, where C means “carbon”, and cat – “catalyst”) was used as a parameter characterizing the efficiency of the Co-Mo/Al₂O₃ catalyst. The specific surface area of the catalyst system was determined using a “Sorbometer-M” analyzer (KATAKON, Novosibirsk, Russia), the principle of which is based on the thermal desorption of an adsorbate gas from the surface of the sample under dynamic conditions.

A scanning electron microscopy (SEM) instrument (Merlin, Carl Zeiss, Germany) was used to assess the morphology of the catalyst system and the CNTs synthesized on it. The degree of the CNTs defectiveness CNTs was determined with a DXR Raman microscope (Thermo Scientific, USA) based on the intensity ratio of the D and G peaks.
The initial reagents intended for preparing the Co-Mo/Al₂O₃ catalyst were dissolved in a small amount of distilled water by vigorous stirring (100-150 rpm) for 15 min at 55 °C. At this stage, a problem of incomplete dissolution of the tribasic carboxylic acid occurred due to the presence of white crystals in the solution. The availability of such crystals in the pre-catalyst at the thermal decomposition stage is highly undesirable, since this leads to a decrease in the efficiency of the catalyst system synthesized. In this case, it is possible to increase the mixing intensity to ~200 rpm and the dissolution time to maximum 5 min, since partial removal of the solvent takes place with a significant increase in the duration of this process, thereby leading to undesirable crystallization of the solution of the initial components even before their dissolution. This was enough to completely dissolve the components of the catalyst system under study; after that, the 50-mL solution was thermally decomposed at 350 °C. The duration of the pre-catalyst decomposition stage was varied from 15 to 50 min, after which the resulting catalyst systems were ground and used for the CNTs synthesis. During the experiment, it was found that the solution decomposition for 5-10 min at 350 °C is impractical, since this time is not enough to completely decompose the organic matter and form an active catalyst system.

3. Results and discussion
The results obtained during the experiment are presented in figure 1. The effectiveness of the obtained Co-Mo/Al₂O₃ catalyst in the CVD process was evaluated by the specific CNTs yield.

![Figure 1. The effect of the heat treatment (thermal decomposition) of the initial components solution of the Co-Mo/Al₂O₃ catalyst on its specific surface area and efficiency during the CNTs synthesis.](image)

Analyzing these data, one can conclude that the most efficient metal oxide Co-Mo/Al₂O₃ catalyst systems with higher specific surface areas (16.8 and 26.0 m²/g) are formed as a result of the thermal decomposition of the pre-catalyst solution during 15 and 30 min at 350 °C. With further increase in the duration of this process, the formation of Co₃O₄ particles on the surface of the catalytic system can be observed. After the reduction of these particles, metal cobalt particles, responsible for nanotubes formation and growth, are formed. The diffractogram obtained for these catalyst conditions is shown in figure 2.
Figure 2. A diffractogram of the Co-Mo/Al₂O₃ catalyst system.

The analysis of figure 2 confirms the availability of Co₃O₄ in the Co-Mo/Al₂O₃ catalyst samples obtained.

The morphology of the resulting catalyst systems obtained under these conditions is shown in figures 3(a) and 3(b), respectively.

Figure 3. The morphology of the Co-Mo/Al₂O₃ catalyst systems obtained as a result of thermal the decomposition at 350 °C for 15 min (a) and 30 min (b).

A further increase in the solution decomposition duration leads only to a significant decrease in the specific surface area and the efficiency of the catalyst synthesized. The use of the Co-Mo/Al₂O₃ catalyst system, formed as a result of the thermal decomposition for 15 min at 350 °C, in the CNTs synthesis via CVD allows to get CNTs having diameters of 20-80 nm (figure 4(a)). The catalyst obtained after the thermal decomposition for 30 min contributes to the synthesis of 5-20-nm CNTs (figure 4(b)).
Figure 4. SEM images of the CNTs synthesized on the Co-Mo/Al₂O₃ catalyst obtained after the thermal decomposition of the pre-catalyst solution at 350 °C for 15 min (a) and 30 min (b).

The analysis of the SEM images recorded shows that the catalyst sample synthesized after the pre-catalyst thermal decomposition at 350°C for 30 min is more uniform, and in both cases, the CNTs formed have a length of more than 2 microns.

The degree of defectiveness (presented by the D/G ratio) of the CNTs synthesized on the catalyst systems obtained was assessed using Raman spectroscopy, the Raman spectra recorded are given in figure 5.
Figure 5. Raman spectra recorded for the CNTs synthesized on the Co-Mo/Al₂O₃ catalyst obtained after the thermal decomposition of the pre-catalyst solution at 350 °C for 15 min (a) and 30 min (b).

The analysis of the Raman spectra makes it possible to estimate the D/R ratios values – 1.05 (figure 5(a), and 0.784 (figure 5(b)). Thus, it was experimentally shown that, by eliminating the second heat treatment stage – calcination – in obtaining the metal oxide catalyst systems through the thermal decomposition, an efficient catalyst for CNTs synthesis can be obtained.

The increase in the pre-catalyst heat treatment duration over 30 min leads to getting a catalyst which provides the synthesis of CNTs with a greater degree of defectiveness. Thus, it seems more rational to carry out the pre-catalyst heat treatment at 350 °C for 30 min.

4. Conclusion
Usually, when a catalyst system is obtained via nitrates thermal decomposition, the pre-catalyst heat treatment is implemented in two stages: thermal decomposition, and calcination. It can be assumed that at the first stage, the formation of active sites takes place, whereas at the second stage, they are activated. After having studied in details the method for producing Co-Mo/Al₂O₃ catalyst system, it became possible to synthesize an effective catalyst avoiding the second heat treatment stage – calcination. Performing the pre-catalyst thermal decomposition at 350 °C makes it possible to develop
catalysts with a small specific surface area (~ 2.0-26.0 m²/g). By varying the pre-catalyst heat treatment duration (10-50 min), one can control not only the characteristics of the catalytic system, but also the parameters of the CNTs synthesized on it. As a result of the study, rational modes of the thermal decomposition stage implementation were selected. The specific yield of the CNTs synthesized on the catalytic system obtained after the pre-catalyst thermal decomposition for 30 min was found to be ~9.4 gC/gcat. Using the Co-Mo/Al₂O₃ catalyst in the CVD process makes it possible to synthesize CNTs with a diameter of 5-30 nm and a degree of defectiveness of 0.784. Besides, reduces the cost of these CNTs.

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