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Synthesis of Carbon Nanotubes from Benzene in a Fluidised Bed Reactor

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Abstract

The paper presents the results of carbon nanotubes synthesis from benzene in fluidised bed reactor. Al_2O_3 spheres with iron and nickel nanoparticles coating were used as a catalyst for the synthesis of carbon nanotubes. To deposit nickel nanoparticles on the surface of Al_2O_3 spheres, the method of solution combustion was used. Optimum temperature conditions and gas flow rates were worked out for each of the catalysts. It was found that the best efficiency in the synthesis of carbon nanotubes from benzene is shown by catalysts based on aluminium oxide coated with iron. The obtained carbon nanotubes were studied by scanning electron microscopy and Raman spectroscopy. It was found that at temperatures above 850 °C from benzene on Al_2O_3 spheres with Ni/NiO, carbon frame structures are formed.

1. Introduction

In the synthesis of carbon nanotubes by the chemical vapor deposition (CVD) method, the main conditions affecting the structure and properties of synthesized carbon nanotubes (CNTs) are the composition and ratio of the gas mixture, the synthesis temperature, the structure and morphology of the catalyst, etc. [1, 2]. Also, for the synthesis of carbon nanotubes, polymer waste can be used, as shown in [3].

The main influence on the structure of CNTs is exerted by the morphology and activity of the catalyst, as well as further processing methods, including treatment with various chemical reagents. [4, 5]. The catalyst is often a system that includes a matrix and an active phase deposited on it. Thermostable and chemically inert compounds, such as silicon and aluminium oxide, are used as support for the catalyst [6, 7]. Carbon nanotubes can be synthesized in a flame using iron and nickel catalysts as shown in [8].

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2. Experimental part

The synthesis of carbon nanotubes was carried out in a vertical CVD reactor. To supply benzene to the reaction zone, nitrogen was passed through a glass bubbler with benzene (Fig. 1). A bubbler with benzene was heated to a temperature of 60–70 °C to intensify the evaporation process, and as a consequence, a higher benzene content in the supplied gas mixture. Nitrogen passing through the bubbler captured benzene molecules, which were transported by nitrogen to the reactor and served as a carbon source for the synthesis of carbon nanotubes.

The temperature regimes for the synthesis of carbon nanotubes from benzene were worked out in the range of 750–860 °C. At temperatures ranging from 750 to 800 °C, the product is mainly amorphous carbon. The nitrogen flow rate varied from 300 to 1000 cm^3/min. At a nitrogen flow rate of less than 650 cm^3/min, the benzene content in the gas mixture is too low and no significant product yield was observed. At a nitrogen flow rate over 700 cm^3/min, due to the intensive flow rate, the gas mixture does not have time to warm up before

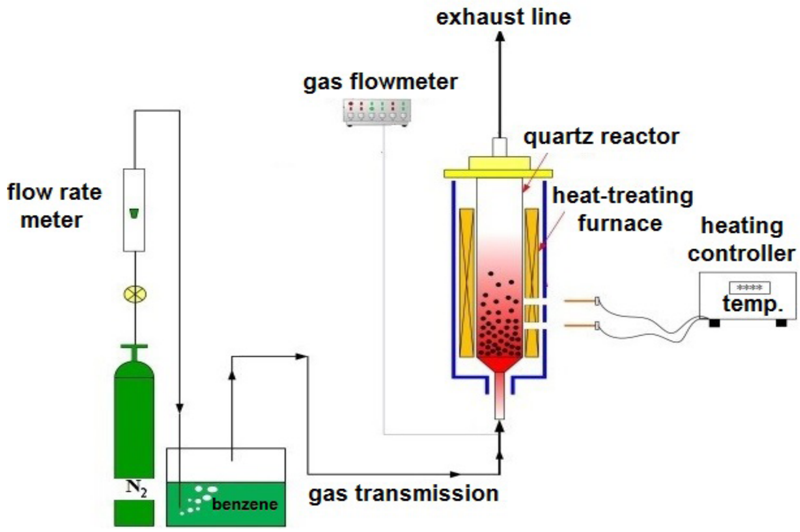

Fig. 1. Schematic of a vertical CVD setup for the synthesis of carbon nanotubes from benzene.

reacting with the catalyst and amorphous carbon is mainly formed. Based on this, the most optimal nitrogen rate is 650–700 cm^3/min.

In this work, Al_2O_3 spheres with a diameter of 0.5–1 mm were used as a matrix for the preparation of catalysts. Al_2O_3 spheres have the following composition: Al_2O_3 – 93.6%, SiO_2 – 0.06%, Fe_2O_3 – 0.18%, Na_2O – 0.45%.

As an active component of the catalyst, we used compounds of the transition group metals: iron and nickel, which are the most used catalysts in the synthesis of CNTs. Ferrocene is the most useful catalyst for the growth of carbon nanotubes. The active component was applied by the impregnation method; Al_2O_3 spheres were impregnated with a saturated solution of $Fe(C_5H_5)_2$ (Sigma Aldrich) in 95% ethanol. After impregnation, the catalyst was placed in an oven until the solvent was completely removed. During the synthesis of CNTs, ferrocene decomposes with the formation of pure iron by the reaction:

$$Fe(C_5H_5)_2 \rightarrow Fe + 2CH_4 + 8C + H_2.$$

During decomposition, iron particles are formed on the surface of the spheres, which play the role of an active phase in the growth of carbon nanotubes. Nickel was deposited on the surface of Al_2O_3 spheres by the method of solution combustion synthesis. For this, the Al_2O_3 spheres were impregnated with an aqueous solution of a mixture of nickel nitrate and fuel. Citric acid ($C_6H_8O_7$) was used as a fuel. After impregnation with Al_2O_3, the spheres were subjected to a drying process at a temperature of 100 °C until the solvent was completely removed. After drying, the Al_2O_3 spheres were subjected to heat treatment at 260 °C in a nitrogen atmosphere, while an exothermic reaction proceeds on the surface with the release of heat and an increase in temperature to 1200 °C and the formation of nickel nanoparticles with a small content of nickel oxide. The resulting Ni/NiO nanoparticles were studied by scanning electron microscopy, optical microscopy, BET (Brunauer, Emmett and Teller) analysis, and X-ray phase analysis.

3. Results and discussion

To establish the phase composition of the Al_2O_3 spheres, an X-ray phase analysis was performed. The results of X-ray phase analysis (Fig. 2) showed that the catalyst matrix consists of γ-Al_2O_3, a trace amount contains impurity compounds, the content of which is less than 1 wt.%. The BET analysis carried out on the SORBTOMETR-M device showed that the specific surface area of the Al_2O_3 sphere is 248 m^2/g, the specific pore volume is 0.106 cm^3/g.

Figure 3 shows the diffractogram and SEM (scanning electron microscope) image of a Ni/NiO sample obtained from nickel nitrate and citric acid.

The interaction of nickel nitrate ($Ni(NO_3)_2$) and citric acid ($C_6H_8O_7$) under the influence of high temperature on the surface of Al_2O_3 spheres forms nanoparticles consisting of 85 % pure nickel (Ni) and 15% nickel oxide (NiO). Particle sizes are 80–300 nm. Thus, based on the results of X-ray phase analysis, the interaction of nickel nitrate and citric acid forms a product consisting of 85% Ni and 15% NiO.

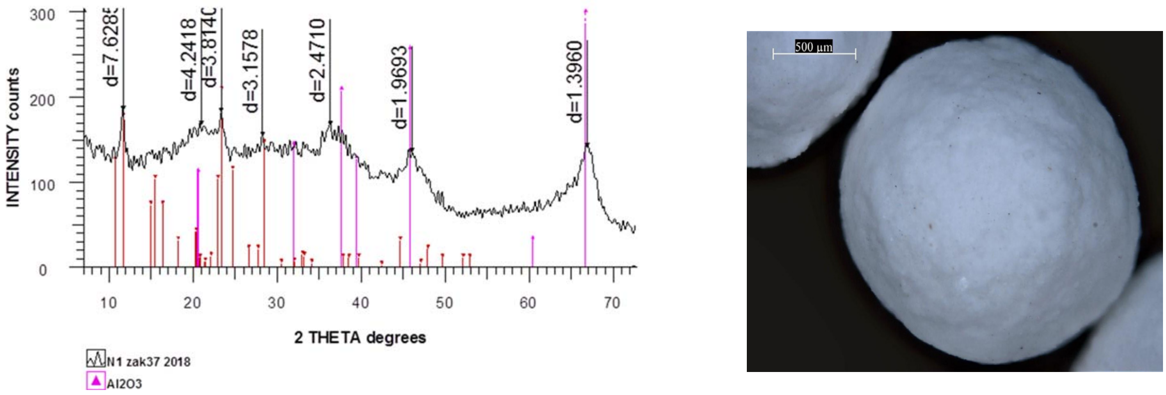

Fig. 2. X-ray diffraction and optical microscopy image of Al_2O_3 spheres.

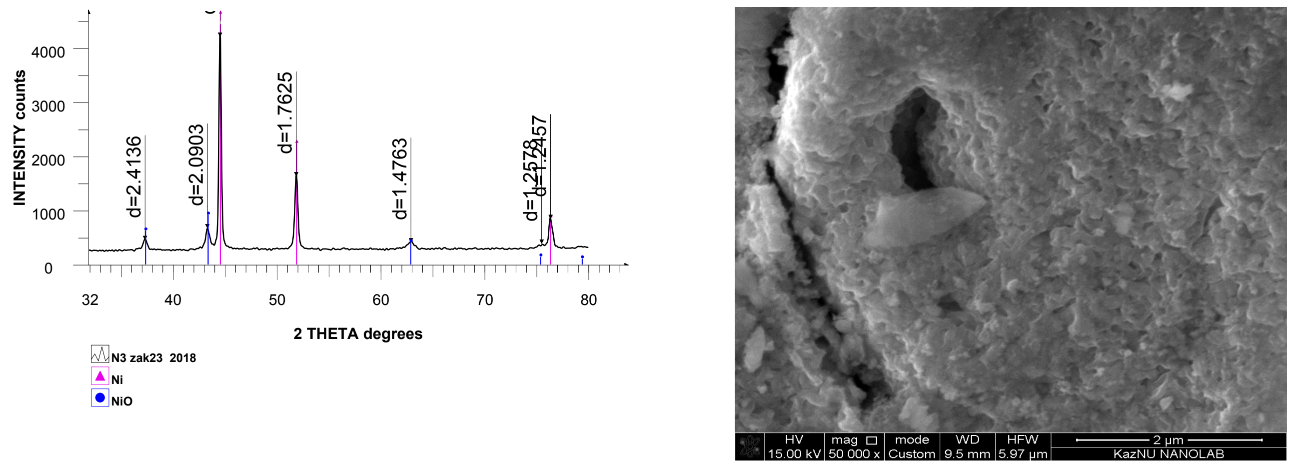

Fig. 3. X-ray diffraction and SEM-image of Ni/NiO.

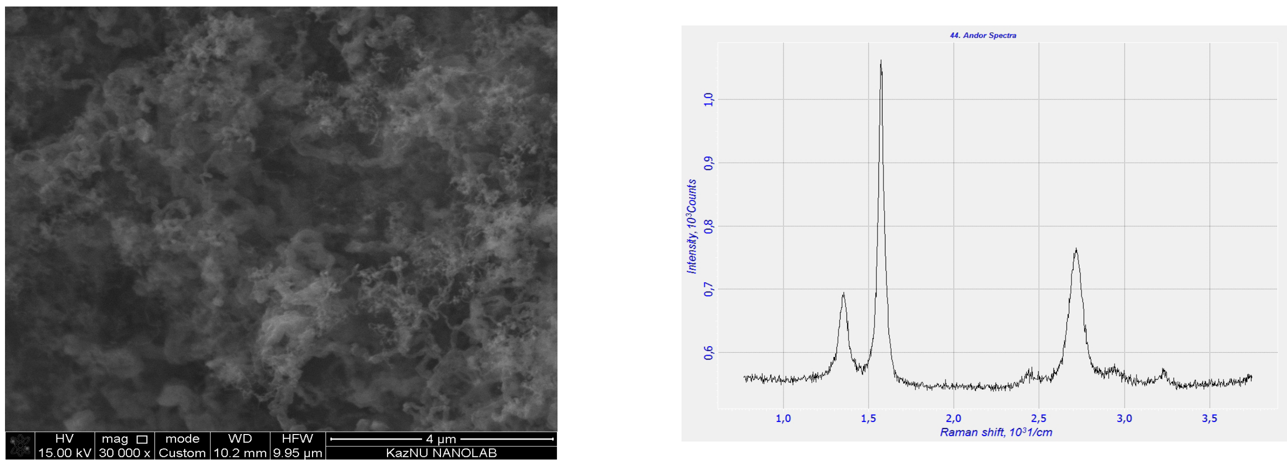

Fig. 4. SEM image and Raman spectrum of carbon nanotubes synthesized on Fe@sp-Al_2O_3 from benzene.

The catalysts synthesized on the basis of Al_2O_3 spheres with iron and nickel particles were used in the synthesis of CNTs from benzene. It was experimentally found that when using Fe $(C_5H_5)_2$ on various carriers and benzene, the optimum temperature was 830 °C.

Figure 4 shows an SEM image and a Raman spectrum of carbon nanotubes synthesized on Al_2O_3 spheres impregnated with a $Fe(C_5H_5)_2$ solution.

Based on the scanning electron microscopy images, it was found that as a result of the synthesis of CNTs on Al_2O_3 spheres impregnated with a solution of $Fe(C_5H_5)_2$ from benzene, carbon nanotubes with diameters from 27 to 135 nm were obtained; helical one-dimensional structures are also present. A small content of the amorphous carbon phase is observed.

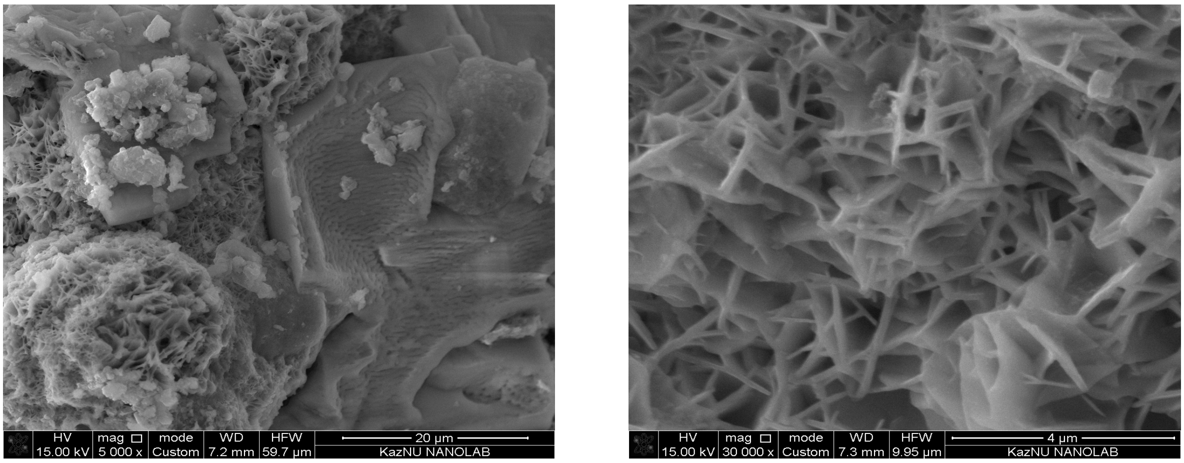

Fig. 5. SEM images of carbon framework structures synthesized on Ni/NiO@ sp-Al_2O_3 from benzene.

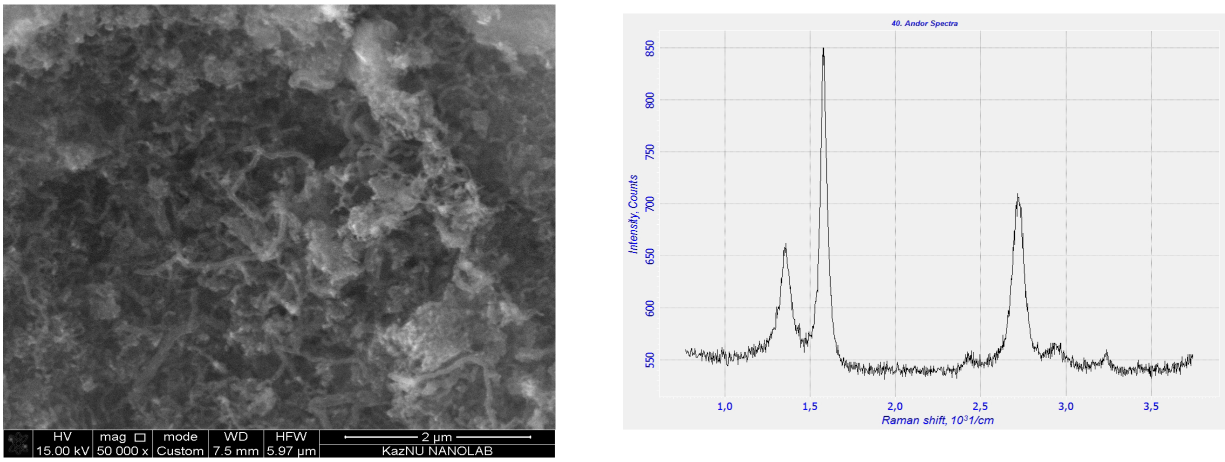

Fig. 6. SEM image and Raman spectrum of carbon nanotubes synthesized on Ni/NiO@ sp-Al_2O_3.

The spectrum of this sample has the following peaks, D-peak at 1360 cm^{-1}, G-peak at 1600 cm^{-1}. For this CNT sample, the peak intensity ratio I_D/I_G is 0.65. This ratio indicates a low defectiveness of the obtained carbon nanotubes.

It was experimentally found that for the Ni/NiO catalyst when using benzene, the most optimal temperature is 850 °C. It was also found that graphene-like structures are formed at temperatures above 850 °C. Figure 5 shows SEM images of these carbon nanostructures synthesized on Al_2O_3 spheres with deposited Ni/NiO nanoparticles.

Analysis of SEM images shows that the thickness of the “walls” of the framework structures varies from 45 to 300 nm. Outwardly, these structures have a graphene-like structure.

Figure 6 shows the SEM image and Raman spectrum of carbon nanotubes synthesized on Al_2O_3 spheres with deposited Ni/NiO nanoparticles.

For the Ni/NiO catalyst on Al_2O_3 spheres, benzene forms multi-walled carbon nanotubes with a diameter of 40–120 nm. The spectrum of this sample has the following peaks, D-peak at 1345 cm^{-1}, G-peak at 1600 cm^{-1}. For this CNT sample, the peak intensity ratio I_D/I_G is 0.78. This ratio indicates a relatively high defectiveness of the obtained carbon nanotubes and the presence of an amorphous phase.

4. Conclusions

As a result of the work carried out, the optimal conditions for the synthesis of carbon nanotubes in a fluidised bed reactor from benzene were determined. For the first time, the solution combustion method was applied to obtain the active phase of catalysts in the form of Ni/NiO on the surface of Al_2O_3 spheres for the synthesis of carbon nanotubes from benzene. It was found that the following synthesis conditions meet the optimal conditions for the synthesis of carbon nanotubes from benzene: nitrogen consumption 650–700 cm^3/min, synthesis temperature 850 °C. The best indicators of catalytic activity during the synthesis of carbon nanotubes were shown by Al_2O_3 spheres impregnated with a $Fe(C_5H_5)_2$ solution. In this case, carbon nanotubes were synthesized with diameters from 27 to 135 nm with an insignificant content of amorphous carbon. It was experimentally found that at temperatures above 850 °C from benzene on Al_2O_3 spheres with deposited Ni/NiO nanoparticles, graphene-like structures with a wall thickness of frame structures from 45 to 300 nm are formed, which opens up the prospect of using this method for the synthesis of graphene structures. For the Ni/NiO catalyst on Al_2O_3 spheres, benzene forms multi-walled carbon nanotubes with a diameter of 40–120 nm.

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