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Generation of carbon nanostructures with diverse morphologies by the catalytic aerosol-assisted vapor-phase synthesis method

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ABSTRACT

The Fe catalyst-supported aerosol-assisted synthesis method was used to prepare carbon products of diverse morphologies from toluene. Aerosol mist generation was accomplished with an ultrasonic device. An open-ended quartz boat for powder collection was placed in the maximum temperature zone of the tube reactor (850 °C or 1000 °C). The morphology of the products was studied by SEM and TEM microscopy. Structural characterization was provided by powder XRD, whereas Raman spectroscopy was used to determine the structural quality/homogeneity of the products. The hydrogen gas sorption capacity of the product prepared at 850 °C was relatively high despite its rather moderate BET specific surface area.

1. Introduction

There are numerous techniques known for the synthesis of carbon nanotubes (CNTs) [1,2]. Aerosol-assisted vapor phase deposition methods are considered to be among the most economically feasible techniques for the large-scale synthesis of CNTs [3–13]. This is due to a relative simplicity of the equipment and to the fact that the carbon precursors, mainly liquid hydrocarbons, usually used in the system with various metal catalysts are inexpensive. One of the investigated precursors has been toluene, an available liquid hydrocarbon. Pinault et al. [14], using either an aerosol generator or an injection system, synthesized aligned multiwalled CNTs (MWCNTs) at 800 or 850 °C from solutions of ferrocene $Fe(C_5H_5)_2$ dissolved in toluene or cyclohexane; for an efficient catalyst residue removal, the annealing treatment of raw carbon nanotubes under flowing argon in the temperature range from 1700 to 2000 °C was applied. Similarly, Meysami et al. [3,15] used an aerosol-assisted chemical vapor deposition technique for investigating the synthesis of CNTs from several liquid hydrocarbons in the system with ferrocene at 800 °C. Singh et al. [16], based on the experimental set-up elaborated by Andrews et al. [4], used toluene solutions of ferrocene to prepare aligned MWCNTs. To this aim, a two-stage furnace was used. The first stage was preheated to 200 °C and served as a zone for vaporization of precursors that were entered by injection with a syringe pump. In the second stage of the furnace, the nanotubes were synthesized at various temperatures in the range from 550 to 900 °C. A mixture of argon and 10% hydrogen was used as a carrier gas. The addition of hydrogen to a carrier gas, first, reduces the decomposition temperature of ferrocene and, second, reduces an average

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molar weight of the gas [17]. The latter factor has a direct influence on collisional phenomena by controlling the size of the catalytic particles and increasing their number density. A modified method of Singh et al. was proposed for the growth of aligned arrays of CNTs from the toluene/ferrocene precursor system [18]. Namely, the activity and lifetime of the catalyst was studied by switching from the precursors solution to a pure toluene feedstock during the growth of nanotubes. Das et al. described the synthesis of MWCNTs by pyrolysis of solutions of ferrocene in benzene, toluene, xylene, and trimethylbenzene [19]. Temperatures in the range 600–800 °C and argon mixed with 10% hydrogen as a carrier gas were used. The solutions were introduced to the preheater by a syringe pump. By using substituted ferrocenes in toluene solution and the same injection method, Mohlala et al. synthesized MWCNTs and carbon fibers at 800–1000 °C and 5% hydrogen in argon [20]. Ma et al. reported the preparation of small carbon "trees" in a quartz tube reactor from the toluene/ferrocene precursor system [21]. Ferrocene was introduced into the reactor through its sublimation at 150 °C in the entrance section of the reactor otherwise preheated in the hottest zone to 1150 °C, whereas toluene was transported to the reactor as vapors by argon bubbling. Fedorovskaya et al. synthesized arrays of vertically aligned CNTs grown on n-doped silicon substrates by means of an aerosol-assisted catalytic chemical vapor deposition technique in flowing argon from ferrocene solutions in toluene that were injected into the reactor preheated to 800 °C [22].

It is apparent from this brief review that the toluene/ferrocene system was frequently utilized in various chemical vapor deposition methods aimed at CNTs synthesis. In our approach, we used a simple experimental set-up equipped with an affordable ultrasound aerosol generator to investigate a possibility to synthesize carbon materials of different morphologies, and not necessarily CNTs, from the common toluene/ferrocene solution system. For this purpose, we used two reaction temperatures, i.e. 850 and 1000 °C. A pure argon gas was used for mist transportation and for the protection of carbon products against oxidation. A study of low-pressure hydrogen adsorption was conducted for the selected product.

2. Materials and methods

Toluene $C_6H_5(CH_3)$ (POCH Poland) and ferrocene $Fe(C_5H_5)_2$ (Sigma Aldrich) were used as received. In this regard, ferrocene served primarily as a source of iron catalyst formed *via* thermal decomposition of this compound. Carbon nanomaterials were prepared by the aerosol-assisted synthesis method in an experimental set-up comprised of an ultrasound aerosol generator, a quartz tube reactor, ID = 20 mm, length = 840 mm, and an open-ended quartz boat support for product collection, the latter placed in the maximum temperature zone. The details of the method were published elsewhere [23]. Post-reaction gases after cooling down in a condenser were directed into the ventilating hood. The reactor was installed in an electrical tube furnace preheated to the selected temperature of 850 °C or 1000 °C. The aerosol mist generated from the toluene solution of ferrocene (4 wt%) was transported through the reactor in argon, 1 L/min. After 50 min, the aerosol-generating system was switched off and the reactor was cooled down to ambient conditions under continuing argon flow. Black-colored raw products were formed that were carefully scraped from the crucible. Based on a check-up microscopic examination, the products consisted of a major fraction with distinct morphological features and of a minor fraction consisting of amorphous carbon. Survey TGA scans in air evidenced that the optimal temperature to remove by mild oxidation the reactive amorphous carbons was 440 °C. The clean-up oxidation of each raw product placed in an alumina crucible was carried out with air at this temperature for 1 h. After oxidation, the resulting materials were refluxed with a 8 M HNO_3 solution for 1 h to dissolve/remove residual iron according to a published procedure [24]; subsequently, they were rinsed with de-ionized water several times until reaching pH = 7. Finally, the filtered solid products were dried in an oven at 150 °C during 2 h.

The efficiency of iron removal *via* acid extraction was evaluated by combustion of the materials samples in oxygen at 900 °C and the determination of the weight of the residue, assumed to be Fe_2O_3 in both cases. The morphology of the samples was investigated with scanning electron microscopy (Hitachi, model S-4700). Individual nanosized carbon objects were studied by transmission electron microscopy (JEOL, model JEM 1011). For investigation of the resistance to oxidation and determination of temperature conditions for amorphous carbon removal *via* mild oxidation, thermogravimetric analyses in air were carried out with a heating rate of 5 °C/min. Raman measurements were conducted on a Horiba Jobin Yvon LabRAM HR micro-Raman spectrometer equipped with a CCD detector, excitation wavelength 532 nm, beam intensity 10 mW. Powder XRD measurements were done with the X'Pert Pro system, Panalytical, using the Cu Kα source. The BET surface areas of the samples were determined by low-temperature adsorption of nitrogen on Micromeritics Gemini 2380. H_2 adsorption experiments were conducted at −196 °C, in the pressure range from 0 to 100 kPa, by the gravimetric method using a low-pressure Sartorius microbalance. Prior to the adsorption runs, the samples were conditioned in air at 105 °C for 2 h. The measurements started with sample outgassing at room temperature for 6 h until a static vacuum of 10^{-2} Pa was reached in the system. As a standard procedure, each experimental point was recorded after a 20-min equilibration time although, routinely, the condition for adsorption equilibrium was met earlier than that.

3. Results and discussion

Fig. 1 presents typical images of the raw product prepared at 850 °C. The prevailing feature is the bundles of not rigidly straight fiber-like objects with lengths of *ca.* 400 μm. They contain visibly rounded bulges originating from Fe particles (Fig. 1B and D). In this regard, the occasional curvature of 1D carbons (nanotubes, nanofibers, etc.) has often been linked to the use of hydrocarbons with a cyclic molecular structure (benzene, xylene, cyclohexane, fullerene, toluene, etc.) as precursors [25–28]. In the