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Hierarchically structured carbon-carbon nanocomposites: The preparation aspects

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ABSTRACT

The hierarchically structured carbon-carbon nanocomposites represent carbon microfibers covered with a layer of carbon nanomaterials. Having properties of both micro- and nano-level, such nanocomposites demonstrate perspectives in polymer reinforcement, membrane technologies and catalysis. The synthesis of the carbon-carbon nanocomposites with controlled properties is a challenging task. This paper describes effect of catalyst deposition technique on the properties of hierarchically structured carbon-carbon nanocomposites. The synthesized samples were analyzed by XRD, SEM, TEM and BET. It was shown how the way of catalyst deposition affects both the yield and structure of the carbon nanofibers grown on the microfiber surface.

1. Introduction

The hierarchically structured carbon-carbon nanocomposites represent a new class of materials consisting of carbon nanostructures deposited on the surface of carbon microfibers. The shape of the nanocomposites is determined by the microfiber (discrete fibers, thread or fabrics), while surface properties mainly depend on the nanoscale component of the composite (carbon nanotubes (CNT), nanofibers (CNF) or fullerenes). These materials considered to be promising in polymer reinforcement [1], membrane technologies [2] and catalysis [3]. As an example, addition of the carbon-carbon nanocomposites into polymers leads to 50% improvement of materials strength [4]. The nanocomposite CNF/'activated carbon fabric' is known to be effective in adsorption of phenol and lead [2]. As we have recently reported, the metal particles anchored on the CNF/ACF composite provide superior catalytic performance due to the stabilization of the active component in a disperse state [5].

Usually, catalytic chemical vapor deposition (CCVD) is used for the synthesis of the carbon nanostructures. Various hydrocarbons can be decomposed on metals of iron subgroup (Ni, Fe, Co). Being versatile, CCVD remains rather complicated technique – the product of synthesis depends on a set of parameters such as nature and composition of the catalyst, type of the hydrocarbon, temperature and duration of the process [6]. Synthesis of the carbon nanomaterials in the form of powders is well described in literature, while the design of hierarchically structured carbon-carbon nanocomposites with pre-determined properties is still required to be investigated.

In this paper, we continue the step-by-step study on the impact of CCVD parameters on the properties of hierarchically structured carbon-carbon nanocomposites. We have already shown that carbon source and catalyst composition influence both the carbon yield and the structure [7], while the nature of microfiber affects the carbon yield and the strength of CNF anchorage [8]. The scope of the present paper is elucidation of the impact of the catalyst deposition technique on the properties of the carbon-carbon nanocomposites. The methods based on an incipient wetness impregnation were used since they are considered as well controllable and easy-to-scale ones [8,9].

2. Experimental

Chopped carbon microfibers UKN-M 5000 (LLC "Argon", Russia) of 5.6 μm in diameter were used as a framework (marked as CMF). A precursor of an active component (Ni) was deposited on the surface of microfibers via an incipient wetness impregnation according to three different routes followed by the thermal treatment procedure:

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1. Impregnation with aqueous solution of nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$. The sample is labeled as Ni/CMF(imp).
2. Deposition of freshly prepared $Ni(OH)_2$ (obtained by reaction of $Ni(NO_3)_2$ with NH_4OH). CMF was impregnated with calculated amount of $Ni(OH)_2$ dispersion. The sample is designated as Ni/CMF (dep).
3. Surface precipitation of $Ni(OH)_2$. Firstly, CMF were impregnated with aqueous solution of nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$, then $Ni(OH)_2$ was precipitated on the surface of the microfiber by adding NH_4OH. The sample is labeled as Ni/CMF(prec).

Amount of metal loading was calculated to be 2.5 wt% and then was controlled by weighing of ash residual after combustion of the sample in air.

The synthesis of the hierarchically structured carbon-carbon nanocomposites (Ni/CNF/CMF) was carried out by CCVD of ethylene at 600 °C in a gravimetric flow setup equipped with McBain balance according the standard procedure with preliminary reduction [7]. The setup allows studying the kinetics of the carbon deposition in a real time regime.

X-ray diffraction (XRD) analysis of the samples was performed on a DRON-RM4 diffractometer using CuKα radiation with a wavelength of 1.54178 Å and a step of 0.05°. The phases were identified by comparison with JCPDS Powder Diffraction File data. The average crystallite size (coherent scattering region, CSR) was calculated using the Scherrer equation [10].

The microstructure of the prepared samples was examined by scanning electron microscopy (SEM) using a JSM 6460 instrument (Jeol, Japan) with magnifications from 8× to 300.000× and transmission electron microscopy (TEM) on a JEM 1400 microscope (Jeol, Japan) operated at 80 kV.

Specific surface area (SSA) of the samples was determined by a low-temperature nitrogen adsorption (BET method) using an ASAP 2400 instrument (Micromeritics, USA).

3. Results and discussion

Prior to the synthesis of the hierarchically structured carbon-carbon nanocomposites, the catalyst precursors ($Ni(NO_3)_2$ or $Ni(OH)_2$) were heated in air (350 °C for nitrates and 360 °C for hydroxides, 30 min) and then reduced in a hydrogen flow (600 °C, 15 min). At each step, XRD analysis was used to control the composition of the samples (Fig. 1). XRD patterns for the sample obtained by impregnation with aqueous solution of nickel nitrate $Ni(NO_3)_2{\cdot}6H_2O$ are given in [8]. XRD data confirm that the total decomposition of the precursors with formation of corresponding oxides takes place under the used conditions. Appearance of the peaks assigned to an oxide phase after reduction in H_2 is accounted for the contact of nickel with air during the sample passivation.

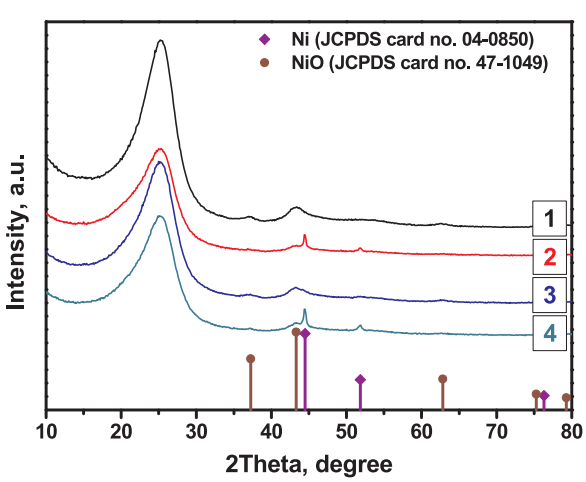

Fig. 1. XRD patterns for the samples obtained via deposition of freshly prepared $Ni(OH)_2$ (1, 2) and surface precipitation of $Ni(OH)_2$ (3, 4): 1, 3 – after calcination; 2, 4 – after reduction in H_2 and passivation in O_2/Ar mixture.

Table 1
Coherent scattering regions for NiO and Ni particles, and average diameter of CNF obtained via CCVD of C_2H_4 at 600 °C.

N	Catalyst	CSR, nm		Average CNF diameter, nm
		Before reduction	After reduction	
1	Ni/CMF(imp)	16	54	52
2	Ni/CMF(dep)	13	48	86
3	Ni/CMF (prec)	10	41	103

The results of CSR calculation are shown in Table 1. As seen, the average crystallite size of NiO phase before reduction was 16, 13 and 10 nm for Ni/CMF(imp), Ni/CMF(dep) and Ni/CMF(prec), respectively. The reduction procedure leads to an enlargement of the crystallite sizes for Ni phase being formed due to the sintering process, which takes place in a hydrogen atmosphere. General trend is that CSR of Ni in metallic state is two times higher than that of NiO which is thought to be resulted from agglomeration of the catalyst particles occurring due to their high mobility on the carbon microfiber surface [11]. The sizes after the reduction were 54, 48 and 41 nm, correspondingly. Taking into account that the accuracy of calculations lies in a range of 10–20%, it can be concluded that the average crystallite size of NiO and Ni does not practically depend on the catalyst deposition technique.

The kinetic studies revealed that the catalytic behavior of the samples is different (Fig. 2). Decomposition of ethylene on Ni/CMF (imp) resulted in the highest yield of CNF (193%). Ni/CMF(prec) and Ni/CMF(dep) samples show 92% and 73%, respectively (Fig. 2, curves 2 and 3). Note that all samples were completely deactivated after relatively short period of time (15–20 min).

Since XRD data revealed no significant differences in a phase composition of the samples, their different catalytic behavior can be explained in terms of the CNF structure. Fig. 3 presents SEM images of the hierarchically structured carbon-carbon nanocomposites with comparable values of the carbon yield.

As clearly seen from Fig. 3, the samples differ significantly in a diameter distribution. Thus, Ni/CMF(imp) gives relatively narrow distribution (d = 20 - 100 nm), which corresponds to the crystalline size of Ni particles after reduction (Table 1). Oppositely, both Ni/CMF(dep) and Ni/CMF(prec) produce nanocomposites with CNF diameters up to 600 nm. The average CNF diameters significantly exceed the CSR values for reduced Ni particles (Table 1), which might be explained by their

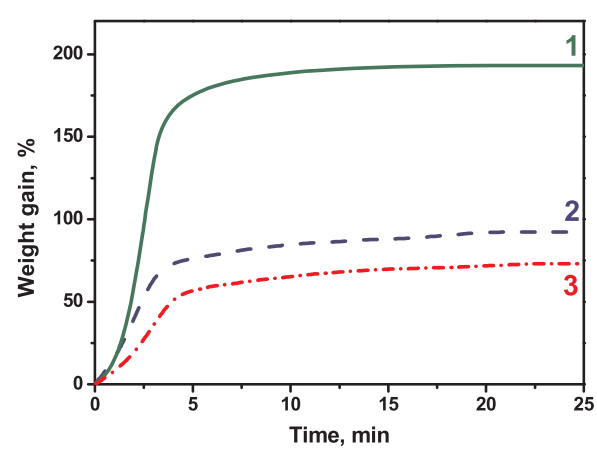

Fig. 2. Kinetics of carbon growth on 1 – Ni/CMF(imp), 2 – Ni/CMF(prec) and 3 – Ni/CMF (dep) samples.