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Article

Comparison of growth mechanisms of undoped and nitrogen-doped carbon nanofibers on nickel-containing catalysts



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ABSTRACT

The growth mechanisms of carbon nanofibers on Ni catalysts and nitrogen-doped carbon nanofibers on Ni and Ni-Cu catalysts were studied. The growth of both types of nanofibers was found to occur by a mechanism that included the formation of surface non-stoichiometric nickel carbide followed by the dissolution and diffusion of carbon, or carbon and nitrogen into the bulk of the catalyst particles.

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1. Introduction

The synthesis of carbon nanomaterials (CNMs) is a rapidly growing area of nanotechnology [1–5]. CNMs possess various useful properties, which extend the scope of the applications of such materials in different fields [1,2,4,6–9]. To ensure efficient control of CNM syntheses, the precise detail of their formation processes should be elucidated. The mechanism underlying the formation of undoped CNMs from hydrocarbons on metal catalysts has been discussed in many works [10–12]. It has been concluded that the formation of CNMs on metal catalysts proceeds by the following steps: (1) catalytic decomposition of a hydrocarbon on the surface of a metal particle to form atomic carbon, and an increase in carbon concentration to limiting values; (2) dissolution of carbon atoms and diffusion through the bulk of the metal particle; (3) formation of graphite phase nucleation centers and growth of the phase to produce carbon

nanotubes or carbon nanofibers (CNFs).

This proposed mechanism suggests that the diffusion of carbon atoms is caused by concentration gradients at the particle surfaces, where hydrocarbons are decomposed and where CNMs are formed. However, irrespective of the substantial progress that has been made in understanding the mechanism of CNM formation, some aspects remain debatable, for example, the type of carbon diffusion (bulk, surface, or subsurface) [13].

The synthesis of nitrogen-doped carbon nanomaterials (N-CNMs) is a new field that is currently receiving much attention [14–19]. Methods and approaches used to produce N-CNMs are based either on the direct formation of material from a nitrogen-containing carbon precursor or on the heat treatment of undoped CNMs in a nitrogen-containing medium. Thus, the synthesis method can be catalytic (low-temperature) or physical (high-temperature). The catalytic synthesis of N-CNMs on the iron subgroup metals (Fe, Co, Ni) is a direct

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method, which proceeds at moderate temperatures and results in selective formation of the target product. This has advantages compared with physical methods such as laser ablation, electric arc synthesis, or magnetron sputtering. The main emphasis in the development of methods for N-CNM synthesis and the investigation of their properties has been placed on carbon nanotubes doped with nitrogen. In contrast to such nanotubes, the multiple edges of graphite planes in CNFs come to the outer surface of the fiber, thus increasing the interaction of the surface with active components and making CNFs especially attractive for catalytic applications [1,4,5,20–25].

It should be noted that there is currently a very limited understanding of the mechanism of the catalytic growth of N-CNMs, in particular N-CNFs, on metal catalysts (Fe, Co, Ni). It is commonly accepted that the growth mechanism of N-CNMs is similar to that of undoped CNMs. The only difference is that the decomposition of the nitrogen-containing compound is accompanied by the additional formation of atomic nitrogen, which also diffuses over the surface of the catalyst particle or through its bulk [26–28]. However, there are limited experimental data in favor of this hypothesis [29–32]. As shown in our earlier works, the conditions of N-CNF formation by decomposition of ethylene-ammonia mixture on a Ni-Cu catalyst, in particular the temperature and ammonia concentration, determine the state of the catalyst during its growth and, as a result, the properties of the resulting N-CNFs [30,32]. The present work aimed to reveal and compare the mechanisms of CNF and N-CNF growth on Ni and Ni-Cu catalysts.

2. Experimental

In this study, a Ni catalyst was synthesized using the reactive “pure” Ni(II) oxide. Metallic nickel was obtained by the reduction of NiO in hydrogen at 300 °C. Reduction, carbide formation, and carbonization of the catalyst were carried out in a flow-type reactor equipped with a quartz balance. This setup made it possible to directly monitor changes in the sample mass during the experiment. Details of the setup design can be found elsewhere [33]. The mass measurement sensitivity was 1×10^{-4} g. The initial catalyst loading was varied within the range 0.002–0.100 g. At the beginning of the experiment, the sample was heated under an argon flow to the chosen working temperature. The argon supply was then shut off and the reaction mixture was fed into the reactor.

The formation kinetics of nickel carbide were studied at 225–300 °C, while those of CNFs on nickel were studied at 500–650 °C in an argon-diluted 1,3-butadiene medium. To prevent sintering of the reduced metallic nickel, the studies at 500–650 °C were conducted with the sample containing 20 wt.% carbon. This sample was synthesized by treating NiO with argon-diluted 1,3-butadiene ($P(\text{C}_4\text{H}_6) = 10.5$ kPa, $T = 600$ °C).

Changes in the phase composition of the nickel catalyst upon decomposition of 1,3-butadiene were investigated using a high-temperature chamber mounted on a standard laboratory diffractometer (DRON-1) with a copper anode and graphite monochromator, as shown in Fig. 1.

X-ray diffraction (XRD) measurements of the decomposition

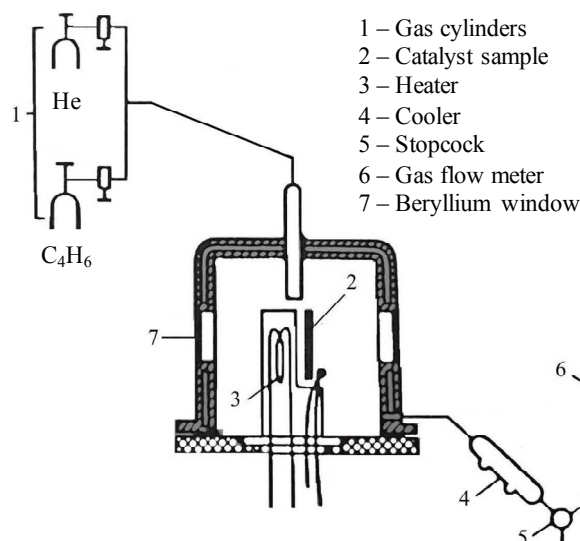


Fig. 1. High-temperature X-ray chamber for study of nickel catalyst during decomposition of 1,3-butadiene.

of ethylene and ethylene-ammonia mixtures were performed using synchrotron radiation at the Siberian Synchrotron and Terahertz Radiation Center (Novosibirsk, Russia) on a diffractometer with a position-sensitive detector and operating wavelength $\lambda = 0.1731$ nm.

The XRD study was carried out with a catalyst composed of 65 wt.% Ni/25 wt.% Cu/10 wt.% Al_2O_3 (Ni-Cu), which has previously been shown to possess high catalytic activity and stability for the formation of N-CNFs by decomposition of ethylene-ammonia mixture [34]. For comparison, a catalyst composed of 90 wt.% Ni/10 wt.% Al_2O_3 (Ni) was also used in the experiments. Both catalysts were synthesized by co-precipitation from an aqueous solution of the required nitrates with an aqueous solution of NaOH. The dried samples were calcined in nitrogen at 350 °C and then reduced in flowing hydrogen at 550 °C.

Time-resolved XRD was used for *in situ* study of the catalysts during N-CNF growth by decomposition of 100% C_2H_4 as well as 75% C_2H_4 /25% NH_3 and 50% C_2H_4 /50% NH_3 mixtures. For this experiment, the diffractometer was equipped with a high-temperature reactor chamber (XRK-900, Anton Paar, Austria). The test sample was loaded into an open holder and mounted in the reactor chamber. The reactor chamber design allowed the reaction mixture to pass through the bulk of the sample. The catalyst was pretreated in hydrogen medium at 550 °C for 15 min to remove adsorbed oxygen from the catalyst surface. The reaction mixture was then fed into the reactor chamber at a rate of 40 mL/min. The sample was held at 550 °C in the reaction mixture flow and XRD patterns were recorded at 30 s intervals.

The amount of nitrogen in the N-CNFs was determined by elemental analysis. The charge states of nitrogen in the N-CNFs and nickel in the CNFs and N-CNFs were analyzed by X-ray photoelectron spectroscopy (XPS). After the reaction, the samples were quenched in argon medium to prevent further changes in the catalysts. Spectra were collected on a KRATOS

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