



Review

Nitrogen-doped carbon nanomaterials: To the mechanism of growth, electrical conductivity and application in catalysis

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ABSTRACT

The doping of carbon nanomaterials with nitrogen produces changes in their electrophysical, adsorption and catalytic properties. The catalytic synthesis of nitrogen-doped carbon nanomaterials (N-CNMs) is performed at moderate temperatures, leads to selective formation of N-CNMs and is therefore more attractive than the physical synthesis methods. The review discusses the mechanism of N-CNMs catalytic growth; the understanding of this mechanism is essential in the synthesis of active and stable catalysts for the production of N-CNMs. Literature data on the surface properties and application of N-CNMs as catalysts and catalyst supports are also reviewed; the effect of nitrogen content and type on physicochemical and catalytic properties of N-CNMs is analyzed.

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1. Introduction

Synthesis of graphite-like carbon nanomaterials (CNMs) is a rapidly growing field of nanotechnology; by now, a large body of knowledge has been accumulated on the subject [1–6]. An increased interest in such materials is caused by their great potential for practical application in nanoelectronics and catalysis, for the development of advanced composite materials, gas or biosensors and sorbents.

In recent years, great efforts were made to find ways to precise control of electrophysical and adsorption properties of CNMs

by modification of the carbon structure with heteroatoms, for example with the nitrogen atom (N-CNMs), for the deliberate synthesis of new functional materials [7–10]. Investigation of N-CNMs was inspired by theoretical calculations which demonstrated that nitrogen-doped carbon nanotubes (N-CNTs) show the metallic behavior [11–14]. Various methods and approaches to the production of N-CNMs are being developed; they can be based on the direct synthesis of material from a nitrogen-containing carbon precursor or a mixture of carbon- and nitrogen-containing precursors as well as on the heat treatment of undoped CNMs under nitrogen-containing atmosphere. Low-temperature (catalytic) and high-temperature (physical) methods of the synthesis are distinguished. The catalytic synthesis of graphite-like N-CNMs on the iron subgroup metals (Fe, Co, Ni) is considered as a direct synthesis method, is performed at moderate temperatures, and leads to

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selective formation of the target product; thus, it is more attractive than the physical methods including laser ablation, electric arc synthesis or magnetron sputtering. An essential feature of the catalytic method is the possibility to control the structural and textural properties of N-CNMs as well as the nitrogen content and type by choosing the appropriate conditions of the synthesis [15–17]. The understanding of the growth mechanism is one of the key factors for the synthesis of active and stable catalysts, which would increase quite low yields of N-CNMs [15,18,19]. In this connection, the first part of the review considers the studies that are devoted to the mechanism of N-CNMs catalytic growth and especially to the state of catalyst during the growth process.

Primarily, it was found that the unique properties of N-CNMs open wide possibilities for application of such materials as the catalysts and catalyst supports in electrochemical devices [20,21]. Many works have demonstrated that platinum catalysts supported on N-CNMs exhibit high electrochemical activity and stability because of a decrease in the platinum particle size and a corresponding increase in the electrochemically active surface; the appearance of specific active sites at the metal-support interface; an enhanced adhesion of platinum to the support; an improved wettability with electrolyte and an increased conductivity of the carbon material. When N-CNMs were employed as supercapacitor electrodes, an increase in capacitance was caused not only by a better wettability of the surface with electrolyte and a higher conductivity of N-CNMs, but also by the appearance of pseudocapacitance.

Lately, N-CNMs have been intensively studied as the catalysts and catalyst supports in various catalytic reactions including oxidation in the gaseous or liquid phase, dehydrogenation, and organic synthesis [4,5,10,22]. The catalytic activity of N-CNMs is likely to be caused also by the following factors: (1) stabilization of metallic particles with a smaller size, narrowing of the particle size distribution, and increasing the metal-carbon binding energy in the case of supported system, (2) alteration of the acid-base properties of the support surface, and (3) acceleration of electron transfer in the catalytic system because of the enhanced conductivity of N-CNMs.

The conclusion about acceleration of electron transfer in the metal-N-CNMs system is based on calculations of the electronic structure of N-CNMs and experimental measurements of electrical conductivity; so, a part of the review is devoted to comparison and analysis of the data on electrical conductivity of N-CNMs. And finally, the review will consider the literature data on the surface properties and application of N-CNMs as the catalysts and catalyst supports in various reactions except for electrocatalysis, which was thoroughly analyzed in the reviews [4,10,20–22]. In the proposed review, particular emphasis will be made on the effect of nitrogen content and type on physicochemical and catalytic properties of N-CNMs.

Among various graphite-like N-CNMs, attention has conventionally been paid to N-CNTs and nitrogen-doped carbon nanofibers (N-CNFs). However, there is a growing interest in nitrogen-doped graphene, which was shown to be highly active in the oxygen reduction reaction, reduction of nitrocompounds or selective oxidation of aromatic hydrocarbons [23]. The analysis of available studies on the use of nitrogen-doped graphene as the catalyst support also deserves a separate review. Our review covers the works dealing mainly with 1D-structured N-CNTs and N-CNFs, and to a smaller extent with other N-CNM species, such as N-activated carbon, onion-like carbon or composite carbon nanomaterials.

2. Mechanism of N-CNMs catalytic growth

A commonly accepted model describing the formation of undoped CNTs and CNFs on metal catalysts consists of three main steps: (1) decomposition of hydrocarbon molecules on the catalyst surface with the formation of adsorbed carbon atoms,

(2) dissolution of the adsorbed carbon atoms followed by their diffusion within the catalyst particle or over its surface, and (3) formation of a nucleus and growth of a carbon tube or fiber outside the catalyst particle [1,2,24–27].

Originally, a correlation between activation energy of the CNFs growth rate in decomposition of acetylene on Ni, Fe, Co, Cr and activation energy of the carbon atoms diffusion within the metallic particle, which was obtained in [1], was used to conclude that the diffusion of carbon atoms limits the growth of carbon material and a temperature gradient at the gas-metal and metal-carbon interfaces serves as the driving force. However, after successful experiments on CNF synthesis using the endothermic reaction of methane decomposition, it was supposed that the driving force is caused by a concentration gradient of carbon atoms at the gas-metal and metal-carbon interfaces [25]. Recently, a novel idea has been proposed by the authors of [28]: they suggest that diffusion of carbon in the catalytic particle occurs only in the subsurface layer and does not involve the entire volume of the particle, because subsurface diffusion is energetically more advantageous than the surface and bulk diffusions.

To reveal the mechanism of CNMs growth, it is necessary to identify the state of carbon on the surface of the catalytic particle and in the bulk of metal during carbon diffusion from the faces where the precursor molecules are decomposed to the sites of carbon atoms segregation. First it was assumed that dissolution of carbon atoms in the bulk of the catalytic particle is accompanied by the formation of a bulk metal carbide [24,29,30]. *In situ* thermomagnetic analysis of Ni and Fe catalysts during their carbonization under the atmosphere of CH₄ and CO has revealed the formation of metastable non-stoichiometric carbides at the first step of the reaction, which was followed by their decomposition into graphite and metal [30]. However, as shown by the analysis of the data obtained, in this case it is rather the subsurface carbide, because its formation involves only the subsurface layers of the catalytic particle [24]. The unstable subsurface carbide, which was formed during the induction period, initiates the reconstruction of metallic particle and becomes a source of carbon atoms for the diffusion through its bulk, thus creating a concentration gradient of carbon.

On the other hand, in a series of works [31–35] the involvement of carbides in the synthesis of CNMs is called into doubt; it is supposed that decomposition of carbon-containing precursors is accompanied by dissolution of carbon in the metallic particle without the formation of the carbide. Thus, investigation of mass transfer at the formation of filamentous carbon on Fe, Co and Ni in [31] demonstrated that metal carbides cannot serve as the process intermediates. *In situ* XRD study [35] showed an increase in the lattice parameter of nickel at decomposition of methane, which indicated the incorporation of carbon into the metal structure. At the same time, the diffraction maxima of the hexagonal nickel carbide phase were not observed. Along with this, the formation of surface metal carbide MeC_x can be considered proven because it was verified by experimental studies using the microscopy and *in situ* XPS methods [28,36]. Dissolution of carbon in the metallic particle can convert it into molten phase since the dissolution of C in Me-C system can significantly decrease the melting temperature of this system [37,38].

It is commonly accepted that the growth mechanism of N-CNMs is similar to that of undoped CNMs. The only difference is that decomposition of the nitrogen-containing compound is accompanied by the additional formation of nitrogen atoms, which also diffuse over the surface of the catalytic particle or through its bulk [39–41]. Indeed, such a mechanism is confirmed by the calculations of thermodynamic stability of metal carbides and nitrides *versus* temperature, which are compared with experimental data on the effect of N-CNTs yield and nitrogen content in N-CNTs reported in [41].

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