

# SYNTHESIS OF NITROGEN-CONTAINING CARBON NANOFIBERS BY ETHYLENE/AMMONIA DECOMPOSITION

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## Introduction

Nanostructured carbon materials doped with nitrogen attract an interest as promising catalyst supports, nanoelectronic devices, composite fillers, chemical and biological sensors and many other applications (Ewels, 2005; Matter, 2006). Obviously, special application requires particular nitrogen doping level as well as specific structural, textural and electrophysical characteristics of material. Nitrogen-containing carbon nanofibers (N-CNFs) with carbon atoms partially replaced by nitrogen ones are of special interest for catalysis. Presence of N sites on the nanofiber surface favours high dispersity of active component, its uniform distribution on the support and sintering stability. Furthermore, enhanced electroconductivity of N-CNFs in comparison with non-doped counterparts (Miyamoto, 1997) makes them very promising in fuel cell applications.

It is well known (De Jong, 2000) that non-doped carbon nanofibers can be grown in controlled manner by decomposition of different carbon precursors over metal catalysts (usually Fe, Co and Ni) and CNF properties can be easily controlled by the growth conditions. Evidently, N-CNF properties can also be tailored by selection of appropriate synthesis parameters. Systematic investigation of physicochemical regularities of N-CNF formation will help to elucidate a mechanism of this process and provide a tool for precise regulating of N-CNF characteristics.

The present work is focused on the study of relationship between synthesis conditions and properties of the resulted N-CNFs. It was found that structural and textural features of N-CNFs, nitrogen incorporation and its electronic state are determined by reaction parameters like catalyst used, precursor composition, temperature and duration. The optimum conditions for production of N-CNFs with regulated N content up to 7 wt. % and high surface area amounting to 350 m<sup>2</sup>/g were established.

## Experimental

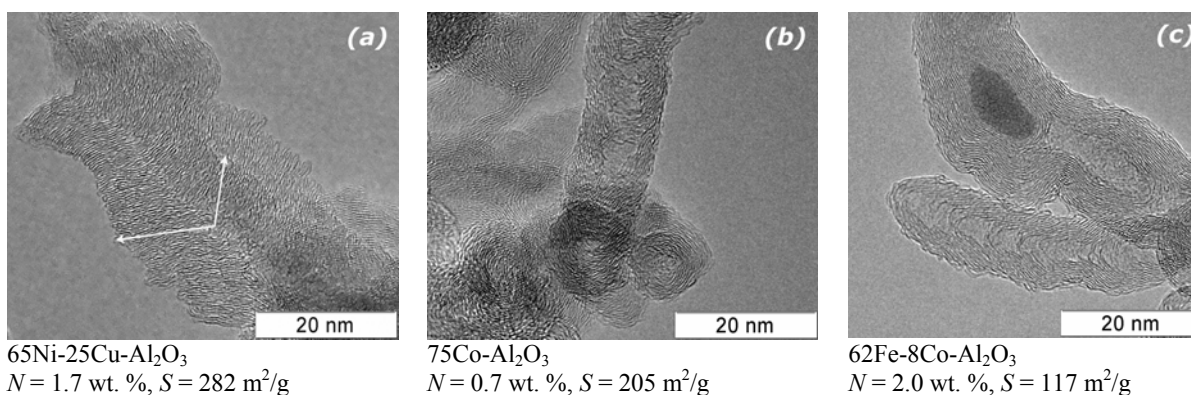
Nitrogen-containing CNFs were synthesized by decomposition of C<sub>2</sub>H<sub>4</sub>/NH<sub>3</sub> mixture at 450 – 675 °C over metal catalysts. The catalysts with high (70 – 90 wt. %) loading of iron-subgroup metals were prepared by coprecipitation of active component and alumina from nitrate solution as described elsewhere (Shaikhutdinov, 1997; Avdeeva, 2002). The following catalysts were used: 90Ni-Al<sub>2</sub>O<sub>3</sub>, 82Ni-8Cu-Al<sub>2</sub>O<sub>3</sub>, 65Ni-25Cu-Al<sub>2</sub>O<sub>3</sub>, 45Ni-45Cu-Al<sub>2</sub>O<sub>3</sub>, 75Co-Al<sub>2</sub>O<sub>3</sub>, 72Co-3Mo-Al<sub>2</sub>O<sub>3</sub>, 90Fe-Al<sub>2</sub>O<sub>3</sub>, 85Fe-5Co-Al<sub>2</sub>O<sub>3</sub>, 62Fe-8Co-Al<sub>2</sub>O<sub>3</sub>. Herein and after in catalyst code number before the element symbol indicates the metal content in initial catalyst, wt %. Alumina content equals to the rest.

The initial ethylene/ammonia mixture contained 25, 50 and 75 vol. % of NH<sub>3</sub>. Synthesis of N-CNFs was carried out in a flow reactor with a fluidized catalyst bed at atmospheric pressure. Catalyst loading was 0.1 g, while feed flow rate was equal to 22.5 l·h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup>.

Synthesized N-CNF samples were characterized by elemental analysis, XRD, TEM, N<sub>2</sub> adsorption at 77 K and XPS methods.

## Results

It is well known that structural type of non-doped CNFs and their textural characteristics strongly depend on preparation conditions, and first of all, on chemical composition of metal catalyst (De Jong, 2000; Reshетенko, 2003). Similarly, structure of nitrogen-containing CNFs was found to be dependent on the catalyst used. Figure 1 represents high-resolution TEM images of N-CNFs synthesized by decomposition of 75%C<sub>2</sub>H<sub>4</sub>/25%NH<sub>3</sub> mixture over 65Ni-25Cu-Al<sub>2</sub>O<sub>3</sub> (a), 75Co-Al<sub>2</sub>O<sub>3</sub> (b), and 62Fe-8Co-Al<sub>2</sub>O<sub>3</sub> (c) catalysts. Nitrogen content and BET surface area are also given under the pictures. It can be concluded that nitrogen incorporation in quantity of 1 – 2 wt. % does not cause any considerable changes of nanofiber structure as compared with non-doped CNFs prepared from pure hydrocarbons (Reshетенko, 2003). TEM images of nickel-copper catalyst after N-CNF growth registered 'herringbone' type structure (Fig. 1 (a)), whereas nanotubular morphologies were observed in the cases of cobalt (Fig. 1 (b)) and iron-cobalt (Fig. 1 (c)) samples. However, nanotubes produced on Fe-Co catalyst showed a specific morphology uncharacteristic for pure ones, exhibiting a so-called 'bamboo' (or 'nano-bell') structure where tubular core contains regularly spaced cone-shaped carbon layers. Probably, nitrogen species produced by ammonia dissociation at catalyst surface alter the ratio between surface and volume carbon diffusion rates during N-CNF growth facilitating the last one.

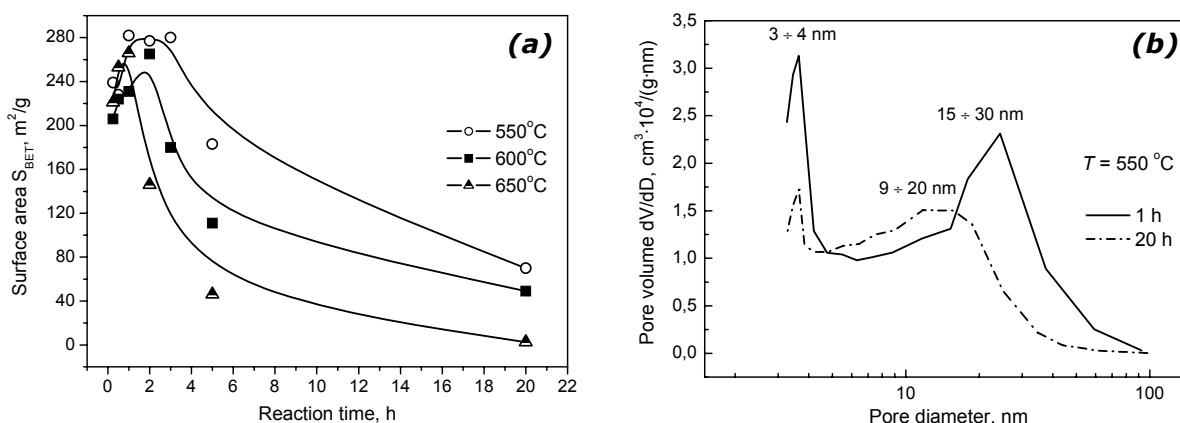


**Figure 1.** TEM Images of Nitrogen-Containing CNFs Synthesized by Decomposition of 75% $C_2H_4$ /25% $NH_3$  Mixture on Different Catalysts: (a) 65Ni-25Cu- $Al_2O_3$ , (b) 75Co- $Al_2O_3$  and (c) 62Fe-8Co- $Al_2O_3$ .

The effectiveness of different metal catalysts in production of N-CNFs was evaluated in respect to carbon yield and nitrogen content in the material. It was found that the amount of carbon prepared on Ni, Ni-Cu, Co and Co-Mo catalysts exceeds that obtained on Fe-based catalysts by a factor of 10 – 30 (Table 1). For example, yield of carbon from 75% $C_2H_4$ /25% $NH_3$  mixture at 625°C on 65Ni-25Cu- $Al_2O_3$  was 13.7 gC/g<sub>catalyst</sub> whereas on 62Fe-8Co- $Al_2O_3$  catalyst it amounted only to 1.3 gC/g<sub>catalyst</sub>. Among the most active catalysts the maximum nitrogen content in N-CNFs was observed in the sample prepared by use of 65Ni-25Cu- $Al_2O_3$  catalyst. So, this catalyst was selected for a more detailed investigation of physicochemical regularities of N-CNF growth from  $C_2H_4/NH_3$  mixture.

Investigation of pore structure and textural characteristics of N-CNFs showed that all materials are mesoporous with specific surface area ( $S_{BET}$ ) strongly dependent on the synthesis conditions and varying from 30 to 350  $m^2/g$  (Table 1, Fig. 2 (a)). Figure 2 (b) represents pore size distribution (PSD) for N-CNFs produced at 1 and 20 h of synthesis duration. The PSD curve of 1h sample has two maxima at 3 – 4 nm and 15 – 30 nm regions. It was found that the maximum at 15 – 30 nm shifts to the lower values of 9 – 20 nm when the duration of process is increased to 20 h. At the same time, BET surface area and pore volume diminishes. Equivalent thermal treatment of 1h sample during 19 h under Ar flow does not decrease  $S_{BET}$  value. It is known that carbon materials themselves are able to catalyze decomposition of hydrocarbons (Muradov, 2001). So, decrease of mesopore volume of 20h sample may be caused by deposition of a new carbon form inside the pores of material on the surface of nanofibers generated during the first hours of reaction.

Specific surface area reduces when the synthesis temperature is increased as it seen from Figure 2 (a). At all studied reaction temperatures from 550 to 675°C, the  $S_{BET}$  dependence on time reveals a maximum at 1 – 3 h (see also Table 1). Evidently, the reaction time of 1 – 3 h is the optimum for ethylene/ammonia decomposition when nanofiber growth occurs. After that time catalytic particles, possibly, become deactivated and ethylene pyrolysis is catalyzed by CNF surface leading to formation of pitch-like carbon, plugging the CNF pores initially produced.



**Figure 2.** Specific Surface Area (a) and Pore Size Distribution (b) of N-CNFs as Functions of Synthesis Duration: 65Ni-25Cu- $Al_2O_3$  Catalyst, 75% $C_2H_4$ /25% $NH_3$  Mixture.

**Table 1.** Effect of Synthesis Conditions on CNF Properties.

Variable parameter	Synthesis Conditions				$G^b$ , g <sub>c</sub> /g <sub>cat</sub>	$N$ , wt. %	Texture		
	Catalyst	Precursor	$T$ , °C	$t^a$ , h			$S_{BET}$ , m <sup>2</sup> /g	$V_{pores}$ cm <sup>3</sup> /g	$D_{BET}^c$ , nm
Catalyst	90Ni	75% $C_2H_4$ / 25% $NH_3$	550	1	11.6	0.5	158	0.43	10.8
	82Ni-8Cu				11.5	0.9	206	0.59	11.4
	65Ni-25Cu				12.4	1.7	282	0.51	7.2
	45Ni-45Cu				11.2	0.7	280	0.44	6.3
	75Co	600	600	1	12.2	0.7	205	0.44	8.7
	72Co-3Mo				14.3	0.7	223	0.61	11.0
	65Ni-25Cu				13.1	1.1	231	0.34	5.9
	90Fe	625	625	1	0.2	n.d. <sup>d</sup>	n.d.	n.d.	n.d.
	85Fe-5Co				0.6	n.d.	n.d.	n.d.	n.d.
	62Fe-8Co				1.3	2.0	117	0.27	9.3
	65Ni-25Cu				13.7	1.0	244	0.59	9.6
Precursor	65Ni-25Cu	100% $C_2H_4$	550	1	14.6	0	214	0.45	8.5
		75% $C_2H_4$ / 25% $NH_3$			12.4	1.7	282	0.51	7.2
		50% $C_2H_4$ / 50% $NH_3$			10.6	3.1	278	0.82	11.8
		25% $C_2H_4$ / 75% $NH_3$			2.5	7.0	191	0.71	14.9
$T$ , °C	65Ni-25Cu	50% $C_2H_4$ / 50% $NH_3$	450	1	6.6	2.1	351	0.83	9.5
			500		10.2	2.3	350	0.74	8.4
			550		10.6	3.1	278	0.82	11.8
			675		7.0	2.6	162	0.32	8.0
Reaction time	65Ni-25Cu	75% $C_2H_4$ / 25% $NH_3$	550	0.25	3.5	0.8	239	0.67	11.2
				1	12.4	1.7	282	0.51	7.2
				2	27.0	1.2	277	0.55	7.9
				3	39.7	n.d.	280	0.50	7.2
				5	56.9	0.7	183	0.39	8.4
				20	70.4	0.8	70	0.23	13.2

<sup>a</sup> Reaction time;<sup>b</sup> Carbon yield;<sup>c</sup> Average BET pore diameter;<sup>d</sup> Not determined.

An investigation of temperature effect within the interval of 450 – 675 °C on carbon yield and nitrogen content in N-CNFs showed that both these values have maxima at 550 °C (Table 1). Increase of the synthesis temperature from 550 to 675 °C results in decrease of carbon yield and nitrogen content. Thus, for 25% $C_2H_4$ /75% $NH_3$  mixture an increase of temperature from 550 to 675 °C leads to decrease of nitrogen content in N-CNFs from 7 to 4 wt. %.

Furthermore influence of synthesis duration on nitrogen content in obtained material was studied. The kinetic curves showed that nitrogen percentage in N-CNFs grows considerably when reaction time is increased from 0.25 to 1 h (Table 1). However, further increase of time up to 20 h leads to decrease of nitrogen concentration. Probably, this phenomenon relates to formation of new carbon product at prolonged synthesis when the catalytic particles become

deactivated or transformed upon exposure to reaction mixture and the reaction proceeds by another route. So, the optimum value of synthesis duration for high nitrogen content was established to be 1 h.

Table 2 contains XPS and elemental analysis data of N content. These data show a good correlation between the bulk and surface compositions when the reaction time is 1 h, but a discrepancy appears when synthesis duration is increased to 20 h. Hence, after 1 h on stream the N-CNF surface composition is identical to the bulk one. Meanwhile, decrease of nitrogen content in the N-CNF subsurface region is observed after long reaction time of 20 h. This effect can also be explained by the formation of new type of carbon material on the surface of N-CNFs with the nitrogen content lower than that in graphitic material.

A percentage composition of initial C<sub>2</sub>H<sub>4</sub>/NH<sub>3</sub> mixture has the most pronounced effect on nitrogen content in N-CNFs (Table 1). For example, an increase of ammonia concentration in feed from 25 to 75 vol. % results in increase of nitrogen content from 1.7 to 7.0 wt.% at 550°C, and from 1.3 to 3.9 wt. % at 675°C.

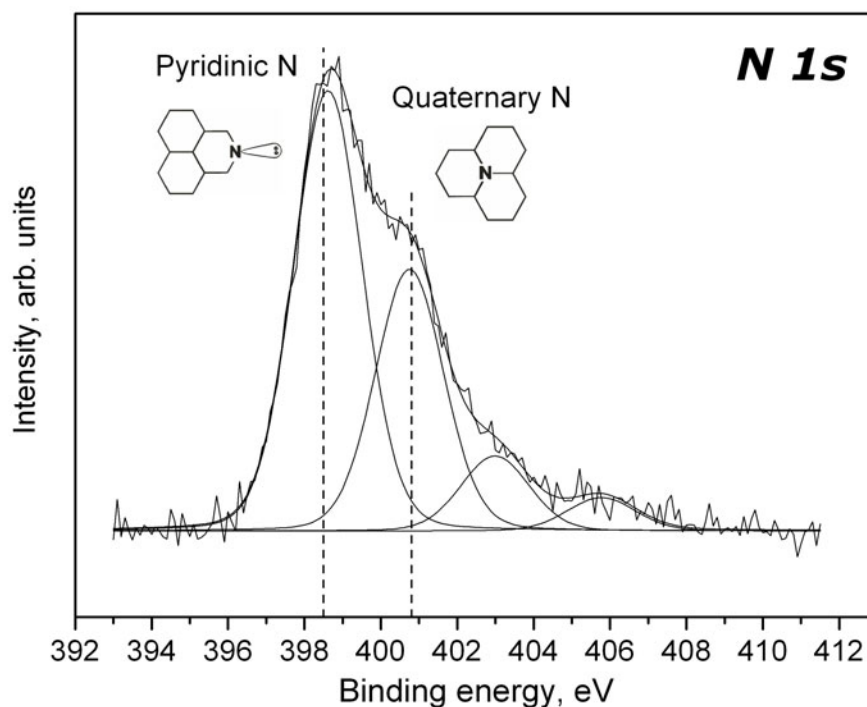
The N 1s XPS spectra of N-CNF samples consist of two main peaks: N<sub>Py</sub> at 398.5 eV and N<sub>Q</sub> at 400.8 eV (Fig. 3). The N<sub>Py</sub> peak is known to represent pyridinic nitrogen form. The N<sub>Q</sub> band is assigned to quaternary N coordination, i.e. more positively charged nitrogen as compared to pyridinic N, being part of an extended aromatic structure where some of carbon atoms are replaced by nitrogen. The relative intensity of N<sub>Py</sub> band grows with increase of nitrogen content, indicating that pyridinic-like functionalities become predominant (Table 2).

**Table 2.** Bulk and Surface Composition of Nitrogen-Containing CNFs.

Reaction mixture	Reaction time, h	S <sub>BET</sub> , m <sup>2</sup> /g	N content from EA data <sup>a</sup> , wt. %	N content from XPS data, wt. %	N <sub>Py</sub> /N <sub>Q</sub> ratio <sup>b</sup>
75%C <sub>2</sub> H <sub>4</sub> /25%NH <sub>3</sub>	1	244	1.0	1.1	1.1
	20	28	0.9	0.6	0.4
50%C <sub>2</sub> H <sub>4</sub> /50%NH <sub>3</sub>	1	278	3.1	2.9	1.3
25%C <sub>2</sub> H <sub>4</sub> /75%NH <sub>3</sub>	1	191	7.0	6.5	1.7

<sup>a</sup> Elemental analysis data;

<sup>b</sup> Atomic ratio of pyridinic N<sub>Py</sub> (BE 398.5 eV) to quaternary N<sub>Q</sub> (BE 400.8 eV) nitrogen states.



**Figure 3.** XPS N 1s Spectrum of N-CNF Sample with 7 wt. % of Nitrogen Content.

## Conclusions

A simple and efficient method for the production of nitrogen-containing carbon nanofibers by decomposition of ethylene/ammonia mixture over metal catalysts was developed. This technique allows regulating nitrogen content and its electronic state in graphitic lattice as well as structural and textural characteristics of N-CNF materials. Ascertained physicochemical dependencies allow to control characteristics of produced N-CNFs and to synthesize the materials with desired properties.

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