Preparation of Carbon Nanomaterials over Ni/ZSM-5 Catalyst Using Simplex Method Algorithm

J. Majewska* and B. Michalkiewicz
West Pomeranian University of Technology in Szczecin, K. Pułaskiego 10, 70-322 Szczecin, Poland

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Carbon nanomaterials were prepared from methane by catalytic decomposition over a nickel-supported ZSM-5 catalyst. The mole ratio of SiO_2 to Al_2O_3 in ZSM-5 was 200–400. The nickel content was varied from 17 to 23 wt% Ni. In order to find the greatest yield and the highest quality of carbon nanomaterials the simplex design method for planning the experiments was applied. Different parameters such as: temperature, methane flow, nitrogen flow and nickel content in the catalyst were evaluated. The carbon nanomaterials were analyzed by the Raman spectroscopy, scanning and transmission electron microscopy, and total organic carbon analyzer.

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1. Introduction

The first mention of carbon filaments production by the thermal decomposition of methane was reported in 1889 [1] but after Iijima paper published in 1991 [2] carbon nanotubes have been receiving great research interest from scientists worldwide due to their unique electrical, mechanical and physical properties [3]. Carbon nanomaterials (CNMs) can be obtained by graphite sublimation followed by its desublimation or catalytic decomposition of organic compounds and CO [4].

Graphite is evaporated in an electric arc or under a laser beam. Very high temperatures are needed to form CNMs with a low selectivity and a low level of homogeneity of the product [5]. The decomposition of organic compounds or chemical vapor disposition [6–10] is considered a potential method for large scale production of CNMs due to its low cost, relative simplicity and capability to scale up as large unit operation. Hydrocarbons are commonly used as a carbon source for the synthesis of carbon nanomaterials [11]. The use of methane is the most economical way to produce CNMs since methane is cheap and abundant [12–15].

Transition metals, especially Fe, Co, Ni [16–23] are commonly used in catalytic decomposition of methane. Supported nickel is the most effective catalyst, active even at a lower temperature (even 450 °C) [24]. Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, SiO_2, Al_2O_3, and SiO_2 were usually used as support [25]. ZSM-5 zeolite was investigated as a support by our research team for 5 years [24, 26, 27] although Choudhary et al. [28] stated that H-ZSM-5 supported nickel cannot be used to produce filamentous carbon.

There is still a problem to find proper processing parameters e.g. temperature, Ni concentration, flow of a gases, for good quality CNMs or a high yield of CNMs synthesis. A classical method for selection of the optimum conditions consists in a procedure for finding a value of the parameters which can give the highest result of the experiment. This method is better than a random search. Because of the smallest number of experiments needed and the simplicity of calculations, the best method, used in chemical studies, is the one involving geometric solids referred to as simplexes [29–31].

In this study, we demonstrate CNMs production by catalytic decomposition of methane utilizing the simplex design method for planning the experiments. Different parameters such as: temperature, methane flow, nitrogen flow, and nickel content in the catalyst were evaluated.

*corresponding author; e-mail: jmajewska@zut.edu.pl

2. Experimental

2.1. Methods

Carbon nanomaterials were examined by transmission electron microscopy (TEM-FEI Tecnai F20). A small part of samples was prepared by ultrasonic dispersion in acetone for 7 min. Then one drop of the resultant suspension evaporated onto a copper grid. The structure of carbon nanomaterials was examined by the Raman spectroscopy (RenishawInVia) equipped with a CCD detector. The Raman band appearing in the 1500–1600 cm^{-1} region is noted as G band (graphite band) and the Raman band appearing in the 1250–1450 cm^{-1} region is noted as D band (disorder band). The G band can be imputed to the in-plane carbon–carbon (C–C) stretching vibrations of graphite layers. The D band is attributed to the structural imperfection of graphite. The intensity ratio of the D- and G-peaks (I_G/I_D) can be regarded as the measure of the quality of a CNMs. Samples were excited by the red laser light of 785 nm. The morphology of as prepared carbon nanomaterials was characterized by a field emission scanning electron microscope (FE-SEM) equipped with a secondary electron (SE) and backscattered electron (BSE) detectors — Hitachi SU 8200. The samples for FE-SEM were dispersed onto a carbon tape without any metal coating. The mass of the carbon was calculated on the basis of total organic carbon (TOC) analyzer measurements.

2.2. Preparation of the catalysts

The catalysts were prepared by trituration to a uniform powder of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) and ZSM-5 at room temperature. The molar ratio of SiO_2/Al_2O_3 in ZSM-5 zeolite was 200–400. The content of nickel was varied from 17 to 23 wt%.

The calcination was performed at 550 °C for 5 h in the air atmosphere. After calcination catalysts were pressed under 10 t for 1 h. Then, they were crushed to obtain grain with a diameter of about 2–4 mm.

2.3. Catalytic decomposition of methane

Nanomaterials were synthesized in a vertical quartz reactor in the temperature range of 675–701 °C. 1 g of the catalyst was placed in the center of the reactor. The catalyst was crushed for grain with a diameter of about 2–4 mm. Gas flow was equal to 5.6 l/h. Nitrogen was passed through the quartz tube as the furnace was heated to reach 700 °C. The catalyst was activated by reduction with hydrogen for 1 h at 700 °C. Methane decomposition was carried out for 15 min after cooling to a desired temperature. After reaction the reactor was cooled to room temperature under nitrogen. Gaseous samples of the products were taken every minute with gas tight syringes (1 ml) and analyzed by GC. After reaction as synthesized carbon nanomaterials were analyzed by the Raman spectroscopy, TOC, SEM, and TEM.

2.4. Simplex method algorithm

Two series of experiments were performed: Simplex A and Simplex B. In Simplex A the criteria for selecting the next experiments was mass of carbon deposit and in Simplex B it was the quality of CNMs. Table I shows the initial values of the parameters of simplex method algorithm such as: temperature, methane flow, nitrogen flow, and nickel content in the catalyst.

TABLE I

The initial values of the parameters of simplex method algorithm.

	Parameter	x_{0n}	Variability unit (Δx_n)
x_1	temperature [°C]	650	50
x_2	methane flow [l/h]	3	2
x_3	nitrogen flow [l/h]	1	1
x_4	nickel content [wt%]	20	5

TABLE II

Matrix A of simplex (a — general form of the matrix, b — numerical values of k_n and R_n in the matrix).

a				b			
k_1	k_2	k_3	k_4	0.5	0.289	0.204	0.158
($-R_1$)	k_2	k_3	k_4	-0.5	0.289	0.204	0.158
0	($-R_2$)	k_3	k_4	0	-0.577	0.204	0.158
0	0	($-R_3$)	k_4	0	0.000	-0.612	0.158
0	0	0	($-R_4$)	0	0.000	0.000	-0.632

Matrix A with the calculated values k_n and R_n for $N = 4$ is shown in Table II, where

$$k_n = \left[\frac{1}{2} n\,(n+1)\right]^{1/2} \quad (1)$$

and

$$R_n = \left[\frac{n}{2}\,(n+1)\right]^{1/2} \quad (2)$$

for $n = 1, 2, ...N$ (n — number of the coefficient matrix).

The initial simplex was used for starting the experiments with M ($M = N + 1$). The corresponding rows and columns of the matrix give the values for each parameter. The initial values of the experiments (base simplex) were calculated using Eq. (3):

$$x_{mn} = x_{0n} + \Delta x_n a_{mn} \quad (3)$$

where x_{mn} — the value of the parameter n in the m experiment, x_{0n} — the initial value of the parameter n, a_{mn} — the value from the matrix A in the row m and column n, Δx_n — unit variability of the parameter n.

After completing the initial simplex and analyzing for series A and B, the next parameters for the process were selected at which the new $M + 1$ experiment was conducted using Eq. (4):

$$x_{M+1,n} = \frac{2}{N} \sum_{m=1}^{M} x_{mn} - x_{jn} \quad (4)$$

where $m = 1, 2, ...M$ ($M = N + 1$), except $m = j$; x_{jn} — value of the rejected experiment.

After the ($M + 1$) experiment was finished and its best value was evaluated, the experiment with the lowest value (mass or G/D ratio) was rejected and then the calculations were repeated in order to determine the parameters for the next experiment $x_M + 2$ for simplex A and simplex B.

3. Results and discussion

The original points of the simplex base are calculated from the formula (3) with values from Tables I and IIb.

$$x_{11} = 500 + (50 \times 0.5) = 675,$$
$$x_{12} = 3 + (2 \times 0.289) = 3.6,$$
$$x_{13} = 1 + (1 \times 0.204) = 1.2,$$
$$x_{14} = 20 + (5 \times 0.158) = 21.$$

The first five experiments ($M = N + 1$) in simplex A and B had the same parameters, then the best value was evaluated and the worst value in each simplex was rejected.

The next point in the simplex was calculated (Eq. (4)):

$$x_{61} = 2/4 \times (675 + 625 + 650 + 650) - 650 = 650,$$
$$x_{62} = 2/4 \times (3.6 + 3.6 + 3.0 + 3.0) - 1.8 = 3.0,$$
$$x_{63} = 2/4 \times (1.2 + 1.2 + 0.4 + 1.0) - 1.2 = 1.9,$$
$$x_{64} = 2/4 \times (21 + 21 + 21 + 17) - 21 = 21.$$

3.1. Simplex A

Taking into consideration the first simplex (experiments 1–5) the lowest mass of carbon nanomaterials was obtained after the third experiment (Table III).

TABLE III

Experiment parameters and mass of carbon deposits in Simplex *A*.

	Temp. [°C]	CH_4 [l/h]	N_2 [l/h]	Ni [wt.%]	Results	
x_{mn}	1	2	3	4	Mass C [g]	Elimination
1 (In)	675	3.6	1.2	21	0.241	E VI
2 (In)	625	3.6	1.2	21	0.166	E II
3 (In)	650	1.8	1.2	21	0.116	E I
4 (In)	650	3.0	0.4	21	0.194	E III
5 (In)	650	3.0	1.0	17	0.208	E IV
6	650	4.8	0.7	19	0.309	E VIII
7	688	3.6	0.5	18	0.241	E V
8	682	4.5	1.3	17	0.298	E VII
9	698	5.3	0.9	21	0.380	
10	665	5.5	1.6	21	0.365	E IX
11	673	6.5	1.1	18	0.370	
12	661	6.6	0.9	23	0.413	
13	699	7.2	1.6	23	0.433	best value
14	701	7.3	0.7	22	0.197	E X/S

Therefore point 3 was rejected. Based on Eq. (4) experiment 6 was calculated. The second simplex, experiments: 1, 2, 4–6. The lowest mass was obtained after the second experiment so point 2 was rejected. Based on Eq. (4) experiment 7 was calculated. The procedure was repeated several times. After the fourteenth experiment, also calculated using Eq. (4), the mass of carbon nanomaterials was the lowest. Therefore the simplex was ended because the result obtained in experiment 14 was worse than the previous ones.

3.2. Simplex B

Taking into consideration the first simplex (experiments 1–5) the lowest I_G/I_D value of carbon nanomaterials was obtained after the fourth experiment and this experiment was rejected (Table IV). The next 6 experiments of Simplex *B* were calculated using Eq. (4).

TABLE IV

Experiment parameters and quality for the nanomaterials carbon in Simplex *B*.

	Temp. [°C]	CH_4 [l/h]	N_2 [l/h]	Ni [wt.%]	Results	
x_{mn}	1	2	3	4	G/D	Elimination
1 (In)	675	3.6	1.2	21	0.503	E II
2 (In)	625	3.6	1.2	21	0.552	
3 (In)	650	1.8	1.2	21	0.566	best value
4 (In)	650	3.0	0.4	21	0.450	E I
5 (In)	650	3.0	1.0	17	0.530	
6	650	3.0	1.9	19	0.528	
7	613	2.1	1.5	18	0.533	
8	619	2.3	0.6	20	0.511	E III/K

E I, E II,... — elimination, In — initial value of simplex.

The second simplex is composed for experiments 1, 2, 3, 5 and 6. The lowest result was obtained in the first experiment. Experiment was calculated using Eq. (4). The procedure was repeated and the lowest value of I_G/I_D was obtained in experiment 8. Therefore, the simplex was ended, because the result obtained in experiment 8 was worse than the previous ones.

3.3. Results

Experiments in Simplex *A* were made in order to maximize the mass of carbon but the I_G/I_D value was calculated as well. It was found that the increase of carbon mass decreases I_G/I_D value (Fig. 1). The same tendency was observed in the experiments performed in Simplex *B*.

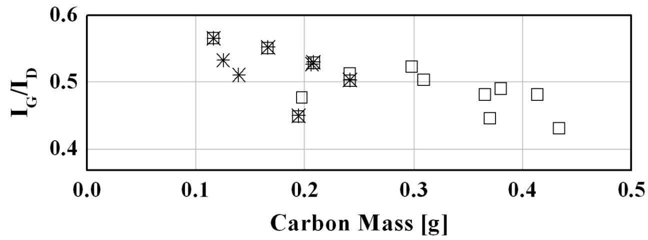

Fig. 1. I_G/I_D value vs. carbon mass. Simplex *A* (*) Simplex *B* (□).

The results obtained by carbon analyzer and the Raman spectroscopy were confirmed by SEM and TEM micrographs. Figure 2 presents carbon nanotubes obtained during experiment 13 (Simplex *A*). One can see a significant amount of braided CNMs. Figure 3 presents carbon nanotubes produced during experiment 3 (Simplex *B*). The quantity of the CNMs produced in experiment 3 is much lower than that in Fig. 2. Only several nanotube bundles are visible. Figures 4 and 5 reveals TEM pictures of carbon nanotubes obtained during experiment 13 (Simplex *A*) and 3 (Simplex *B*), respectively. The quality of carbon nanotubes obtained with the highest yield is the lowest.

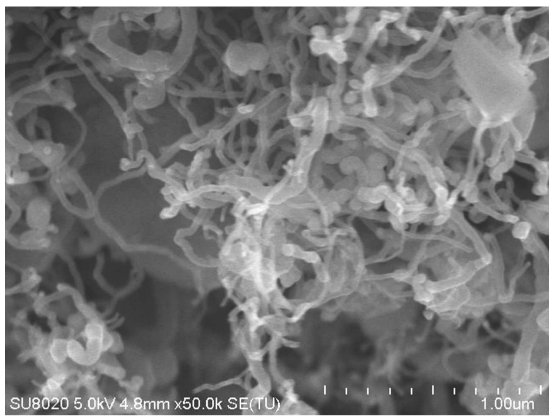

Fig. 2. SEM image for sample prepared at 699 °C, under 7.2 l/h of methane flow, 1.6 l/h of nitrogen flow and 23 wt% Ni (experiment 13 in Simplex *A*).

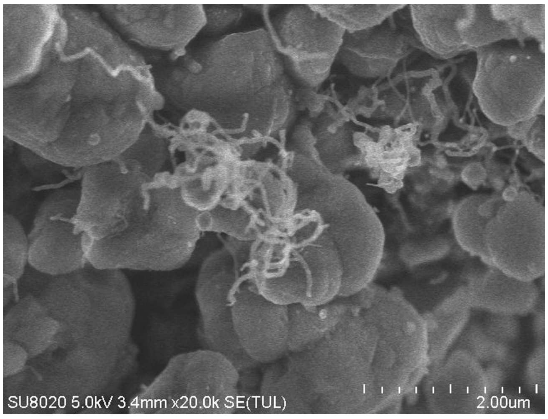

Fig. 3. SEM image for sample prepared at 650 °C, under 1.8 l/h of methane flow, 1.2 l/h of nitrogen flow and 21 wt% Ni (experiment 3 in Simplex *B*).

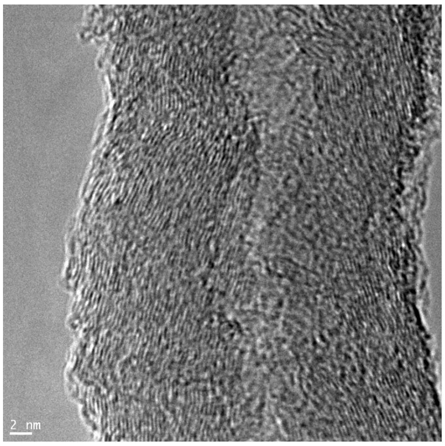

Fig. 4. TEM image for sample prepared at 699 °C, under 7.2 l/h of methane flow, 1.6 l/h of nitrogen flow and 23 wt% Ni (experiment 13 in Simplex *A*).

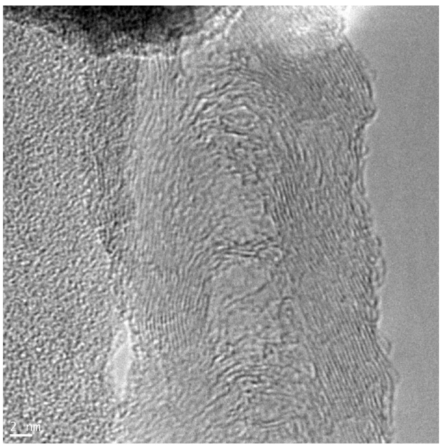

Fig. 5. TEM image for sample prepared at 650 °C, under 1.8 l/h of methane flow, 1.2 l/h of nitrogen flow and 21 wt% Ni (experiment 3 in Simplex *B*).

4. Conclusion

The nanomaterials synthesized after methane decomposition by the simplex method algorithm were carbon nanotubes. The best result in Simplex *A* was obtained with experiment parameters: the temperature of 699 °C, methane flow of 7.2 l/h, nitrogen flow of 1.6 l/h and nickel content in catalyst of 23 wt% (experiment 13). The carbon mass was 0.433 g. In Simplex *B* the highest value of I_G/I_D ratio (0.566) was obtained in experiment 3. The parameters of the 3. experiment were: the temperature of 650 °C, methane flow of 1.8 l/h, nitrogen flow of 1.2 l/h and nickel content in catalyst of 21 wt%. The increase of carbon mass decreases the quality of carbon nanomaterials.

Acknowledgments

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