Morphology and dispersion of FeCo alloy nanoparticles dispersed in a matrix of IR pyrolized polyvinyl alcohol

A A Vasilev1,2, E L Dzidziguri1, D G Muratov2, N A Zhilyaeva2, M N Efimov2 and G P Karpacheva2

1 Department of Functional Nanosystems and High-Temperature Materials, National University of Science and Technology “MISiS”, Moscow 119049, Russia
2 Chemistry of Polyconjugated Systems Laboratory, A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow 119991, Russia

E-mail: raver.vasiljev@mail.ru

Abstract. Metal-carbon nanocomposites consisting of FeCo alloy nanoparticles dispersed in a carbon matrix were synthesized by the thermal decomposition method of a precursor based on polyvinyl alcohol and metals salts. The synthesized powders were investigated by X-ray diffraction (XRD), X-ray fluorescent spectrometry (XRFS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Surface characteristics of materials were measured by BET-method. The morphology and dispersity of metal nanoparticles were studied depending on the metals ratio in the composite.

1. Introduction
At present days the development of new materials with predefined properties is relevant task in both scientific and applied aspects. Metal-carbon nanocomposites based on pyrolyzed polymers are attractive due to the diversity and uniqueness of their physico-chemical properties providing their high potential for commercial application [1–3].

It is well known that Fe and Co have a great importance in different scientific fields and engineering due to their catalytic and magnetic properties [4–8]. Fe-Co bimetallic system allows to improve various physico-chemical properties significantly. For example, Fe-Co bimetallic system is characterized by high Curie temperature, large saturation magnetization, great magnetic permeability [2, 5–9] and gives rise to a synergistic effect in catalysis [5, 10].

Using of carbon based materials is one of the best way to stabilize nanoparticles. The carbon encapsulation increases electrical conductivity, mechanical performance, capability of nanoparticles to absorb the electromagnetic waves, biocompatibility of nanoparticles and decreases interparticle interaction [3, 7, 11]. In addition, carbon is a good catalyst support material due to its various porous structure, resistance to acid and basic environments, low cost and easy accessibility. Furthermore, metal nanoparticles stabilized by carbon materials can be considered as models of the dimensional effect influence on catalytic activity [12]. Thus, metal-carbon nanocomposites based on Fe and Co are promising as catalysts, absorber of electromagnetic waves, carriers for magnetically-driven drug delivery and in development new magnetic materials based on these nanocomposites [13–17].

The goals of this work were the preparation of metal-carbon nanocomposites based on FeCo nanoparticles immobilized in IR pyrolized polyvinyl alcohol support and the investigation of the phase
formation, morphology and dispersity of FeCo bimetallic nanoparticles depending on the intensity of IR-annealing and metals ratio in the composite.

2. Materials and methods
Metal-carbon nanocomposites were prepared under the conditions of infrared (IR) pyrolysis of a precursor based on solution of polyvinyl alcohol (PVA) and iron and cobalt hydronitrates (Fe(NO$_3$)$_3$$\cdot$9H$_2$O and Co(NO$_3$)$_2$$\cdot$6H$_2$O) with the follow ratio of metal components 9 : 1; 3 : 1; 1 : 1; 1 : 3; 1 : 9 (mole) at different temperatures (300 – 700 °C). The concentration of PVA in water was 5 % wt. and the summary metal concentrations in polymer was 20 % wt.

The pyrolysis was carried out in the quartz reactor of IR heating device. IR annealing was accomplished at two-step mode: preliminary annealing at presence of the air at 150 and 200 °C for 15 minutes in order to remove the solvent and start the initial structuring of PVA followed by the main annealing in an argon atmosphere at a necessary temperature. The main annealing step takes 2 minutes at desired temperature.

The size and morphology of the metal nanoparticles were evaluated by TEM (LEO 912 AB) and SEM (JSM 6700F) analysis. Histograms of particle size distribution were obtained via estimation of particle size from TEM micrographs.

XRD analysis was carried out at room temperature on a DIFRAY-401 diffractometer using Cr-Kα radiation source with the Bragg-Brentano focusing geometry. Spherical crystallite diameter distribution was estimated from XRD data.

The elemental composition of the samples was determined by X-ray analytical microscope RAM-30μ.

The N$_2$ adsorption/desorption isotherms of metal-carbon nanocomposites were measured with an accelerated surface area and porosimetry system (ASAP-2020 «Micromeritics») for determining the surface areas.

3. Results and discussion
The elemental composition of the composites determined by X-ray fluorescence analysis is given in table 1. It was found that initial and measured metals content were similar.

| Ratio of metals | Annealing temperature, °C | Fe content, at. % | Co content, at. % |
|----------------|---------------------------|------------------|------------------|
| Fe : Co        |                           |                  |                  |
| 9 : 1          | 700                       | 90               | 10               |
| 3 : 1          | 700                       | 75               | 25               |
| 1 : 1          | 300                       | 48               | 52               |
| 1 : 1          | 400                       | 48               | 52               |
| 1 : 1          | 500                       | 49               | 51               |
| 1 : 1          | 600                       | 49               | 51               |
| 1 : 1          | 700                       | 49               | 51               |
| 1 : 3          | 700                       | 24               | 76               |
| 1 : 9          | 700                       | 7                | 93               |

Figure 1 shows the TEM images of samples obtained at different temperatures with the equal ratio of components. FeCo spherical nanoparticles dispersed in translucent carbon matrix are observed and have a uniform distribution. Figure 2 demonstrates the TEM images of composites synthesized at 700 °C with different ratio of components. Morphology of metal nanoparticles are the same at different ratio of components, however the carbon matrix uniformity is changed in the sample with the ratio of metals Fe : Co = 1 : 9.

Figure 3 shows the SEM images at high magnification on which nanoparticles also have spherical forms localized on the carbon matrix surface. The particle size distribution histograms were obtained
via estimation of particle size from TEM micrographs (figure 4) and described by the log-normal distribution function. Table 2 represents the average particle sizes $D_{el}$.

![Figure 1](image1.png)

**Figure 1.** TEM micrograph of IR-PVA/Fe-Co samples with the equal ratio of components obtained at: (a) 600 °C; (b) 700 °C

![Figure 2](image2.png)

**Figure 2.** TEM micrograph of IR-PVA/Fe-Co samples obtained at 700 °C: (a) Fe : Co = 9 : 1; (b) Fe : Co = 1 : 9

![Figure 3](image3.png)

**Figure 3.** SEM micrographs of IR-PVA/Fe-Co samples with the equal ratio of components obtained at: (a) 600 °C; (b) 700 °C
Figure 4. Particle size distribution histograms of FeCo nanoparticles obtained at:
(a) 600 °C (Fe : Co = 1 : 1); (b) 700 °C (Fe : Co = 1 : 1); (c) 700 °C (Fe : Co = 9 : 1);
(d) 700 °C (Fe : Co = 1 : 9)

XRD analysis of samples confirms the formation of FeCo solid solution. For a better visual perception the XRD patterns are shifted relative to each other by the same scale along the intensity axis on figure 5. FeCo nanoparticles with body-centered cubic (bcc) structure start forming at 400 °C. In the temperature range of the IR-annealing from 300 to 500 °C the XRD patterns peaks corresponding to iron and cobalt oxides are observed, which are superimposed on one another.

Figure 6 represents the reflection lines corresponding to the maximum intensity peak of FeCo solid solution, the crystal plane of (110). It is observed that the FeCo reflection peaks at the range from 600 to 700 °C have a symmetrical shape and are aligned relative to each other, whereas at 500 °C the diffraction maximum is shifted towards larger angles. Therefore, FeCo solid solution formation with unequal ratio and with a smaller lattice constant occurs at 500 °C. The observed iron oxide peaks at 500 °C indicate that FeCo solid solution formation is incomplete. The diffraction maximum corresponding to the graphite appears on the diffraction pattern from 600 °C. The crystalline phase amount of carbon is increased with rising temperature.

Figure 7 shows XRD patterns of composites synthesized at 700 °C with different ratio of metals. FeCo solid solution with bcc structure is formed in all samples except the composite with the ratio of component Fe : Co = 1 : 9. FeCo phase based on faceted-centered cubic structure (β-Co) is becoming visible for the samples containing more than 70 at. % of cobalt in the solid solution. The XRD pattern of composite containing 90 at. % of cobalt characterized by the presence of FeCo nanoparticles based on β-Co lattice only.
All picks have a symmetrical shape and are shifted toward larger angles with increasing cobalt content in the samples (figure 8). It indicates that the lattice constant is decreased and the chemical composition of solid solution is changed.

The coherent scattering region (CSR) distribution was calculated according to the method of Selivanov and Smislov [18]. The sample obtained at 600 °C has the most narrow distribution and smaller size of the CSR. The average crystallite size for all composites obtained at 700 °C is approximately the same (20 – 24 nm) and doesn't depend on the ratio of components.

According to the table 2 nanoparticles consist of a single crystallite in all samples. In the composite annealed at 700 °C, the average crystallite size larger than the average particles size. This can be explained by the locality of the TEM method, while X-ray analysis is an integral.

Figure 5. X-ray diffraction patterns of IR-PVA/Fe-Co samples

Figure 6. X-ray diffraction patterns of IR-PVA/Fe-Co samples with the equal ratio of components obtained at 500 – 700 °C, the crystal plane of (110)
Figure 7. X-ray diffraction patterns of IR-PVA/Fe-Co samples synthesized at 700 °C:
(1) Fe : Co = 9 : 1; (2) Fe : Co = 3 : 1; (3) Fe : Co = 1 : 1; (4) Fe : Co = 1 : 3; (5) Fe : Co = 1 : 9

Figure 8. X-ray diffraction patterns of IR-PVA/Fe-Co samples with different ratio of components obtained at 700 °C, the crystal planes of (110) and (111)

Figure 9. Crystallite size distribution of the FeCo phase (BCC): (a) with the equal ratio of metals; (b) with different ratio of metals: (1) Fe : Co = 9 : 1; (2) Fe : Co = 3 : 1; (3) Fe : Co = 1 : 1; (4) Fe : Co = 1 : 3
The specific surface area was determined from nitrogen adsorption-desorption isotherm data and collected in table 2. The specific surface area is higher for samples with a predominant Fe content. This fact corresponds to the results obtained in [19, 20] where iron-containing carbon composite characterized by higher surface area in comparison to cobalt-containing material. Hence, the metals affect on porosity and structure of the metal-carbon composites.

Table 2. Dimensional characteristics of FeCo nanoparticles and specific surface area of nanocomposites

| Ratio of metals Fe : Co | Annealing temperature, °C | Metal phase | Specific surface area, m²/g | Dsr, nm | DCSR, nm |
|------------------------|---------------------------|-------------|-----------------------------|---------|----------|
| 9 : 1                  | 700                       | BCC         | 195                         | 27      | 23       |
| 3 : 1                  | 700                       | BCC         | 187                         | 25      | 21       |
| 1 : 1                  | 600                       | BCC         | -                           | 7       | 7        |
| 1 : 1                  | 700                       | BCC         | 21                          | 12      | 24       |
| 1 : 3                  | 700                       | FCC         | 58                          | 17      | 48       |
| 1 : 9                  | 700                       | FCC         | 17                          | 48      | -        |

4. Conclusions.
The obtained research results show that FeCo nanoparticles with bcc structure start forming at 400 °C. The metallic phase of samples synthesized at 600 and 700 °C consists of FeCo solid solution only. Nanoparticles have spherical form and uniform distribution in a carbon matrix. Equal ratio of components and iron predominance in the samples lead to formation of FeCo nanoparticles with the structure based on α-Fe lattice whereas an excess of cobalt leads to form a FCC-lattice based on β-Co. The sample at the ratio of Fe : Co = 1 : 9 is characterized by larger particle sizes and destruction of carbon matrix uniformity.

Acknowledgements
The equipment of the collective exploitation center "New petrochemical processes, polymer composites and adhesives" was used.

This work was done as part of TIPS RAS (№ 79) State Plan.

References
[1] Kulikova M V, Zemtsov L M, Sagitov S A, Efimov M N, Krylova A Y, Karpacheva G P, Khadzhiev S N 2014 Solid Fuel Chemistry 48 32
[2] Zaharov Yu A, Pugachev V M, Popova A N 2013 Bulletin of the Russian Academy of Sciences: Physics 77 142
[3] Afghahi S, Shokuhfar A 2014 Journal of Magnetism and Magnetic Materials 370 37
[4] Sourmail T 2005 Progress in Materials Science 50 816
[5] Sedighi B, Feyzi M, Joshaighani M 2015 Journal of the Taiwan Institute of Chemical Engineers 50 108
[6] Chokprasombat K, Harding P, Pinitsootorn S, Maensiri S 2014 Journal of Magnetism and Magnetic Materials 369 228
[7] Nautiyal P, Seikh M M, Lebedev O I, Kundu A K 2015 Journal of Magnetism and Magnetic Materials 377 402
[8] Karipoth P, Thirumarugan A, Josephyus R J 2013 Journal of Colloid and Interface Science 404 49
[9] Chaubey G S, Barcena C, Poudyal N, Rong C, Gao J, Sun S, Liu J P, Am J. 2007 Chemical Society 129 7214
[10] Diaz J A, Romero A. García-Minguillán A M 2015 Fuel Processing Technology 138 455
[11] Castrillon M, Mayoral A, Urtizberea A, Marquina C, Irusta S, Meier J G, Santamaria J 2013 *Nanotechnology* **24** 505702
[12] Pomogailo A D, Rozenberg A S, Uflyand I E 2000 *Metal nanoparticles in polymers* (Moscow: Khimiya) p 672
[13] Galaburda M V, Bogatyrov V M, Tomaszewski W, Oranska O I, Borysenko M, Skubiszewska-Zieba J, Gun’ko V 2017 *Colloids and Surfaces A* **529** 950
[14] Xing W, Zhue S, Gao X 2009 *Materials Letters* **63** 1177
[15] Liu L, Concepcion P, Corma A 2016 *Journal of Catalysis* **340** 1
[16] Tsurin V A, Ermakov A E, Uimin M A, Mysik A A, Schegoleva A A, Gaviko V S, Maikov V V 2014 *Physics of the Solid State* **56** 287
[17] Kozhitov L V, Kozlov V V, Kostikova A V, Popkova A V 2013 *Russian Microelectronics* **42** 498
[18] Selivanov V N, Smislov E F 1993 *Crystallography Reports* **38** 174
[19] Wu M, Zhang E, Guo Q, Wang Y, Qiao J, Li K, Pei P 2016 *Applied Energy* **175** 468
[20] Han C, Bo X, Liu J, Li M, Zhou M, Guo L 2017 *Journal of Alloys and Compounds* **710** 57