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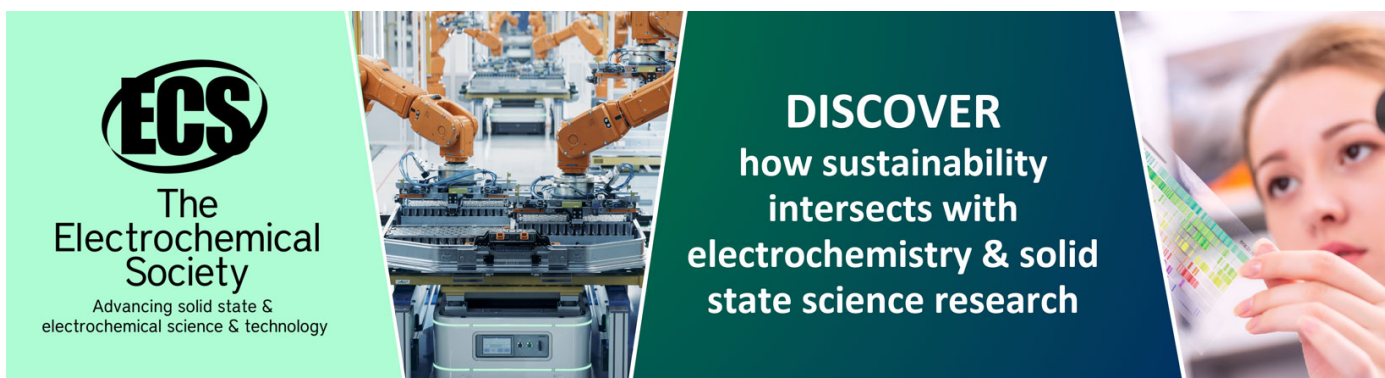
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Metal-carbon nanosystem IR-PVA/Fe-Co for catalysis in the Fischer-Tropsch synthesis

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Abstract. Metal-carbon nanosystems consisting of nanodimensional bimetallic particles of Fe-Co dispersed in a carbon matrix for the Fischer-Tropsch synthesis were studied. Prepared metal-carbon nanopowders samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). It was shown formation of FeCo nanoparticles with body-centered cubic structures started at 400 °C. FeCo nanoparticles have spherical form, the mean size is 7 – 12 nm and uniform distribution in a carbon matrix. The metal-carbon nanosystem demonstrates a catalytic activity in the Fischer-Tropsch synthesis. The maximum yield of liquid hydrocarbons C₅₊ was 92 g/m³ while the selectivity for the target product – 35 %.

1. Introduction

Associated petroleum gas (APG) utilization is one of the priority tasks facing the Russia's oil and gas complex. Imbalance of petroleum production and processing of APG has led to the fact that the volume of the gaseous hydrocarbons which are annually burned on torch installations exceeds 20 billion m³ that is equivalent to losses to 500 billion roubles per year [1]. As the decree of the Government of the Russian Federation № 1148 dated 08.11.12 about the increase of payment for excessive APG flaring was approved most large companies have started paid more attention to the program based on the petroleum products synthesis, namely, APG processing into motor fuel, methanol and other valuable products via the "gas to liquid" technology. This technology is based on the chemical Fischer-Tropsch synthesis [2, 3].

Fischer-Tropsch (FT) synthesis is a catalytic process that converts syngas (CO and H₂) into components of liquid fuels [4]. Mainly cobalt and iron are applied as commercial catalysts [5]. At the present time these catalysts based on Co and Fe, used by Shell (Malaysia), Sasol (South Africa) and Qatar Petroleum (Qatar), require the recovery stage before FT process [6]. Synthesis of metal-carbon nanosystem containing a catalytic non-pyrophoric nanoscale particles which don't require recovery procedures is an important task, which will reduce excess expenses.

Thus, the goals of this work were preparation of metal-carbon nanosystems based on FeCo nanoparticles in infrared (IR) pyrolyzed polyvinyl alcohol support and investigation their structure and catalytic properties depend on synthesis conditions.



2. Materials and methods

Metal-carbon nanosystems were prepared under the conditions of IR pyrolysis of a precursor based on solution of polyvinyl alcohol (PVA) and iron and cobalt hydronitrates ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) at 5 different temperatures (300, 400, 500, 600, 700 °C), with a mole ratio of metal components 1 : 1. The concentration of PVA in water was 5 % wt. and the summary metal concentrations in polymer was 20 % wt.

Pyrolysis was conducted in the IR-chamber of pulse photon annealing device [7]. IR-annealing was accomplished at two-step mode: preliminary annealing in air at 150 and 200 °C for 15 minutes during which there is removal the solvent and initial structuring of PVA and then the main annealing in an argon atmosphere at a specified temperature. The main annealing time was 2 minutes.

The size and morphology of the metal nanoparticles were evaluated by TEM (JEM-1011) and SEM (JSM 6700F) analysis. Histograms of particle size distribution were obtained via estimation of particle size from TEM micrographs.

X-ray diffraction analysis was conducted at room temperature on a DIFREY-401 diffractometer using Cr-K α radiation source with the Bragg-Brentano focusing geometry. Spherical crystallite diameter distribution was estimated from X-ray diffraction data.

The Fischer–Tropsch synthesis was carried out in catalytic flow system with a fixed catalyst bed under conditions of continuous operation at 20 bar and bulk velocity of the feed syngas 1000 h⁻¹ (molar ratio CO : H₂ = 1 : 1) in the temperature range from 220 to 380 °C. The temperature rise was accomplished stepwise (20 °C every 12 hours). Gas sampling and fluid analysis is accomplished at the end of each isothermal regime.

Catalytic tests were conducted without the preliminary stage of recovery. Initial syngas and gaseous products of synthesis were analyzed by the method of gas-solid chromatography on the chromatograph "Cristallux-4000".

3. Results and discussion

Figure 1 shows the TEM images of samples synthesized at different temperatures. FeCo spherical nanoparticles dispersed in translucent carbon matrix are observed and have a uniform distribution. Particle size distribution histograms (Figure 2) were obtained via estimation of particle size from TEM micrographs. Table 1 represents the average particle sizes D_{av} .

SEM images at high magnification in Figure 3 demonstrate a spherical form of nanoparticles localized on the carbon matrix surface.

Figure 4 shows XRD patterns of samples obtained at annealing temperatures of 300, 400, 500 and 600 °C. For a better visual perception the XRD patterns are shifted relative to each other by the same

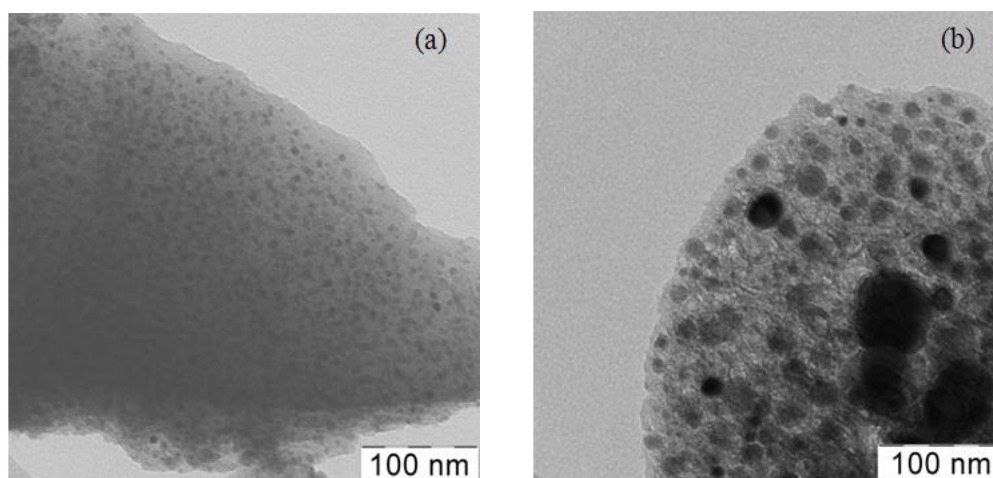


Figure 1. TEM micrographs of IR-PVA/Fe-Co samples obtained at: (a) 500 °C; (b) 700 °C.

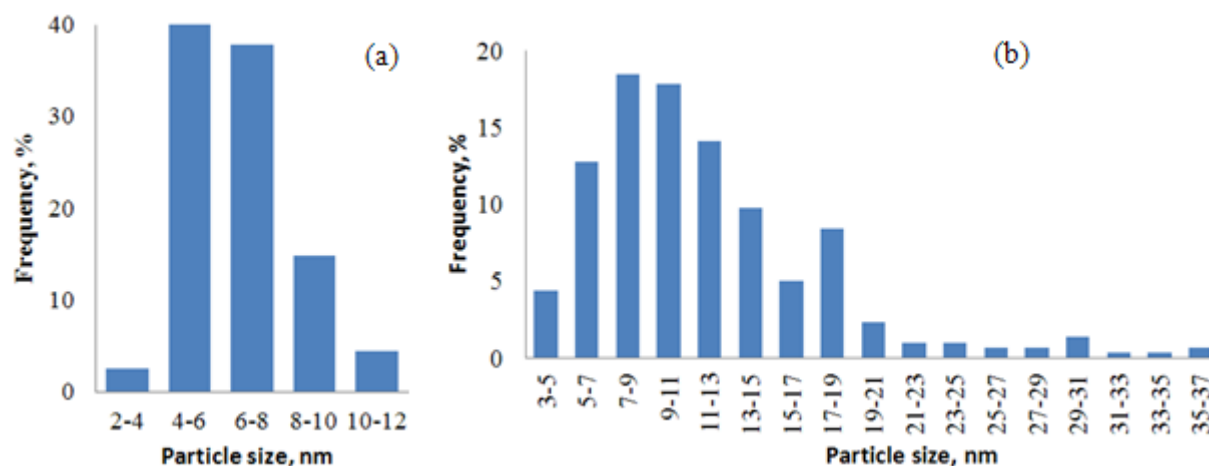


Figure 2. Particle size distribution histograms of FeCo nanoparticles obtained at: **(a)** 600 °C; **(b)** 700 °C.

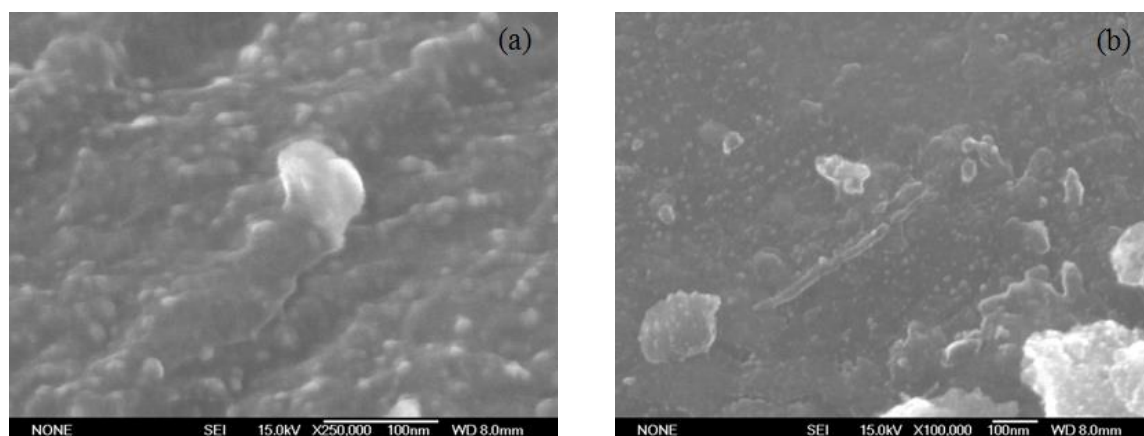


Figure 3. SEM micrographs of IR-PVA/Fe-Co samples obtained at: **(a)** 600 °C; **(b)** 700 °C.

scale along the intensity axis. X-ray phase analysis showed that FeCo nanoparticles with body-centered cubic 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 each other.

X-ray diffraction analysis shows that FeCo reflection peaks at the range from 600 to 700 °C have a symmetrical shape and are not displaced relative to each other, whereas at 500 °C the diffraction maximum is shifted towards larger angles. This fact indicates FeCo solid solution formation with unequal ratio of components and with a smaller lattice constant at 500 °C. The observed iron oxide peaks at 500 °C indicate that FeCo solid solution formation is not completed.

Figure 5 represents the reflection lines corresponding to the maximum intensity peak of FeCo solid solution, the crystal plane of (110). The diffraction maximum corresponding to graphite on the diffraction pattern of 600 °C sample appears (Figure 4). The crystalline phase amount of carbon increases as temperature increases. At the same time there are structural changes in FeCo solid solution detected by the narrowing of the intensity peaks (Figure 5).

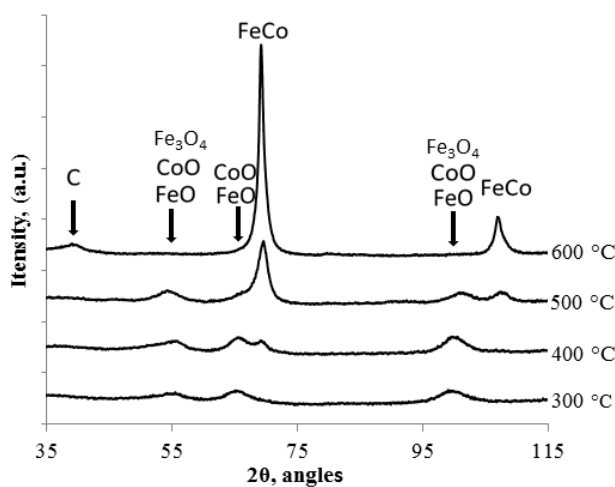


Figure 4. X-ray diffraction patterns of IR-PVA/Fe-Co samples.

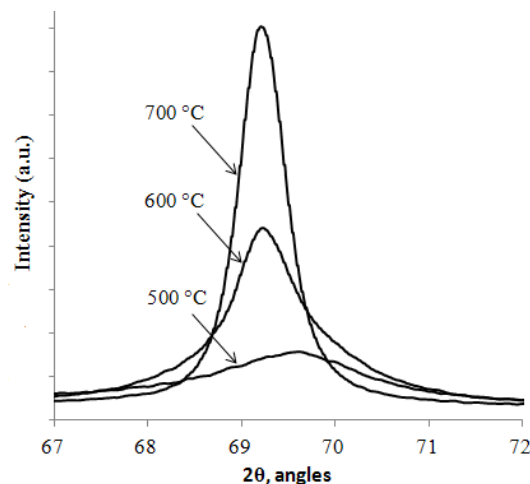


Figure 5. X-ray diffraction patterns of IR-PVA/Fe-Co samples obtained at $T = 500 - 700$ °C, the crystal plane of (110).

Table 1 shows the calculation results of the structural characteristics of FeCo phase according to X-ray analysis. The lattice constant a in the material is smaller than in a bulk analogue due to specific features of nanoscale metal condition.

Figure 6 shows the estimated lattice constant dependence on Fe content assisting in quantitative assessment of the composition of FeCo forming phases. The starting point of the expected dependence for nanoscale material was determined by extrapolation of lattice period values of FeCo solid solution with different compositions synthesized via the method described above. It is expected that the further graph course is similar to bulk material. The lattice period values of iron and FeCo solid solution for bulk samples were taken from reference data [8].

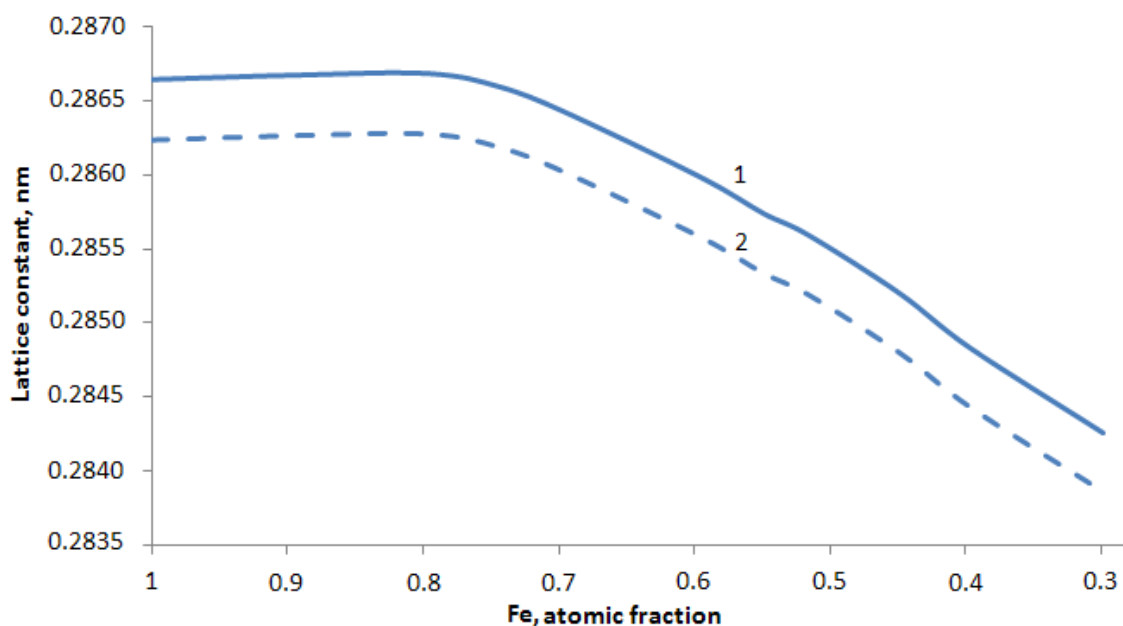


Figure 6. The curves of FeCo lattice constant dependence on iron content; 1 – bulk material, 2 – nanosize material.

Table 1 also represents the results of compositions determination of FeCo solid solutions by lattice periods experimentally obtained. In the sample synthesized at 500 °C FeCo composition is 30 : 70 due to an incomplete reduction of iron oxide.

Figure 7 shows the calculation result of the coherent scattering region (CSR) size distribution by the method of Selivanov-Smyslov [9]. The sample obtained at 600 °C has the most narrow distribution and smaller size of the CSR.

According to data of Table 1 particles consist of a single crystallite in the sample synthesized at 600 °C. The average crystallite size larger than the average particles size in the sample annealed at 700 °C. This can be explained by the locality of the TEM method, while X-ray analysis is an integral.

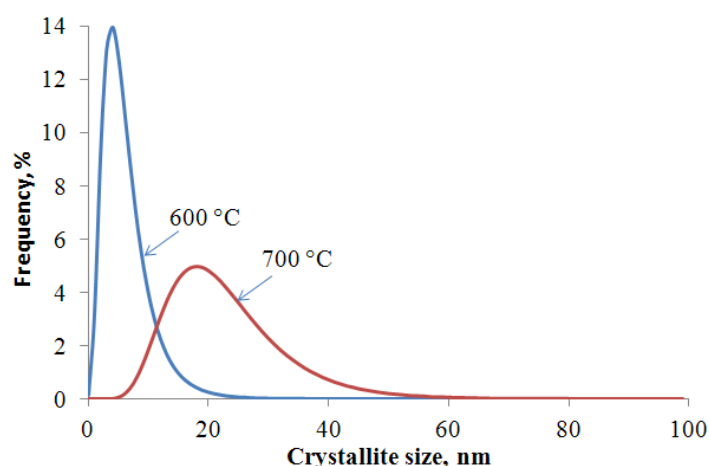


Figure 7. Crystallite size distribution.

Table 1. Dimensional and structural characteristics of FeCo phase

T, °C	<i>a</i> , nm	<i>D_{el}</i> , nm	<i>D_{CSR}</i> , nm	Fe : Co in mass percent
500	0.2838	-	-	30 : 70
600	0.2852	6.(6)	7	50 : 50
700	0.2852	12	23	50 : 50

It is known that the metal-carbon nanosystems obtained by the IR-annealing of polymer materials, exhibit a high catalytic activity in Fischer-Tropsch synthesis [10].

The catalytic activity study was conducted for two samples obtained at 600 and 700 °C. Table 2 shows the main indicators of the Fischer-Tropsch synthesis in the presence of the sample IR-PVA/FeCo (600 °C). The CO conversion reaches values close to 100 %. The yield of liquid hydrocarbons C₅₊ is 92 g/m³ while selectivity was relatively low – 35 %. The thermodynamic yield of the group [–CH₂–] is 208.5 g/m³ conceding a synthesis gas [11].

Table 2. The main indicators of the Fischer-Tropsch synthesis in the presence of catalyst IR-PVA/Fe-Co (600 °C)

Synthesis temperature, °C	CO conversion K _{CO} , %	Yield of liquid hydrocarbons C ₅₊ , g/m ³	Productivity, g/kg FeCo h	Selectivity for liquid hydrocarbons C ₅₊ , %
220	2.8	8.1	218	100.0
280	12.1	16.9	456	52.2
320	33.8	32.0	862	35.3
340	96.0	92.4	2488	35.7
360	98.7	50.4	1358	18.9

Increasing of the catalytic indicators during synthesis in the range of 220 – 300 °C are observed. In the range of 320 to 360 °C, the synthesis indicators reach their maximum values due to the optimum performance of the catalyst. Above 380 °C a rapid decrease of the synthesis indicators is observed that may be associated with the system deactivation, i.e. agglomeration of active phase or matrix destruction. The selectivity value of a liquid product is not high due to intensive secondary processes: methane generation, water-gas reaction).

Table 3 represents the main indicators of the Fischer-Tropsch synthesis in the presence of the sample IR-PVA/FeCo (700 °C). The CO conversion value is 90 - 95 % but the yield of liquid hydrocarbons, selectivity and productivity are lower compared with the previous sample.

Table 3. The main indicators of the Fischer-Tropsch synthesis in the presence of catalyst IR-PVA/Fe-Co (700 °C)

Synthesis temperature, °C	CO conversion K_{CO} , %	Yield of liquid hydrocarbons C_{5+} , g/m ³	Productivity, g/kg FeCo h	Selectivity for liquid hydrocarbons C_{5+} , %
220	4.7	10.1	221	78.7
280	10.0	9.4	206	34.3
320	29.7	32.6	716	39.8
340	91.6	74.9	1645	30.0
360	94.7	73.8	1621	28.5

4. Conclusions

The obtained research results show that FeCo nanoparticles with body-centered cubic structure start forming at 400 °C. The metallic phase of samples synthesized at 600 and 700 °C consist of FeCo solid solution only. Nanoparticles have spherical form, the mean size is 7 – 12 nm.

Catalytic tests in Fischer-Tropsch synthesis revealed activity of investigated samples (conversion of CO reached 95 – 100 %). The yield of synthetic hydrocarbons in the presence of nanosystems obtained at 600 and 700 °C was 92 and 75 g/m³, respectively, while selectivity was relatively low (30 – 35 %).

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