STUDY OF Fe-MgO CATALYST STRUCTURAL TRANSFORMATIONS IN THE PROCESS OF PYROLYTIC SYNTHESIS OF CARBON NANOMATERIALS

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Introduction

There are a few main methods of carbon nanotube and nanofiber synthesis. The most commonly used amongst them are sublimation of graphite with subsequent desublimation and pyrolysis of hydrocarbons. The pyrolysis does not demand so high temperatures as needed for graphite sublimation, is not connected with high level of energy consumption, and can be realized using cheap raw materials in standard chemical equipment. Relatively low synthesis temperature predetermines moderate level of nontubular forms of carbon admixture concentration: in the course of nanofiber synthesis this level can be lowered to 1 – 3% (during electric arc synthesis it is equal up to 50 – 60%) [1].

In all cases the carbon nanomaterial is formed in the presence of catalysts – Fe, Co, Ni or alloys of these metals [2].

One of the features of the catalysts for production of carbon nanofibers and especially nanotubes consists in a big role of catalyst particle size besides the catalyst chemical composition. The size can not be assigned in advance, and only the change of synthesis method or synthesis condition allows to produce the most active particles. Chemical composition of the catalyst can be changed during pyrolysis.

The aim of our study is to investigate the chemical composition of the catalyst Fe-MgO and to monitor structural changes of the catalyst during the pyrolysis of methane.

Results and discussion

Pyrolitic synthesis was carried out on gravimetric installation at the temperature 900^{0}C. The catalytic mixture Fe and Mg with mutual ratio 20:80 was prepared from homogeneous Fe(NO3) x $6H_2O$ and $Mg(NO_3)$ x $6H_2O$ mix with a citric acid and placed on 15 mines in the furnace heated up to temperature 600 ^{0}C. The rests of the catalyst after pyrolysis were washed in hydrochloric acid. Structural researches of the catalyst samples before and after synthesis, and also the washed product were carried out by means of X-ray diffraction and Mossbauer spectroscopy (fig.1, 2). Besides the control of pyrolysis products morphology was performed by means of electron microscopy.

It was found out, that the initial catalyst represents a high dispersed mixture of two compounds: $MgFe_2O4_4$ and MgO. After pyrolytic synthesis realization at the temperature 900 ^{0}C, the catalyst with carbon nanostructures formed on it, represents much more complex mix of connections.

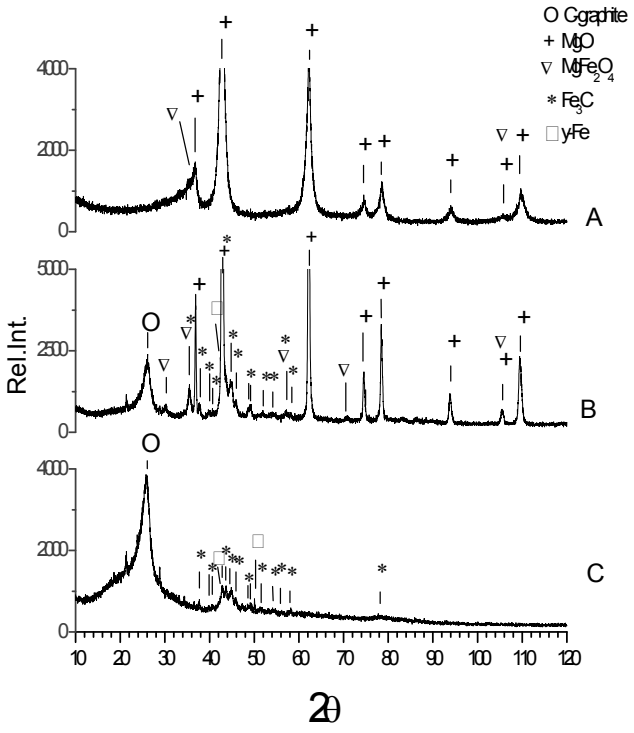

Fig 1. X-ray spectra of samples: A - Initial catalyst, B - Catalyst with formed on it carbon nanostructures, C - washed carbon nanostructures

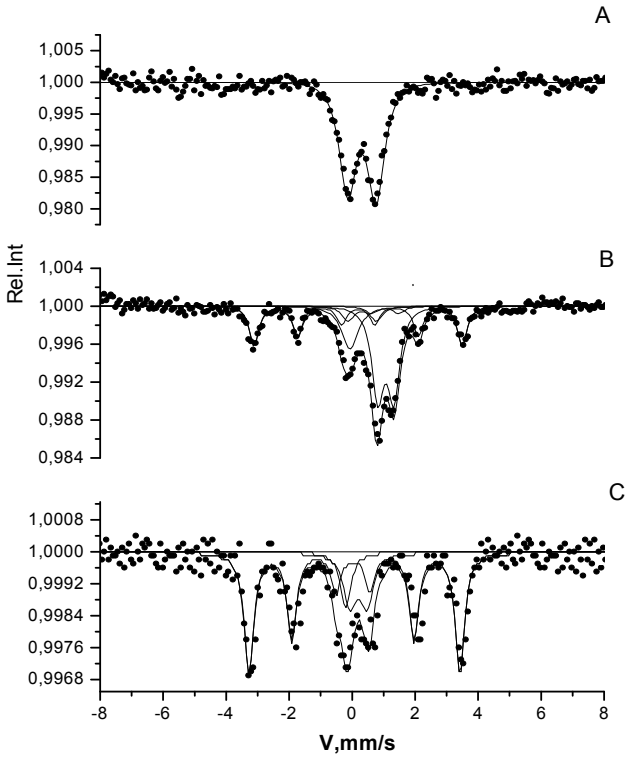

Fig 2. Mossbouer spectra of samples:
A - Initial catalyst,
B - Catalyst with formed on it carbon nanostructures,
C - washed carbon nanostructures

There is a plenty of chemical transformations in the catalyst during the synthesis. Besides carbon nanofibres formation, we observed ions Fe implantation in the lattice of MgO, formation of Fe_3C, γ-Fe, and also iron - carbon compound which we have defined as an iron - graphite complex [3-4].

Measured temperature dependence of Mossbauer spectra in the temperature range 80-300K allowed us to estimate the average size of catalyst active particles. The revealed steady superparamanetic state of the catalyst particles in that temperature range testifies that the size of particles does not exceed 30 nm. The component of Fe-Mg-graphite complex is observed in washed carbon nanostructure spectrum. This complex is a nucleation center of carbon nanotubes formation.

Conclusions

The structure of metane pyrolysis catalyst and its changes was investigated during pyrolysis.

References

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