MASS-SPECTROMETRIC INVESTIGATION OF THE GASES EVOLVED IN HEATING C_{60} FULLERITE DOPED WITH METHANE

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Introduction

Recently it has been found that nanostructured single wall carbon may be used as medium for methane storage [1]. Capacity by methane demonstrated by this material is160 cm^3/cm^3 at 3.5 MPa and 30° C what exceeds the known requirement of Energy Department, USA that (150 cm^3/cm^3). The spacing (pores) among convex surface of graphene sheets, flakes or closed fullerene-like formations plays an important part in sorption capacity of such materials.

We have developed the method that allows the introduction of small molecules into the fullerite pores in its precipitating from the solution at low temperature [2]. In this work we describe the first experiments with the fullerite contained a low amount of methane, about 1 cm^3/cm^3. Note that the sample with this amount of methane was prepared at 23° C and only 100 kPa. Surprisingly, methane has been found to be kept in the fullerite material until sublimation of the latter begins. As known, the sublimation proceeds at the considerable rate at the temperatures above 500° C.

Experimental

The experiment with the fullerite precipitation from the solution has been performed as follows. The fullerite solution in 1,2-dichloro-benzene (DCB) (10 mg/ml) was saturated with methane by bubbling for several hours. Then isopropyl alcohol (IPA) was added into the solution. The IPA volume was about 5 times greater than that of the initial solution. Preliminary IPA was also saturated with methane. The salting out process was continued until the solution became light. The formed suspension was filtered. The fullerite powder collected from the filter was dried in air for 5-10 hours. The methane concentration was determined by the volumetric method after heating the sample at high temperature (550 °C) and condensing higher hydrocarbons.

The structure of the formed precipitates was determined based on analysis of IR spectra and X-ray diffraction patterns. Analysis of compositions of the gases formed in heating the precipitates studied was performed using a mass spectrometer. Methane is not practically conden-sed at the temperature of liquid nitrogen and low pressure. Therefore the gas analyzed and comprised a considerable amount of IPA was passed through a nitrogen trap. This has simplified interpretation of the taken spectra.

Results and discussion

The produced samples were brown powders. The microscopic studies have shown that powders comprises rather large (up to several millimeters) various particles with rough edges, coarse layered surface and have no specular planes characteristic of monocrystals. In the IR spectrum of the sample studied, besides four absorption bands characteristic of fullerite, there are also bands that may be assigned to IPA and DCB. The absorption bands that might be attributed to methane present in the sample have not been found. This is conditioned by a low concentration of methane. The *fcc* lattice parameter (a_o) for the sample studied is 14.22±0.01 Å (for the sample produced by sublimation a_o = 14.16 ± 0.01 Å).

Fig.1 shows mass spectra for the gas evolved in heating the sample. At heating temperatures 20-70° C the most intensive peak in the spectrum is that with m/z =28. This peak may be assigned to $[N_2]^+$ or $[CO]^+$ ions. However, the larger contribution to intensity of this peak should be attributed to $[N_2]^+$ ions as the peak with m/z= 14 is in the spectrum and the peak with m/z = 12 is practically absent in it. The spectrum has no peaks that might be assigned to IPA and DCB. Obviously, this is associated with the fact that these molecules are condensed in a nitrogen trap.

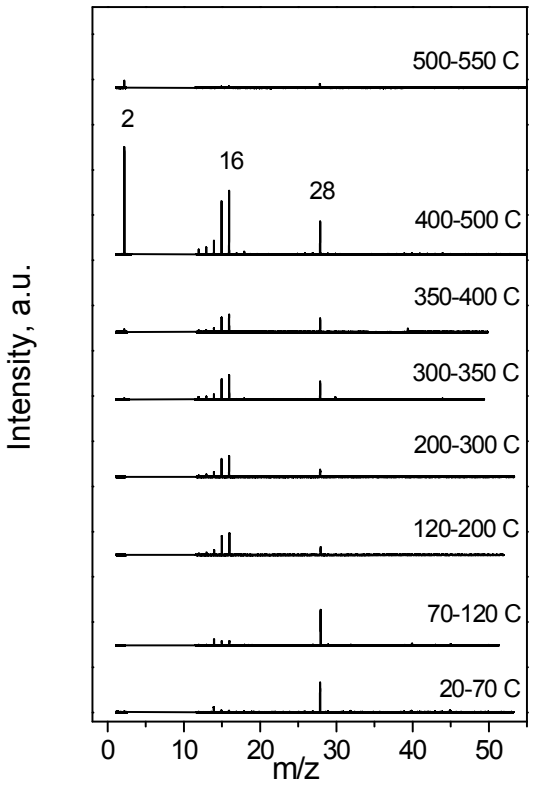

Fig.1. Mass spectra of the gas evolved from the sample studied. After being cooled in a nitrogen trap, the gas was introduced into the ionization camera of a mass spectrometer.

In the region of m/z = 16 the mass spectrum shows two peaks with m/z = 15.995 and 16.031. According to the known data on exact values of atomic mass (see for example [3]), the peak with lower mass is assigned to the $[O]^+$ ion, and the peak with higher mass and intensity is assigned to the $[CH_4]^+$ ion. At the next stage of heating (70-120 C) the relative intensity of the peak determined by $[O]^+$ ions decreases further. Starting with the temperature range 120-200° C and up to 350-400° C intensity of the peak with m/z = 16 becomes the most prominent in the spectrum. Moreover, the intensity ratio of the peaks 16:15:14:13 proves to be practically similar to that in the spectrum for pure methane. In the range of 400-500° C we observe the highest concentration of the gases that are not condensed at the temperature of liquid nitrogen. In this case the peak with m/z = 2 shows the highest intensity. At the temperature above 500 °C, when the fullerene sublimation proceeds with the considerable rate (it is seen when the brown film appears on the cold part of a quartz ampoule and then this film is becoming darker), the content of hydrogen and methane molecules in the gas phase drastically drops.

Conclusions

Mass spectrometry has shown that in the range of temperatures from room to 550 °C methane evolves from the fullerite intercalated with methane during salting out. As this takes place, the highest pressure of methane over fullerite is attained in the temperature range of 400-500 °C when sublimation of fullerene molecules proceeds at the considerable rate. However, only to 300°C can we advocate uniquely that the methane trapped during the fullerene lattice formation evolves. At higher temperatures the chemical transformations which nature has not been understood yet begin in the fullerite studied. It has been found that molecular hydrogen is present over the sample in the gas phase at 400 °C and higher temperatures.

The work has been done under financial support of Russian fund for fundamental research (project No 03-03-32796) and INTAS (03-51-3779).

References

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