Interaction in fullerene—ammonia system at 423—773 K

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The interaction of C_{60} fullerite and C_{60}—NH_4Cl mixture (8 wt. % of NH_4Cl, promoter of reaction) with ammonia was investigated at a starting NH_3 pressure of 0.6—0.7 MPa in the temperature range 423—773 K. Raising the temperature to 723 K is accompanied by hydrogenation and nitrogenation of the C_{60} matrix. Treatment of fullerite with ammonia at 773 K is followed by the decomposition of the fullerene framework and formation of X-ray amorphous product. The physico-chemical properties of hydride-nitride phases formed during the interaction were investigated.

Key words: fullerene, ammonia, ammonium chloride, hydronitrogenation, hydride-nitride phase, X-ray phase analysis, spectroscopy.

Recently, chemistry of fullerenes and carbon nanotubes has been developing rapidly. Considerable attention is paid to functionalization of such systems;[1,2] this is thought to be a route to novel carbon materials with useful properties.

For instance, it was found that certain types of single-wall and multiwall carbon nanotubes are characterized by high hydrogen sorption capacity (5—10 wt. %).[1—3] However, usually both ends of a nanotube are capped with fullerene hemispheres,[4] which creates severe obstacles to absorption of hydrogen inside the nanotubes. Selective opening of the nanotube ends, *i.e.*, breakdown of fullerene hemispheres, is attained by heating in CO_2[5] or in oxygen,[6] and by oxidation[7] in the presence of $KMnO_4$, OsO_4, and RuO_4. Nanotube opening techniques also include acid etching followed by *in vacuo* heat treatment, which results in the formation of carboxyl and quinone groups at the nanotube ends (IR spectroscopy data). As the temperature raises to 1073 K, these functional groups decompose with liberation of CO, CO_2, CH_4, and H_2. Refluxing of nanotubes in nitric acid provides a means of selective breakdown of up to 80% pentagons in the fullerene structure.[8] Breakdown of groups that block defects on the outer nanotube walls was also established; this creates additional "windows" for gas absorption into nanotubes.[9]

In this work we studied the interaction of fullerite with ammonia at 423—773 K and determined the temperature ranges corresponding to hydronitrogenation of fullerene and breakdown of the fullerene framework. The results obtained can found application in studies of nanotube end opening in ammonia atmosphere.

Experimental

Starting reactants. Experiments were carried out using crystalline fullerite C_{60} (99.8% purity, specific area of 1 $m^2 g^{-1}$). According to X-ray phase analysis data, this is a single-phase material with a face-centered cubic lattice. The lattice constant, *a*, equals 14.16 Å, which is in good agreement with the published data.[10] Fullerene C_{60} or a C_{60}—NH_4Cl mixture (8 wt. % of NH_4Cl) was preliminarily stirred in an agate mortar in argon atmosphere (specific areas of the powders obtained were 4 or 1.4 $m^2 g^{-1}$, respectively). Ammonium chloride ("chemically pure" grade) was dried by evacuation at 423 K for 9 h. Ammonia dried with metallic sodium was of 99.99% purity.

Experimental procedure. The interaction of C_{60} or C_{60}—NH_4Cl mixture with ammonia (NH_4Cl acted as promoter of reaction) was carried out at an initial ammonia pressure of 0.6—0.7 MPa in the temperature range 423—773 K in a laboratory high-pressure setup (volume 60 mL). A preset amount of fullerite or mixture (0.3—0.4 g) was placed in a stainless steel container, loaded in an autoclave, evacuated to a residual pressure of ~1 Pa at ~293 K for 30 min, NH_3 was supplied, and then the system was kept at the same temperature for 30 min. Then, the reactor was heated to a preset temperature, kept at this temperature for 3 h, cooled to 293 K, and heated again. Since the process under study is accompanied by an increase in the pressure in the system due to the decomposition of NH_3 and NH_4Cl involving liberation of gaseous products, the process was conducted until a constant pressure. After carrying out the necessary number of the heating—cooling cycles, the gas phase was removed to the buffer vessel, and the reaction products were unloaded in inert atmosphere and analyzed.

In order to remove NH_4Cl and other possible chlorine-containing admixtures, the nitrogenation products were washed using two procedures. One of them involved the addition of absolute EtOH (10 mL) to a weighted sample (~0.1 g) followed by

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stirring the reaction mass at room temperature for 3 h. Usually, the procedure was performed three times. The second method involved evacuation of the mixture of products until a pressure of 10^{-3} Torr at 623 K for 1 h. The elemental and X-ray phase analyses of the residues thus obtained confirmed almost complete absence of ammonium chloride.

Analytical methods. IR absorption spectra were recorded with Specord IR-75 and Perkin—Elmer Spectrum BX spectrometers. Samples to be studied were prepared in the form of KBr pellets (2 mg of the substance under study and 300 mg of KBr).

Mass spectra of gases evolved in the autoclave during the synthesis were studied with the MI-1201V spectrometer (electron impact, electron energy of 70 eV). Measurements were carried out in the m/z range from 4 to 90. Positive ions were detected.

X-Ray diffraction studies were performed on an automated setup comprising a DRON ADP-1 diffractometer (Cu-Kα radiation) connected to a computer. The error in determination of interplanar distances was at most 0.005 Å.

The specific areas of the specimens were calculated by the BET method based on the low-temperature adsorption of krypton after *in vacuo* ($1.3 \cdot 10^{-3}$ Pa) removal of volatile products from the solid phase at 573 K for 15 h. The error was ±10%.

The amount of hydrogen in reaction products was determined using a conventional technique involving combustion of the specimens in oxygen stream. Nitrogen was analyzed according to Kjeldahl and chlorine was analyzed turbidimetrically.

Results and Discussion

The reaction conditions and the results of our study of fullerite—ammonia interaction are listed in Table 1.

According to the data of elemental and X-ray phase analyses, almost no interaction occurs at 423 K (specimen **1**).

On heating to 723 K (specimens **2—6** and **8—13**) fullerene remains relatively stable in ammonia atmosphere irrespective of the presence or absence of NH_4Cl and retains its crystal structure. But as the temperature increases, the content of hydrogen (≤2 wt. %) and nitrogen (≤1 wt. %) gradually increases and hydride-nitride phases with the composition $C_{60}H_xN_y$ are formed in the fullerite structure. In the absence of NH_4Cl the composition with the maximum content of nitrogen, $C_{60}H_4N_{0.4}$ (a = 14.720 Å), was obtained at 723 K (specimen **6**). The presence of ammonium chloride (specimens **8—13**) favors the absorption of hydrogen and nitrogen into the fullerite matrix at 473 K. The phase with the maximum content of nitrogen attained at 723 K (specimen **13**) has the composition $C_{60}H_8N_{0.6}$. According to X-ray phase analysis data, raising the temperature generally causes only minor variations of the lattice constant between 14.15 and 14.23 Å.

Retention of the fullerene cage on heating in ammonia to 723 K was also confirmed by the results of mass-spectrometric analysis. Namely, the gas phase coexisting with the solid phase at these temperatures contains only the ammonia, N_2 and H_2 molecules (sampling and mass-spectrometric analysis were carried out at room temperature).

The IR spectra of the specimens treated with ammonia at 723 K and at lower temperatures exhibit the absorption bands corresponding to fullerene, hydrofullerite (2900 cm^{-1}), and NH_4Cl (for specimens **8—13**).

Ammonium chloride can be removed with ease by washing the specimens with ethanol. Taking specimen **9** as an example, it was established that after this procedure

Table 1. Reaction conditions and results of investigation of fullerite—ammonia interaction

Specimen	Synthesis conditions			Interaction products		
	T/K	τ/h	$P(NH_3)$ /MPa	Composition	Lattice constant, a/Å	Specific area/$m^2 g^{-1}$
1	423	34	0.67	C_{60}	14.180	1.2
2	523	28	0.72	$C_{60}H_8N_{0.2}$	14.190	0.9
3	573	34	0.70	$C_{60}H_0N_{0.2}$	14.167	2.2
4	623	36	0.65	$C_{60}H_2N_{0.3}$	14.189	0.7
5	673	32	0.65	$C_{60}H_2N_{0.3}$	14.202	0.6
6	723	32	0.65	$C_{60}H_4N_{0.4}$	14.720	0.7
7	773	32	0.70		—[a]	4.2
8[b]	473	30	0.72	$C_{60}H_8N_{0.6}$	14.203	12.4
9[b]	523	32	0.64	$C_{60}H_8N_{0.4}$	14.165	7.9
10[b]	573	32	0.60	$C_{60}H_6N_{0.4}$	14.152	9.8
11[b]	623	30	0.68	$C_{60}H_2N_{0.8}$	14.189	3.2
12[b]	673	32	0.64	$C_{60}H_4N_{0.6}$	14.226	4.1
13[b]	723	30	0.68	$C_{60}H_8N_{0.6}$	14.223	2.3
14[b]	773	30	0.68		—[a]	26.7

[a] X-ray amorphous specimen.

[b] Synthesized in the presence of NH_4Cl (8 wt. %).

the content of chlorine decreased from 4.1 to 0.2 wt. %, the content of nitrogen decreased from 2.8 to 0.9 wt. %, and the content of hydrogen decreased from 1.4 to 1.1 wt. %. NH_4Cl can also be efficiently removed from the hydronitrogenation products by evacuating the specimens for 1 h at 623 K (for instance, the content of chlorine in specimen **12** decreased from 1.6 to 0.1 wt. %).

Irrespective of the presence of NH_4Cl in the starting mixture, hydronitrogenation of fullerite at 773 K leads to destruction of the fullerene framework and formation of an X-ray amorphous product having the composition $C_{60}H_{10}$ and containing no nitrogen (according to elelmental analysis data).

Experiments carried out at 723 K in order to elucidate the effect of cycling on hydronitrogenation showed that the crystal lattice of fullerite is expanded after two heating—cooling cycles (a = 14.192 Å). The lattice constant a is equal to 14.396 Å after seven and to 14.720 Å after eighteen heating—cooling cycles.

Our experiments with specimen **5** showed that treatment with ammonia does not reduce the hydrogen sorption capacity of fullerene. The specimen was degassed *in vacuo* at 523 or 623 K for 1 h and then treated with high-purity hydrogen released from a $LaNi_5$-based hydrogen accumulator at a pressure of 2 MPa and at 673 K or 723 K. Hydrogenation products were compounds of compositions $C_{60}H_{24}N_{0.15}$ and $C_{60}H_{30}N_{0.1}$ containing 3.2 and 4.0 wt. % of hydrogen, respectively.

Crystalline products of hydronitrogenation carried out in the presence of ammonium chloride are characterized by the specific areas of up to 12.4 $m^2 g^{-1}$ (*cf.* 26.7 $m^2 g^{-1}$ for the X-ray amorphous product).

We believe that the breakdown of the fullerene framework in ammonia atmosphere at T = 773 K can be used for opening the ends of nanotubes capped with fullerene hemispheres. Comprehensive experimental check of this assumption will be a part of the studies on the behavior of the multiwall and single-wall nanotubes in ammonia atmosphere. The results of investigations of the gas sorption properties suggest the possibility of using fullerite as a "hydrogen pump" at $T \leq 723$ K.

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