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IRON IN ENDOMETALLOFULLERENES

We study the experimental and theoretical works concerned with the description of state-of-the-art methods for the preparation of iron-containing endohedral metallofullerenes (EMF), as well as works, which dispute such results due to the extremely low efficiency of the used methods. We discuss the features of traditional methods for the fabrication of endometallofullerenes, their advantages and disadvantages, and indicate the areas of possible application of the synthesis products. As shown, the EMF is obtained mainly by two methods, namely, arc discharge (plasma) and synthesis using ablation and implantation methods. Despite a very small number of works on iron endometallofullerenes, the group of authors achieved some progress in their analysis. Thus, the fact of obtaining the Fe-containing endometallofullerenes with their isolation from a mixture of synthesis products is proved. In addition, the influence of the magnetic state of metal atoms on the stability of endohedral fullerenes is predicted, a relationship between the EMF output and the plasma tem-

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perature as well as the chemical nature of the precursor of Fe atoms are established. Particularly, as found, with an increase of the group number in the periodic table, in which the metal is located, the EMF yield decreases exponentially. We conclude that, due to the magnetic properties of EMF, they are prospective materials in the field of clinical diagnostics (*e.g.*, as a contrast agents in the magnetic resonance imaging) and medicine (for magnetically controlled delivery of drugs directly to a diseased organ).

Keywords: endofullerene, endometallofullerene, iron-containing endofullerene, magnetic state, ablation, implantation, arc discharge, synthesis, precursor.

1. Introduction

The problem of hydrogen storage is relevant today [1–5]. It is also possible that, in the future, the system ‘fullerite–metal–hydrogen’ will compete with modern advanced means of hydrogen accumulation as the cleanest source of energy [6–8].

Currently, the synthesis of carbon nanotubes [9–11] and other carbon nanostructures [12] is carried out by various methods: laser action on metal–graphite electrodes, electric arc evaporation of graphite in the gas phase [13–16] and in the liquid medium in the presence of catalysts [17], catalytic pyrolysis of hydrocarbon structures [18] and others.

The method of electric arc evaporation in an inert gas medium is relatively common and quite effective because it allows obtaining both soluble [19–23] and insoluble nanotubes. Today, a variety of carbon nanomaterials is actively used in the creation of new composites [24–30].

Fullerene molecules are capable of encapsulating atoms of different elements and even small molecules, including iron atoms. The physical properties of endometallofullerenes formed by various elements are determined by the structural features of the electron shells, as well as by the charge and mass of the nuclei of metal atoms enclosed in the fullerene shell, *i.e.*, physical properties of encapsulated atoms.

The study of the influence of the physical properties of metal atoms on the formation of a new class of materials, namely, different endometallofullerenes, is one of the important tasks of modern science. Using atoms of different metals in the synthesis of endometallofullerenes (*i.e.*, changing the physical properties of the atom enclosed in a fullerene), we can synthesize the endometallofullerene molecules with different physical properties.

One of the important problems in the physics of metals and the chemistry of fullerenes is the introduction of metal atoms into a hollow fullerene molecule (Fig. 1). Encapsulation of a metal atom cannot be achieved by simple chemical interaction of metal atoms with an already formed fullerene molecule. The introduction of a metal atom into the interior of a hollow fullerene sphere is possible only during the forma-

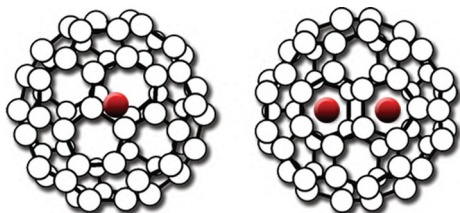


Fig. 1. Endohedral fullerenes containing 1 and 2 metal atoms in the volume [31] (open and solid circles denote C and metal atoms, respectively)

tion (synthesis) of the endofullerene molecule itself. These molecules are known as the endohedral fullerenes (endofullerenes).

Iron endofullerenes as a prospective novel material for scientific and applied purposes. Here, first of all, we should mention: the obtained new class of superhard materials based on fullerenes; superconducting compounds of fullerenes with atoms of alkali and alkaline earth metals, which have been known since 1991 [32–37]; thin films and fullerene solutions with nonlinear optical characteristics [38–41]; various chemical compounds and polymers based on fullerenes with unique physicochemical and mechanical properties [39].

This review scopes on the experimental works on obtaining iron endofullerenes and the theoretical works questioning such results are considered.

An interest in the metal endofullerenes (wherein the metal is Fe, Co, Ni, and their alloys) is determined by their magnetic properties due to iron atoms and the possibility of their application as contrast agents in magnetic resonance imaging (MRI), which can find promising applications in clinical diagnostics and for magnetically controlled drug delivery to a diseased organ.

As shown, obtaining metal endofullerenes of low-active *d*-metals and, particularly, Fe, has proved to be rather ineffective despite numerous attempts by many researchers. Iron endofullerenes are synthesized mainly by two traditional methods: either in an arc discharge or using a laser.

It was theoretically established that in all endohedral metal fullerenes the stabilizing effect of Sc is markedly stronger than that of Ti and significantly stronger than that of Fe. The effect of the magnetic state of metal atoms on the stability of endohedral fullerenes was predicted.

The cavity in a fullerene C₆₀ with a diameter of 7 Å is large enough to be a ‘host’ and accept atoms of various elements and even small molecules inside [42], including iron atoms. Among the first attempts to obtain fullerene molecules with metal atoms inside was the work of Yan Chai and Richard E. Smalley [43] in 1991. They synthesized fullerenes with a lanthanum atom trapped inside the framework, La@C₆₀, La@C₇₀ and La@C₈₂ (the most stable of them), by laser evaporation of a graphite rod filled with a mixture of graphite powder and lanthanum oxide in an argon stream at 1200 °C.

As known, the main methods of obtaining metal endofullerenes (MEF) are [44]: (i) laser ablation (laser-furnace synthesis), (ii) dc arc-discharge synthesis, and (iii) ion implantation technique. The book ‘Endohedral Metallofullerenes. Fullerenes with Metal Inside’ (2015) [44] can be a handbook for any researcher in the field of metal endofullerenes. A comprehensive review of the current state of endohedral metal fullerenes, from preparation to functionalization, reactivity, and applications, is provided in the book. It reviews synthesis, extraction, separation and purification methods, and provides insight into molecular and crystal structures; various categories of encapsulated particle-based endohedral metal fullerenes are discussed, including carbides, nitrides, sulphides, oxides, non-metallic and non-IPR (violating the isolated pentagon rule) endohedral metal fullerenes, followed by scanning tunnelling microscopy and studies of electronic, vibrational, magnetic, and optical methods.

2. Experimental Studies of the Endohedral Iron–Fullerene Complexes

The beginning of the works on the experimental obtaining of endohedral iron–fullerene complexes dates back to the 90th of the last century [34]. Besides being purely scientific, the interest in these compounds, primarily water-soluble, was fuelled by the possibility of using them as contrast agents in MRI [46, 47], as well as for the magnetically-controlled delivery of drugs to a diseased organ [48]. Since mass spectrometry was mainly used for characterization, it is unknown whether the metal atom is inside or outside the spherical hollow fullerene framework [49].

One of the first attempts to obtain iron compounds with fullerenes was performed under the supervision of B.S. Freiser [50, 51], in which exohedral compounds of metal fullerenes with this element were obtained. As known, the aromatic nature of fullerenes with 5- and 6-membered rings and low reduction potentials suggests that they can act as ligands, like cyclopentadienyl or benzene, and form complexes with metal atoms as electron donors. For example, the FeC_{60}^+ exohedral complex was obtained in 1991 in Ref. [50] using the following technique on a Nicolet FTMS-2000 Fourier mass spectrometer:

- Fe^+ was generated by laser evaporation of the Fe target in the external solenoid magnet source;
- then, the Fe^+ particles reacted with alkenes at $1 \cdot 10^{-6}$ Torr to form $\text{Fe}-(\text{C}_n\text{H}_{2n})^+$ ($n = 2-5$);
- after that, these particles were subjected to ligand-exchange reactions with previously obtained C_{60} and C_{70} at 350°C and, as a result, FeC_{60}^+ and FeC_{70}^+ and other particles with lower masses were generated; the complex of FeC_{60}^+ and FeC_{70}^+ particles did not react further with the background alkene.

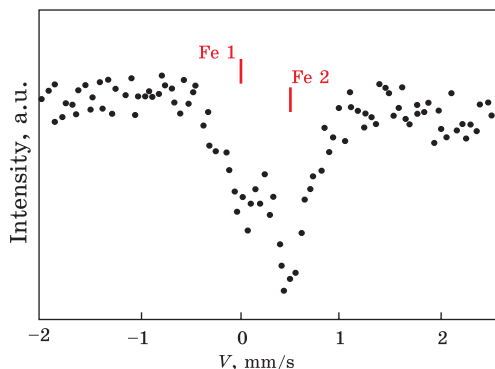


Fig. 2. Mössbauer spectrum of the plasma chemical product synthesis of fullerenes with iron [52]

In Ref. [51], $\text{Ni}(\text{C}_{60})^{2+}$ was obtained in the gas phase in several stages by a similar method, as a result of direct addition of C_{60} to NiC_{60}^{+6} and observed in the Fourier transform mass spectrometer Nicolet FTMS-2000.

Let us note for ourselves that the experimental conditions were not conducive to the penetration of metal ions inside the fullerene molecule: pre-formed fullerene molecules and the low temperature of 350 °C ensured that only exchange reactions took place.

In 1992, T. Pradeep [49] obtained FeC_{60} by electric arc evaporation of graphite in an atmosphere of iron pentacarbonyl $\text{Fe}(\text{CO})_5$. The reaction chamber was evacuated to a vacuum of about 10^{-6} Torr. Helium was then pumped into it to about 50 Torr through a needle valve. $\text{Fe}(\text{CO})_5$ and He were passed at the same rate. The resulting soot was washed with diethyl ether. The residue was treated by Soxlet extraction with toluene for 3 hours. The extract was dried in vacuum at 380 K to remove volatile iron compounds. Mass spectrometry of the synthesis product extract showed peaks with the mass numbers 776, 752, and 728 corresponding to FeC_{66} , FeC_{58} , and FeC_{56} .

G.N. Churilov *et al.* [52] used infrared, ultraviolet spectroscopy, electron paramagnetic resonance, and Mössbauer spectroscopy to identify iron endofullerenes in 1997 (Fig. 2, Table 1). They used a plasma-chemical reactor to synthesize iron-containing fullerene complexes. The operation of this reactor is based on a self-blowing and self-focusing jet of carbon plasma that flows through a conical hole in the outer graphite electrode into a water-cooled copper column (tube). The central electrode was a C-3 rod for spectral analysis with an axial hole filled with carbonyl iron powder (TU 6-09-3000-78). Helium with the flow rate of

Table 1. Mössbauer parameters of the product of the plasma-chemical synthesis of complexes of fullerenes with iron [52] (here, δ is a chemical shift relative to the α -Fe, ε is a quadrupole splitting, Γ is the spectral line width, and S is the share population of the Fe phase)

	δ	ε	Γ	S
Fe 1	-0.15	0	0.37	0.34
Fe 2	0.36	0	0.38	0.66

3–4 l/min was fed into the jet, and the arc was fed with the current with the frequency of 66 kHz and the amplitude of 300 A. Then, soot was poured with a nonpolar solvent. Benzene or toluene were usually used. The solution was filtered and evaporated. The dry residue (fullerene mixture) was studied. The strong covalent bonding, or high local symmetry, and the presence of an additional line in the EPR spectrum of iron-containing fullerene complexes, according to the authors of the paper, prove that the iron atom is located inside the fullerene cell.

In the paper by K. Sueki *et al.* [45], the formation of metal fullerenes has been studied for 23 elements. Experimental evidence was obtained for metallofullerenes with Zr, Hf, and Nb. It was found that the relative yields of metal fullerenes are approximately the same as those of $M@C_{82}$ (M = elements of groups 2 and 3), but exponentially decrease as the group number increases. The yields for Fe and Co, namely group 8 elements, were estimated as less than one hundredth of the yield for $M@C_{82}$ (M = lanthanide).

Special attention should be paid to the works of the group of researchers from Japan (T. Uchida, H. Minezaki *et al.*) [53–59]. They used electron cyclotron resonance (ECR) as an ion source (ECRIS) [53] and endofullerene implantation method [54–56] to obtain endohedral metal fullerenes. The authors developed a technology for the synthesis of $Fe@C_{60}$ iron-endohedral fullerenes by the same ion implantation method by irradiating C_{60} thin films with Fe^+ ions [57–59].

In these works, a thin film of C_{60} was irradiated with a low-energy beam of Fe^+ ions obtained using a deceleration system. The flux energy of iron ions varied from 50 to 250 eV. The dose of this irradiation was controlled from $6.67 \cdot 10^{12}$ to $6.67 \cdot 10^{14}$ ions/cm². The C_{60} thin film irradiated with Fe^+ was analysed by high-performance liquid chromatography and laser desorption/ionization time-of-flight mass spectrometry, confirming the presence of a peak with a mass/charge of 776. Mass/charge 776 corresponds to Fe^+C_{60} . The authors investigated the performance of the inhibition system using a low-energy Fe^+ beam and obtained the maximum intensity of the peak with mass/charge 776 when irradiated with a flux of iron ions with energies and doses of 50 eV and $3.30 \cdot 10^{13}$ ions/cm², respectively. Then, separation of the material with mass 776 was performed using high-performance liquid chromatography. They were able to separate Fe^+C_{60} from a thin film of C_{60} irradiated with iron ions. As a result, they synthesized the Fe^+C_{60} complex as a new material. However, the yield was quite low because only the surfaces of the C_{60} thin films were irradiated with ion beams (*i.e.*, very small amounts of the treated starting material).

Therefore, researchers attempted to synthesize iron-endohedral fullerenes in plasma using the same method of obtaining Fe ions [60]. By this time, it was already possible to obtain $N@C_{60}$ in the ECR plasma

[61, 62]. However, most fullerene molecules were destroyed in plasma and the yield of the product was minimal. High-temperature electrons probably damaged fullerenes and metal endofullerenes. The fact is that the energy required to generate iron plasma is much higher than that required to generate fullerene plasma. Since the conditions for the two plasmas are significantly different, it is currently difficult to create dense mixed plasma. Therefore, the researchers needed to develop a technique that would not damage the metal fullerenes at the higher power of the microwave energy source. They used a gas mixing method to cool the plasma and thereby reduce fullerene dissociation. Based on the results, the method of adding helium and He–Ar, He–Xe gas mixtures to the plasma was effective against fullerene dissociation [60].

Despite our attempts to find confirmation of the obtained results to increase the yield of Fe@C₆₀ in ECR plasma by the group of researchers (T. Uchida, H. Minezaki *et al.*), a positive result could not be found. Summarizing the work of these authors was the article [56]. It reports materials science experiments conducted recently using bio-nanoelectronic cyclotron resonance ion source (ECRIS) at the University of Toyo. They investigated several methods for synthesizing endohedral C₆₀ using ion–ion and ion–molecule collision reactions in ECRIS. It turned out that because of the simplicity of the configuration, a wide range of additional equipment can be installed in the ECRIS setup. Bio-Nano ECRIS is not only suitable for material production testing, but also for technical development testing to improve or understand ECRIS performance.

The work of the team of authors also attract attention, namely, V.T. Lebedev, M.V. Suyasov, A.A. Szhogin, [47], in which electric arc synthesis of 3*d*-metal endofullerenes is carried out in helium medium with graphite electrodes containing an additive of pyrolysis of 3*d*-metal taftalocyanine. This is an unusual precursor in the synthesis of metal endofullerenes. Usually metal oxides are used in this process, for iron–iron pentacarbonyl. Iron phthalocyanine powder was heated at 840 °C for 1.5 hours in a helium flow. A pyrolysis product with Fe content of 30 wt.% was obtained. As can be seen from the text of the invention, the chemical composition of the pyrolysate was not determined. The electric arc evaporation of graphite electrodes containing the pyrolysis additive of 3*d*-metal tephthalocyanine was performed in helium environment (constant current 140 A and helium pressure 380 mm Hg) resulting in the formation of fullerene-containing soot containing empty fullerenes and metal endofullerenes of 3*d*-metals. Then, empty fullerenes and 3*d*-metal endofullerenes were isolated from carbon black in two stages. First, the empty fullerenes were separated by extraction with o-xylene. Then, the 3*d*-metal endofullerenes were isolated by extraction as a complex with the solvent, which was N,N-dimethylformamide with the addition of hydrazine hydrate. The yield of endofullerenes of 3*d*-

metals increased. What was new was that graphite electrodes containing a pyrolysis additive of 3d-metal tephthalocyanine were used in the electric arc evaporation, and the separation of empty fullerenes and 3d-metal endofullerenes was performed in two stages.

It should be noted that in spite of many years of fairly successful synthesis work, the possibility of forming iron fullerenes has been disputed throughout the research in this field, both in theoretical (*e.g.*, [63]) and experimental (*e.g.*, [64]) studies.

For example, the authors of the paper [63] (2016), including the authoritative theoretical researcher A.A. Popov, argue that iron endometal fullerenes (3d-metal group) are not synthesized in the electric arc and plasma due to the fact that the Fe–C bonds formed are weak and exist for a short time, which is not long enough for endofullerene formation.

In 1994, E.M. Brunsman *et al.* [64] obtained endofullerenes of 3d-metals by electric arc evaporation of graphite electrodes filled with a powdery mixture of a metal source: Fe, Ni, Co oxides and graphite in the molar ratio metal/carbon ≈ 0.04 . Magnetic nanocrystallites were extracted from carbon black by the magnetic gradient field method. No iron-endohedral fullerenes were detected in the products. From our point of view, this is possible for two reasons: the theoretically calculated weakness of the Fe–C bonds [63] and the experimentally established exponential decrease in the MEF yield with increasing number of the Mendeleev table group, in which the element is located [45].

3. Formation of the Endohedral Iron–Fullerene Complexes: Theoretical Calculations

In Ref. [65], Chun-Mei Tang *et al.* applied the generalized gradient approximation (GGA) method based on a density functional theory (DFT) to analyse the structural and electronic properties of Fe@C₆₀ and C₅₉Fe for comparison. According to the calculation results, it appeared that among the six possible optimized geometries of Fe@C₆₀, the most favourable endohedral location of the Fe atom is under the centre of the hexagonal ring, that is, Fe@C₆₀-6. The energy gap of Fe@C₆₀-6 was lower than that of C₅₉Fe and C₆₀, indicating a higher chemical reactivity of this complex. The magnetic moment of the Fe atom in Fe@C₆₀-6 was preserved to some extent, although hybridization between the Fe atom and the C atoms of the framework was observed. In Ref. [66], R.E. Estrada-Salas *et al.* also studied the structural and electronic properties of M@C₆₀ (*M* = Mn, Fe, Co, Ni, Cu, or Zn) by another DFT method, namely, BPW91/DNP. Energy structures with minimal energy were calculated for each endohedral metal fullerene. As found, there is hybridization between the 3d-valent orbitals of Mn, Fe, Co, and Ni and the

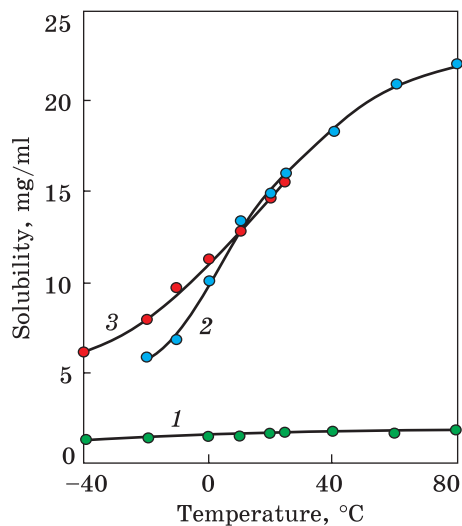
cellular orbitals of C_{60} , which suggests the presence of chemical bonding between the M and C atoms of the fullerene molecule. At the same time, this phenomenon was not observed between the Cu and Zn orbitals and the C_{60} cell orbitals. These results were obtained when the metal atom was preferentially located inside the fullerene framework. The endohedral metal fullerenes $Mn@C_{60}$, $Fe@C_{60}$, $Co@C_{60}$, and $Cu@C_{60}$ possess paramagnetism.

Based on calculations using density functional theory, Guohua Gao *et al.* [67] showed that C_{60} can act as a Faraday chemical cell, into which a metal cluster with high magnetic activity and high chemical reactivity can be encapsulated. As an example, the authors found that C_{60} can encapsulate a Fe_3 cluster, while it is much less likely to encapsulate a Fe_2 cluster. The spin set ($= 9$) of $Fe_3@C_{60}$ is very large and comparable to that (of 11 \AA) a free Fe_3 cluster. Geometrically, the triangular plane of the cluster is perpendicular to the S_6 axis of the fullerene.

M.B. Javan *et al.* [68] (2010) theoretically, by the same generalized gradient approximation (GGA) in density functional theory (DFT) method as in [65], calculated the total energy of a C_{60} nanocage doped with Fe and Co transition metals (TM), endohedral and exohedral, *i.e.*, inside and outside the fullerene. Full geometry optimization near the minimum of the bonding energy curves showed that the most stable position of the Fe atom in the $TM@C_{60}$ system is below the carbon atom and the position of the Co atom is below the middle of the double bond between the carbon atoms. In addition, the most stable position of both TM atoms in the $TM@C_{60}$ systems is above the double bond. The results showed that for all investigated structures Co atom has higher bonding energy than Fe atom. As found, for all complexes, the additional peaks introduced by the $TM-3d$ -, $4s$ -, and $4p$ -states appear in the highest occupied molecular orbital (HOMO) slot and lowest unoccupied molecular orbital (LUMO) slot of the host cluster, which is perfectly reasonable and understandable. The mid-slit states are mainly due to hybridization between the $TM-3d$ -, $4s$ -, and $4p$ -orbitals and the π -orbitals of the framework. Because of the interaction between the TM atom and the fullerene framework, the charge of the $TM-4s$ -orbital decreases to the $TM-3d$ - and $4p$ -orbitals, and the magnetic moment of the included TM atom decreases in all cases. In addition, the Mulliken charge analysis shows that the general charge transfer takes place from the TM atom to the framework.

A relatively recent theoretical work by S.G. Semenov *et al.* [69] again refers to a 'hypothetical endocomplex' $Fe@C_{60}$. It is argued, with references to other authors, that the production of metal fullerene containing a natural iron isotope is limited only by the lack of efficient synthesis methods, rather than by the shortage of feedstock [49, 60, 73, 74]. We should add for ourselves that this production is limited by

Fig. 3. Temperature dependence of the solubility of fullerene C_{70} in toluene (1), xylene (2), and CS_2 (3) [75]



small yields and difficulties in separating the synthesis products from the mixture.

In the work [69], the structural parameters of this complex were determined at the (U) level of PBE0/cc-pVDZ density functional theory (DFT). It was found that the (A1//C3v)-Fe@C₆₀ state characterized by an electron spin square of 3.07 a.u., a free valence of 4.15, a dipole moment of 1.15 D, and a Fe nuclear shift of 172 pm relative to the C₆₀

centre of inertia corresponds to an energy minimum. The Stone–Wales transposition in the quasi-triplet state increases the endocomplex energy by 1.56 and 0.79 eV in the quasi-quintet state. The authors applied the same method in [70] to study the structure of the Fe@C₆₀(OH)₃₀ endocomplex molecule. It was shown that the triplet state of the endocomplex is energetically the lowest among its four states corresponding to different spin sets and positions of the Fe nucleus in the fullerene cavity. This state is characterized by a bond between the iron atom and one of the two benzoidal cycles of the carbon frame, six Fe–C internuclear distances (208 pm) and the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{7.24} 4s^{0.14} p^{0.3}$ for iron with a spin population of 2.36.

In the work of M.V. Ryzhkov *et al.* [71] of the same 2017 theoretical (*ab initio* method Dmol3) calculated the electronic structures of endohedral forms of fullerenes C₂₈, C₄₀, C₆₀ and C₈₀ encapsulating 3d atoms of Sc, Ti and Fe, and in the case of C₈₀ with M₂C₂ carbide clusters (M = Sc, Ti, Fe). For the C₆₀ and C₈₀ frameworks, the authors found the preferred positions of the metal atoms and their carbon clusters near the inner surface of the fullerene shell. We found that, in all endohedral metal fullerenes, the stabilizing effect of Sc is markedly stronger than that of Ti and significantly stronger than that of Fe. The stability of the complexes M@C₆₀ and M₂C₂@C₈₀ with Sc becomes higher than that of the systems with Ti and Fe. The effect of the magnetic state of metal atoms on the stability of endohedral metal fullerenes was predicted.

In Ref. [72], using density functional theory (DFT), the authors (Tianwei *et al.*) first predicted the possibility of using endohedral metal fullerenes M@C₆₀ (M = Na, K, Rb, Cs, Sc, Ti, Mn, Fe) as catalysts for a promising highly efficient hydrogen evolution reaction (HER). The cat-

Table 2. Solubility of C₆₀ fullerene at different temperatures [75]

Solvent	T, K	Solubility		Solvent	T, K	Solubility	
		mg/ml	mole fraction, 10 ⁴			mg/ml	mole fraction, 10 ⁴
<i>n</i> -Hexane	195		0.011	Toluene	253		1.93
	238		0.03		258		2.79
	273		0.07		273		4.79
	283		0.12		278		4.93
	288		0.1		283		3.79
	298		0.09		288		3.93
	318		0.07		295		4.21
	338		0.07		298		4.07
	338.1		1.8		313		3.29
Toluene	298.1		0.8	353		1.57	
	308.1		0.9	383		1.29	
	328.1		1.2	1,2-Dimethylbenzene	253	1.6	
	338.1		1.5		263	2.5	
	233	0.75			273	3.5	
	243	0.96			283	5.0	
	248	1.30			288	6.2	
	253	1.5			293	7.7	
	258	1.9			298	9.3	
	263	2.5			300.5	10.2	
	268	3.2			303	10.3	
	273	4.0			305.5	9.3	
	278	3.9			308	8.4	
	283	3.7			313	7.4	
	293	3.3			323	6.1	
	298	2.9		333	5.3		
	303	2.7		343	4.9		
	313	2.3		353	4.4		
	323	2.2		1,2-Dichlorobenzene	298.1		11.1
	333	1.9			308.1		13.4
	353	1.5			318.1		15.1
	195		0.14		328.1		17.8

alytically active centre in this case is a non-metallic C-atom, and the HER characteristics of $M@C_{60}$ are even better than those of modern Pt and MoS₂ catalysts. The excellent catalytic properties are related to the charge transfer between the metal atom and the C₆₀ framework. Since endohedral metal fullerenes can be easily implemented in the experiment, these results, according to the authors, create a new class of inexpensive and efficient HER catalysts in hydrogen production.

4. Conclusions

Obtaining endofullerenes of low-active *d*-metals, and iron, particularly, has proved to be rather ineffective in spite of numerous attempts of many researchers. Some authors theoretically deny the possibility of Fe-endofullerenes formation at all due to extremely weak bonds between iron atoms and fullerene carbon atoms [63]. Others point to an exponential decrease in the MEF yield with the increase in the number of the periodic table group, in which the metal is located [45].

Nevertheless, Fe-containing endofullerenes are still obtained, just with very small yields and great difficulties in their extraction from the mixture of products (see Fig. 3 and Table 2), because the completeness of endofullerenes extraction from carbon black is not provided (the solubility of fullerenes in toluene does not exceed 2 mg/ml [75]).

Iron-containing endofullerenes are obtained mainly by two traditional methods: in plasma generated by electric arc or using laser (ablation and implantation methods). In contrast to obtaining and studying the properties of MEF substances of other metals, there are significantly fewer works on iron endofullerenes. Let us focus our attention on the obvious dependence of the yield of these MEF on the plasma temperature (primarily in the processes of involving iron atoms in the forming fullerene molecule [60–70]). We can note the presence of gases in the reaction medium that do not form complexes with fullerenes, and the probable dependence on the chemical nature of the precursor of iron atoms. For example, in Ref. [47], iron phthalocyanine pyrolizate was used in electric arc synthesis rather than iron oxides or iron pentacarbonyls.

The interest of researchers in iron MEF is determined by their magnetic properties due to iron atoms and the possibility of their application as contrast agents in MRI [46, 47], which can find promising applications in clinical diagnostics and for magnetically-controlled delivery of drugs to a diseased organ [48–63].

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ФЕРУМ В ЕНДОМЕТАЛОФУЛЛЕРЕНАХ

Вивчаються експериментальні та теоретичні роботи, присвячені опису сучасних методів одержання ферумвмісних ендедральних металофуллеренів (ЕМФ), а також роботи, що ставлять під сумнів подібні результати через вкрай низьку ефективність застосовуваних методик. Розглядаються особливості традиційних методів одержання ендедральних фуллеренів, їхні переваги та недоліки, а також зазначаються сфери можливого застосування продуктів синтезу. Показано, що ЕМФ одержують в основному двома способами: дуговим розрядом у середовищі гелію та синтезом із застосуванням методів абляції й імплантації. Незважаючи на дуже малу кількість робіт стосовно ендедральних фуллеренів Феруму, групі авторів вдалося досягти певного прогресу в їх аналізі. Так, було доведено факт одержання ферумвмісних ендедральних фуллеренів із виділенням їх із суміші продуктів синтезу. Крім того, було прогнозовано вплив магнітного стану атомів металу на стабільність ендедральних фуллеренів, встановлено зв'язок між виходом ЕМФ і температурою плазми, а також хімічною природою прекурсору — атомів Fe. Зокрема, було встановлено, що зі збільшенням номера групи періодичної таблиці елементів, в якій знаходиться метал, вихід ЕМФ експоненційно знижується. Робиться висновок про те, що завдяки магнітним властивостям ЕМФ є перспективними матеріалами в області клінічної діагностики (наприклад, у якості контрастних речовин магніторезонансної томографії), а також медицини (для магнітокерованої доставки лікарських препаратів безпосередньо до хворого органу).

Ключові слова: ендфуллерен, ендедральний фуллерен, ферумвмісний ендфуллерен, магнітний стан, абляція, імплантація, дуговий розряд, синтез, прекурсор