

# Chapter 17

## The Peculiarities of Hydrogenation of Fullerene Molecules C<sub>60</sub> and Their Transformation

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**Abstract** This chapter provides an explanation for the kinetic features of C<sub>60</sub> molecule hydrogenation by analyzing the state and structure of double bonds in the frame of fullerene molecule. The status of these bonds, that changes the chemical activity of C<sub>60</sub> molecules, and hence the ability of fullerene molecule to accept different number of reagents particles, has been proposed. The special features of fullerene molecule formation and mechanism of structural transformations of fullerene molecule in solutions and fullerite have been considered.

**Keywords** Peculiarities of hydrogenation • Fullerene molecules • Transformation of fullerene molecules

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## 17.1 Introduction

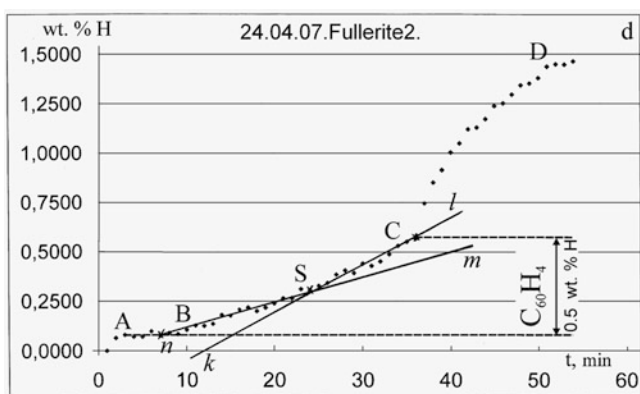
The solution of the problem of reverse hydrogenation of each carbon atom in the frame of fullerene molecule will allow to create an effective energy storage. The fullerite properties as volume ( $8.25 \cdot 10^{22}$  H atoms/cm<sup>3</sup>), weight (7.7 wt.% H) and electrochemical (2,000 mA h/g) capacities exceed many similar properties of metal hydrides and hydrocarbons.

Over the past two decades many scientific papers have been devoted to solving this particular problem. We have shown that hydrogen in the fcc lattice of fullerite can be found in the lattice (absorbed) and fullerinated (chemisorbed) states [1]. It has also been shown that when  $T \rightarrow 0$  K up to 18 hydrogen atoms in the absorbed state can be contained per one molecule of C<sub>60</sub> in the fcc lattice of fullerite. However, under normal conditions, octahedral and tetrahedral interstitial sites should be considered as a possible position of hydrogen atoms arrangement. Theoretical justification for the possibility of hydrogenation of all carbon atoms in the fullerene frame has been given in this paper.

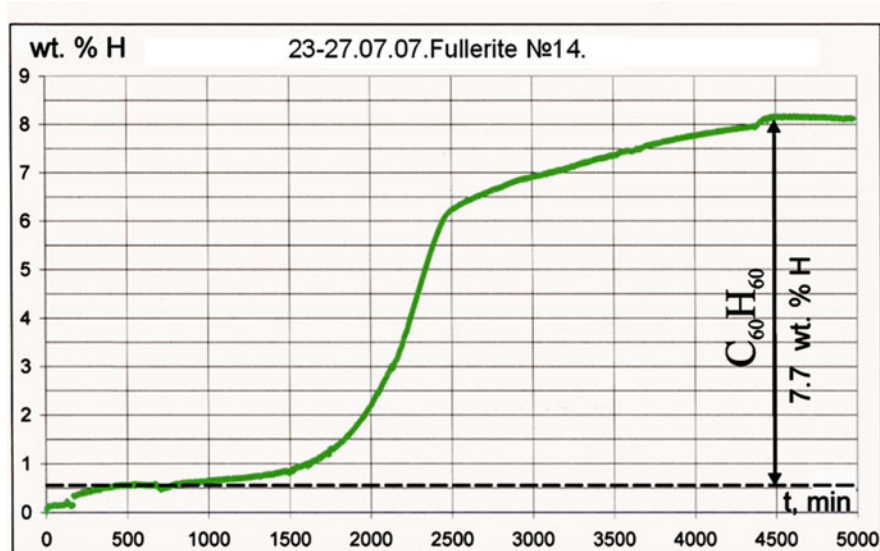
Experiments have shown that the kinetic curve of hydrogen interaction with fullerite C<sub>60</sub> notes two stage of the process. There are good grounds to believe that the process of physical absorption of hydrogen by crystallites belongs to the first stage (Fig. 17.1) [2]. This stage is determined by the content of the lattice hydrogen corresponding to 0.5 wt.% of hydrogen.

The reaction of chemisorptions of hydrogen atoms by fullerene molecules occurs at the second stage. The experimental curve of hydrogenation of fullerene molecule C<sub>60</sub> is shown in Fig. 17.2. The fullerinated hydrogen content is marked by an arrow (H<sub>F</sub>).

The second stage of reaction of hydrogen atoms chemisorption by fullerene molecules is defined by concentration – 7.7 wt.% of hydrogen (i.e. by formula



**Fig. 17.1** The adsorption of H<sub>2</sub> and two-stage atomic-molecular absorption of hydrogen in fcc lattice of fullerite. *Arrowed line* shows the content of lattice hydrogen (H<sub>L</sub>)



**Fig. 17.2** Kinetics of interaction of gaseous hydrogen with fullerite. *Arrowed line* shows the fraction of fullerinated hydrogen ( $H_F$ ) (see color plates)

$C_{60}H_{60}$ ). However the chemisorption stage has the kinetic features. The kinetic curve has a break at the hydrogen concentration of 6.2 wt.% H. As this takes place, this concentration corresponds to 48 fullerinated hydrogen atoms that are attached to the frame of fullerene molecule, is relevant to the formula  $C_{60}H_{48}$  (Fig. 17.2). In this point the energy of process activation has undergone a change and the interaction rate reduces.

In our opinion, the multi-stepwise character of process of fullerene molecule formation in plasma conditions [3] reflects later on the behavior of molecule itself in the crystal lattice and on its interaction with chemical elements and compounds. This multi-step process of fullerene molecule formation, observed on the way of carbon atom from atomic state to the spherical molecule formation, can be presented by the sequence of the following steps: atom – chain of atoms – pentagon (pentatomic molecule) – pentagon pair (pyracyclene unit) – sphere.

The pentagon plays a special role in the structure of  $C_{60}$  molecule, it often acts as an independent (separate) energetic centre on the molecule surface. These centers are responsible for the existence of molecule in the free and bound states, as well as for its behavior in solutions and crystals [4–14].

In the present paper through analysis of the state of double bonds structure in the frame of fullerene molecule, an attempt has been made to interpret the kinetic features of  $C_{60}$  molecule hydrogenation. The status of these bonds, changing the chemical activity of  $C_{60}$  molecule, and hence the ability of fullerene molecule to accept different number of reagent particles, will be considered in this paper.

## 17.2 Correlation of the Rate of Interaction with the Rate of Temperature Rise

We have pointed out some features of hydrogen interaction with fullerite during the experimental investigations of this interaction process. These peculiarities include the processes occurring both in the crystal lattice of fullerite, and in the frame of fullerene molecule itself.

At the prolonged holding of fullerite in hydrogen, the effect of cross-correlation of the interaction rate and the rate of temperature rise was found (Fig. 17.3) [2]. This effect can be explained by the fact that with sufficient time of interaction of hydrogen atom (sufficient for hydrogen atom diffusion and chemical bond

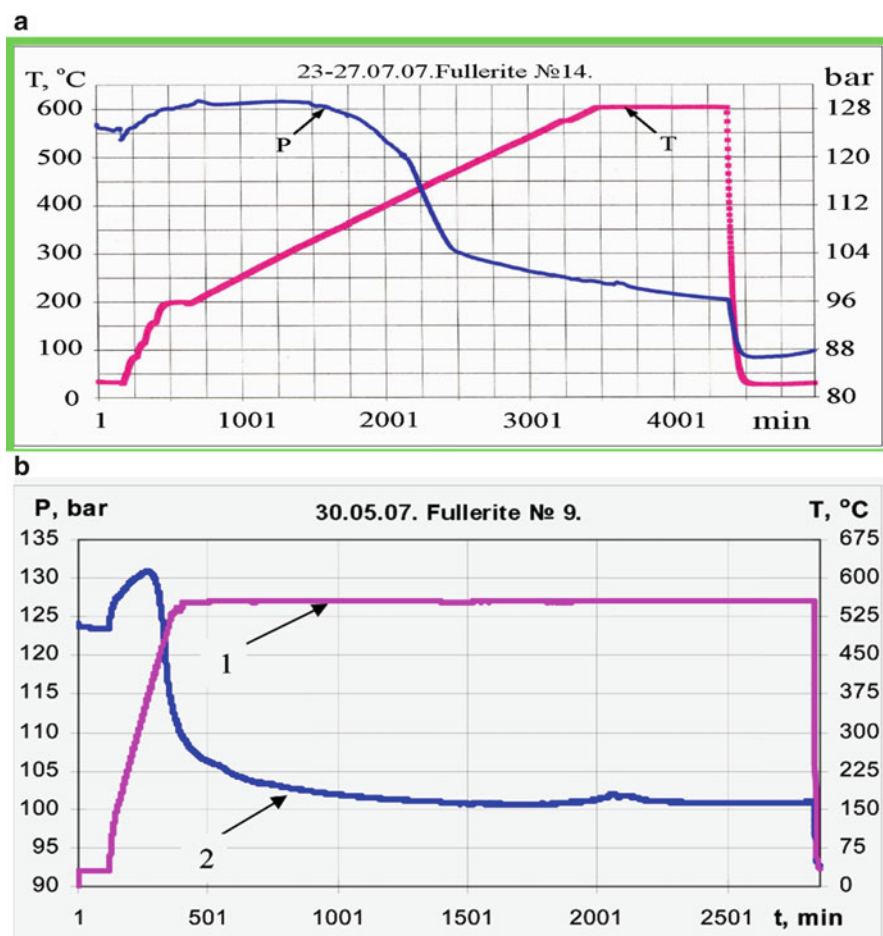


Fig. 17.3 The dependence of the rate of interaction between hydrogen – fullerene (2) the rate of temperature rise (1) (a) 0.2° per hour, and (b) 3.2° per minute (see color plates)

formation) with carbon atom the energy state (i.e., activation energy of each subsequent elementary act of interaction) of this system is a limiting parameter.

With a rise in temperature, each accepted atom of hydrogen leads to the transformation of the initial compound  $C_{60}H_n$  (fullerene molecule with  $n$ -attached hydrogen atoms) to the new  $C_{60}H_{n+1}$  compound. The newly formed system requires this additional energy for the formation of new C–H bond. The system gets this energy by raising the temperature. A certain temperature range corresponds to a strictly specified number of hydrogen atoms.

Working with metals and alloys, researchers usually have to deal with the metal hydrides where all atoms are energetically equivalent and at the creation of certain thermodynamic conditions it is likely that all atoms interact with the hydrogen atoms. Only surface and diffusion processes in solids interfere with this interaction.

The fact that each molecule  $C_{60}$  can be found in 61 (a minimum) energy states ( $C_{60}, C_{60}H, \dots, C_{60}H_n$ , where  $1 \leq n \leq 60$ ) must be taking into account when you consider the processes of hydrogenation of fullerene molecule. Each energy state corresponds to a specific chemical compound, which has its own physical and chemical properties. Thus, the benzene molecule changes its properties during the replacement of one, two, etc., hydrogen atoms. During the hydrogenation process the fullerene molecule also changes its electron density, and physical and chemical properties by changing its chemical composition.

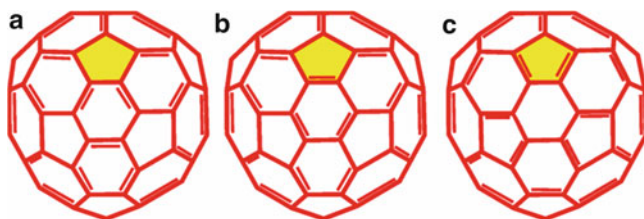
According to experimental data, with a rise in temperature the thermodynamic probability of occurrence of all 60 chemical reactions increases. However, at the final stage of interaction due to the increase of the intermolecular electron density, another process occurs, and these processes limit the interaction rate.

We think that the parabolic character of interaction hydrogen-fullerene (after the addition of hydrogen atoms above the amount corresponding to  $H_{36}$ ) is due not only to the complication of diffusion processes in the fullerite crystal. At the concentrations higher than 48 atoms of hydrogen ( $H_{48}$ ) this interaction is complicated by the processes of transformation in the fullerene molecule itself. These transformations are primarily determined by the rearrangement of five double bonds in the pentatomic cycles responsible for the association of pentatomic molecules with each other.

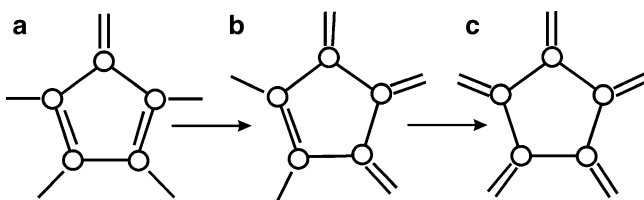
Thus, the effect of correlation of interaction rate with the rate of temperature rise can be explained by the fact that the activation energy of each subsequent act of hydrogen atom adding is higher than of the previous act. For this reason an explanation for kinetic features of  $C_{60}$  molecule hydrogenation should be found in the structural changes of fullerene molecule itself.

### 17.3 The Peculiarities of Formation of Fullerene Molecule

Bochvar and Gal'pern [15] performed calculations of the molecule electronic structure, made the quantum-chemical analysis of the stability of fullerene (well before the experimental discovery of fullerene molecule), and predicted the possible existence of stable fullerene molecules  $C_{20}$  and  $C_{60}$ .



**Fig. 17.4** The covalent resonance structures of carbo-*s*-icosahedron (a) – with the axis of fifth order (one structure); (b) and (c) – with the axis of the third order (Ten equivalent structures in each). All of structures are with 30 double bonds [15] (see color plates)



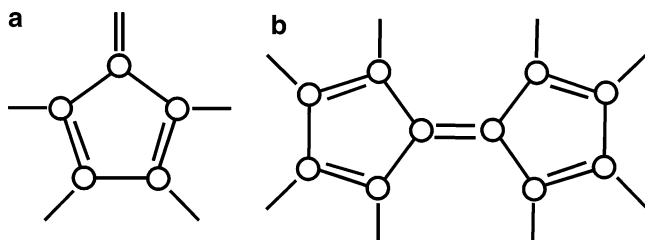
**Fig. 17.5** The transformation of the pentadiene molecule into radialene (a) pentadiene molecule, (b) – pentaene molecule, (c) – radialene

In addition, this work made an important conclusion, according to the calculations of electronic structure of fullerene molecule (by the Huckel molecular orbital method (HMO)), and orders of bonds between carbon atoms. It lies in the fact that three basic resonance structures (Fig. 17.4a–c) exist among the large family of fullerene isomers  $C_{60}$ .

The structure of (Fig. 17.4a) is the most stable among them. In fact, these structures represent the stepwise graphitization (annealing) of fullerene molecule in the reverse sequence ( $c \rightarrow b \rightarrow a$ ) [1, 16, 17]. During the course of graphitization (annealing), there is reorganization of the double intramolecular bonds into the intermolecular for the pentatomic molecules of carbon, forming the fullerene molecule. The cyclopentadiene carbon molecule is transformed into the cyclopentaene molecule and then becomes radialene (Fig. 17.5).

Due to the presence of unpaired electrons, these molecules combined in six pairs in the  $C_{60}$  frame can form the stable structures in the form of the pyracyclene units. The existence of such pairs or so-called pyracyclene units distinguishes the fullerene molecule from all other allotropies of carbon and exerts influence on its chemical activity. Figure 17.6 shows the state of the cyclopentadiene molecule at the formation of pairs or the pyracyclene units.

Every fourth electron, in the remaining four electrons, in the 12 pentatomic cyclic molecules in the frame of the  $C_{60}$  fullerene molecule is used for the intra- and extramolecular bonds [17] (depending on thermodynamic conditions). All of these  $\pi$ -electrons are 48 ( $4 \times 12 = 48$ ) in each molecule  $C_{60}$  and they determine the physical and chemical properties of fullerene molecule  $C_{60}$  [18, 19].



**Fig. 17.6** The state of pentatomic molecule at the formation of cyclopentadiene pairs (a) – single pentatomic molecule with one double (external) intermolecular bond; (b) – pyracyclene-similar unit in the frame of fullerene  $C_{60}$  molecule

## 17.4 The Features of Structural Transformations of Fullerene Molecule and Fullerite

As shown in our previous papers [3, 16–20], the phase transition f.c.c.  $\rightarrow$  s.c. in fullerite the process proceeds through the intermediate stage of the b.c.c. lattice formation. In this case, in the f.c.c. lattice, the pentatomic cyclic molecule in the frame of fullerene molecule exists at high temperatures in the form of radialene, but  $C_{60}$  molecule itself is in the  $\gamma$ -state (Fig. 17.7a).

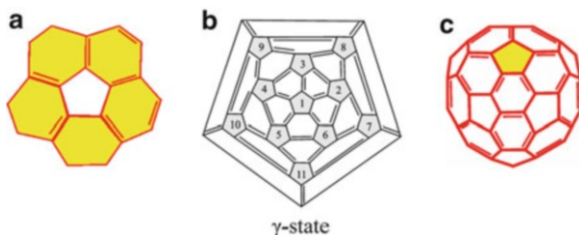
In the frame of fullerene molecule, 12 radialenes interact with radialenes of the 12 nearest fullerene molecules, forming the f.c.c. structure. The radialene is turned into the pentaene molecule (Fig. 17.5) as the temperature decreases below 280 K.

These molecules, interacting with each other, form eight cyclic hexatomic structures in the frame that obey the rule of Huckel. Due to the magnetic interaction, excited by ring currents, these structures attract the eight nearest neighbouring fullerene molecules that form the b.c.c. structure (transitional  $\beta$ -state Fig. 17.8b).

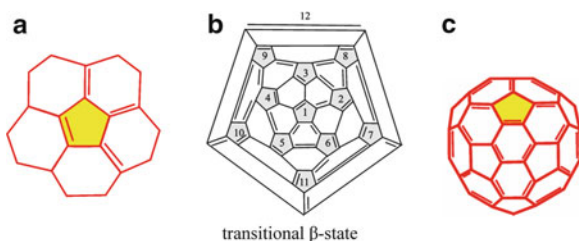
At the temperature below 260 K, the phase transition b.c.c.  $\rightarrow$  s.c. occurs and all extramolecular bonds (except for the pairing) of pentatomic molecule transform into intramolecular bonds. The molecule itself becomes pentadiene (Fig. 17.6a).

In these conditions, the fullerene molecule is formed in the  $\alpha$ -state and it has the structure presented in Fig. 17.9b, c. As can be seen from the Shlegel diagram of Fig. 17.9b, this structure has 30 double bonds, 24 of which are intramolecular for the pentadiene molecules, but six other intermolecular bonds combine molecules into six pyracyclene-similar pairs.

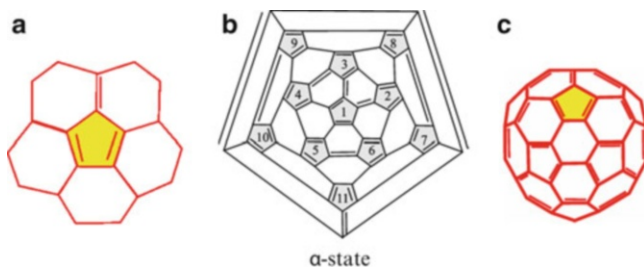
In this case, the pairing bonds between the pentatomic molecules become more active and chemically centers in the frame of fullerene molecule. Six pyracyclene units represent aromatic structures and, interacting with the similar structures in the six neighboring fullerene molecules, form the s.c. structure.



**Fig. 17.7**  $\gamma$ -state of the covalent resonance structure of carbo-s-icosahedron with an axis of fifth order, forming the f.c.c. lattice of fullerite (a) – pentatomic molecule in the state of radialene; (b) – Shlegel diagram; (c) – the frame of molecule  $C_{60}$  (see color plates)



**Fig. 17.8**  $\beta$ -state of the covalent resonance structure of carbo-s-icosahedron with an axis of third order, forming the b.c.c. lattice of fullerite (a) – pentatomic molecule in the state of pentaene; (b) – Shlegel diagram with the marked hexatomic structures (1, 2, 3, 4, 5, 6, 7, 8) that obey the Huckel rule; (c) – the frame of molecule  $C_{60}$  (see color plates)

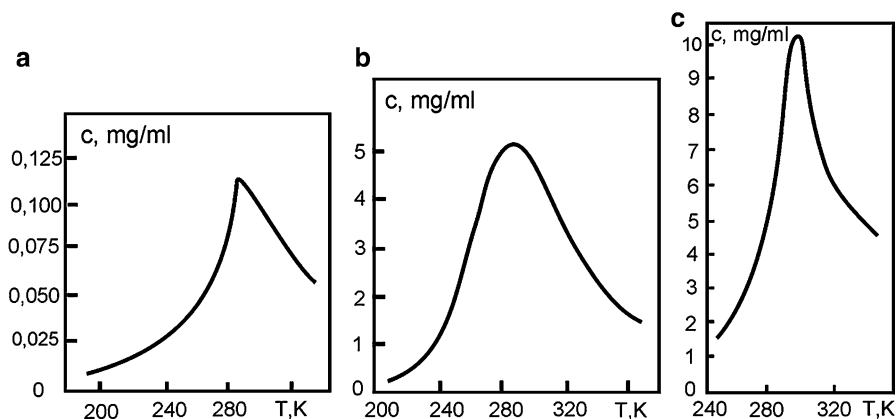


**Fig. 17.9**  $\alpha$ -state of the covalent resonance structure of carbo-s-icosahedron with an axis of third order, forming the s.c. lattice of fullerite (a) – pentadiene molecule; (b) – Shlegel diagram with the marked double bonds (1, 2, 3, 4, 5, 6) that combine pentadiene molecules in pyracylene pairs; (c) – the frame of molecule  $C_{60}$  (see color plates)

## 17.5 Fullerene Molecule in the Solution

The note on the anomalous solubility of fullerene molecule appeared in 1993, in the journal “Nature” in the section “Letters to Nature” [4]. The experimental results on the solubility of  $C_{60}$  molecules were reported in this paper. The anomalous was the fact that  $C_{60}$  solubility in the shown organic solvents has a maximum room temperature of 280 K. The revealed dependence did not fit into the existing concepts about solubility of organic bodies in the organic solvents. It is agreed





**Fig. 17.10** Experimental plots of temperature dependence of fullerite C<sub>60</sub> solubility in hexane (a), toluene (b), xylol (c)

that the increase in solubility with the increasing temperature is regular. Neither of these presentations or papers of the next 20 years [5–14 and others], did not give an answer to this question.

In our paper [16] in the year 2008, it was demonstrated that the anomalous behavior of fullerene molecule in solutions at the temperature change is determined by the transformations taking place in the frame of fullerene molecule. So it was shown that the fullerene molecule reaches the maximum solubility in the  $\beta$ -modification. Because this  $\beta$ -modification is metastable, the curve of solubility has a maximum at the point where its concentration in the solution reaches 100 % respectively (Fig. 17.10).

The rise in temperature at the fullerene dissolving leads to the transformation of fullerene molecule. Its  $\alpha$ -modification is changed into  $\beta$ -modification, and fullerene molecule becomes more chemically active. This is due to the formation of two double external-molecular bonds in each pentatomic molecule in the frame of the C<sub>60</sub> molecule (Fig. 17.8). These bonds by  $\pi$  – electrons connect X molecules of solvent per each fullerene molecule [21–23] (X – is the number of solvent molecules per one fullerene molecule).

The further increase in temperature transforms  $\beta$  – modification into  $\gamma$ -modification that has two external-molecular bonds more in each pentatomic molecule in the frame of C<sub>60</sub> molecule (Fig. 17.4). It will double the chemical activity of each fullerene molecule. These bonds, using  $\pi$ -electrons twice as much, connect 2X molecules of solvent per each fullerene molecule. Such situation increases (double) the demands in the solvent molecules that in its turn reduces by one half the fullerene solubility.

The  $\beta$ -modification exists at the temperature of 273 K, with the  $\alpha$ -modification at  $T \leq 260$  K, and the  $\gamma$ -modification at  $T \geq 280$  K. However, these temperatures correspond to the moments in which molecules of one kind exist. In the intervals between these temperatures, the mixtures of two type of fullerene molecules are in existence, the concentration ratio of which changes depending on the temperature (Fig. 17.10).

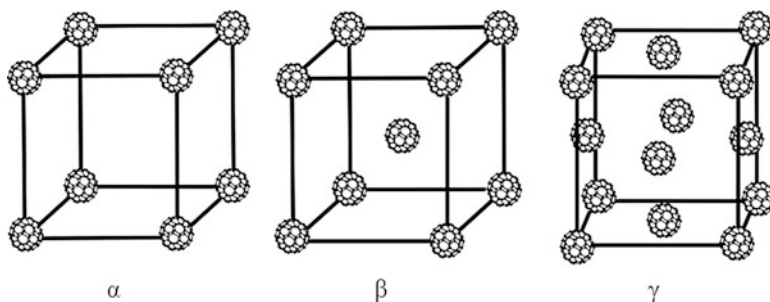
Thus, the anomalous solubility demonstrates the chemical activity of four of the five external-molecular bonds in the 12 pentatomic cycles ( $4 \times 12 = 48$ ) in the frame of fullerene molecule, that can be the place of priority interaction of fullerene molecule with hydrogen atoms.

## 17.6 Fullerene Molecule in Crystal

Another confirmation of transformations occurring in the frame of fullerene molecule under changes of temperature can be the transitions in the crystal lattice of fullerite. At the temperature of orientational transition between phases (260 K), the concentration of one or other kind of molecules become more than 50 %. This determines the fullerite structure under these thermodynamic conditions. Thus, the solid-phase transition in the fullerite is possible with the existence of more than 50 % of any modification of fullerene molecule in the system.

When temperature increases the phase transformation s.c.  $\rightarrow$  f.c.c. ( $\alpha \rightarrow \gamma$ ) in the fullerite as well as when temperature decreases takes place through the formation of an intermediate  $\beta$ - phase with b.c.c. lattice (Fig. 17.8). On heating the fullerite higher, the temperature of 260 K and the rearrangement of bonds are found in the frame of fullerene molecule. When fullerene molecules rearrange their frame, causes a change in the structure of the crystal lattice. Fullerene molecule transformations from the  $\alpha$ -state (Fig. 17.9) into the intermediate  $\beta$ -state at higher temperatures are replaced by a more stable  $\gamma$ -state (Fig. 17.7). In consequence of this, the crystal lattice of fullerite changes the structure (s.c.  $\rightarrow$  b.c.c.  $\rightarrow$  f.c.c. transformation, Fig. 17.11) [24]. In the intervals between these temperatures, the mixtures of two types of fullerene molecules exist, the concentration ratio of which determines the type of crystal lattice in fullerite (Fig. 17.10).

By this means over the long run the density of the inner and outer electron layer of fullerene molecule is changed at the phase transitions  $\alpha \rightarrow \beta \rightarrow \gamma$  in the frame of fullerene molecule, initiating the changes in the crystal lattice. This affects the chemical activity of  $C_{60}$  molecule and the ability of fullerene molecule to interact with hydrogen atoms.



**Fig. 17.11** Phase transition s.c.  $\rightarrow$  b.c.c.  $\rightarrow$  f.c.c. in the fullerite lattice with increasing temperature

## 17.7 Features of Structural Transformations of Fullerene Molecule at Its Interaction with Hydrogen

As mentioned above, each fourth electron of four carbon atoms in the 12 pentatomic cyclic molecules in the frame of  $C_{60}$  molecule is used for intra- and extra-molecular bonds (depending on the thermodynamic conditions). In all, there are 48 of these  $\pi$ -electrons ( $4 \times 12 = 48$ ) in each  $C_{60}$  molecule and they define the physic-chemical properties of the fullerene molecule. As follows from the consideration of processes in the fullerene frame, all 48 carbon atoms (or their  $\pi$ -electrons) become chemically active for the environment in the  $\gamma$ -modification, which exists at room and high temperatures.

Thus, we can assume that the first stage of chemisorptions process is determined by the interaction of these 48 carbon atoms with hydrogen.

Every fourth electron of fifth carbon atoms (in the 12 pentatomic cyclic molecules in the  $C_{60}$  molecule frame) is used for the formation of pyracyclene unit. For pairing each pentatomic molecule uses one  $\pi$ -electron. This leads to the production of the double bond between the pentatomic molecules and formation of the pyracyclene unit. In this way each fifth  $\pi$ -electron (i.e., all 12  $\pi$ -electrons) in the frame of  $C_{60}$  molecule is used for the production of pyracyclene units forming the fullerene molecule frame. Also, this bond contributes to the retention of fullerene molecule in the sites of the fcc lattice of fullerite.

From the above discussion, it follows that the kinetic features of process of fullerene molecule interaction with hydrogen, manifesting itself at hydrogen concentration higher 6,2 wt.% (more than 48 atoms of hydrogen), can be explained by the change in the mechanism of interaction. The change in the activation energy of process and decrease in the interaction rate are due to the expenditure of additional energy on the destruction of pyracyclene units, which are the frame-forming basis for fullerene molecule. As a result, this bond is intra-molecular for pyracyclene unit. In view of the fact that this bond makes contribution to the retention of fullerene molecule in the sites of the fcc fullerite lattice, this gives us grounds to believe that this bond is stronger than the other four in the pentatomic cycle.

Thus, it can be argued that the process of fullerene molecule with hydrogen (at its concentration higher 6.2 wt.%) goes by the way of the breaking of one of two bonds uniting pentagons into the pyracyclene units.

## 17.8 Conclusions

This chapter presents the study of a multi-step process of the fullerene molecule formation in the plasma conditions that is further reflected on its behavior in the crystal lattice and its interaction with chemical elements and compounds. This multi-step character of the formation process of fullerene molecule, observed in the passing of the carbon atom from the atomic state to the formation of spherical

molecule, can be presented by the following sequence of steps: atom – chain of atoms – pentagon – pentagon pair – sphere.

The pentagon plays an important role in the structure of the  $C_{60}$  molecule, acting often as an independent (autonomous) energetic center in the molecule. These energy centers are responsible for the existence of fullerene molecule in the free and bound states.

In our opinion, the kinetic features of the  $C_{60}$  molecule hydrogenation can be accounted by the change of structure of the double bonds in the fullerene frame. The status of these bonds modify the chemical activity of the  $C_{60}$  molecule, and consequently the ability of this molecule to attach a different number of the reagents particles. The status of the double bonds depends on the state of pentatomic molecules, formed the  $C_{60}$  frame, and on the interaction between these molecules.

In cooling the pentatomic molecules in the  $C_{60}$  frame transform from the radialene state into pentaene, and then into the pentadiene state. In the course of this process, the double bonds in the  $C_{60}$  frame turn from the intermolecular into the intra-molecular bonds for the pentatomic molecules. This conclusion follows from the physical and chemical features of effects observed both in the solid and in the solution at the certain temperature range.

The phase transitions  $\alpha \rightarrow \beta \rightarrow \gamma$  in the frame of fullerene molecule demonstrate clearly the dependence of structural transformations in the crystal lattice on the status of the double bonds in the frame of this molecule.

So, at the  $C_{60}$  molecule hydrogenation in the fcc lattice of fullerite the activation energy for the reaction of the hydrogen interaction with fullerite changes sharply after the addition of 48 hydrogen atoms to each molecule; in this case there is a decrease in the rate of reaction. By virtue of the fact that each molecule in the fcc lattice has 12 nearest neighbors, it is quite possible that each of 12 electrons is responsible for the bond with each neighbor and in this case these electrons are not yet bonded with hydrogen (12 electrons from 60  $\pi$ -electrons responsible for the intermolecular bonds of fullerene).

It is obvious that each of the 12 electrons belongs to one of the local energetic centers in the fullerene molecule and 12 pentagons can be such identical energetic centers on the surface of the frame of  $C_{60}$  molecule.

After the addition of 48 hydrogen atoms, each of the pentagons has a  $\pi$ -electron paired with the same electron in the neighboring pentagon of the pyracyclene unit. On the breaking of these bonds, the  $C_{60}$  molecules loose bonds between each other in the crystal lattice adding the hydrogen atoms to the remaining bonds. As this takes place, the crystal lattice is destroyed and the fullerite transforms into hydrocarbon or hydrofullerene, which is a dense resin-like mass. This stage of hydrogenation process of the fullerene molecule is more energy-intense, because this process is accompanied by the previous processes of destruction of the fcc lattice and of the pyracyclene unit.

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## References

1. Schur DV, Zaginaichko S, Veziroglu TN (2008) Peculiarities of hydrogenation of pentatomic carbon molecules in the frame of fullerene molecule  $C_{60}$ . *Int J Hydrog Energy* 33:3330–3345
2. Schur DV, Zaginaichenko SY, Savenko AF, Bogolepov VA, Anikina NS, Zolotareno AD et al (2011) Experimental evaluation of total hydrogen capacity for fullerite  $C_{60}$ . *Int J Hydrog Energy* 36:1143–1151
3. Schur DV, Zaginaichenko SY, Lysenko EA (2008) The forming peculiarities of  $C_{60}$  molecule. In: *Carbon nanomaterials in clean energy hydrogen systems*, NATO science series. Springer, Dordrecht, pp 53–65
4. Ruoff RS, Malhotra R, Huestis DL, Tse DS, Lorents DC (1993) Anomalous solubility behaviour of  $C_{60}$ . *Lett Nat* 362:140–141
5. Ying Q, Marecek J, Chu B (1994) Slow aggregation of buckminsterfullerene ( $C_{60}$ ) in benzene solution. *Chem Phys Lett* 219:214–218
6. Suzuki E et al (1998) *Molecular nanostructures*. World Scientific, Singapore
7. Sivaraman N, Dhamodaran R, Kaliappan I, Srinivasan TG, Rao PRV (1992) Solubility of  $C_{60}$  in organic solvents. *J Org Chem* 57:6077–6079
8. Doome RJ, Fonseca A, Nagu JB (1999)  $^{13}C$ -MAS-NMR investigation of solutions saturated with fullerenes: study of the anomalous solubility behaviour. *Colloids Surf A Physicochem Eng Asp* 158(1–2):137–143
9. Beck MT, Mandi G (1996) *Fuller Sci Technol* 3:32
10. Bezmel'nitsyn VN, Elets'kii AV, Okun' MV (1998) Fullerenes in solutions. *Uspekhi Fiz Nauk* 168(11):1195–1220 (in Russian)
11. Ruoff RS, Tse DS, Malhotra R, Lorents DC (1993) Solubility of fullerene ( $C_{60}$ ) in a variety of solvents. *J Phys Chem* 97:3379–3383
12. Scriven WA, Tour JM (1993) Potent solvents for  $C_{60}$  and their utility for the rapid acquisition of  $^{13}C$  NMR data for fullerenes. *J Chem Soc Chem Commun*, p.1207
13. Beck MT, Mandi G (1996) *Fuller Sci Technol* 5(2):291–310
14. Letcher TM et al (1993) Solubility buckminsterfullerene,  $C_{60}$ , in Benzene and Toluene. *S Afr J Chem* 46:41
15. Bochvar DA, Gal'pern EG (1973) About hypothetical system: carbododecahedron, s-icosahedron and carbo-s-icosahedron. *Dokl Akad Nauk SSSR* 209(3):610–612 (in Russian)
16. Schur DV, Zaginaichenko SY, Zolotareno AD, Veziroglu TN (2008) Solubility and transformation of fullerene  $C_{60}$  molecule. In: *Carbon nanomaterials in clean energy hydrogen systems*, NATO science series. Springer, Dordrecht, pp 85–95
17. Schur DV, Zaginaichenko SY, Matysina ZA (2008) The special features of formation of carbon nanostructures, their classification and site on the state diagram of carbon. In: *Carbon nanomaterials in clean energy hydrogen systems*, NATO science series. Springer, Dordrecht, pp 67–83
18. Schur DV, Zaginaichenko SYu, Lysenko EA, Golovchenko TN, Vlasenko AYu (2007) The peculiarities of molecule  $C_{60}$  formation. In: *Proceedings of 10th international conference "hydrogen materials science and chemistry of carbon nanomaterials"*, Sudak, Crimea, Ukraine, p 716–721
19. Schur DV, Zaginaichenko SY, Matysina ZA (2007) Effects of stimulation of hydrogen solubility in fullerite  $C_{60}$ . *Nanosyst Nanomater Nanotechnol* 5(2):385–409
20. Schur DV, Matysina ZA, Zaginaichenko SY (2007) Carbon nanomaterials and phase transformations in them. *Nauka i obrazovanie*, Dnepropetrovsk, p 678
21. Zaginaichenko SY, Anikina NS, Zolotareno AD, Krivushenko OJ, Shur DV (2007) Regularity of  $C_{60}$  fullerene dissolving in methyl derivatives of benzene. In: *Proceedings of 10th international conference "hydrogen materials science and chemistry of carbon nanomaterials"*, Sudak, Crimea, Ukraine, p 668–671
22. Anikina NS, Shur DV, Zaginaichenko SYu, Zolotareno AD, Krivushenko OYa (2008) On the donor-acceptor mechanism of  $C_{60}$  fullerene dissolving in aromatic hydrocarbons. *Ibid.* pp 676–679

23. Anikina NS, Shur DV, Zaginaichenko SYu, Zolotarenko AD, Krivushenko OYa (2008) The role of chemical and physical properties of  $C_{60}$  fullerene molecules and benzene derivatives in processes of  $C_{60}$  dissolving. *Ibid.* pp 680–683
24. Matysina ZA, Schur DV, Zaginaichenko SY (2009) The solid-phase transformations in fullerite stimulated by rearrangement of the structure of fullerene molecules. *Met Phys Adv Technol* 31(2):147–163