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Quantum-mechanics simulation of carbon nanoclusters and their activities in reactions with molecular oxygen

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Abstract

The mechanism and energy characteristics (activation energy and enthalpy) of interaction of linear and graphene carbon nanoparticles with an oxygen molecule are investigated by semiempirical PM3 method. The oxidation activation energy depends on the structure of clusters and the interposition of the O_2 molecule and a carbon cluster. Linear clusters are oxidized mainly to CO_2; graphene clusters are oxidized to CO.

Keywords: Carbon nanoparticle; Oxidation; Activation energy; Semiempirical calculations

1. Introduction

Carbon nanoparticles and nanosystems (fullerenes, nanotubes, nanographites, soots and so on) are objects of intensive theoretical and experimental studies during the last years. Investigations of soot are of special interest. On the one hand, soot is widely used as a good reducer for metal-oxides; on the other hand, it is a product of incomplete combustion of organic substances (oil, gas, coal, diesel fuel, etc.). In the first case, it is important to define a type of soot, which particles would interact most actively with oxides of metals. In the second case, the problem consists of selection of catalysts promoting the fast combustion of soot.

There is a lot of works devoted to studying of the soot particles' structure (see [1–16]. A part of authors suppose that soot particles are formed from graphite-like nanocrystallites bonded by sp^3 bonds [6]. Other researches suggest that the main components of soot are fullerenes and their aggregates [7,15]. As far as soot particles can be of different origins, there cannot be the only model of their structure here, and one needs to use different structure models to describe different types of soot.

A modern review of soot structure models is presented in Ref. [7]. The following stages of soot formation are noted there:

1. formation of carbon linear chains;
2. formation of carbon hexagon-based (graphene) clusters;
3. coalescence of grapheme sheet particles (soot precursors);
4. growth of soot precursors due to their reactions with carbon-contained substances.

The structure of soot particles depends on their origin, however their usual build elements are linear and graphene clusters, graphite-like nanocrystallites, as well as perfect and defect fullerenes. A theoretical study (by different methods) has shown [17–22] that linear carbon chains with the odd numbers of atoms (N) are stable up to N equal to 21 with the binding energy of about

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4 eV per atom. Clusters with the even numbers atoms have cyclic structures. The hexagon and pentagon contained clusters with binding energies of about 6 eV are formed if the number of carbon atoms is larger than 21. The final stage of the soot formation is the growth of fullerenes, nanotubes, graphite-like nanocrystallites and their aggregates.

Combustion of soot can be complete or incomplete. Complete combustion produces CO_2, while the product of incomplete combustion is CO. The value of the CO_2/CO relation depends on temperature and catalyst concentrations (if any are present).

According to literature data, the energy of soot oxidation varies from 1.5 to 2.6 eV [15,23–27] depending on a soot type and the combustion temperature. However, when researches discuss types of soot they usually write only about its origin (a type of fuel, a method and temperature of combustion, and so on). However, it is known that a change of structure leads to a change of activity. In particularly, it has been shown [28] that the activation energy for oxidation of hexagon sheets depends on the position of a reactive atom and on the curvature of the sheet. The most active are the edge atoms.

The present study is devoted to investigation of stability and activity of typical carbon clusters (linear chains and plane graphene particles) in their reactions with molecular oxygen.

2. Details of simulation

To optimize atomic geometries and to calculate the total energies of clusters we employed the quantum mechanical semiempirical PM3 method [29] that is widely used for carbon and oxygen-contained systems [see for example 12,30,31]. The PM3 method is an optimized version of the AM1 method [32]. The AM1 (Austin Model 1) method is a version of the modified neglect of differential overlap (MNDO) method [33–35]. All these methods use the self-consistent field approach to calculate the ground electronic state, to optimize the system geometry and the total energy. There is a number of popular codes realized these methods (MOPAC [36], HyperChem [37] GAMESS [38] and so on). We used here the CLUSTER-Z1 code [30] developed and provided to us by Ukraine researches. This code allowed us to carry out both the spin-restricted and spin-polarized calculations. For every studied system we carried out calculations in the both spin-restricted and spin-polarized cases and used the case with the lowest energy.

Studying the oxidation reaction, we placed an oxygen molecule near a reactive atom of the carbon cluster and found the total energy of the system depending on the distance between this carbon atom and the center of the oxygen molecule. The reaction enthalpy (ΔH) was calculated as the difference between the final system energy, E_{system} (final), and the summary energy of non-interacted, separated oxygen molecule, $E(O_2)$, and an N-atomic carbon cluster, $E(\text{cluster}, N)$: $\Delta H = E_{\text{system}}(\text{final}) - E(O_2) - E(\text{cluster}, N)$.

The activation energy E_a was calculated as the difference between the initial state energy, $E(O_2) + E(\text{cluster})$, and the maximum value of the energy, $E_{\text{system}}(\text{max})$, going from the initial system state to the final one

$$E_a = E_{\text{system}}(\max) - E(O_2) - E(\text{cluster}, N).$$

Besides, we calculated the mean binding energy for a carbon atom in a cluster, E_b, and the energy of separation of one atom from a carbon cluster, E_{sep}

$$E_b = \frac{N \cdot E(\text{atom}) - E(\text{cluster}, N)}{N},$$

$$E_{\text{sep}} = E(\text{cluster}, N-1) + E(\text{atom}) - E(\text{cluster}, N)$$

where $E(\text{atom})$ is the energy of a free carbon atom, N is the number of atoms in the cluster.

3. Results and discussions

3.1. Linear and graphene clusters without oxygen

In spite of the comparative stability of linear and graphene carbon clusters has been studied in Refs. [17–22], we have carried out a similar investigation in order to testify the used computer code [30] and to analyze the energetics of carbon nanoclusters. Results of our calculations are plotted in Fig. 1. Their analysis shows a presence of binding energy oscillations. Small clusters (until 10 carbon atoms) have linear structures. Linear and hexagonal structures compete with each other in clusters consisting of 11–21 atoms. As a rule, the carbon clusters have linear structures for the odd numbers of atoms and cyclic structures for the even

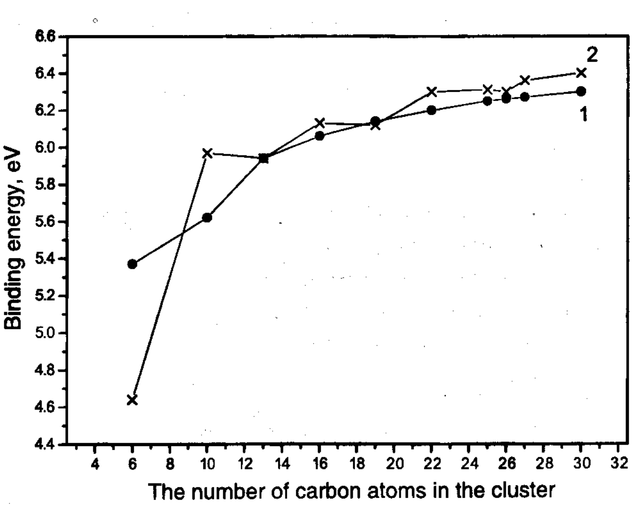

Fig. 1. The binding energy for carbon clusters calculated using the PM3 method: (1) linear clusters and (2) graphene clusters.

numbers. If a cluster has more than 21 atoms, it has a hexagonal structure. These results correlate with literary data [17–22].

As far as we study oxidation reactions with formation of CO or CO_2 molecules, we must be sure that our approach is able to give us the correct value for the energy of separation (E_{sep}) of one atom from a carbon nanocluster. Therefore, we additionally have testified the PM3 method using the data of Ref. [8] where the dissociation of carbon nanochains was studied experimentally and the energy of the separation of one carbon atom from the four-atomic chain has been found to be 4.71 eV. Our calculation gives 5.0 eV, very close to the value of 5.08 eV calculated by the Monte Carlo method convoluted PST distribution [39]. Comparing these values, we can conclude that the PM3 method describes the energy of separation of one atom from carbon nanoclusters rather satisfactorily.

We have calculated also the energies of separation of one carbon atom from linear clusters of different sizes and have plotted them in Fig. 2 versus the number of atoms. The dependence of E_{sep} on the number of atoms is not monotonous. It has minimums and maximums at the even and odd numbers, respectively. To be sure that this non-monotonous dependence is not an artifact of the semiempirical PM3 method but demonstrates the real nature of studied systems, we have analyzed the corresponding literary data. Comparison of our results and literary data [40] obtained by the Hartree–Fock (HF) method (see Fig. 2) allows us to conclude than the PM3 method describes the energetic of carbon nanoparticles rather well. As one can see, the HF and PM3 plots are very similar, especially for large clusters.

3.2. Oxidation of linear clusters (chains)

A usual tactics for the theoretical simulation of combustion is to find the minimal activation energies for the oxidation reactions (Table 1). Because the large linear chains are not stable, we studied here only chains up to C_6. Studying interactions of linear carbon chains with an oxygen molecule, we have found that the minimal activation energies correspond to the cases where the O_2 molecule approaches to the edge atom of the chain and is oriented normally to its binding line.

Therefore, the main part of our investigations was fulfilled for these cases. A typical plot for the dependence of the total system energy on the distance between reagent components (a carbon cluster and an oxygen molecule) is shown in Fig. 3.

The oxidation process can be divided to two stages—adsorption and reaction ones. The adsorption stage is characterized by overcoming of the adsorption barrier (B) with the height of E_{bar} and by reaching of the metastable adsorption state (A) with the binding energy E_{bind} From the geometry point of view the adsorption state (A) is a state where the oxygen and carbon atoms present a united, bonded system. This state is separated from the reaction state (R) by a barrier of very a small weight ($\leqslant$0.1 eV) for all C_2–C_6 chains. The reaction state

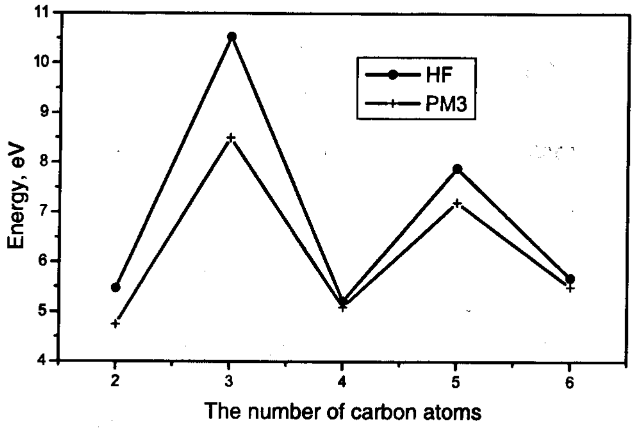

Fig. 2. The energy of separation of one atom from linear carbon clusters (E_{sep}) calculated using PM3 and HF [40] methods.

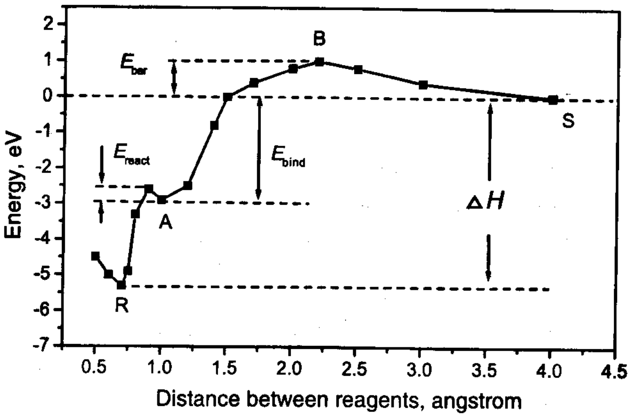

Fig. 3. The oxidation energy scheme for linear carbon clusters (C_2–C_6).

Table 1
Energy parameters for oxidation of the C_n (n = 2–6) linear carbon clusters with an oxygen molecule

n	2	3	4	5	6
Reaction products	CO + CO	C_2O + CO	C_3 + CO_2	C_4 + CO_2	C_5 + CO_2
$E_{act} = E_{bar}$, eV	0.2	0.9	1.0	0.5	0.3
E_{react}, eV	$\leqslant$0.1	$\leqslant$0.1	$\leqslant$0.1	$\leqslant$0.1	$\leqslant$0.1
ΔH, eV	−11.5	−4.6	−5.3	−4.3	−5.2

consists of reactions products (free CO_2 or CO molecules and a rest of the carbon chain). The energy difference between the reaction (R) and initial state (S) is the reaction enthalpy ΔH. Therefore, in reality, the activation energy for this oxidation reaction is equal to the adsorption barrier: $E_{act} = E_{bar}$.

Energy parameters for oxidation of the C_n ($n = 2$–6) linear carbon clusters are listed in Table 1. Atomic schemes of the reaction are shown in Fig. 4.

As it follows from Table 1 and Fig. 4, the oxidation mechanism is the same for the C_4–C_6 carbon chains. After getting over the barrier (the B state at Fig. 3), a system consisted of an oxygen molecule and a carbon cluster reaches to the final stage of the reaction R, the products of which are a free CO_2 molecule and the carbon cluster diminished by one atom. The energy difference between the initial and final states is the reaction enthalpy ΔH or the evolved energy. The value of ΔH also depends on the size of the linear cluster by a non-monotonous way (Table 1) and lies in the region of 4–5 eV. As it was to be expected, the evolved energy ΔH is much larger than the activation energy E_{act}. In the other words, oxidation of linear carbon chains is a self-supported process or combustion.

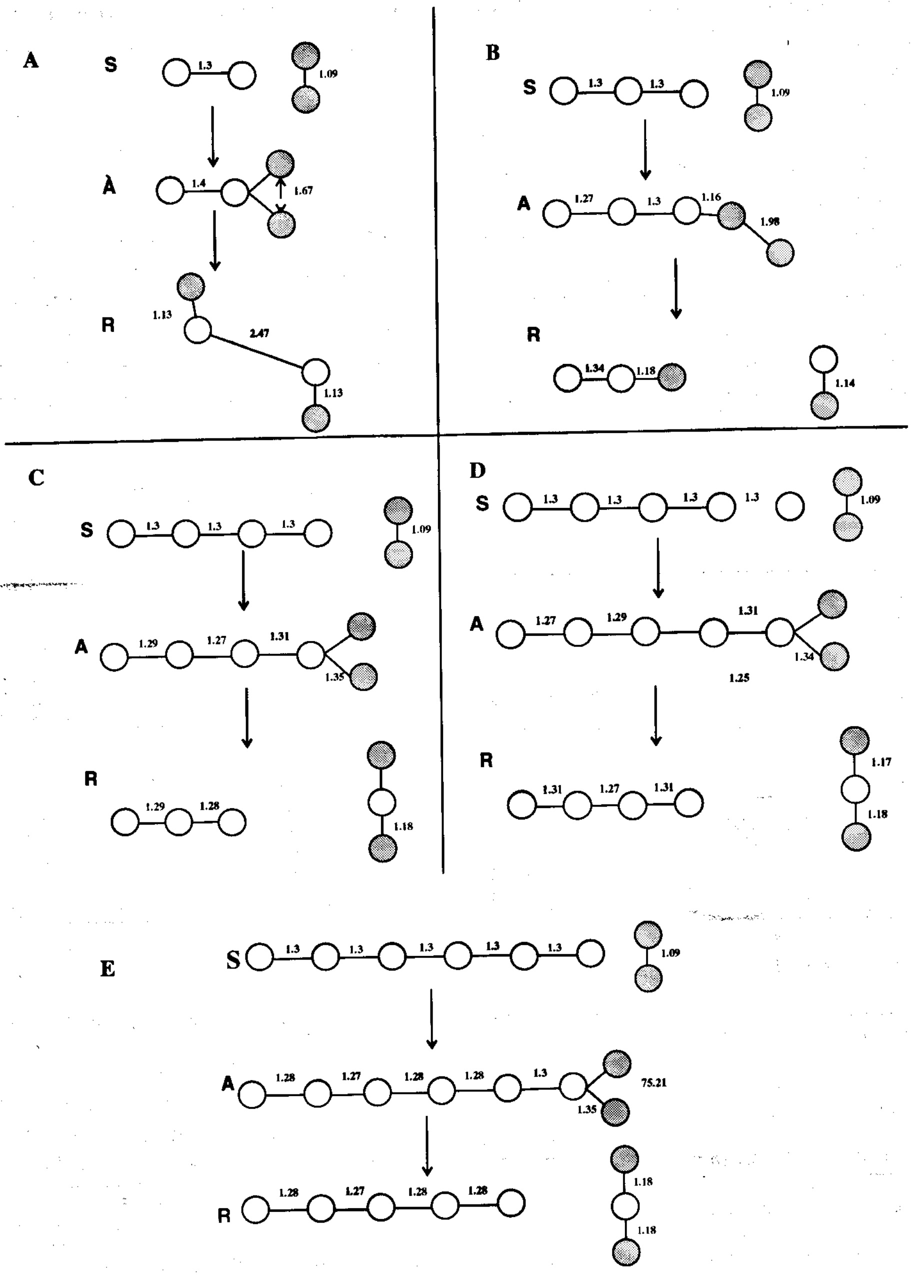

Fig. 4. The oxidation mechanism is the same for the C_4–C6 chains: (◎) oxygen atoms; (○) carbon atoms; (S) start position; (A) adsorption state and (R) reaction product.

The limit stage is the adsorption of the molecular oxygen at the edge of the chain. The adsorption activation energy varies between 0.3 and 1.0 eV (the energy difference between the S and B states a Fig. 3). The separation of the CO_2 molecule occurs with the energy barrier (=0.1 eV): the A–R transition at Fig. 3.

Some special cases are the oxidations of the C_2 and C_3 chains. The products of the C_2 chain oxidation are the two CO separated molecules ($\Delta H = -11.6$ eV). Another possible reaction (formation of the CO_2 molecule) needs to make one of the C atoms to be free, without any bonding; the enthalpy of this reaction is equal to −6.2 eV.

In the C_3 case three reactions are possible:

$$C_3 + O_2 \rightarrow C_2 + CO_2 \ (\Delta H = -2.4\ \text{eV});$$
$$C_3 + O_2 \rightarrow C + CO + CO \ (\Delta H = -3.1\ \text{eV});$$
$$C_3 + O_2 \rightarrow C_2O + CO \ (\Delta H = -4.6\ \text{eV}).$$

The third reaction (with one CO molecule separated) is energetically more favorable because the first and seconds reactions have smaller enthalpies.

As for geometry details, the O_2 molecule had the O–O calculated distance of 1.09 Å before the interaction with carbon, and the initial C–C distances in all studied linear chains were of 1.3 Å. In the adsorption state, the oxygen molecule keeps its molecular nature, but the O–O distance increases to 1.6–1.7 Å, and a typical C–O distance for this case is 1.35 Å. The distance between the edge reactive carbon atom and the nearest atom of the chain increases slightly, but the internal C–C distances for small chains decrease more appreciably (see Fig. 4).

4. Oxidation of graphene nanoclusters

As far as the C_{22} hexagons-contained cluster is a minimal stable graphene cluster we used it as a model to study the oxidation of graphene carbon nanoparticles. A scheme of this study is illustrated in Fig. 5 where two cases are shown: (1) the interaction of oxygen with an edge carbon atom having two neighbors: (2) the interaction of oxygen with a basal (internal) atom having three neighbors.

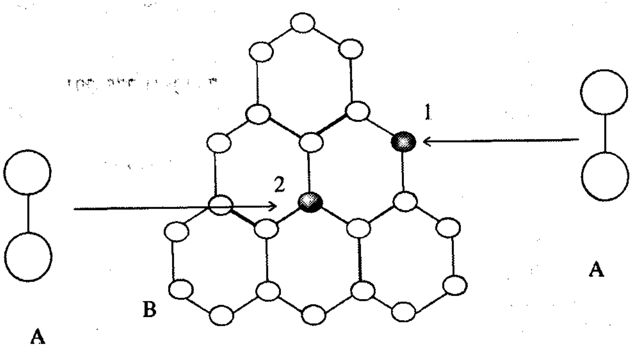

Fig. 5. The schemes of studied cases for oxidation of the C_{22} graphene nanocluster.

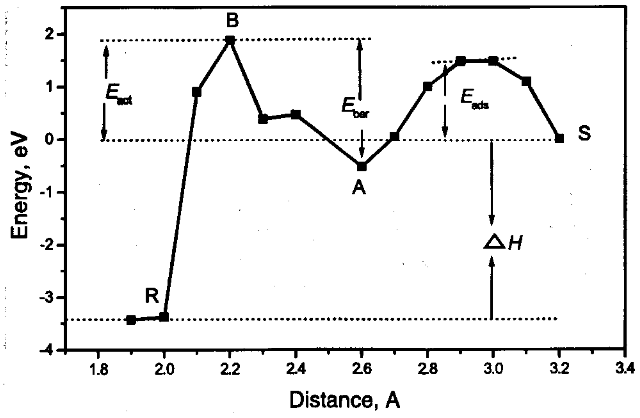

Fig. 6. The energy scheme for oxidation of the C_{22} hexagon cluster. The O_2 molecule approaches to the edge C atom. The reaction product is CO.

At the first case (Fig. 6) the dependence of the total energy on the distance between the reagents (an oxygen molecule and a reactive atom of the graphene cluster) looks very like to that for the linear cluster case described above. Namely, the chemical adsorption state (A) is separated by the energy barrier E_{ads} (of 1.5 eV) from the initial state (S). Then the oxygen molecule dissociates and one carbon atom separates from the hexagon cluster (the R state) with the overcoming of the energy barrier E_{bar} of 2.3 eV. The total activation energy of this two-steps process is determined by the energy difference between the initial state (S) and the maximal point of the second barrier (B). The value of this activation energy E_{act} is equal to 1.8 eV.

Products of this reaction do not contain CO_2 molecules. They consist of a CO molecule and the carbon cluster that has lost one carbon atom but has trapped one oxygen atom. The formation (and separation) of the second CO molecule is unfavorable energetically: the activation energy of this process is equal to 4.5 eV and the enthalpy is +3.3 eV. The detail analysis shows that the formation of a CO_2 molecule is also possible (Fig. 7). However, the activation energy E_{act} of this reaction is 2.8 eV, much larger than the 1.8 eV value obtained for the reaction with the CO formation.

As for the reaction enthalpy, it exceeds the activation energy only for the reaction followed by one CO molecule creation (see Table 2). It means that other reactions (with formation of two CO molecules or one CO_2 molecule) are not self-supported and cannot proceed without an external source of energy.

The oxidation scheme for an internal atom of the graphene cluster C_{22} is presented at Fig. 8. One can see that in this case the oxygen molecule can be adsorbed physically (the P state) with the adsorption

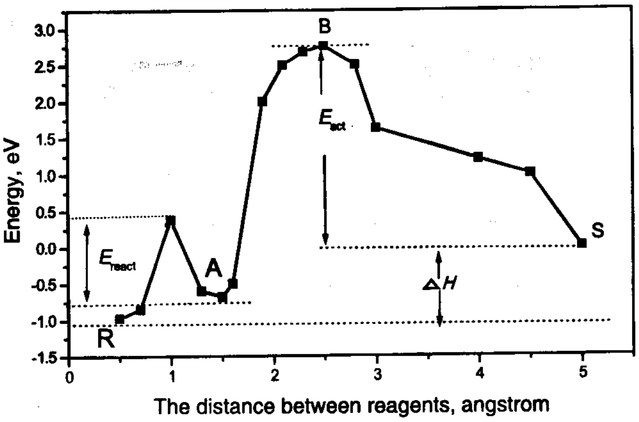

Fig. 7. The energy scheme for oxidation of the C_{22} hexagon cluster. The O_2 molecule approaches to the edge C atom. The reaction product is CO_2.

Table 2
The results of oxidation of graphene carbon clusters

Reaction products	Internal C atom	Edge C atom	
	CO	CO	CO_2
E_{act}, eV	5	1.8	2.8
ΔH, eV	+3.2	−3.4	−0.9

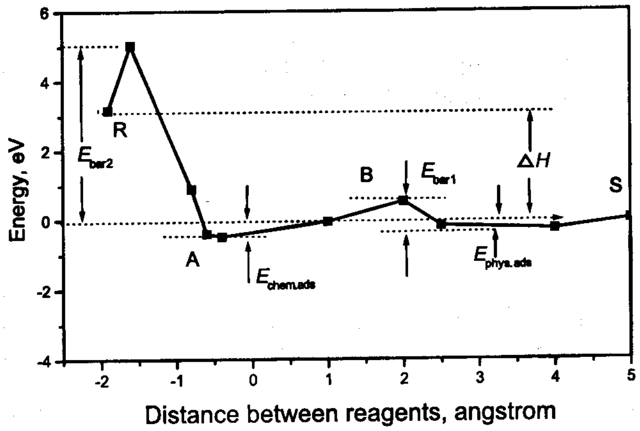

Fig. 8. The energy scheme for oxidation of the C_{22} hexagon cluster. The O_2 molecule approaches to the internal C atom. The reaction product is CO.

energy $E_{phys.ads} = -0.1$ eV. Then the O_2 molecule can go over the barrier B ($E_{bar1} = 0.5$ eV) to the chemical adsorption state A. The energy of the chemical adsorption $E_{chem.ads} = -0.3$ eV. In this state two oxygen atoms are bonded similar an O_2 molecule: the O–O distance is equal to 1.26 eV. The next part of Fig. 8 (the region A–R) corresponds to the dissociation of the adsorbed O_2 molecule with a simultaneous formation of a CO molecule. On can see that the formation of a CO molecule needs the activation energy of 5.0 eV, and the enthalpy of this reaction is positive (+3.2 eV). Thus, our study of the O_2 interaction with internal atoms of the C_{22} cluster has shown that the internal atoms of graphene are much less active than the edge ones and do not participate in the combustion reaction until the combustion front comes close to them and they become the edge atoms.

5. Summary

Our semiempirical PM3 calculations show that a mechanism of oxidation of carbon clusters by molecular oxygen depends on the structure of clusters. Linear clusters, as a rule, produce CO_2 molecules while hexagon clusters give mainly CO molecules.

The activation energy for the oxidation of linear chains is caused by the barrier of the chemical adsorption of the O_2 molecule at the edge of a linear carbon chain. The values of this activation energy (0.2–1.0 eV) are much less than the absolute value of the reaction enthalpy (4–11 eV), therefore the linear carbon chains have to combust very well.

The activation energy for oxidation of the C_{22} hexagon (graphene) cluster depends on the position of reactive carbon atom. It is minimal for the edge atoms (1.8 eV) and maximal for the internal atoms (5 eV). Products of these reactions are CO molecules.

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References

[1] V.S. Samoilov, N.D. Senin, B.I. Smirnov, et al., in: V.F. Surovinin (Ed.), Production and Properties of Carbon Soot, Omsk, 1972, pp. 96–112 (in Russian).
[2] B.S. Haynes, H.G. Wagner, Prog. Energy Combust. Sci. 7 (1981) 229–273.
[3] J. Lahaye, Carbon 30 (3) (1992) 309.
[4] O.I. Smith, Prog. Energy Combust. Sci. 7 (1981) 275–291.
[5] B.R. Stanmore, J.F. Brithae, P. Gilot, Carbon 39 (2001) 2247–2368.
[6] V.B. Fenelonov, Porous Carbon, Publishing House of Institute of Catalysis the Siberian Branch of the Russian Academy of Science, Novosibirsk, 1995, 518 (in Russian).
[7] V.I. Berezkin, Fiz. Tverd. Tela 42 (3) (2000) 567–572 (in Russian).
[8] H. Choi, R.T. Bise, A.A. Hoops, D.H. Mordaunt, D.M. Neumark, J. Phys. Chem. A 104 (2000) 2025–2032.
[9] Q.L. Zhang, S.C. O'Brien, J.R. Heath, Y. Liu, R.F. Curl, H.W. Kroto, R.E. Smalley, J. Phys. Chem. 90 (1986) 525.
[10] Ph. Gerhardt, S. Löffler, K.H. Homann, Chem. Phys. Lett. 137 (4) (1987) 306.

[11] C.J. Pope, J.A. Marr, J.B. Howard, J. Chem. Phys. 97 (42) (1993) 11001.

[12] M. Frenclach, L.B. Ebert, J. Phys. Chem. 92 (2) (1988) 561.

[13] L.B. Ebert, Science 247 (1990) 1468.

[14] P. Kappler, P. Ehrburger, J. Lahaye, J.-B. Donnet, J. Appl. Phys. 50 (1) (1979) 308.

[15] O.P. Gorelik, G.A. Djuzhev, D.V. Novikov, V.M. Ojchenko, G.N. Fursej, Zh. Tekh. Fis 76 (11) (2000) 125 (in Russian).

[16] L. Randy, Vander Wal, J.A. Tomasek, Combust. Flame 134 (2003) 1–9.

[17] B.R. Eggen, R.L. Johnston, J.N. Murrell, J. Chem. Soc. Farady Trans. V90 (20) (1994) 3029–3037.

[18] J.M.L. Martin, J. El-Yazal, J.-P. Francois, Chem. Phys. Lett. 252 (1996) 9–18.

[19] J.M.L. Martin, J.P. Francois, R. Gijbels, J. Comput. Chem. 12 (1991) 52.

[20] P.A. Withey, L.N. Shen, W.R.M. Graham, J. Chem. Phys. 95 (1991) 820.

[21] H. Handschuh, G. Gantefor, B. Kessler, P.S. Bechthold, W. Eberhardt, Phys. Rev. Lett. 74 (1995) 1095.

[22] T. Guo, M.D. Diener, Y. Chai, M.J. Alford, R.E. Haufler, S.M. McClure, T. Ohno, J.H. Weaver, G.E. Scuseria, R.E. Smalley, Science 257 (1992) 1661.

[23] E.S. Golovina, Phys. Combust. Explos. 35 (4) (1999) 48 (in Russian).

[24] V.S. Babenko, Kinet. Catal. 39 (1) (1998) 62 (in Russian).

[25] C. Hyeon, T.B. Ryan, A.A. Hoops, D.H. Mordaunt, D.M. Neumar, et al., J. Phys. Chem. A 104 (2000) 2025.

[26] M.A. Hasan, M.I. Zaki, K. Kumari, L. Pasupulety, Termochim. Acta 320 (1998) 23–32.

[27] Y. Matsuo, Y. Sugie, Carbon 36 (3) (1998) 301–303.

[28] P.A.J. Neeft, T.X. Nijhuis, E. Smakman, M. Makkee, J.A. Moulijn, Fuel 76 (1997) 1129–1136.

[29] J.J.P. Stewart, J. Comp. Chem 10 (2) (1989) 221–264.

[30] V.A. Zayetz, CLUSTER-Z1 Quantum Chemical Software, Institute of Surface Chemistry, National Academy of Science of Ukraine, Kiev, 1990;
V.D. Khavryutchenko, A.V. Khavryutchenko Jr., DYQUA-MOD, Dynamical Quantum Modeling Software for Personal Computers, Joint Institute for Nuclear Researches, Dubna and Institute of Surface Chemistry, National Academy of Science of Ukraine, Kiev, 1993.

[31] S. Erkoc, L. Türker, Phys. E 8 (2000) 50–56.

[32] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.

[33] N.C. Baird, M.J.S. Dewar, J. Chem. Phys. 50 (1969) 1262.

[34] M.J.S. Dewar, E. Haselbach, J. Am. Chem. Soc. 92 (1970) 590.

[35] R.C. Bingham, M.J.S. Dewar, D.H. Lo, J. Am. Chem. Soc. 97 (1975) 1285.

[36] J.J.P. Stewart, MOPAC: a semiempirical molecular orbital program, J. Comput. Aided Mol. Des. 4 (1990) 1–105.

[37] Available from: <http://www.chemistry-software.com>.

[38] M.W. Schmidt, K Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomegy, J. Comput. Chem. 14 (1993) 1347.

[39] K.A. Gingerich, H.C. Finkbeiner, W. Schmude Jr., Chem. Phys. Lett. 207 (1993) 23.

[40] A.F. Jalbout, S. Fernandez, J. Molec. Struct. (Theochem) 584 (2002) 169–182.