Computer Investigation of Carbon Nanoclusters and Their Activities in Reactions with Molecular Oxygen

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The mechanism and energy characteristics for the interaction of linear and graphene carbon nanoparticles with molecular oxygen are investigated numerically using the semiempirical PM3 method and the density functional theory. It has been shown that the cluster geometry influences the mechanism and the activation energy of oxidation. Linear clusters are oxidized mainly up to CO_2; the oxidation product for graphene clusters is CO. Comparison of activation energies for linear (0.3–1.0 eV) and graphene (1.9 eV) clusters with the experimental data for soot (1.5–2.6 eV) allows us to conclude that linear carbon chains can play an important role at the first stage of the soot combustion while the temperature is not high. However, the process of stable combustion is mainly limited by the oxidation of graphene particles.

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 pick up the type of soot whose 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 the study of the soot particles structure (see Refs. [1–16]). Some 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 graphene sheet particles (soot precursors);
4. growth of soot precursors due to their reactions with carbon-containing substances.

Although the structure of soot particles depends on their origin, the usual building elements are linear and graphene clusters, graphite-like nanocrystallites, as well as perfect and defect fullerenes. A theoretical study (the PM3 semiempirical method) has shown [17] that linear carbon chains are stable up to 20–25 atomic sizes with the binding energy of about 4 eV per atom; then the hexagon and pentagon contained clusters are formed with binding energies of about 6 eV. 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 CO_2/CO ratio depends on temperature and catalyst concentrations (if any are present).

According to the literature data, the energy of soot oxidation varies from 1.5 to 2.6 eV [8, 15, 18, 19] depending on the soot type and combustion temperature. However, when researches discuss types of soot they usually write only about its origin (type of fuel, method and temperature of combustion, and so on). However, it is known that a change in the structure leads to a change of activity. In particular, it has been shown [20] 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 [21, 22] that is widely used for carbon and oxygen-containing systems [12, 23].

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 as a function of 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 total energy of a non-interacted, isolated oxygen molecule, $E(O_2)$, and an N-atomic carbon cluster, E(cluster,N):

$$\Delta H = E_{system}(\text{final}) - E(O_2) - E(\text{cluster},N), \tag{1}$$

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_{system}(max), occurring when going from the initial system state to the final one:

$$E_a = E_{system}(\text{max}) - E(O_2) - E(\text{cluster},N), \tag{2}$$

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

$$E_b = \frac{NE(\text{atom}) - E(\text{cluster}, N)}{N}, \tag{3}$$

$$E_{sep} = E(\text{cluster}, N - 1) + E(\text{atom}) - E(\text{cluster}, N), \tag{4}$$

where E(atom) is the energy of a free carbon atom, N is the number of atoms in the cluster.

3. Results and discussion

3.1. Linear and graphene clusters without oxygen

Although stabilities of linear and graphene carbon clusters have already been compared in Ref. [17], we have carried out a similar investigation in order to verify the employed computer code [22] and to analyze the energetics of carbon nanoclusters. Results of our calculations are plotted in Fig. 1.

Figure 1 demonstrates that graphene carbon clusters are more favorable energetically than linear clusters when the number of atoms is larger than 20 (in good agreement with the results of Ref. [17]). However, if 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 have additionally checked the PM3 method using the data of Ref. [8] where dissociation of carbon nanochains was studied experimentally and the energy of separation of one carbon atom from the four-atomic chain has been found to be 4.71 eV. Our calculation
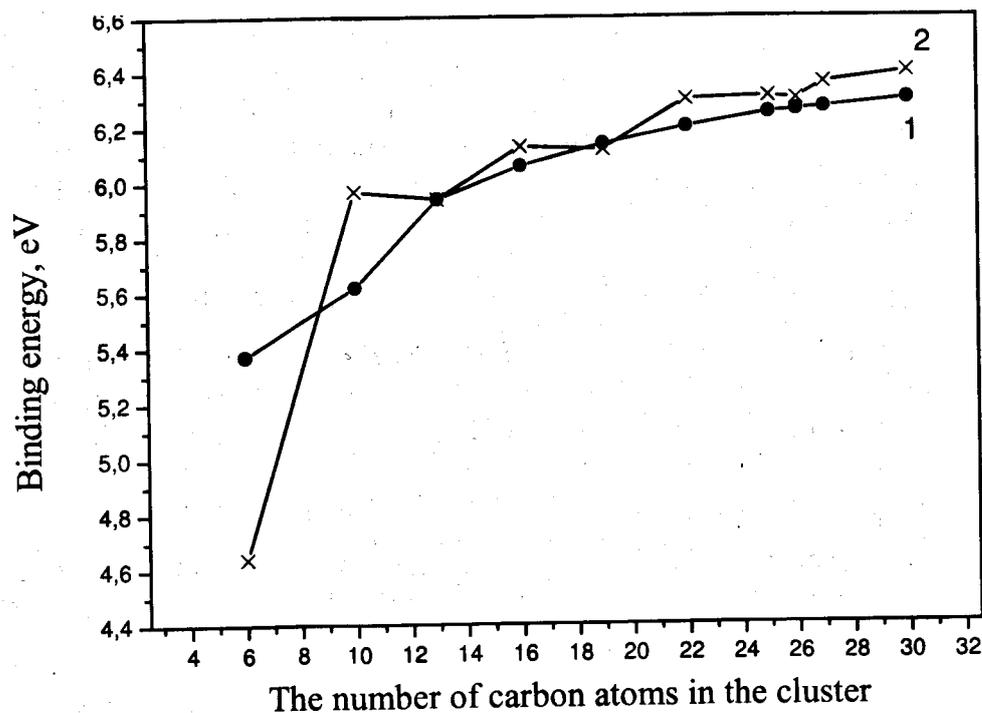
Figure 1. Binding energy for carbon: 1 – linear clusters, 2 – graphene clusters.

gives 5.04 eV, very close to the value of 5.08 eV calculated in Ref. [25]. 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 the separation energies of one carbon atom for linear clusters of different sizes and 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 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 carried out the same calculations using a non-empirical (*ab initio*) method based on the density functional theory (DFT) [26–28] in the framework of the FHI96md code [29]. The DFT and PM3 results are compared in Fig. 2. As one can see, the DFT and PM3 plots look very similar. The main difference between them is that the DFT values overestimate the PM3 ones systematically by the value of about 1.5–2.0 eV. This is the usual DFT overestimation for carbon systems [30].
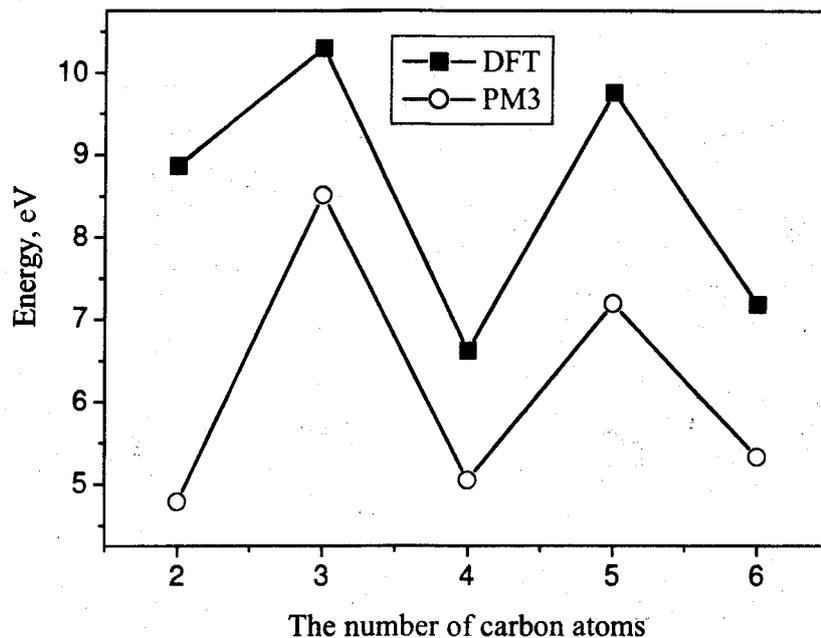
Figure 2. Energy of separation of one atom from linear carbon clusters (E_{sep}).

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. By studying the interaction of linear carbon chains with an oxygen molecule we have found that the minimal activation energies correspond to the case where the O_2 molecule approaches the edge atom of the chain and is oriented normally to it. Therefore, the main part of our investigations was fulfilled for this case. Atomic schemes of the oxidation for the n-atomic linear carbon clusters (C_n, $n = 2 - 6$) are presented in Fig.3. The case of C_{22} is shown in Fig.4.

The oxidation process can be divided to two stages (Fig. 5): adsorption and reaction ones. The adsorption stage is characterized by overcoming the adsorption barrier B_1 with the height of E_{bar} and by reaching the metastable adsorption state (A) with the binding energy E_{bind}. From the geometry point of view the adsorption state 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 B_2 whose height E_{react} is very small (less than 0.1 eV) for the C_2–C_6 clusters and is equal to 0.3 eV for the C_{22} linear chain. The reaction state consists of reaction products (free CO_2 or CO molecule) and the rest of the
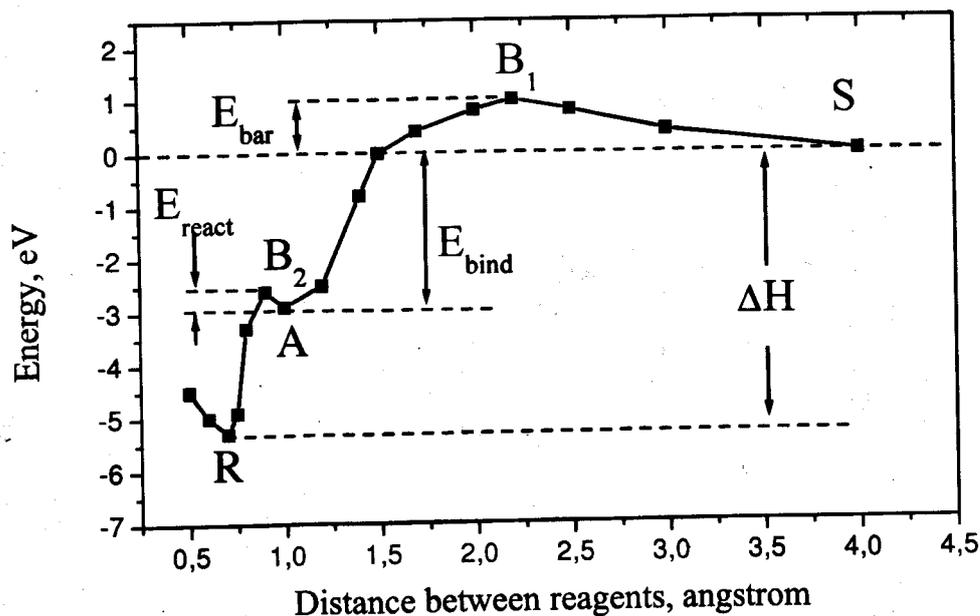
**Figure 5.** Energy scheme for the oxidation of linear carbon clusters.

n	2	3	4	5	6	22
$E_{act} = E_{bar1}$	0.2	0.9	1.0	0.5	0.3	0.4
E_{bind}	−3.6	−2.3	−2.9	−3.2	−3.0	−2.7
E_{react}	0.1	0.1	0.1	0.1	0.1	0.3
ΔH	−11.5	−2.5	−5.3	−4.3	−5.2	−4.5
Reaction products	$CO+CO$	C_2O+CO	C_3+CO_2	C_4+CO_2	C_5+CO_2	$C_{21}+CO_2$

Table 1. Energy parameters for the oxidation of C_n (n = 2–6, 22) linear carbon clusters with an oxygen molecule.

carbon chain. The energy difference between the reaction and initial states (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 the oxidation of C_n (n = 2–6, 22) linear carbon clusters are listed in the Table 1. As it follows from these data, the oxidation mechanism is the same for the C_4–C_{22} chains. The limit stage is the adsorption of the molecular oxygen at the edge of the carbon chain. The oxidation activation energy varies between 0.3 and 1.0 eV. Separation of the CO_2 molecule occurs with the energy barrier whose height for the small carbon chains is less than the actual accuracy of our numerical simulation technique (less than 0.1 eV). The absolute value of the reaction enthalpy (4–5 eV) is much larger than the reaction activation energy (0.3–1.0 eV), so that the reaction is a self-supported process
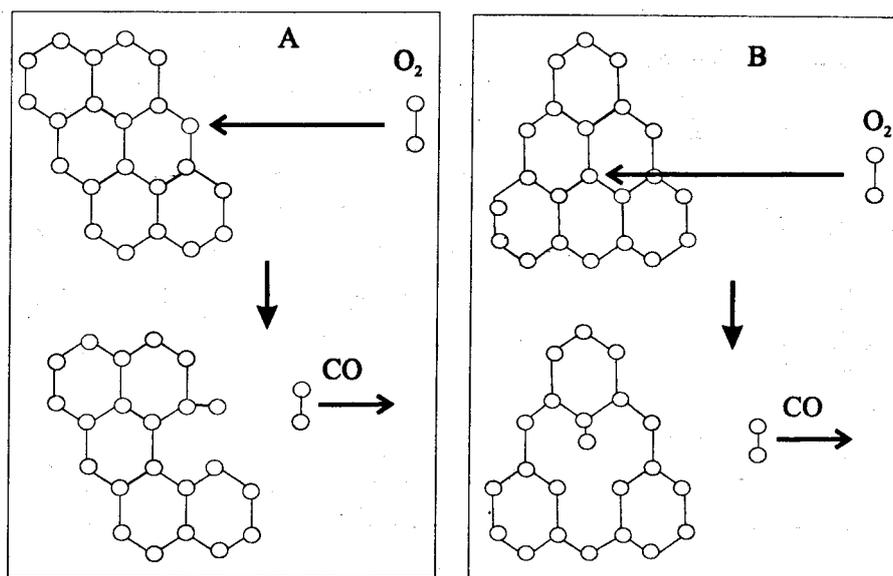
Figure 6. The schemes of studied cases for the oxidation of the C_{22} graphene nanocluster: A) oxygen reacts with an edge atom; B) oxygen reacts with a basal atom. White circles are carbon atoms, gray circles are oxygen atoms.

Structure	Graphene, C_{22}		
Reactive C atom	internal	edge	
Product of reaction	CO	CO	CO_2
Activation energy	5.0	1.9	2.7
Enthalpy	+3.2	−3.4	−0.9

Table 2. Results of oxidation for graphene carbon clusters.

or combustion.

Some special cases are the oxidation of the C_2 and C_3 chains. The products of the C_2 chain oxidation are two CO separated molecules because the formation of the CO_2 molecule needs to make one of the C atoms to be free, without any bonding, but this state it is very unfavorable. In the C_3 case only one CO molecule separates because the separation of the second CO molecule also needs to make one of the C atoms to be free which is again unfavorable.

Before interaction with carbon, the O_2 molecule has the O–O distance equal to 1.09 Å, and all initial C–C distances in the linear chains are 1.3 Å. In the adsorption state, the oxygen molecule keeps its molecular nature, but the O–O distance increases up to 1.6–1.7 Å, and a typical C–O distance for this case is
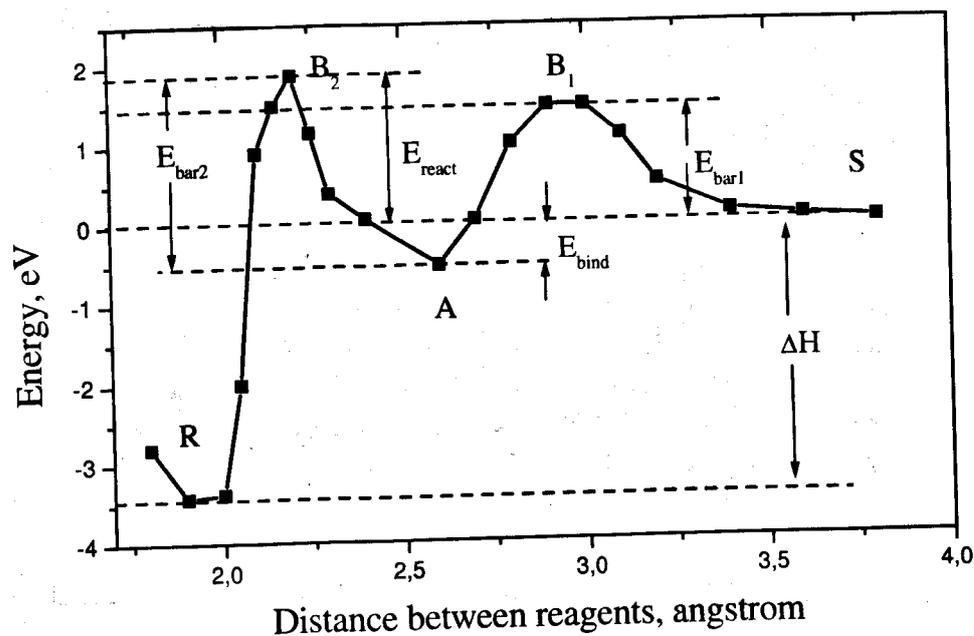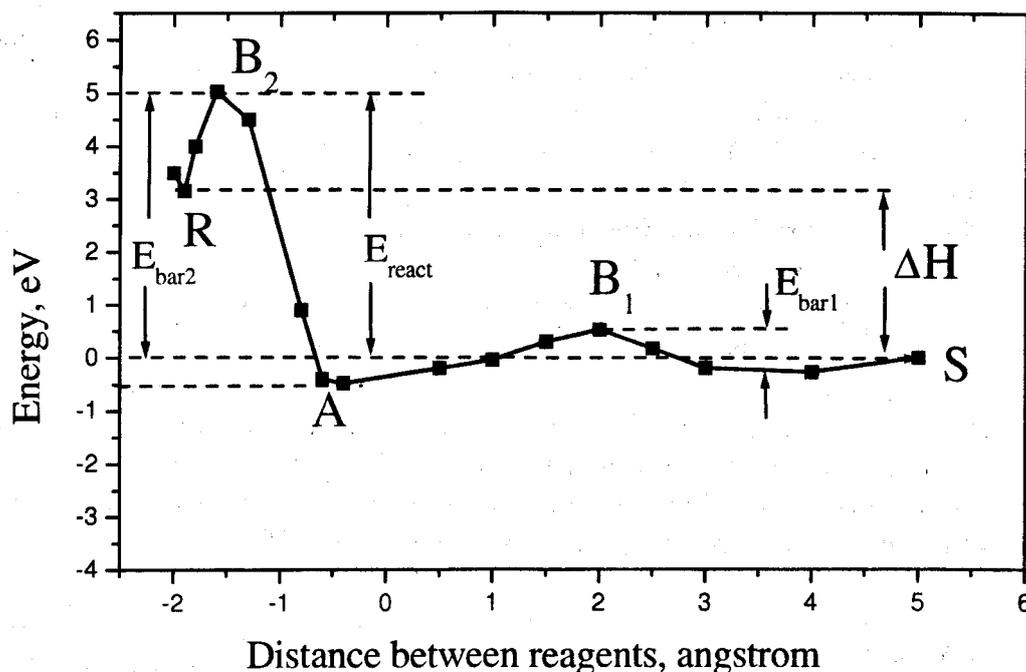
Figure 7. Energy scheme for the oxidation of the C_{22} hexagon cluster (an edge atom is taken as reactive). This reaction produces a CO molecule. Another oxygen atom is bound to the rest of the graphene particle.

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 (for the C_4–C_6 chains). In the case of the C_{22} chain, the changes of C–C distances have a more complicated character. As it is seen from Fig. 4, the C–C bond nearest to the O_2 molecule increases to 1.4 Å, whereas the inter-chain distances are periodically larger or less than 1.3 Å.

3.3. Oxidation of graphene nanoclusters

According to our calculations, graphene (hexagons contained) clusters are more stable than linear chains for the number of atoms equal to 22 or larger. We have used this minimal 22-atomic graphene cluster as a model to study the oxidation of graphene carbon nanoparticles. A scheme of this study is illustrated in Fig. 6 where two cases are shown: A) molecular oxygen interacts with an edge carbon atom having two neighbors; B) molecular oxygen interacts with a basal (internal) carbon atom having three neighbors.

In the case of graphene systems, the dependence of the total energy on the distance between the reagents (an oxygen molecule and a reactive atom of the graphene cluster) looks similar to that of the linear cluster case described above.

Figure 8. The energy scheme for oxidation of the C_{22} hexagon cluster. The O_2 molecule approaches the internal C atom.

The energy scheme of this reaction (with an edge reactive atom) is shown in Fig. 7), where the adsorption stage is characterized by overcoming the adsorption barrier B_1 and by reaching the adsorption state (A). However, the adsorption state is separated from the reaction state by a rather high-energy barrier B_2. (E_{bar2} is larger than E_{bar1}); thus, the reaction is limited by the second barrier. The reaction energy E_{react} may be calculated as a difference between E_{bar2} and the energy of the initial state. In our case $E_{react} = 1.9$ eV. The reaction products consist of a CO molecule and the carbon cluster that has lost one carbon atom but has trapped one oxygen atom (Fig. 6A). The formation (and separation) of the second CO molecule is unfavorable energetically. The activation energy of this process is equal to 3.9 eV. The detailed analysis shows that formation of a CO_2 molecule is also possible. However, the activation energy of this reaction is 2.8 eV which is much larger than the value of 1.9 eV obtained for the reaction with the CO formation. As for the reaction enthalpy, it exceeds the activation energy only for the reaction followed by creation of a single CO molecule (see Table 2). This 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.

A study of the O_2 interaction with the internal atoms of the C_{22} graphene cluster has shown that the internal atoms are much less active than the edge ones (Fig. 8). In this case, the formation of a CO molecule needs the activation energy of 5.02 eV. Enthalpy of this reaction is positive ($\Delta H = +3.2$ eV). In other words, this reaction cannot proceed without an external source of energy. Therefore, the internal atoms do not participate in the combustion reaction until the combustion front comes close to them and they become the edge atoms. The same conclusion has been made in Ref. [31] where the oxidation of graphenes with atomic oxygen was studied using the Hartree-Fock method.

Comparing activation energies for linear (0.3–1.0 eV) and graphene (1.9 eV) clusters with the experimental data for soot (1.5–2.6 eV [15,18–22]), one can conclude that linear carbon chains can play an important role at the first stage of the soot combusting while the temperature is not high. However, the process of stable combustion is mainly limited by the oxidation of graphene particles.

4. Summary

Our PM3 calculations confirm that linear carbon clusters are more stable than graphene (hexagons contained) clusters when the number of atoms is less than 22. The mechanism of oxidation of carbon clusters by molecular oxygen depends on the structure of the cluster. Linear clusters produce CO_2 molecules while graphene clusters give mainly CO molecules. Activation energy for the oxidation of linear clusters shows a non-monotonous dependence on the number of atoms featuring maximums at even numbers and minimums at odd numbers. Activation energy for the oxidation of the C_{22} hexagon cluster depends on the position of reactive carbon atom. It is maximal for the edge atoms and minimal for the internal atoms. Linear carbon chains can play an important role at the first stage of the soot combustion while the temperature is not high. However, the process of stable combustion is mainly limited by the oxidation of graphene particles.

Acknowledgements

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