Catalytic pyrene and pyrene butyric acid condensation as a means of producing graphene

O. A. Shinkarenko[1,2], M. V. Pozharov[3], A. S. Kolesnikova[2], A. S. Chumakov[1,2], A. J. K. Al-Alwani[4], O. Yu. Tsevtkova[2], E. G. Glukhovskoy[1,2]

[1]Department of Nano- and Biomedical Technologies, Saratov State University, Saratov, Russia

[2]Education and Research Institute of Nanostructures and Biosystems, Saratov State University, Saratov, Russia

[3]Institute of Chemistry, Saratov State University, Saratov, Russia

[4]Babylon University, Babylon, Iraq

oksana.sh63@mail.ru, dm89@yandex.ru, kolesnikova.88@mail.ru, lehahares@rambler.ru, ammarhamlet2013@yahoo.com, olgatsvetkova77@gmail.com, glukhovskoy@gmail.com

In the present study, we have conducted molecular modeling of a potential method of graphene sheet formation. As the nano-sized blocks from which graphene can be synthesized, pyrene and pyrene butyric acid are chosen. The potential of several compounds (namely, Pt, Pd, Ni, $AlCl_3$ and $PdCl_4$) as catalysts for hydrocarbon condensation has been estimated by semiempirical calculations. The heat of formation in the series Pt, Pd, Ni, $PdCl_4$, $AlCl_3$ for pyrene is reduced to a minimum and reaches a value of 99 kJ/mol, and for pyrene butyric acid in the series Pt, Ni, Pd, $PdCl_4$, $AlCl_3$ decreases to 295 kJ/mol. According to the results of calculations, Pt and Ni can be the most effective catalysts for this reaction. As a substrate (or 2D nanoscale), we propose to use a surface of water or a monolayer of surfactants on water (this method is realized by the Langmuir–Blodgett method) having a 2D crystal structure whose state can be controlled by external conditions.

Keywords: graphene, catalytic condensation, Langmuir–Blodgett method, polycyclic aromatic hydrocarbons, semiempirical computations, 2D nanotemplate.

Received: 20 June 2017

Revised: 31 October 2017

1. Introduction

Graphene is a promising material, as it possesses unique properties, very interesting from the point of view of practical implementations in the form of unique instruments and of nanoelectronics devices. Currently there are a number of areas where graphene could be used [1–3]. But, in spite of a vast array of potential applications, a universal methodology that would allow obtaining high-quality graphene samples of a large area on a production scale has not yet been found. All published methods for obtaining samples have drawbacks and graphene samples can only be used for a specific purpose. Consequently, the development of new methods for the synthesis of graphene is an area of intense interest and relevant topics in its study.

Contemporary methods of monolayer graphene synthesis can be divided into two main groups – "top-down" methods and "bottom-up" methods. The "top-down" methods [4, 5] involve transforming a graphene slab into thinner layers by breaking the bonds between layers of initial sheet and stabilizing the resulting compound structure. This can be achieved by chemical cleavage or mechanical exfoliation of its precursors (graphite, carbon nanotubes, etc.) using Scotch tape, centrifugation, exposure to ultrasound, strong acids, etc.

"Bottom-up" methods involve cross-linking of various molecular fragments to produce large-scale graphene sheets [6, 7]. One of the most common is the method of deposition from the gas phase, which makes it possible to obtain large sheets of graphene, but its main disadvantages are the use of high temperatures and the possibility of contamination of the product obtained. Another example of this approach is the production of graphene from so-called nanografens. As such substances, polycyclic aromatic hydrocarbon molecules are used. These methods are a promising direction in the field of graphene synthesis.

In this study, we propose the next stage in the development of the method that we described in [8, 9]. By analogy with the Shole reaction, we have described a method for producing graphene sheets by crosslinking molecules of polycyclic aromatic hydrocarbons (such as naphthalene, pyrene, pyrene butyric acid). However, in the synthesis methods (like the Shole method), the mutual approach to the required distance and the favorable orientation of the reacting molecules is a critical condition. For these purposes, most often any solid surfaces are used on which synthesis reactions are carried out. Such surfaces (for example, plates of copper, nickel, etc.)

simultaneously serve as an orienting surface and catalyst. As a rule, such reactions require vacuum conditions, the use of plasma as a stimulating action, the supply of particularly pure reagents, etc.

In this article, we develop a previously-proposed approach, according to which the water-air interface or the surface of an ordered monomolecular surfactant layer formed at the water-air interface is used as a 2D nanoscale. Experimentally, this approach can be implemented without high vacuum or high temperatures. All the processes are realized in Langmuir baths with the help of the Langmuir-Blodgett method, which is based on the principles of self-organization of surfactant molecules at interfaces.

In this paper, we assume that the molecules lie on some 2D template and, for simplicity, are located one below the other and lie in the same plane.

2. Materials and methods

In this paper, we studied the effect of various catalysts (Pt, Pd, Ni, PdCl$_4$ and AlCl$_3$), chosen as a result of the analysis of scientific information, on the condensation reaction of pyrene and pyrene butyric acid, to select the most promising catalyst for subsequent synthesis using semiempirical calculations. Semiempirical calculations of potential intermediate complexes between catalysts and compound have been performed using PM7 method implemented in MOPAC2012 software.

3. Results and discussions. Quantum chemical computations

Pyrene and pyrene butyric acid, which belong to the class of aromatic hydrocarbons, were chosen as starting materials for the further graphene formation (Fig. 1a,b). They were chosen because of their structural similarity to graphene and interesting physicochemical characteristics – they have low water solubility, are solid under normal conditions. Also, the selected substances are soluble in chloroform, which is an important aspect for further synthesis. Since using the Langmuir–Blodgett technique it is necessary to dissolve the substance in a volatile solvent (e.g., chloroform).
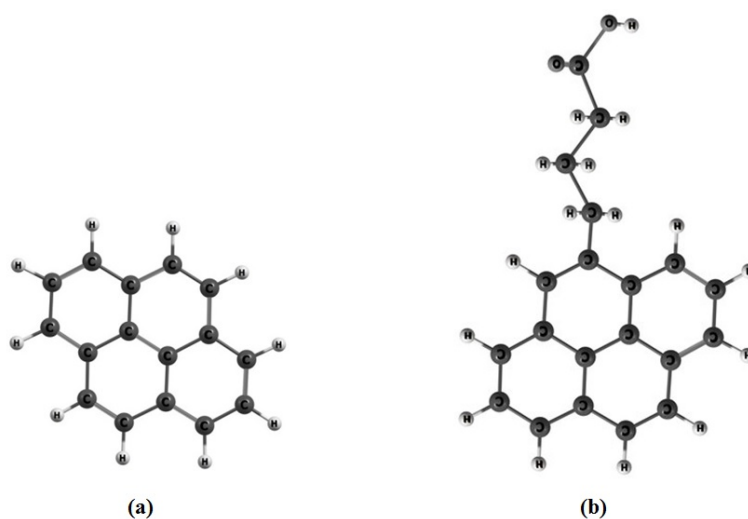

(a) (b)

FIG. 1. Molecules: a) pyrene; b) pyrene butyric acid

To form the required structure of graphene from molecules of aromatic hydrocarbons, it is necessary to carry out the dehydrogenation reaction, as a result of which hydrogen atoms located at the edges of the molecules are removed from the molecule. To carry out the dehydrogenation reaction, different catalysts were used in our approach. As a result of the analysis of literature data, the following catalysts were selected for calculations: Pd, Pt, AlCl$_3$, Ni and PdCl$_4$. The influence of the nature of catalysts on the state of hydrogen atoms in hydrocarbon molecules was investigated. In the presence of catalysts, the crosslinking in graphene was simulated for a given distance between the molecules. The reaction mechanisms for pyrene and pyrene butyric acid are shown in Figs. 2 and 3.

Simulating the reaction of the interaction of aromatic hydrocarbons and catalysts, the heat of formation of the catalysts, the starting molecule and the intermediate complex formed during the reaction was found. On the basis
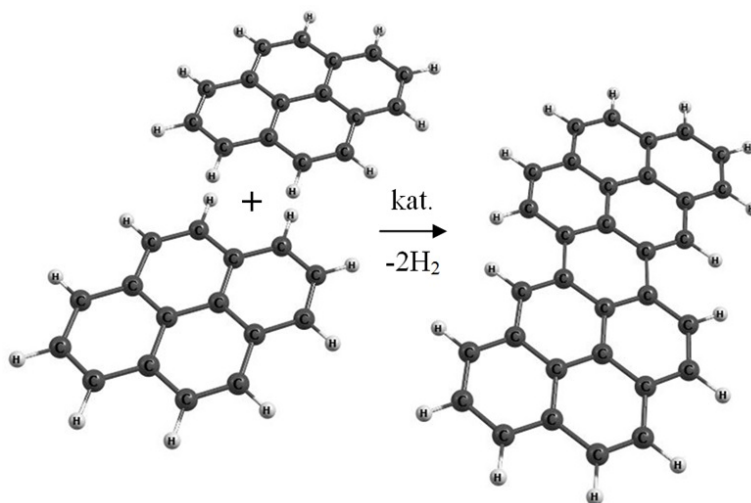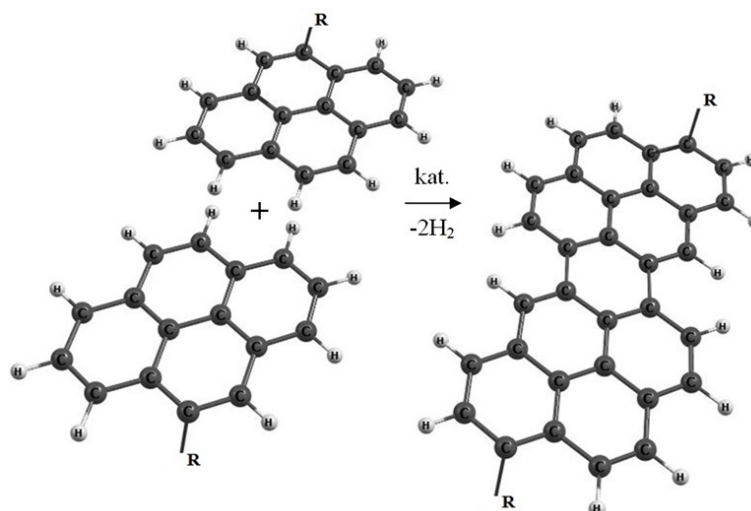
FIG. 2. The mechanism of the condensation reaction for pyrene

FIG. 3. The mechanism of the condensation reaction for pyrene butyric acid, where R is CH_2–CH_2–CH_2–COOH

of these data, the enthalpy of the reaction was calculated by the following formula:

$$\Delta H_r = \Delta H_{fcomp} - (\Delta H_{fkat} - \Delta H_{fpyrene}), \qquad (1)$$

where ΔH_r – enthalpy of reaction ΔH_{fcomp} – heat of formation of intermediate complex, ΔH_{fcat} – heat of catalyst formation $\Delta H_{fpyrene}$ – heat of formation of initial compound.

The results of calculations are presented in Table 1.

Thus, according to the results of calculations, the use of platinum and nickel, as the most effective catalysts, can be recommended for the condensation reaction of pyrene or pyrenbutanoic acid. This can be suggested, as the catalyst component system has a higher heat of formation than the other studied catalysts, 1768 kJ/mol and -361 kJ/mol, respectively.

4. Conclusion

The potential of several compounds, including Pt, Pd, Ni, $AlCl_3$ and $PdCl_4$ as catalysts for pyrene and pyrene butyric acid condensation has been estimated by semiempirical calculations. According to calculation results, the most efficient catalyst for proposed selected substances condensation is Pt, followed by Ni.

TABLE 1. Calculated enthalpies of studied compounds

	Pyrene		Pyrene butyric acid	
	ΔH_f, kJ/mol	ΔH_r, kJ/mol	ΔH_f, kJ/mol	ΔH_r, kJ/mol
Compound	262	–	233	–
Pt	1660	–	1660	–
Compound-Pt system	416	−1768	115	−2000
Pd	377	–	377	–
Compound-Pd system	333	−568	144	−953
Ni	631	–	631	–
Compound-Ni system	794	−361	−31	−1120
AlCl$_3$	−593	–	−593	–
Compound-AlCl$_3$ system	−240	−99	−422	−295
PdCl$_4$	−83	–	−83	–
Compound-PdCl$_4$ system	342	−347	−88	−571

References

[1] Mattevi C., Eda G. Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films. *Adv. Funct. Mater.*, 2009, **19**, P. 1–7.

[2] Narita A. New advances in nanographene chemistry. *Chem. Soc. Rev.*, 2015, **44**(18), P. 6616–6643.

[3] Al-Alwani A.J.K., Chumakov A.S., Shinkarenko O.A., Gorbachev I.A., Pozharov M.V., Venig S., Glukhovskoy E.G. Formation and optoelectronic properties of graphene sheets with CdSe/CdS/ZnS quantum dots monolayer formed by Langmuir-Schaefer hybrid method. *Applied Surface Science*, 2017, **424**, P. 222–227.

[4] Novoselov K.S., Jiang D., Schedin F., Booth T.J., Khotkevich V.V., Morozov S.V., Geim A.K. Two-dimensional atomic crystals. *PNAS*, 2005, **102**(30), P. 10451–10453.

[5] Hamilton C.E., Lomeda J.R. High-yield organic dispersions of unfunctionalized graphene. *Nano Lett.*, 2009, **9**(10), P. 3460–3462.

[6] Zhang L. Catalyst-Free Growth of Nanographene Films on Various Substrates. *Nano Res.*, 2011, **4**(3), P. 315–321.

[7] Rempala P., Kroulík J. Investigation of the Mechanism of the Intramolecular Scholl Reaction of Contiguous Phenylbenzenes. *J. Am. Chem. Soc.*, 2004, **126**, P. 15002–15003.

[8] Kolesnikova A.S., Safonov R.A., Shinkarenko O.A., Chumakov A.S., Soldatenko E.M., Glukhovskoy E.G. Graphene Synthesis from Naphthalene Molecules on Top of Langmuir Monolayer. *J. Surf. Invest.-X-ray+*, 2017, **11**(3), P. 510–516.

[9] Shinkarenko O.A., Safonov R.A., Kolesnikova A.S., Al-Alwani Ammar J.K., Pozharov M.V., Glukhovskoy E.G. Naphthalene condensation as a means of producing nanostructured graphene. *Appl. Surf. Sci.*, 2017, **424**, P. 177–173.