Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Density Functional Theory Study on the Reaction of Finite-Sized Graphene with Methyne

Tomoya Takada [a], Yosuke Komatsu [a] & Tsukasa Takagi [a]
[a] Department of Materials Chemistry, Asahikawa National College of Technology, Asahikawa, Japan
Published online: 11 Sep 2013.

To cite this article: Tomoya Takada, Yosuke Komatsu & Tsukasa Takagi (2013) Density Functional Theory Study on the Reaction of Finite-Sized Graphene with Methyne, Molecular Crystals and Liquid Crystals, 579:1, 62-68, DOI: 10.1080/15421406.2013.805087

To link to this article: http://dx.doi.org/10.1080/15421406.2013.805087

Mol. Cryst. Liq. Cryst., Vol. 579: pp. 62–68, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.805087

Taylor & Francis
Taylor & Francis Group

Density Functional Theory Study on the Reaction of Finite-Sized Graphene with Methyne

TOMOYA TAKADA,* YOSUKE KOMATSU, AND TSUKASA TAKAGI

Department of Materials Chemistry, Asahikawa National College of Technology, Asahikawa, Japan

We studied the reactivity of finite-sized graphene with methyne (CH radical) theoretically by means of density functional theory (DFT) calculations. We identified a favorable reaction site for model graphene by comparing the total energies of the adducts corresponding to the inequivalent reaction sites. The addition of methyne to an edge site of the graphene was energetically favorable rather than an inner site. The potential energy barrier for the methyne addition became lower as the model size became larger. We also discuss the reactivity of methyne with graphene discussed on the basis of our calculation results.

Keywords Density functional theory; graphene; methyne

Introduction

Graphene, a component of graphite, is a planar sheet composed of carbon atoms. Graphite is composed of a number of stacked graphene sheets, and these sheets are bound to each other through the van der Waals interaction. Graphite is important as a coverage material for nozzles used in combustion gas exhaustion [1], and thus knowledge of the chemistry of the reaction of graphene with combustion products will be important for the future design of structural materials related to fuel combustion instruments. For example, Xu et al. studied the mechanism of the reaction of pristine and defective graphene with many small species (H_2O, OH radical, O atom, O_2, NO, NO_2, and so on) by means of desity functional theory (DFT) [2–6]. Tachikawa et al. also studied the interaction between graphene and small species (H_2O clusters, H atom) by means of DFT [7–9]. Wang et al. Recently reported their theoretical study of H atom addition to graphene by DFT and coupled cluster (CC) methods [10].

One of the important combustion products is hydrocarbon radical. For example, in the combustion of hydrocarbon fuel, the following reaction occurs and methyne (CH radical) is formed:

$$C_2 + OH \rightarrow CH + CO \tag{1}$$

*Address correspondence to Dr. Tomoya Takada, Department of Materials Chemistry, Asahikawa National College of Technology, 2-2-1-6, Syunkodai, Asahikawa 071-8142, Japan. Fax: +81-166-55-8036. E-mail: takada@asahikawa-nct.ac.jp

Here, C_2 and OH are formed at the initial stage of combustion. Since CH is highly reactive, it rapidly reacts with oxygen gas (O_2) to form OH and CO [11]:

$$CH + O_2 \rightarrow OH + CO \tag{2}$$

In the hydrocarbon combustion, methyne is thus diminished by the second reaction. With the presence of other carbon materials such as graphite, methyne would react also with them and form surface defects of carbon materials. This process seems to affect mechanical, electric and chemical properties of carbon materials. However, the detailed mechanism of the reaction of graphene (the surface component of graphite) with hydrocarbon radicals is still unclear.

In the present study, we studied the reaction process of graphene with methyne by means of DFT calculations employing finite-sized (ring number: 7 and 19) model graphenes. A favorable reaction site was identified by our calculations of the total energy of the reaction products. Model size dependence of the potential energy barrier of the reaction was preliminarily confirmed. On the basis of the calculation results, we discuss the reactivity of methyne with graphene.

Method

To represent graphene's structure, we first used a model graphene consisting of seven benzene rings. The structure of the model is shown in Figure 1. Its edges were terminated with hydrogen atoms. The optimized structure and total energy of the model and methyne were separately obtained by DFT calculations at the B3LYP/6–31G(d) level. The structure and total energy of the products of methyne addition to the model graphene were also obtained, in the same manner. All calculations were performed with the Gaussian 03 program package [12].

To compare the potential energy change of methyne addition to graphenes with different sizes, we calculated the total energies of the graphene-methyne complexes as a function of graphene-methyne distance. In this calculation, the larger model graphene consisting of 19 benzene rings was used.

Results and Discussion

Favorable Reaction Site of Graphene with Methyne

First, we identified a thermodynamically favorable reaction site for methyne addition by comparing the total energy of the products. Possible reaction sites are labeled in the optimized structure of model graphene shown in Fig. 1. The smallest model (ring number: 7) has four inequivalent sites. The relative energies obtained for the products are listed in Table 1. The zero level of energy corresponds to the sum of the individual total energies of graphene and methyne.

The optimized structures of the products of methyne addition are shown in Fig. 2. The graphene before methyne addition was completely planar, whereas after the reaction the graphene changed to a bent structure; bridge-type adducts in which methyne carbon bonded to two adjacent surface carbons of graphene were obtained by methyne addition to sites A, B and D. In the case of addition to site C, an insertion product containing a planar seven-membered ring structure was obtained. A similar type of insertion was suggested

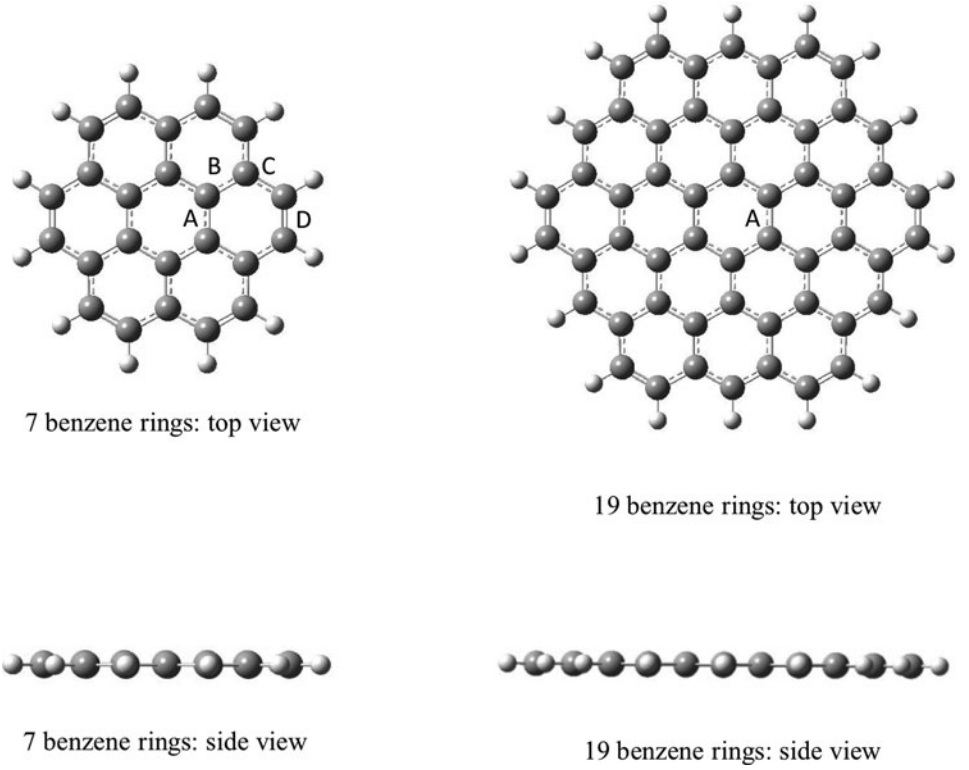


Figure 1. Optimized structures of model graphenes. White and gray spheres represent hydrogen and carbon, respectively.

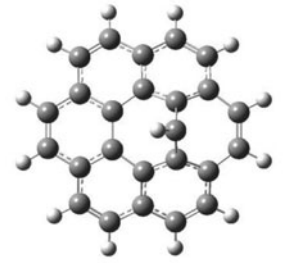
regarding the reaction of ethylene and cyclopentadiene with reactive carbon species [13, 14]. This seven-membered ring product has the lowest total energy.

Similarly, we found that in a comparison of the total energy of the three-membered adducts, the reaction site at the edge region (site D) had relatively low total energy. This tendency is due to the hybrid orbital deformation at the reaction site; in the edge sites an sp^2 hybrid orbital is smoothly deformed by its interaction with methyne. The change of

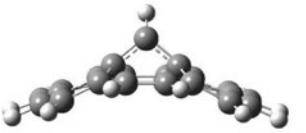
Table 1. Relative energies obtained for the products of methyne addition to model graphene (ring number: 7)

Reaction site	Relative energy / eV
Graphene + CH*	0
site A	−1.75
site B	−1.81
site C	−4.28
site D	−2.95

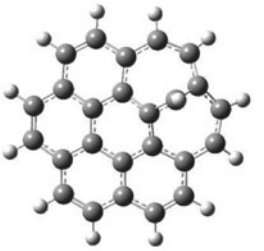
*The zero level of energy corresponds to the sum of individual total energies of graphene and methyne.



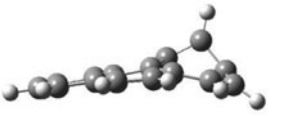
Addition to site A: top view



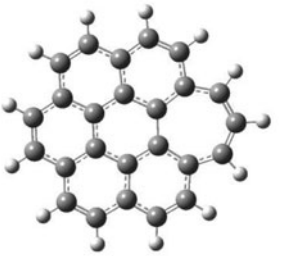
Addition to site A: side view



Addition to site B: top view

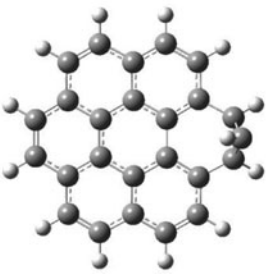


Addition to site B: side view



Addition to site C: top view

Addition to site C: side view



Addition to site D: top view

Addition to site D: side view

Figure 2. Optimized structures of reaction products of methyne addition.

hybrid orbital is restricted at the inner sites because of the hindered movement of carbon atoms. The total energies of the adducts corresponding to the inner sites (sites A and B) are almost equal.

In a widely extended real graphene sheet, the number of edge sites would be quite limited compared to the number of inner sites (site A). Therefore, the edge sites appear to be favorable for methyne addition from the energetic viewpoint, while the reaction frequency at an inner reaction site will be much higher than that at an edge site. The identification of the actual favorable reaction site will be the subject of a future study.

Potential Energy Change in the Course of Methyne Addition to Model Graphenes

The relative energy change of the graphene-methyne system as a function of graphene-methyne distance is shown in Fig. 3. We used the model graphene with the 19-benzene ring in this calculation. Methyne approached the inner site (corresponding to site A) of the graphene surface perpendicularly. The C-H bond of methyne inclined 45 degrees to the graphene surface. This angle was fixed to reduce the variables to be optimized because of the limitations of our computational environment; to obtain the information on a potential energy change for a fully optimized structure, this angle should also be optimized, but full optimization of the geometrical parameters is difficult to perform under the calculation conditions in this work. The geometry of graphene moiety was fully optimized.

Figure 3 provides the relative energies of the reactants, products and transition states of the methyne addition. We observed an activation barrier in the potential energy curve; this barrier is formed by the change of hybrid orbital. The barrier height for larger graphene is lower than that of smaller graphene; the barrier height decreases with the size of the model graphene. The real graphene sheet will be much larger than the models examined in this study, and thus the activation barrier height of the reaction of real graphene will be lower than that calculated for the finite-sized models. According to classical reaction kinetics, the barrier height corresponds to the reaction rate. The reaction with a lower activation barrier proceeds faster than a reaction with a higher barrier. We therefore expect methyne addition

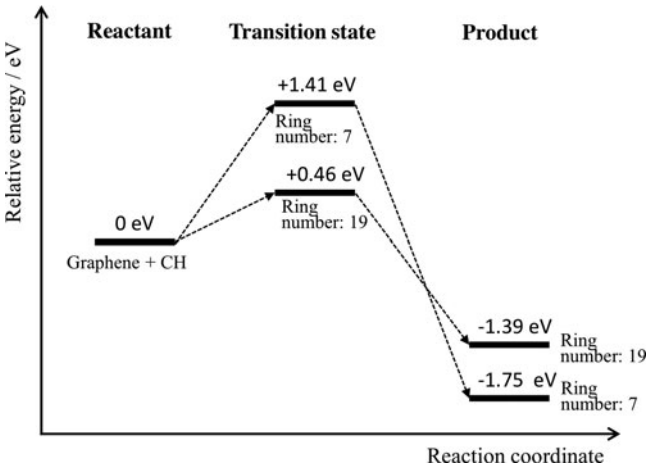


Figure 3. Schematic illustration of relative energy change in the course of methyne addition to graphene. The zero level of energy corresponds to the sum of individual total energies of graphene and methyne.

to widely extended graphene to proceed faster than the addition to smaller graphene. The size of the graphene sheet thus affects its reactivity with methyne, and the widely extended graphene sheet consisting of a number of carbon atoms seems to be easily attacked by methyne. This methyne addition will change the structure of the graphene and affect its mechanical and electric properties. In addition, the reaction will induce the formation of surface defects, and the chemical stability of graphene may be lessened by the defect formation.

Conclusions

The new findings obtained in this work are summarized as follows:

- From the energetic viewpoint, methyne is most likely to react with graphene at the edge sites to give a bridge-type or insertion-type product. However, in a real graphene sheet, the number of inner reaction sites is much larger than that of edge sites. The identification of the favorable reaction site in the case of real graphene remains for further studies.
- In the potential energy curve of the methyne addition, an activation barrier exists. This barrier is formed by the change of the hybrid orbital of carbon atoms. The barrier height decreases with the size of graphene; methyne addition to large graphene is expected to occur smoothly. The reaction will affect the mechanical, electric and chemical properties of graphene-based carbon materials.

We found that in the calulation of potential energy changes during the methyne addition, the reaction site was limited to the inner carbon of the graphene sheet in this work; the methyne addition to the edge site was not considered. As mentioned in the Discussion section, in a widely extended real graphene sheet, the number of edge sites would be quite limited compared to the number of inner sites. Thus, it is rational to take particular notice of the reaction at the inner site. However, to enable more detailed knowledge of the reaction pathway, the potential energy change of the reaction at the edge site should also be calculated. This is also a subject for future studies. And of course, the potential energy change calculated for a fully optimized reaction system will also be necesssary for the elucidation of the overall mechanism of the methyne addition.

Acknowledgment

This work was financially supported by the the Institute of National Colleges of Technology, Japan.

References

[1] Keswani, S. T., Andiroglu, E., Campbell, J. D., & Kuo, K. K. (1985). *J. Spacecraft and Rockets*, *22*, 396.
[2] Xu, S., Irle, S., Musaev, D. G., & Lin, M. C. (2005). *J. Phys. Chem. A*, *109*, 9563.
[3] Xu, S. C., Irle, S., Musaev, D. G., & Lin, M. C. (2007). *J. Phys. Chem. C*, *111*, 1355.
[4] Xu, S. C., Irle, S., Musaev, D. G., & Lin, M. C. (2009). *J. Phys. Chem. C*, *113*, 18772.
[5] Xu, S. C., Irle, S., & Lin, M. C. (2010). *J. Phys. Chem. C*, *114*, 8375.
[6] Xu, S. C., Chen, H.-L., & Lin, M. C. (2012). *J. Phys. Chem. C*, *116*, 1841.
[7] Tachikawa, H., Iyama, T., & Kawabata, H. (2010). *Jpn. J. Appl. Phys.*, *49*, 01AH06.
[8] Tachikawa, H., & Iyama, T. (2010). *Jpn. J. Appl. Phys.*, *49*, 06GJ12.
[9] Abe, S., Nagoya, Y., Watari, F., & Tachikawa, H. (2011). *Jpn. J. Appl. Phys.*, *50*, 01BJ02.

[10] Wang, Y., Qian, H.-J., Morokuma, K., & Irle, S. (2012). *J. Phys. Chem. A.*, *116*, 7154.
[11] Carl, S. A., Van Poppel, M., & Peeters, J. (2003). *J. Phys. Chem. A.*, *107*, 11001.
[12] Frisch, M. J. *et al.* (2003). *Gaussian 03, Revision B. 03*, Gaussian Inc.: Pittsburgh, PA.
[13] Rose, T., MacKay, C., & Wolfgang, R. (1966). *J. Am. Chem. Soc.*, *88*, 1064.
[14] Nicholas, J., MacKay, C., & Wolfgang, R. (1966). *J. Am. Chem. Soc.*, *88*, 1065.