Theoretical study on the adsorption behavior of CO and C$_2$H$_2$ on graphene sheet: Active sites and basal surface

T. Hosseinnejad*$^a$, F. Nazari$^b$, Z. Zarbi$^b$, R. A. Mirzaei$^b$

$^a$Department of Chemistry, Faculty of Science, Alzahra University, PO Box: 19835-389, Vanak, Tehran, Iran
$^b$Department of Chemistry, Faculty of Science, Shahid Rajaee Teacher Training University, Tehran, Iran
*Tayebeh.Hosseinnejad@gmail.com

Abstract: The adsorption of CO and C$_2$H$_2$ on perfect and defective graphene surfaces has been investigated by adopting cluster models in conjunction with semi-empirical molecular orbital calculations. The interaction potential energy curves for three different orientations of CO and C$_2$H$_2$ molecules with respect to the inert basal plane graphene have been calculated with approximate step size of 0.5 Angstrom. Moreover, the calculated adsorption energies of CO and C$_2$H$_2$ on the clean basal surface revealed their weak interaction nature and consequently their physisorped behavior on this surface model. Moreover, it was found that the defect edge sites of zigzag and armchair surface models exhibit the significant catalytic role toward the chemisorptions and activation of molecular CO and C$_2$H$_2$ while these molecules not only able to strongly bind to these edge sites but also C-O and C-C bond strength is obviously weakened.

Keywords: Graphene; Carbon monoxide; Acetylene; Adsorption energy; Semi-empirical methods.

Introduction

One of the most important methods of producing carbon compounds is Chemical Vapor Deposition (CVD). The growth of carbon material, such as carbon fibers, carbon nano-tubes [1,2], pyrolytic carbons[3,4] and carbon nano-spheres (that are all related mainly to graphite structures) on substrates by catalytic CVD also has received much attention in recent years.

Carbon monoxide and acetylene are used industrially in the pyrolysis reaction for production of carbon materials including graphite, via a growth process. Since the extended honey comb structure of graphene surface is the basic building block of other important allotropes such as 3D graphite, 1D nanotubes and 0Dfullerene, we have studied polycyclic aromatic hydrocarbons (PAHs) to model the adsorption of CO and C$_2$H$_2$ molecules on the active sites of graphene nano-layers. These PAHs [5,6] themselves are of great research interest due to their high stability, their rigid planar structure and their characteristic optical spectra [5,6].

Generally, the investigations regarding the adsorption on planar surfaces can roughly be classified into two categories. One is the adsorption on perfect surface that is chemically inert towards the adsorption and dissociation of small molecules, the other happens on the defective surface which exhibits relatively high surface reactivity and thus contributes to the catalytic reactions.

In this research, we have mainly focused on the theoretical effective cluster models of graphene layer and its growth via the pyrolysis reaction of CO and C$_2$H$_2$ using semi-empirical AM1, PM3 and PM6 quantum computational methods [7,8].

Computational details

As the first step in survey of interaction potential energy between graphene sheet with CO and C$_2$H$_2$ molecules, three cluster models were employed in our calculations, considering that they can offer an excellent compromise between accuracy and time-saving efficiency with respect to graphite surface[9,10]. These cluster models that entitled as basal, zigzag and armchair sheets respectively (shown in Fig.1) represent different adsorption sites of graphite surface, since they can yield parameters in excellent agreement with experimental data[9-11].

In the next step, three different relative orientations were considered for the approach of CO and C$_2$H$_2$ molecules towards each graphene sheet models [12,13]. All calculations were carried out in the framework of semi-empirical AM1, PM3 and PM6 levels of theory implemented in MOPAC 2009 software.

Results and Discussion

The adsorption energy at each distance R, were defined according to the expression:

$$E_{ad}(R) = E(G-m) - E(G) - E(m)$$

Where E(m) is the energy of an isolated molecule, E(G) is the energy at its optimized relaxed geometry in the absence of the adsorbed species and E(G-m) corresponds to the energy at its optimized geometry upon molecule adsorption on graphene sheet.

Firstly, the adsorption of CO and C$_2$H$_2$ molecules on graphene surface has been considered in the three relative
configurations for basal, armchair and zigzag structure models of graphene. These relative orientations have been displayed schematically in Fig.1.

However, the calculated results based on the optimized structure of CO-graphene and C\textsubscript{2}H\textsubscript{2}-graphene and their adsorption energies on basal cluster model reveal that CO and C\textsubscript{2}H\textsubscript{2} species can only be physisorbed on the perfect basal sheet while the adsorption energy is about -3 kJ.mol\textsuperscript{-1} at PM6 level, suggesting the weak nature of interactions. From the structural viewpoint, it can be clearly seen that the optimized computed C-O and C-C bond distances in the aforesaid basal models is about 0.1124 nm and 0.1202 nm respectively, the same as that of calculated free CO and C\textsubscript{2}H\textsubscript{2} in the gas phase.

It should be noted that the calculated CO-graphene interaction energies in basal cluster model is slightly more strong than the obtained C\textsubscript{2}H\textsubscript{2}-graphene adsorption energies, which can be attributed to the greater polarizability of graphene sheet in the presence of CO molecule. The CO-graphene and C\textsubscript{2}H\textsubscript{2}-graphene interaction potential energy curves were calculated for the three relative orientations in basal model using AM1, PM3 and PM6 levels and have been illustrated for PM6 results in Figs.2 and 3 respectively. As it can be seen in these figures, the relative orientation in which CO and C\textsubscript{2}H\textsubscript{2} molecules approach the graphene sheet perpendicularly has more potential depth and consequently depicts more strong interactions.

In order to investigate the chemisorption of CO and C\textsubscript{2}H\textsubscript{2} molecules on the edge sites of the defect graphene surface, the armchair and zigzag cluster models have been employed. Based on the obtained results for unsaturated zigzag and armchair structures, a chemisorbed C-O and C-C species bonded to the underlying C-C bond was identified with the value of about -400 kJ.mol\textsuperscript{-1}at PM6 level for the adsorption energies. Moreover, the C-O and C-C bond length was elongated to 0.1195 nm and 0.1355 nm respectively that indicated the adsorbed CO and C\textsubscript{2}H\textsubscript{2} were activated at these defect sites of zigzag and armchair surfaces. It is important to mention that analysis of the calculated results for those orientations that CO and C\textsubscript{2}H\textsubscript{2} approach to armchair and zigzag sheets from the clean and inert sides shows the weak adsorption energies of about -3 kJ.mol\textsuperscript{-1}.

**Conclusion**

To summarize, semi-empirical molecular orbital calculations have been used to study and analyze the adsorption behavior of CO and C\textsubscript{2}H\textsubscript{2} molecules on three different graphene cluster models from the energetic and structural viewpoints. A comparative study on the calculated physical interaction potential energy curves of CO and C\textsubscript{2}H\textsubscript{2} with the clean basal surface model shows that i) CO-graphene interaction energies in basal cluster
model is slightly more strong than the obtained C$_2$H$_2$-graphene adsorption energies and ii) the relative orientation in which CO and C$_2$H$_2$ molecules approach the graphene sheet perpendicularly has more potential depth and consequently depicts more strong interactions. This means specifically that the graphite prefers to increase its thickness via the pyrolytic reaction of CO and C$_2$H$_2$.

In addition, we have found that the edge sites on zigzag and armchair surface models exhibit the active catalytic reactivity toward the adsorption and dissociation of CO and C$_2$H$_2$. Not only the large adsorption energies have been obtained but also obvious C-O and C-C bond strength weakening was found with respect to the adsorption of CO and C$_2$H$_2$ at these active sites.

![Graphene adsorption energy](image)

**Fig.3.** The C$_2$H$_2$-graphene physical interaction potential energy curves for the three relative orientations in basal model at PM6 level.

**Acknowledgment**

The first author gratefully acknowledges partial financial support from the research council of Alzahra University.

**References**


