INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 15254–15265

Available online at www.sciencedirect.com

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Effect of boron doping in sumanene frame toward hydrogen physisorption: A theoretical study

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ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form
3 July 2016
Accepted 5 July 2016
Available online 21 July 2016

Keywords:
Hydrogen adsorption
Physisorption
Sumanene
Carbon nanostructure
Boron doping
NBO

ABSTRACT

Because of carbon-based materials have shown excellent results for the adsorption of hydrogen as an energy source, in this study, adsorption properties of 26 boron disubstituted sumanene isomers were investigated using MP2/6-311++G(d,p)//B3LYP/6-31+G(d) level of theory. The influence of sumanene modifications on its adsorption properties towards the hydrogen molecule was evaluated and zero point energy (ZPE) and basis set superposition error (BSSE) corrections were applied to calculate interaction energies (IE). Molecular electrostatic potential (MEP) surfaces were also employed to better understanding the adsorption sites and additional details about adsorption. The adsorption properties were discussed by using density of states (DOS), projected density of states (PDOS), overlap population density of states (OPDOS) and natural bond orbital (NBO) analysis. Stability and reactivity, natural population analysis (NPA), dipole moment, HOMO–LUMO gap (HLG) and bowl depth of the isomers were discussed and temperature effects on the interaction energy were evaluated. The results indicate a physisorption mechanism and insignificant perturbation of isomers after adsorption. Also, respect to position of boron atoms in frame of sumanene, interaction energy increases or decreases in comparison with pristine sumanene. The best and the worst isomers and the best and the worst classes of isomers were proposed for future experimental studies.

Introduction

Today, the world needs a substitute to the present energy source i.e. fossil fuels because of environmentally problems and limited sources. Hydrogen is an ideal energy carrier for mobile applications among other alternatives. It is an environment friendly, renewable and the third most abundant element on the earth's surface. It is expected that a desirable hydrogen storage system have these properties: low-sized, light and capable of releasing hydrogen gas at standard condition of temperature and pressure [1–3]. One of the main areas that use hydrogen for clean energy is proton exchange membrane fuel cell (PEMFC) technology which converts chemical to electrical energy. It has been vastly studied in the literature [4–9]. In PEMFCs, the membrane electrode assembly is a major factor in the unit lifespan and cost and the commercialization of PEMFCs is dependent on it. Insufficient durability mainly because of the downfall of the proton exchange membrane (PEM) component is one of the major factors inhibiting the widespread distribution of this technology. Therefore, an essential step to perform the commercialization requirements for PEMFCs is to enhance the membrane lifetime [4,6,8].

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http://dx.doi.org/10.1016/j.ijhydene.2016.07.027

Recently, carbon nanostructures with light weight and high surface-to-volume ratio are a candidate for hydrogen adsorption purposes and are center of attentions [10–14]. But, interaction of hydrogen in molecular form with pristine carbon nanostructures is weak (physisorption) and the interaction energy is very low at conventional temperature. This low interaction energy is not suitable for hydrogen storage applications and must be modified. Doping with suitable elements is one of the best approach to increase its interaction energy and hydrogen storage value [15,16].

Theoretical considerations are very suitable for discovering and improving new materials for hydrogen storage applications, while experimental evaluating the hydrogen storage capacity of a new material requires not only synthesis of it but also the high precision equipments. There are various candidate materials for hydrogen storage applications such as fullerenes [17], carbon nanotubes [18], organic molecules as liquid organic hydrogen carrier [19], boron sheets [20], graphene [21,22] etc.

Bowl-shaped π-conjugated compounds such as sumanene ($C_{21}H_{12}$), corannulene ($C_{20}H_{10}$) and circumtrindene ($C_{36}H_{12}$) which are sub-fullerene structures, are model compounds of fullerenes with their own chemical and physical properties. They have been attracting great interest because of their promising potential for electrical materials [23,24].

Sumanene is an unsaturated hydrocarbon and a polycyclic aromatic hydrocarbon containing six fused rings (five and six-membered rings, alternatively) around a central six-membered ring. It was synthesized by Sakurai et al. [25], it is a partly novel synthesized molecule and so far it is not enough investigated theoretically or experimentally. Exploring the structure, bowl-to-bowl inversion dynamics, population and charge analysis, vibrational spectra, and some other physicochemical properties of sumanene were studied theoretically by Priyakumar and Sastry before that it will be synthesized [26]. Also, they estimated the strain energy through the isodesmic equations. It has two accessible different faces: concave (inside) and convex (outside). As shown in Fig. 1, it has four kinds of C atom and six kinds of C–C bonds. Sumanene has the molecular bowl-depth equal to 1.11 Å [27] in comparison to the bowl-depth of corannulene that is equal to 0.87 Å.

In a theoretical study, Armaković et al. indicated that the sumanene can be very useful in the practical application for storage of hydrogen [27,28]. In 2012, Armaković et al. evaluated specificities of boron disubstituted sumanene (16 isomers). The stability of isomers, NMR parameters, nucleus independent chemical shift (NICS), aromaticity, bowl to bowl inversion barrier and NBO/NPA analysis were considered [29]. Adsorption of CO, CO_2 and NH_3 molecules onto sumanene was studied theoretically and a physisorption mechanism was proposed for them [30].

Recently, Armaković et al. investigated the influence of sumanene modifications with boron and nitrogen atoms (only in benzylic positions) on its adsorption properties towards the hydrogen molecule [31]. Their results indicated a physisorption mechanism. Moreover, the significance of charge separation by inducing boron and nitrogen atoms was discussed. In our recent published paper, functionalization of the sumanene by nitrous oxide was studied, theoretically and a mechanistic study of the cycloaddition reaction of nitrous oxide onto sumanene nanostructure was done [32]. Thirteen pathways for reaction of nitrous oxide with different kinds of C–C bond of sumanene were investigated.

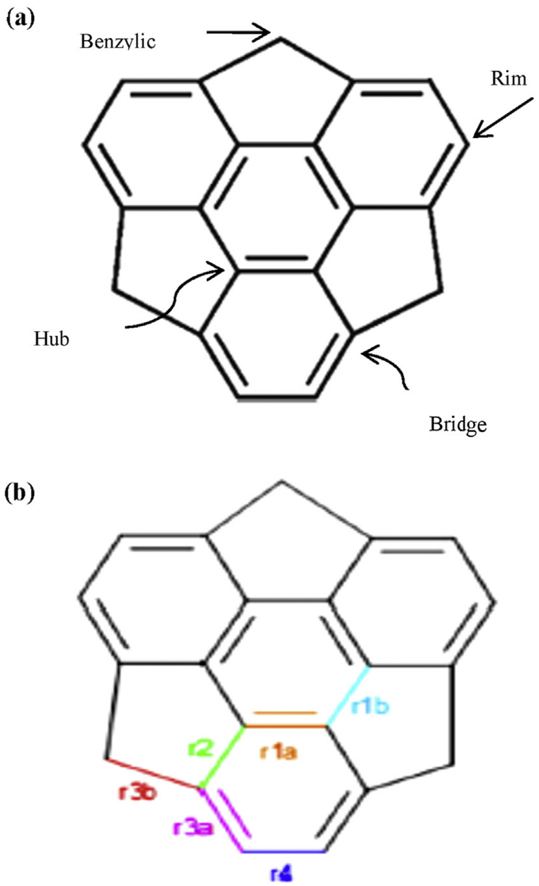

Fig. 1 – Various type of: (a) carbon atoms, and (b) C–C bonds.

In the past decade, there are few studies for sumanene and its derivatives [33–46]. To our knowledge, except to Armaković's work that mentioned above and only benzylic positions substituted with boron atoms, there is no theoretical or experimental study of hydrogen adsorption onto disubstituted boron doped sumanene. In this work, we investigated 26 disubstituted boron doped sumanene isomers obtained by substitution of two C atoms with two B atoms in various positions (except benzylic position). We have investigated the effect of doping of two boron atoms and their positions on the hydrogen adsorption of sumanene. Interaction energies with respect to zero point energy (ZPE) and basis set superposition error (BSSE) corrections have been calculated and the best isomer was assigned for the hydrogen adsorption. MEP surfaces were also employed to better understanding the adsorption sites and additional details about adsorption. The adsorption properties were discussed by using DOS, PDOS, OPDOS and NBO analysis. Stability and reactivity, dipole moment, HOMO–LUMO gap and bowl depth of the isomers were discussed and temperature effects on the interaction energy were evaluated.