Hydrogenation of Substituted Fullerenes – a DFT Study

K. Muthukumar, M. Sankaran and B. Viswanathan*

Department of chemistry, Indian Institute of Technology Madras, Chennai - 600 036, India

Abstract

Hydrogen storage by carbon materials is a topic of current interest. In order to exploit fullerenes as one of the new forms of carbon for hydrogen storage, it is shown that an activator for hydrogen is necessary in the fullerene network. Even though one can generate stoichiometric hydrides the formation of such hydrides have to be established. In this present study we have examined what type of species on carbon surfaces may be able to activate hydrogen molecule and lead to hydride formation. The Density Functional Theory calculations have been carried out on some typical model systems wherein the fullerene molecule is substituted in the network with heteroatoms like N, P and S and the reduction in the dissociation energy of hydrogen molecule is considered as a measure of the ability to hydride the carbon materials. On the basis of the reduction in the dissociation energy for the hydrogen molecule it was shown that heteroatom substitution in the fullerene net work may be suitable for the activation and dissociation of hydrogen molecule.

Introduction

Hydrogen storage is one of the critical components of the hydrogen based energy economy. Various storage options have been tried in the past and the successful development of an economically viable medium to store hydrogen of 6.5 weight percent is essential. Storage in solid matrices appears to be the option available since in this state, one could achieve usable capacity ratio greater than 1 [1], which means that in presence of solids the amount of hydrogen stored is higher than what can be stored in the absence of the absorbent. For hydrogen storage in solid matrices, the options available are metals, intermetallics, porous solids and carbon materials. In the case of metals and intermetallics, the adverse factors are the limitation in the storage capacity or the reversibility of stored hydrogen under favourable experimental conditions. Storage of hydrogen by a new generation of carbon materials like carbon nanotubes, carbon nanofibers and fullerene appears to be promising route to achieve the DOE standards of storage of 6.5 weight percent. After the recent report that carbon nanomaterials can store hydrogen, (though this observation has not been reproduced to any satisfactory extent) [2] a variety of investigations dealing with modification of carbon materials like metal loading, preparing carbon materials in various geometrical forms, phase purity, addition of metal oxides have been tried to establish reversible hydrogen storage.

The objective of this report is to focus on the logic behind this contention that carbon materials may be the possible candidates for hydrogen storage applications as well as to outline the fullerene and fullerene-based materials may be the promising medium for hydrogen storage. Fullerenes have recieved attention due to their unusual hydrogen – sorbing properties and the process of reversible reaction with hydrogen. When one considers fullerenes as the storage medium, theoretically they can store up to about 7.7 wt.% of hydrogen, which is greater than the required amount for an economically viable storage medium. Even though the storage capacity of fullerenes is high, currently the hydrogenation of fullerene requires high pressure and temperature for the reaction to take place to overcome the reaction barrier [3-5]. The hydrogenation of fullerenes involves formation of C–H bonds as a result of breakage of C=C double bonds and dissociation of hydrogen molecule to form hydrogen atoms. From the experimental results, the activation energy for the hydrogenation was estimated to be 1.0 eV/H_2 and for dehydrogenation to reestablish C=C and reforming hydrogen molecule is higher about 1.6 eV/H_2. To over come this potential barrier high temperatures (> 673 K) and pressures (> 60 MPa) are required.

*corresponding author. E-mail: bvnathan@iitm.ac.in

There have been a number of attempts to prepare hydro-fullerenes. Initially the experiments were carried out by direct gas phase hydrogenation of fullerenes under elevated temperatures and high pressures (673-723 K, 60-80 MPa), which resulted in compounds with hydrogen content up to 6.1 wt.% [6]. In order to reduce the high energy required for the activation of hydrogen molecule various approaches have been adopted like, selecting and optimizing the metal catalyst for the reaction to take place, however the addition of metal catalysts [7] shows decrease in the temperature and pressure but the storage capacity is not significant, because of the high polarisabilty of the metal towards hydrogen when compared to carbon. Alternatively the reaction was carried out in the liquid phase, which involves the utilization of solvent molecules and by this process the experimental conditions required are temperatures in the range 453-523 K and pressure of 12 MPa [8-10]. However the storage capacity of hydrogen decreased.

In order to establish the feasibility of hydrogenation of fullerene molecules, number of theoretical calculations have been carried out in various levels and the results, essentially indicate that the fullerenes are capable of forming stoichiometric hydrides ($C_{60}H_{12n}$ series). Among all the stoichiometric hydrides the $C_{60}H_{36}$ seems to be stable one and has the lowest enthalpy of formation [11-13]. By lowering the activation energy reversible hydrogenation of fullerenes is thermodynamically feasible at low temperatures. In order to lower the activation energy for the hydrogenation, other approaches is to modify the electronic structure of the fullerenes. In this approach, doping the fullerene with alkali metals (Na, K and Li) resulted in the formation of fulleride anions [14]. However it improves the hydrogenation process at lower temperatures and pressures but the dehydrogenation of hydrides is difficult and also the storage capacity is low. Though the metal sites are capable of activating hydrogen, the transport to the carbon surface is not a facile process and also the carbon surface by nature is not heterogeneous so as to promote the migration of hydrogen species from the metallic sites. In order to achieve high storage capacity there must be an activator, which should be easily hydridable than carbon and the dissociated hydrogen should then migrate to carbon surface (equipotential). While considering these aspects, heteroatoms like N, P and S seem promising to function as activator and the heterofullerenes are stable and

the energy difference is minimum when compared to the pristine fullerene C_{60} molecule [15,16]. All these possibilities predicts heterofullerenes may show higher hydrogen storage capacity. Several methods for production and isolation of heterofullerene have been developed [17,18] however the hydrogenation of heterofullerene has been reported only through the in situ analyses of species by the mass spectrometric technique [19].

The present investigation therefore has been undertaken with the following objectives (i) Hydrogenation of fullerenes is possible only in presence of activators, which can activate the hydrogen molecule. Taking the clue from nature, it is postulated that the presence of heteroatoms in the fullerene may be the appropriate sites for activation of hydrogen and (ii) if heterofullerenes were to be one of the materials appropriate for hydrogen storage, then the questions to be addressed are: (a) what is the gradation of materials containing various heteroatoms? (b) What are the geometrical positions in the fullerene that are active?

In order to understand the interaction of hydrogen molecule in pure fullerene and heteroatom (N, P and S) substituted fullerene, cluster model calculations have been carried out using Density Functional Theory (DFT) and semi-empirical method. For this study fullerene (C_{60}) molecule has been taken as the cluster to study the hydrogen interaction. Where as to study the reaction mechanism of hydrogenation in fullerene, a simpler cluster model (Fig. 1) of pyracyclene ring structure has been taken, which is the subunit of C_{60} molecule consisting of two pentagons and two hexagons shows fulvalenelike character and responsible for the facile reaction to take place in fullerene molecule. The geometrical parameters of the cluster used for proposing the mechanism are listed in the Table 1 shows the similarity to the fullerene molecule (C_{60}).

Theoretical methods

The Fullerene (C_{60}) cluster was used for the study and the geometry of the cluster is minimized using Universal Force Field (UFF 1.02) approach. The hydrogen molecule is allowed to interact with minimized C_{60} cluster and the geometry of the system is optimized. Cerius2 software was used for force field calculations. Using force field optimized parameters DFT single point energy calculations were done by Becke's three parameter hybrid functional with LYP
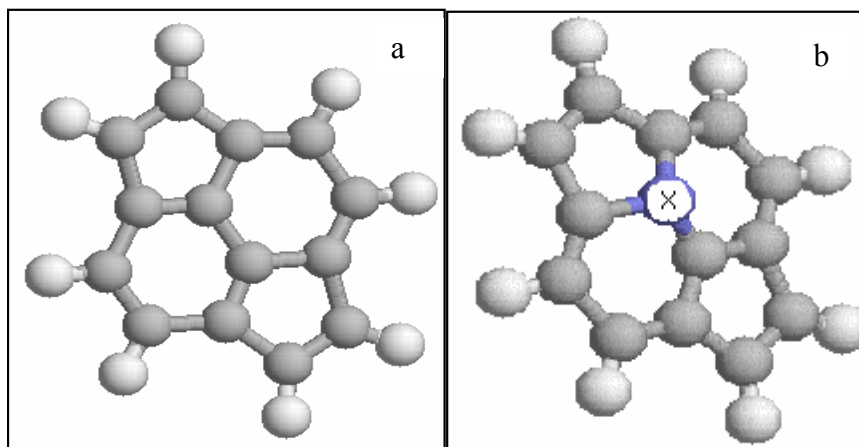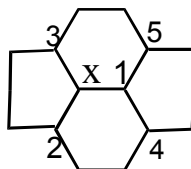
a. Unsubstituted and b. Heteroatom substituted.
Fig. 1. Optimized structure of the simple cluster taken for the proposed mechanism.

Table 1
Optimized geometrical parameters of the simple cluster taken for the reaction mechanism

Cluster	X–C$_1$, Å	X–C$_2$, Å	X–C$_3$, Å	C$_4$–C$_1$–X, deg	C$_2$–X–C$_1$, deg	C$_4$–C$_1$–X–C$_2$, deg	C$_5$–C$_1$–X–C$_3$, deg
C$_{60}$	1.40	1.40	1.42	108.09	119.99	0.01	0.00
UNSUB	1.35	1.43	1.43	122.63	122.63	0.00	0.00
N-SUB	1.35	1.42	1.40	124.54	120.31	-8.83	9.28
P-SUB	1.60	1.68	1.69	124.90	101.48	-32.59	34.25
S-SUB	1.58	1.70	1.70	124.38	101.49	31.73	-31.73

correlation functional (B3LYP) and 6-31G(d) basis set using Gaussian 98W. Similar procedure was adopted for heteroatom substituted cluster models. For proposing the mechanism of the hydrogenation simple cluster used and the ends of the cluster were saturated with hydrogen in order to avoid the edge effect. AM1 calculations were done to study the transition state structures by using MOPAC 6.0 package.

Results and discussions

The hydrogen molecule is allowed to interact with the carbon atoms of the unsubstituted fullerene and the dissociation energy of hydrogen was calculated (Table 2). The dissociation energy of hydrogen in its free state is 4.74 eV, and remains unaltered when it is allowed to interact with pure fullerene (4.61 eV).

In order to study the influence of heteroatoms towards the activation of hydrogen, various heteroatoms (N, P and S) are substituted at different positions of the fullerene showing the minimum potential energy and the hydrogen interaction is monitored. In the presence of heteroatom the dissociation energy of hydrogen molecule is considerably decreased compared to that of pure fullerene as can be seen from the values presented in Table 2. This indicates that heteroatom can activate the hydrogen molecule and its presence favors the dissociation of hydrogen. This conclusion can also be arrived at from the redox potential values of the couples involved. For instance, redox potentials of heteroatoms are higher than that of carbon (S/S^{2-}, N/N^{3-}, P/P^{3-}, C/C^{4-} are respectively, 0.171, 0.057, -0.111 and -0.132 V). The

Table 2

The Bond length and dissociation energy of hydrogen on the fullerene

S. No	Substitution	Total Energy, (a.u.)	Bond length H_1-H_2, (Å)	Dissociation Energy, (eV)
1	Hydrogen	-1.175	0.708	4.74
2	Unsubstituted Fullerene	-2286.042	-	-
3	Unsubstituted Fullerene + H_2	-2287.211	0.707	4.61
4	N-substituted Fullerene	-2302.653	-	-
5	N-substituted Fullerene + H_2	-2303.640	0.831	0.36
6	P-substituted Fullerene	-2589.253	-	-
7	P-substituted Fullerene + H_2	-2590.276	0.813	0.64
8	S-substituted Fullerene	-2646.036	-	-
9	S-substituted Fullerene + H_2	-2647.013	0.815	0.62

same fact can be further independently supported by the Ellingham diagram which indicates that free energy of formation for N−H bond is more favourable than that of C−H bond. The bond length of the hydrogen molecule is elongated in heteroatom substituted fullerene compared to that of pure fullerene, indicating that there is considerable activation of hydrogen molecule in hetero fullerene.

In order to understand the role of heteroatoms in hydrogen activation in fullerene, the simple cluster model calculations have been carried out for the proposed mechanism given in the Fig. 2 and the activation energy for each of the steps of hydrogen activation and migration of hydrogen within the framework of Transition state theory were calculated and the essential results are given in Table 3. From the values of activation energy, one can state that the heteroatoms are favourable for the hydrogen interaction and possibly favour migration to the carbon surface. These results support our contention that heteroatoms are the appropriate sites for activation of hydrogen on fullerene.

Conclusions

Theoretical calculations have shown that substitution of heteroatom in fullerenes seems to be one of the methods suitable for hydrogen storage applications. The heteroatom containing fullerenes are able to activate the hydrogen compared to unsubstituted
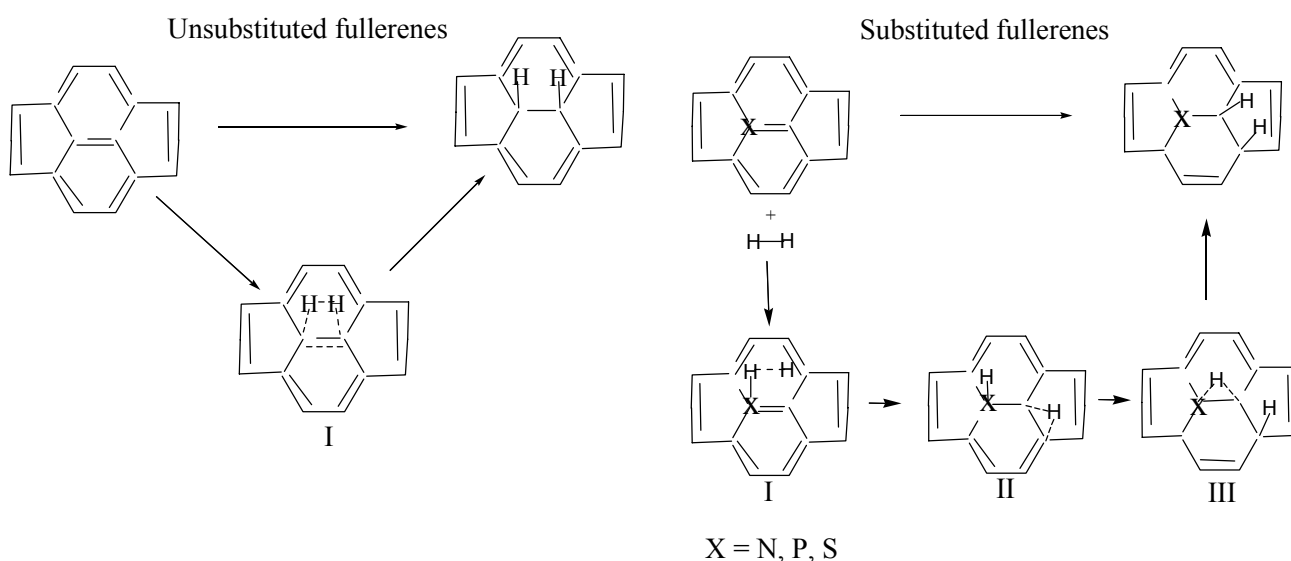

X = N, P, S

Fig. 2. Proposed transition state path ways for hydrogen interaction with fullerene and heteroatom (N, P and S) containing fullerene.

Table 3

The transition state optimized parameters for various clusters and energy of activation for each pathway

Substitution	E_a I, (eV)	E_a II, (eV)	E_a III, (eV)	H_1-H_2, Å	X-H_1, Å	C_1–X, Å	C_2–X, Å	C_3–X, Å
Carbon	18.49	–	–	0.70	–	–	–	–
Nitrogen	3.24	3.15	3.08	1.85	1.04	1.44	1.50	1.50
Phosphorus	1.73	1.52	1.52	1.85	1.26	1.48	1.62	1.62
Sulphur	2.56	6.48	1.86	1.13	1.60	1.70	1.70	1.70

fullerene. This activated hydrogen can then migrate to other sites. The implications of these results for hydrogen storage applications are yet to be realized.

References

1. S. Hynek, W. Fuller and J. Bentley., Int. J. Hydrogen Energy, 1997, 22, 601.
2. A. Chambers, C. Parks, R.T.K. Baker and N.M. Rodriguez J. Phys. Chem.B 1998, 102, 4253.
3. C. Jin, R. Hettich, R. Compton, D. Joyce, J. Blencoe, and T. Burch., J. Phys. Chem. 1994, 98, 4215.
4. A.G. Avent, A.D. Darwish, D.K. Heimbach, H.W. Kroto, M.F. Meidine, J.P. Parsons, J. Chem. Soc. Perkin Trans. 1994, 2, 15.
5. S.Yu. Zaginaichenko, D.V. Schur, B.P. Tarasov, V.K. Pishuk, T.N. Veziroglu, Yu.M. Shul'ga, A.G. Dubovoj, N.S. Anikina, A.P. Pomytkin and A.D. Zolotarenko, Int. J. Hydrogen Energy. 2002, 27, 1063.
6. R.O. Loutfy, and E. M. Wexler, 2001. In Metal Hydrides and Carbon for Hydrogen Storage (Final Report for IEA Task 12) http://www.eren.doe.gov/hydrogen/iea
7. R.E. Haufler, J. Conceicao, L.P.F. Chibante, Y. Chai, N.E. Byrne, S. Flanagan., J. Phys. Chem. 1990, 94, 8634.
8. S. Meier, S. Corbin, K. Vance, M. Clayton, and M. Mollman, Tetrahedron Letters, 1994, 35, 5789.
9. R. Banks, J. Dale, I. Gosney, G. Hodgson, K. Jennings, C. Jones, J. Lecoultre, R. Langridge, P. Maier, H. Scrivens, C. Smith, J. Smyth, T. Taylor, P. Thorburn and S.Webster, J. Chem. Soc., Chem. Commun., 1993, 1149.
10. I. Attalla, M. Vassallo, N. Tattam and V. Hanna, J. Phys. Chem. 1993, 97, 6329.
11. L.E. Hall, D.R. McKenzie, M.I. Attalla, A.M. Vassallo, R.L. Davis, J.B. Dunlop et al., J. Phys. Chem. 1993, 97, 5741.
12. A. Rathna and J. Chandrasekhar, Chem. Phys. Lett. 1993, 206, 217.
13. C. Hendrson and P. Cahill, Chem. Phys. Lett. 1992, 198, 570.
14. V. Schur, P. Tarasov, M. Shul'ga, Yu. Zaginaichenko, A. Matysina, P. Pomytkin, Carbon, 2003, 41 1331.
15. W. Andreoni, F. Gygi, and M. Parrinello, Chem. Phys. Lett. 1992, 190, 159.
16. N. Kurita, K. Kobayashi, H. Kumahora, K. Tago, and K. Ozawa, Chem. Phys. Lett. 1992, 198, 95.
17. J. C. Hummelen, B. Knight, J. Pavlovich, R. Gonzalez, F. Wudl, Science 1995, 269, 1554.
18. B.Nuber, A. Hirsch, Chem.Comm. 1996, 1421.
19. Y.V. Vasil'ev, R.R. Abzalimov, R.F. Tuktarov, S.K. Nasibullaev, A. Hirsch, R. Taylor, T. Drewello, Chem. Phys. Lett. 2002, 354, 361.