

Computational investigation of hydrogen adsorption in silicon-lithium binary clusters[#]

NARESH K JENA, K SRINIVASU and SWAPAN K GHOSH*

Theoretical Chemistry Section, Bhabha Atomic Research Centre and Homi Bhabha National Institute,
Department of Atomic Energy, Mumbai 400 085, India
e-mail: skghosh@barc.gov.in

Abstract. Theoretical studies on hydrogen adsorption properties of silicon-lithium binary clusters are carried out. We have considered three different clusters viz., Si_5Li_5^- , Si_5Li_6 and Si_5Li_7^+ and for each cluster, the geometries of different possible isomers are optimized. In all the minimum energy isomers of the three clusters considered, two of the lithium atoms are found to be situated in the axial positions and the remaining lithium atoms are in the equatorial position in the Si_5 plane. The lithium atoms which are in Si_5 plane are bonded to the Si-Si edge through a bridged bond instead of a corner in the Si_5 ring. From the calculated atomic charges, it is found that there is a charge transfer from lithium to silicon leaving a partial positive charge on the Li atoms and the axial lithium atoms are more charged as compared to the remaining lithium atoms. In the case of Si_5Li_6 and Si_5Li_7^+ , the Li sites can trap a total of 14 and 17 H_2 molecules, respectively, with each bridge bonded Li site adsorbing three H_2 molecules and each axial Li adsorbing one H_2 molecule which corresponds to a gravimetric density of 13.33 wt% and 15.25 wt%, respectively.

Keywords. *Ab initio* calculation; hydrogen adsorption; silicon-lithium binary clusters.

1. Introduction

To meet the ever-increasing energy demands for the world at large, hydrogen in recent years has emerged as a preferred candidate for an alternate source of energy.¹ The choice of hydrogen energy is obviated from considerations like high utilization efficiency and most importantly it being a green, environment friendly and clean source of energy. Realization of this goal, however, rests on the design and development of novel materials for hydrogen storage.² The bottleneck for designing these kinds of materials is the requirement of high gravimetric and volumetric density, fast sorption kinetics and favourable thermodynamics. Moreover, the hydrogen interaction energy should be somewhere in-between that of chemisorption and physisorption, typically in the range of 5.0 to 9.0 kcal/mol for room temperature applications.³ Though a large number of materials have been studied for hydrogen storage, none of the presently existing materials satisfies all the requirements to reach the target of 6.5 mass ratio and 62 kg/m³ volume density set by the Department of Energy (DOE).⁴ Hence, exploration of new hydrogen storage materials for onboard hydrogen storage is an essential and active area of research.

Last few years have witnessed an active research, both theoretically and experimentally, addressing the rational approaches towards the development of materials for hydrogen storage. These materials span the wide range of metal hydrides, porous materials like zeolites and metal organic frame works (MOFs), carbon based nano materials starting from graphene to fullerenes and also nanotubes, etc.^{5–9} These nanomaterials, in their pristine as well as metal doped forms have been explored in all its lengths and depths in recent years. Transition metal atom decorated fullerenes and nanotubes are shown to be effective hydrogen adsorbing materials.¹⁰ However, later it has been shown that transition metals aggregate to form clusters at high temperatures which diminishes their hydrogen storage capacity.¹¹ In an interesting work, Chandrakumar *et al.*¹² have shown that alkali metal atom doped C_{60} fullerenes can be a high capacity hydrogen storage material. In the transition metal decorated nanomaterials, H_2 binds to the metal centres by Kubas interactions whereas in the alkali metal decorated systems the H_2 binds through ion-quadrupole and ion-induced dipole interactions. Apart from extended systems like MOFs, graphenes and nanotubes, molecular systems having the desired properties of hydrogen storage are equally important. Molecular systems from the main group elements having interesting structures and properties have not been widely explored from the viewpoint of hydrogen storage. Recently, we

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

*For correspondence

have explored the possibilities of hydrogen storage by Li-doped *closo*-boranes and proposed an extended 3D network for this application.¹³

In one of our earlier studies,¹⁴ we showed that alkali metal ion decorated $C_5H_5^-$ can adsorb molecular hydrogen with 12 wt% of H_2 and discussed the role of aromaticity in stabilizing these systems. Jemmis *et al.*¹⁵ studied the structure and stability of $C_3Li_3^+$ and showed that the Li atoms form bond to C-C edges. Minkin *et al.*¹⁶ proposed the structure and stability of a series of perthioannulenes C_nLi_n ($n = 3-6$). An interesting 3D molecular star like structures such as $Si_5Li_n^{n-6}$ ($n = 5-7$), have been reported very recently by Tiznado *et al.*¹⁷ where they have shown that the central unit of Si_5^{6-} ring interacts with Li cations. These fascinating molecular structures which essentially contain lighter elements like Si and Li can be important for hydrogen storage with higher gravimetric density. Moreover, alkali metal atoms like Li, which is present in these systems favourably bind multiple hydrogen molecules. These attractive features have prompted us to undertake extensive *ab initio* theoretical investigations of hydrogen adsorption by these systems.

2. Computational details

All the energy calculations and structural optimization of the cluster systems have been carried out by using the electronic structure theory based GAMESS software.¹⁸ We have employed the density functional theory (DFT) with the Perdew-Wang (PW91)¹⁹ exchange correlation functionals. Since the molecular hydrogen interaction is weak in nature, it is important to include proper electron correlation effects. Although the performance of the DFT based exchange-correlation functionals is reasonably good in some of the cases, most of the existing functionals like B3LYP are not good enough for the description of weak interactions. Hence, we have also carried out all the calculations using the second order Moller-Plesset (MP2) perturbation method. We have used the extensive split-valence basis sets with diffuse and polarization functions, 6-31++G(2d,2p). The highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps are calculated as the energy difference between the corresponding orbitals. The initial geometries and all the reported structures have been obtained using the graphical software MOLDEN.²⁰ The adsorption energy per molecular hydrogen on the Si-Li clusters is calculated using the relation

$$\Delta E(H_2) = \{E[Si_5Li_m(H_2)_n] - [E(Si_5Li_m) + nE(H_2)]\} / n.$$

We have also calculated the chemical hardness (η) and electrophilicity (ω) values to verify the stability of the systems using molecular electronic structure principles like the principle of maximum hardness²¹ and minimum electrophilicity principle.²² The hardness and electrophilicity parameters are calculated using the following formulae

$$\eta = I - A$$

and

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta},$$

where, I is the vertical ionization potential and A is the vertical electron affinity values calculated for an N electron system as $I = E(N - 1) - E(N)$ and $A = E(N) - E(N + 1)$.

3. Results and discussions

3.1 Structure and energetics of silicon-lithium clusters

The equilibrium geometries of the possible isomers of the three different silicon-lithium binary clusters, $Si_5Li_5^-$, Si_5Li_6 and $Si_5Li_7^+$, optimized at MP2/6-31++G(2d 2p) level of theory, are given in figure 1. $Si_5H_5^-$ can be considered as the analogue of $C_5H_5^-$ which is known to be aromatic and form stable Ferrocene like complexes. If all the protons are replaced with Li ions, it generates the $Si_5Li_5^-$ binary cluster and can be expected to have a geometry similar to that of $C_5H_5^-$. However, the planar D_{5h} geometry of $Si_5Li_5^-$ shown in figure 1(a-iv) is found to be a higher energy isomer in comparison to the lowest energy isomer (a-i) with an energy difference of 60.69 kcal/mol. The lowest energy isomer is found to have two different types of lithium sites with C_{2v} symmetry shown in figure 1(a-i). Two of the five lithium atoms are found to occupy the axial positions, with one below and one above the Si_5 plane and the remaining three are bonded to the Si-Si edges with an average Si-Si bond distance of 2.38 Å. The Si-Li distance for the axial Li is found to be 2.56 Å whereas the same is 2.41 Å for the equatorial lithium atoms. From the calculated atomic charges, it is found that the axial Li sites carry a positive charge of 0.78 while the equatorial Li has a charge of 0.44 which shows that the axial Li sites are more ionic in nature. The second lowest energy isomer (a-ii) is found to have C_{2v} symmetry with three adjacent bridge bonds and two axial lithium atoms which is just 3.19 kcal/mol higher in energy as compared to the lowest energy isomer. The next higher energy isomer (a-iii) with one axial lithium

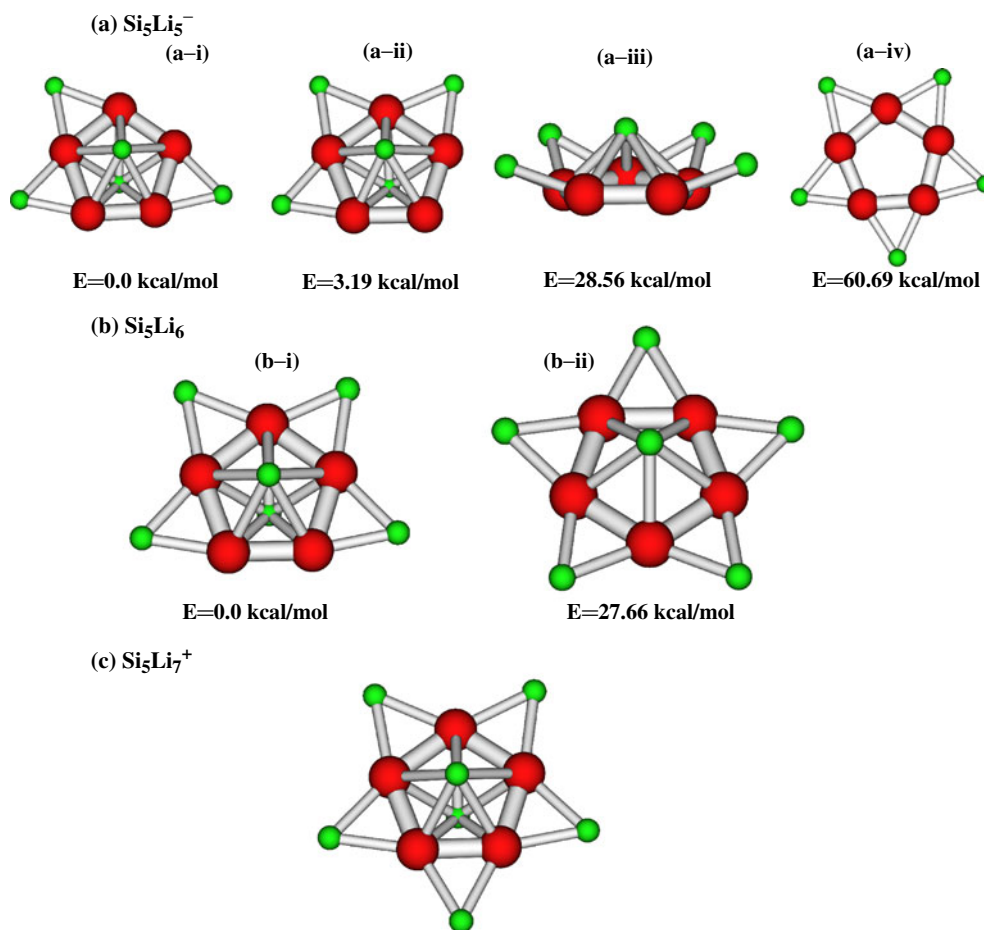


Figure 1. Equilibrium geometries of (a) Si_5Li_5^- , (b) Si_5Li_6 and (c) Si_5Li_7^+ .

and four equatorial Li is 28.6 kcal/mol higher in energy as compared to the lowest energy isomer. In this isomer, the equatorial lithium atoms are not in the Si_5 plane, but have moved towards the axial Li with bridge Li-axial Li distance of 3.5 Å.

In the case of Si_5Li_6 , two different isomers are geometry-optimized and the minimum energy structure is found to be the one with four equatorial Li and two axial Li as shown in figure 1(b-i). The optimized geometry of this isomer has the symmetry C_{2v} with an average Si-Si bond length of 2.35 Å. The calculated atomic charges on the axial Li and equatorial Li are found to be 0.92 and 0.63, respectively. The next higher energy isomer (b-ii) with one axial Li and five equatorial Li is found to have 27.66 kcal/mol more energy and the symmetry C_{5v} . In the case of Si_5Li_7^+ , we have optimized only one isomer with two axial Li and the remaining five equatorial Li are bridged to all the five edges of Si_5 ring and is found to have D_{5h} symmetry as shown in figure 1(c). In this case, as all the edges are bonded to Li, all the Si-Si bonds are equivalent and the Si-Si bond distance is found to be 2.33 Å. The calculated

atomic charge on axial Li is found to be 1.1 and that on the equatorial Li is 0.81. All the minimum energy structures Si_5Li_5^- , Si_5Li_6 and Si_5Li_7^+ are in good agreement with the earlier reported global minima by Tiznado *et al.*¹⁷ For all the isomers considered here, we calculated the Hessian at MP2/6-31++G(2d 2p) level of theory and found none of them to have imaginary frequencies indicating that all these structures correspond to the local minima on their respective potential energy surfaces. The minimum vibrational frequencies are also found to be considerably large to ensure the stability of the binary clusters considered.

3.2 Hydrogen adsorption properties of Si_5Li_6 and Si_5Li_7^+

Although molecular hydrogen does not have a permanent dipole moment, it has a large quadrupole moment and polarizability and hence, when it approaches a charged site it can bind to that site through ion-quadrupole and ion-induced dipole interactions. First,

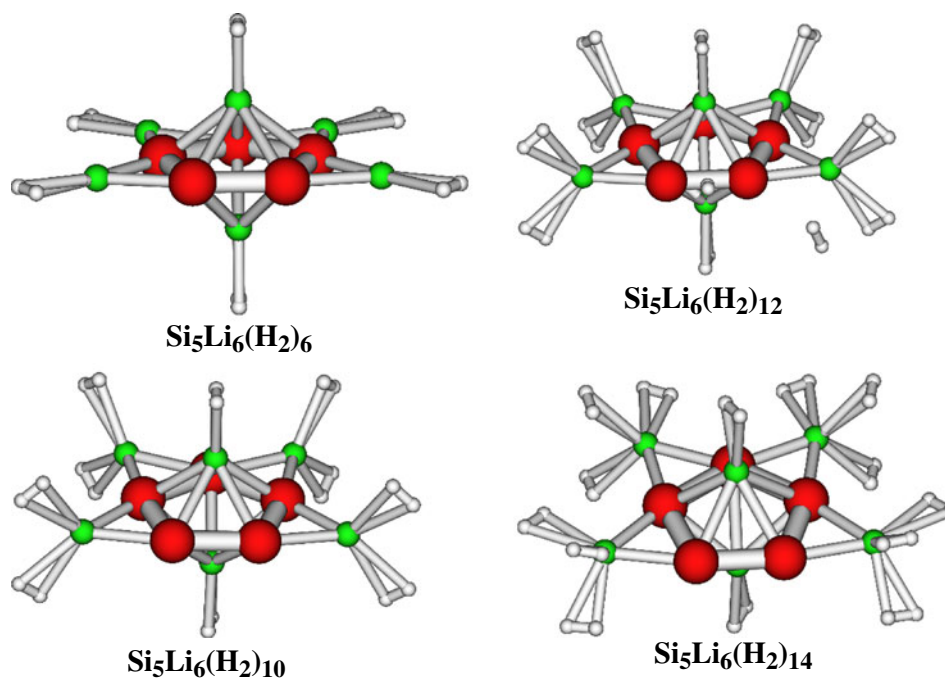


Figure 2. Equilibrium geometries of $\text{Si}_5\text{Li}_6(\text{H}_2)_n$.

we discuss the hydrogen adsorption properties of Si_5Li_6 with different number of molecular hydrogen adsorbed as shown in figure 2 and the corresponding results are reported in table 1. In the case of $\text{Si}_5\text{Li}_6(\text{H}_2)_6$ where each Li site binds one molecular hydrogen, the average adsorption energy per H_2 calculated at MP2/6-31++G(2d 2p) level of theory is found to be -3.63 kcal/mol. The Li- H_2 distance in the case of axial Li is found to be 1.98 Å which is shorter as compared to that in the case of bridged Li- H_2 (2.1 Å) distance which can be attributed to the relatively higher charge on axial Li as compared to that on bridged Li. This difference in Li-H bond distance shows that H_2 molecules bonded to axial Li are more strongly bonded as compared to others bonded to equatorial Li. When the second H_2

molecule approaches each Li site, the axial Li sites cannot trap the second H_2 and thus two of the twelve H_2 in $\text{Si}_5\text{Li}_6(\text{H}_2)_{12}$ move away from the binary cluster as shown in figure 2 which might be attributed to the steric repulsion from molecular hydrogen already adsorbed. Hence, we re-optimized the structure by removing the two H_2 molecules which are not bound as $\text{Si}_5\text{Li}_6(\text{H}_2)_{10}$ and the structure is shown in figure 2. The interaction energy per molecular hydrogen in this case is found to be -3.03 kcal/mol. In the case of $\text{Si}_5\text{Li}_6(\text{H}_2)_{14}$ the interaction energy per molecular hydrogen is found to be -2.47 kcal/mol. As we have seen in our earlier studies, each Li site can adsorb a maximum of three molecular hydrogens. Also, from the optimized geometry of $\text{Si}_5\text{Li}_6(\text{H}_2)_{14}$, one can see that the adsorbed hydrogen

Table 1. Interaction energy, charge on lithium atom and HOMO-LUMO gaps of hydrogenated Si_5Li_6 and Si_5Li_7^+ binary clusters.

System	Interaction energy (kcal/mol)		Charge on Li (a.u)		HOMO-LUMO gap (eV)		η (eV)	ω (eV)
	PW91	MP2	PW91	MP2	PW91	MP2		
Si_5Li_6			0.89	0.92	1.96	5.49	4.93	0.79
$\text{Si}_5\text{Li}_6-6\text{H}_2$	-2.613	-3.632	0.789	0.958	2.03	5.44	5.54	0.69
$\text{Si}_5\text{Li}_6-10\text{H}_2$	-2.511	-3.032	0.637	0.743	1.97	5.30	5.36	0.67
$\text{Si}_5\text{Li}_6-14\text{H}_2$	-2.361	-2.472	0.556	0.635	2.15	5.21	5.50	0.68
Si_5Li_7^+			1.07	1.10	2.51	6.71	6.22	2.43
$\text{Si}_5\text{Li}_7^+-7\text{H}_2$	-3.238	-4.300	0.975	1.069	2.45	7.06	6.12	2.22
$\text{Si}_5\text{Li}_7^+-12\text{H}_2$	-2.881	-3.788	0.818	0.848	2.41	6.98	6.02	2.11
$\text{Si}_5\text{Li}_7^+-17\text{H}_2$	-2.725	-2.979	0.450	0.618	2.39	6.92	5.83	2.20

molecules are already crowded and introduction of further hydrogen molecules is difficult. Hence, we have studied up to a maximum of three H_2 per Li with a total number of 14 molecular hydrogens adsorbed resulting in $Si_5Li_6(H_2)_{14}$, with a gravimetric density of 13.33 wt% of hydrogen.

The next binary cluster studied for hydrogen adsorption is $Si_5Li_7^+$ and the optimized geometries of the corresponding hydrogenated species with different number of molecular hydrogen are given in figure 3 with the results reported in table 1. The average interaction energy per molecular hydrogen in $Si_5Li_7^+(H_2)_7$ calculated at MP2/6-31++G(2d 2p) level of theory is found to be -4.3 kcal/mol and the optimized structure is found to have C_s symmetry. The adsorption energy of molecular hydrogen in this cluster is found to be more than that in the Si_5Li_6 case as the Li sites here are more ionic in nature as compared to the Li sites in Si_5Li_6 . Similar to the earlier case, on introduction of two molecular hydrogens per Li, two of the 14 H_2 move away from $Si_5Li_7^+(H_2)_{14}$ as shown in figure 3 and hence we optimized the structure again with 12 H_2 as $Si_5Li_7^+(H_2)_{12}$ and the interaction energy per molecular hydrogen is found to be -3.79 kcal/mol. In the case of $Si_5Li_7^+(H_2)_{17}$, the five bridged Li adsorb 15 H_2 molecules and the two axial Li adsorb two H_2 which

corresponds to a gravimetric density of 15.25 wt%. The adsorption energy per molecular hydrogen is found to be -2.98 kcal/mol and the optimized structure is found to have C_s symmetry.

The interaction energies calculated by MP2 method are found to be larger than the corresponding PW91 results as is evident from results reported in table 1. This kind of observation with the correlated methods giving improved results as compared to the commonly used DFT functionals, is well-known in the literature, particularly in the case of weakly interacting systems. In all the hydrogenated clusters, the adsorbed hydrogen are mainly in molecular form and the bond length in adsorbed H_2 is little elongated to 0.743 Å from 0.736 Å in the free molecular hydrogen optimized at same level of theory. The calculated HOMO-LUMO gaps for all the hydrogenated clusters are reported in table 1 and all of them are found to have large HOMO-LUMO gaps which are indications of their stability. In addition, we also report the calculated values of the electrophilicity (ω) as well as hardness parameters in table 1. It is observed that there is a gradual decrease in electrophilicity with increase in the number of hydrogen molecules adsorbed per metal site, in line with the minimum electrophilicity principle. The hardness (η) values are found to show trends quite similar to the

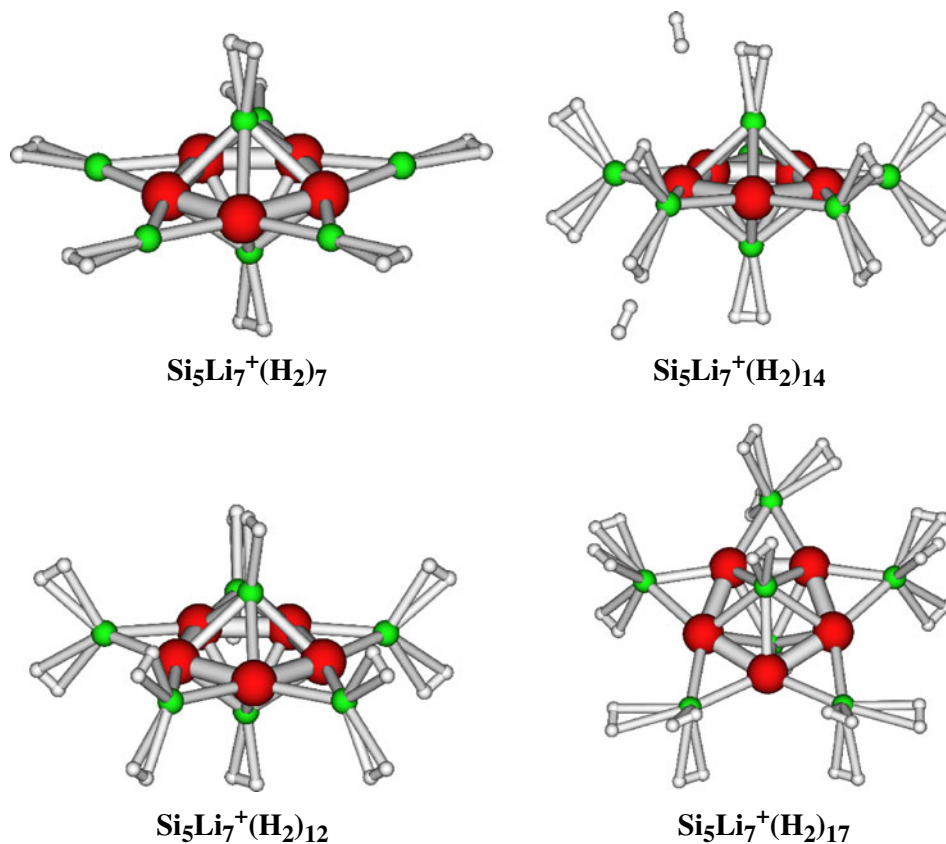


Figure 3. Equilibrium geometries of $Si_5Li_7^+(H_2)_n$.

HOMO–LUMO gap values, reaffirming the conclusion about the stability of the hydrogenated species. This trend demonstrates the stability of the hydrogenated metal clusters. We have also calculated the Hessian for all the hydrogenated clusters at MP2/6–31++G(2d 2p) level of theory and found only real frequencies which shows that these structures are at the local minima on their respective potential energy surfaces. As all the lithium sites in these star like binary clusters are positively charged, it might be possible to design three-dimensional materials by choosing a proper ligand. It is also possible to construct multidecker sandwich type of materials which are well known in the case of $C_5H_5^-$ (Cp^-).

4. Conclusions

Through *ab initio* based calculations, we have shown here that silicon can form perlithioannulene type of structures with the general formula $Si_5Li_n^{n-6}$ ($n = 5-7$). Three-dimensional structures with two axial lithium and remaining ($n-2$) lithium in the Si_5 plane are found to be more stable structures. In all the binary systems considered, the lithium sites are found to carry partial positive charges. In the case of Si_5Li_6 the maximum number of molecular hydrogen adsorbed is found to be fourteen which correspond to a gravimetric density of 13.3 wt% of hydrogen. The corresponding density in the case of $Si_5Li_7^+$ is found to be 15.25 wt% with a total of seventeen molecular hydrogen adsorbed around the binary cluster. It is possible to construct multidecker sandwich type of materials using this $Si_5Li_n^{n-6}$ binary clusters as building units which are common in the case of Cp^- . The future work in this direction is in progress in our laboratory.

Acknowledgements

We thank the Bhabha Atomic Research Centre (BARC) computer centre for providing the high performance parallel computing facility. One of the authors, NKJ, gratefully acknowledges a Senior Research Fellowship from Homi Bhabha National Institute, Department of Atomic Energy, India. This work has also been supported by the INDO-EU project HYPOMAP, in the area of Computational Materials Science. The work of SKG is also supported through Sir J.C. Bose Fellowship from the Department of Science and Technology (DST), India.

References

- (a) Schlapbach L and Züttel A 2001. *Nature* **414** 353; (b) Coontz R and Hanson B 2004, *Science* **305** 957;
- (c) Lewis N S and Nocera D 2006 *Proc. Natl. Acad. Sci. USA* **103** 15729
- (a) Dresselhaus M S and Thomas I L 2001 *Nature* **414** 332; (b) Eberle U, Felderhoff M and Schüth F 2009 *Angew. Chem. Int. Ed.* **48** 6608
- Lochan R C and Head-Gordon M 2006 *Phys. Chem. Chem. Phys.* **8** 1357
- <http://www1.eere.energy.gov/hydrogenandfuelcells/storage/>
- (a) Orimo S -I, Nakamori Y, Eliseo J R, Züttel A and Jensen C M 2007 *Chem. Rev.* **107** 4111; (b) Chattaraj P K, Bandaru S and Mondal S 2011 *J. Phys. Chem. A* **115** 187
- (a) Rowsel J L C, Millward A R, Park K S and Yaghi O M 2004 *J. Am. Chem. Soc.* **126** 5666; (b) Klontzas E, Tylianakis E and Froudakis G E 2010 *Nano Lett.* **10** 452
- (a) Dillon A C, Jones K M, Bekkedahl T A, Kiang C H, Bethune D S and Heben M J 1997 *Nature* **386** 377; (b) Patchkovskii S, Tse J S, Yurchenko S N, Zhechkov L, Heine T and Seifert G 2005 *Proc. Natl. Acad. Sci. USA* **102** 10439; (c) Barman S, Sen P and Das G P 2008 *J. Phys. Chem. C* **112** 19963
- (a) Prakash M, Elango M and Subramanian V 2011 *Int. J. Hydrogen Energy* **36** 3922; (b) Srinivasu K, Ghosh S K and Chandrakumar K R S 2008 *Phys. Chem. Chem. Phys.* **10** 5832; (c) Chandrakumar K R S, Srinivasu K and Ghosh S K 2008 *J. Phys. Chem. C* **112** 15670
- (a) Maark T A and Pal S 2010 *Int. J. Hydrogen Energy* **35** 12846; (b) Han S S and Goddard III W A 2007 *J. Am. Chem. Soc.* **129** 8422; (c) Blomqvist A, Araújo C M, Srepusharawoot P and Ahuja R 2007 *Proc. Natl. Acad. Sci. USA* **104** 20173
- (a) Zhao Y, Kim Y -H, Dillon A C, Heben J M and Zhang S B 2005 *Phys. Rev. Lett.* **94** 155504; (b) Yildirim T and Ciraci S 2005 *Phys. Rev. Lett.* **94** 175501
- Sun Q, Wang Q, Jena P and Kawazoe Y 2005 *J. Am. Chem. Soc.* **127** 14582
- Chandrakumar K R S and Ghosh S K 2008 *Nano Lett.* **8** 13
- Srinivasu K and Ghosh S K 2011 *J. Phys. Chem. C* **115** 1450
- Srinivasu K, Chandrakumar K R S and Ghosh S K 2009 *Chem. Phys. Chem.* **10** 427
- Jemmis E D, Subramanian G, Kos A J and Schleyer P v R 1997 *J. Am. Chem. Soc.* **119** 9504
- Minkin V I, Minyaev R M, Starikov A G and Gribanova T N 2005 *Russ. J. Org. Chem.* **41** 1289
- Tiznado W, Perez-Peralta N, Islas R, Toro-Labbe A, Ugalde J M and Merino G 2009 *J. Am. Chem. Soc.* **131** 9426
- Schmidt M W, Baldridge K K, Boatz J A, Elbert S T, Gordon M S, Jensen J H, Koseki S, Matsunga N, Nguyen K A, Su S J, Dupuis M and Montgomery J A 1993 *J. Comput. Chem.* **14** 1347
- Perdew J P and Wang Y 1992 *Phys. Rev. B.* **45** 13244
- Schaftenaar G and Noordik J H 2000 *J. Comput.-Aided Mol. Design* **14** 123
- (a) Parr R G and Chattaraj P K 1991 *J. Am. Chem. Soc.* **113** 1854; (b) Ayers P W and Parr R G 2000 *J. Am. Chem. Soc.* **112** 2010
- Chamorro E, Chattaraj P K and Fuentealba P 2003 *J. Phys. Chem. A.* **107** 7068