NANOTOROUS: A SUITABLE SYSTEM TO STORAGE HYDROGEN

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ABSTRACT

Looking for novel systems to storage hydrogen, we found that a toroidal carbon C_{120} nanostructure, a nanotorous, is a suitable system that could meet the hydrogen storage of 6 weight %, proposed by the DOE (Department of Energy of the United States). This result is obtained from ab initio density functional calculations studying the different equilibrium configurations for an increasing number of hydrogen molecules adsorbed outside this nanostructure. The influence of the coating scandium or beryllium atom on the external surface of the nanotorous shows that with ten Sc atoms, sixty hydrogen molecules could be adsorbed. This means at least a total of 6.01 wt % of hydrogen can be stored by the Sc-coated C_{120} nanotorous. This result has been complemented with the corresponding charge densities, total energies and Mulliken population analysis for each one of the studied systems. Still we explore if the quantity of adsorbed hydrogen can be increased.

Oral presentation.

1. - Introduction

With the proposal [1] of a new carbon nanostructure with a toroidal shape, a nanotorous, all carbon nanostructures such as graphene have gained great interest for their nanoscale device applications. Here we explore the C_{120} nanotorus, as a hydrogen storage system. First we determine if hydrogen can be adsorbed in the system without any other atomic species. A similar behavior is seen with carbon nanotubes respect to the relatively low hydrogen storage capacity. Next the different curvature and geometry of those systems, nanotubes and nanotorous, makes a little difference in the hydrogen adsorption, independently of other atoms used to increase the quantity of sorbet hydrogen. In particular we discuss the beryllium and scandium effect on the hydrogen adsorbed on the outer surface of the nanotorous.

Once we build and relaxed the entire nanotorous structure, total energy, dimensions of the system, charge density and Mulliken population analysis, for example, were obtained. This time the results of the DFT (density functional theory) computational study for a C_{120} carbon nanotorus were obtained using Dmol^3 code [2, 3] as implemented in the Materials Studio program [4]. Stability for the isolated C_{120} nanotorus and also for each one of the beryllium-coated or scandium-coated nanotorous with $n$$H_2$ molecules was obtained. The large specific area for the nanotorous, suggest that this system should be efficient for H_2 storage.

2. - Method

To study the stability of the nanotorus, first we used the initial structure with only 12 carbon atoms, proposed by Sigeo Ihara and coworkers [5]. Next, the coordinates of the 120 carbon atoms of the nanotorus were obtained by successive five-fold rotations of this set of 12 atoms followed by a reflection and final rotation of $\pi/5$ radians. The generated structure is composed by ten pentagonal, forty hexagonal and ten heptagonal rings. Even the effect of the beryllium atom on the hydrogen storage could be described properly, making use of the LDA (local density approximation); this could not be the case for the scandium atom. By this reason we decided to use the generalized gradient approximation of DFT implemented in the Materials Studio v.4.3 code, as proposed by Perdew and Wang (PW91) [6]. In particular, the Dmol^3 module was used to calculate, for example, total energy, electronic

charge density, HOMO-LUMO and Mulliken population analysis. To calculate the interaction energies of the hydrogen molecules with the C_{120} nanotorus, the DFT is complemented with a double numerical plus polarization basis set, (DNP). For occupied orbitals, two atomic orbitals are considered in the basis set. For C and H atoms polarization, *d*-function and *p*-function are used, respectively. The employed basis set has the advantage to be equivalent to the analytical basis set 6-31G**. Real frequencies were obtained for the isolated nanotorus. Hydrogen storage of the BeC_{120} and ScC_{120} systems was studied after these calculations were performed.

3.-Results and discussion

We first investigate hydrogen adsorption on the bare nanotorous. For example, the adsorption energy of a single H_2 to the outer wall of C_{120} nanotorous is only 0.115 eV, a little bit greater than the corresponding adsorption energy of a hydrogen molecule on the outer wall of a (5, 5) or a (6, 6) carbon nanotube [7]. This means that pure C_{120} nanotorus is not a good candidate for hydrogen storage directly. This was expected by the similarity with the H_2 poor adsorption on a pristine carbon nanotube. Table 1 contains the type of ring (pentagonal, hexagonal or heptagonal) for a pair of carbon atoms identified by their labels. For example, carbon atoms labeled 27 and 78 are neighbors in a pentagonal ring and the respective bond length is 1.458 Å, with a Mulliken bond order of 0.875, which makes difficult to assign either single or double bond character. For comparison, for ethane and ethane molecules C - C bond lengths turn out to be 1.523 and 1.369 Å, while Mulliken bond orders are 1.050 and 0.742, respectively. For the pentagonal, hexagonal and heptagonal rings, the average bond lengths are 1.460, 1.452 and 1.447 Å, respectively. Table 2 contains, for the pentagonal, hexagonal and heptagonal rings, the angle formed by three adjacent carbon atoms. For example, for atoms 27, 78 and 74, the angle is 107.3°. In a similar way as for the bond length, the average angle for each type of ring, pentagonal, hexagonal and heptagonal, is 107.5°, 118.9° and 118.0°, respectively. Next, we study hydrogen adsorption capabilities of the toroidal carbon C_{120} structure with a single Be atom externally attached. Although Be atom can occupy different sites outside the toroidal carbon C_{120} structure, we consider it is adsorbed between carbon atoms labeled 88 and 86, which belong to neighboring pentagonal and hexagonal rings with a bond length of 1.473

Å. The optimized structures of BeC_{120}-nH_2, for n = 1-3, are shown in Figure 1. The geometry and energy information of Beryllium-toroidal carbon C_{120} are presented in Table 3.

The binding energy E_b of the Be atom adsorbed on the outer surface of the bare nanotorus is defined as [8]

$$E_b = E_t(\text{Be}) + E_t(\text{C}_{120}) - E_t(\text{C}_{120}\text{-Be}) \quad (1)$$

where E_t (Be), E_t (C_{120}) and E_t (C_{120}-Be) are the total energies of a free Be atom, the pure C_{120} nanotorus and the C_{120}-Be system, respectively. E_b was found to be equal to 2.948 eV, which indicates that the C_{120}-Be system is strongly bonded. The strength of the interaction is consistent with the formation of a C-Be bond, which indicates that the whole system can be considered as one single species. The spatial HOMO–LUMO distributions for the bare BeC_{120} and hydrogenated BeC_{120}-nH_2 system, for n = 1-3 were obtained. Figures 2 correspond to the system with 3 hydrogen molecules. Blue lobes show the positive and yellow lobes show the negative values of the wave function. In other figures not shown here, the density distribution in the LUMO of BeC_{120} systems is mainly located in the neighborhood of the Be atom, indicating that the adsorption of the first H_2 molecule is expected to take place in this region. For the BeC_{120}-nH_2 systems with n = (1-2) the HOMO density is concentrated in the vicinity of the Be atom, suggesting that the second and third molecules of H_2 would also be absorbed in this region. However, there is no density concentration on the vicinity of Be for the BeC_{120}-$3H_2$ system. This suggests that the fourth H_2 molecule, and probably any other after that, would be absorbed in a non-coated region of the nanatorous. Therefore their binding energies are expected to be of similar magnitude that those involving H_2 adsorptions on the surface of the bare toroidal carbon C_{120} nanostructure.

We have also computed the average adsorption energy per H_2, [9]

$$E_{ave} = \{E[\text{BeC}_{120}] + nE[\text{H}_2] - E[\text{BeC}_{120}\text{-}n\text{H}_2]\}/n \quad (2)$$

Table 1. C-C bond lengths (Å) and Mulliken bond orders for pentagonal, hexagonal and heptagonal rings in the optimized C_{120} nanotorus.

C-C Atom label and ring type			C-C bond lengths (Å) and ***Mulliken bond orders***		
Pentagon	Hexagon	Heptagon	Pentagon	Hexagon	Heptagon
27-78	33-35	91-104	1.458	1.457	1.440
			0.875	***0.867***	***0.891***
78-74	35-36	104-105	1.458	1.470	1.463
			0.846	***0.917***	***0.814***
74-75	36-32	105-92	1.470	1.458	1.417
			0.917	***0.866***	***0.959***
75-77	32-31	92-80	1.458	1.454	1.462
			0.845	***0.813***	***0.811***
77-27	31-30	80-79	1.457	1.417	1.439
			0.874	***0.962***	***0.894***
	30-33	79-40		1.454	1.456
				0.816	***0.806***
		40-91			1.456
					0.807
Average bond lengths (Å)			1.460	1.452	1.447

Table 2. Angle (degrees), formed by three adjacent carbon atoms for the pentagonal, hexagonal and heptagonal rings in the optimized C_{120} nanotorus.

C-C-C Atom labels and ring type			Angle (degree)		
Pentagon	Hexagon	Heptagon	Pentagon	Hexagon	Heptagon
27-78-74	33-35-36	91-104-105	107.3	122.7	116.9
78-74-75	35-36-32	104-105-92	107.6	122.7	117.7
74-75-77	36-32-31	105-92-80	107.7	110.0	117.7
75-77-27	32-31-30	92-80-79	107.2	124.0	116.8
77-27-78	31-30-33	80-79-40	107.7	124.1	122.6
	30-33-35	79-40-91		110.0	111.7
		40-91-104			122.5
Average angle			107.5	118.9	118.0

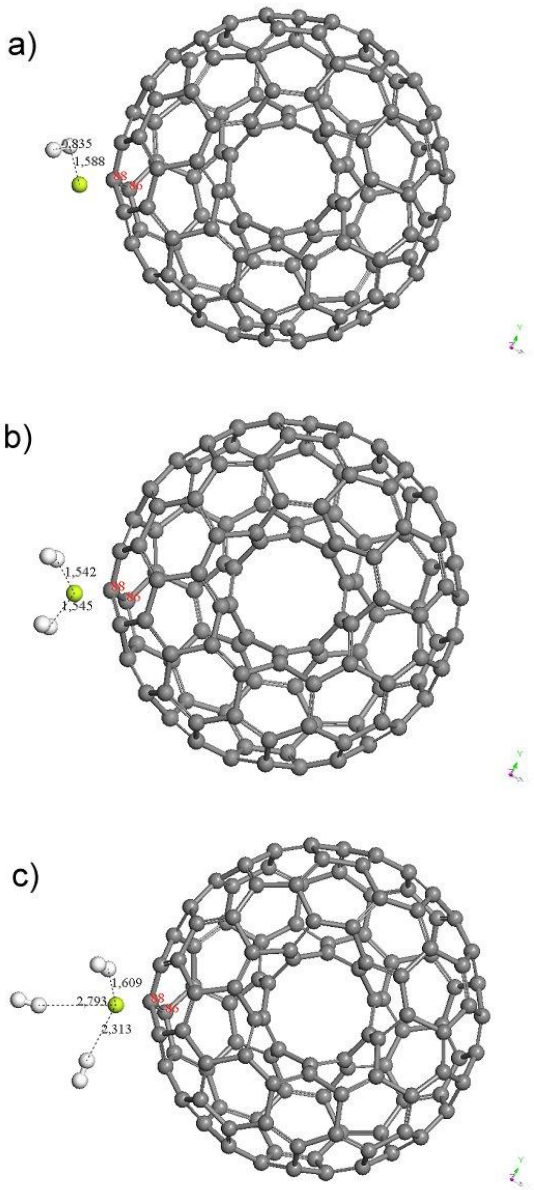

Figure 1. a, b and c. Optimized structures of BeC_{120}-nH_2 systems, for n = 1, 2 and 3, respectively. The beryllium atom is shown in yellow color.

and consecutive adsorption energy of H_2

$$E_t = E[BeC_{120}\text{-}(n\text{-}1)H_2] + E[H_2] - E[BeC_{120} - nH_2] \quad (3)$$

where $E[BeC_{120}]$, $E[H_2]$, $E[BeC_{120}\text{-}nH_2]$ and $E[BeC_{120}\text{-}(n\text{-}1)H_2]$ are the total energies of relaxed BeC_{120}, H_2 molecule, BeC_{120}-nH_2 and the BeC_{120}-$(n\text{-}1)H_2$ system, respectively, and n is the number of H_2 molecules, see Table 4.

Table 3. Bond length, HOMO-LUMO Gap (Δ) and Mulliken atomic charges of BeC_{120}-nH_2 system.

Number of H_2 molecules (*n*)	C(88)-Be distance (Å)	C(86)-Be distance (Å)	Be-H distance (Å)	H-H bond length (Å)	Δ (eV)	Mulliken atomic charges
Be 0 H_2	1.840	1.808	-	-	0.78	Be 0.039
Be 1 H_2	1.807	1.778	H1 1.532 H2 1.500	0.895	0.31	Be -0.019 H1 0.079 H2 0.062
Be 2 H_2	1.852	1.810	H1 1.544 H2 1.539 H3 1.542 H4 1.551	0.856 0.855	0.45	Be -0.098 H1 0.089 H2 0.082 H3 0.087 H4 0.085
Be 3 H_2	1.845	1.808	H1 1.609 H2 1.602 H3 2.313 H4 3.082 H5 2.793 H6 3.524	0.827 0.775 0.765	0.70	Be -0.041 H1 0.098 H2 0.104 H3 -0.035 H4 0.018 H5 0.025 H6 -0.033

Although the adsorption energy of the first H_2 on BeC_{120} reaches up to 0.261 eV, that of the second H_2 is 0.359 eV. The stronger binding of H_2 to BeC_{120} and the relatively larger HOMO-LUMO gap of BeC_{120}-H_2 imply that this structure is of high stability. Thus, the second H_2 molecule is very easy adsorbed.

Next, we give some of the principals results obtained when the nanotorous is coated with one through ten Sc atoms. A single Sc atom can adsorb up to 6 H_2 molecules. Then, the system was increased gradually until 10 Sc atoms, which can adsorb up to 60 H_2 molecules. This leads to 6.01 wt %, which fulfils the current requirement (6 wt %, at 2010, specified by US Department of Energy (DOE)). Accordingly, the scandium-coated C_{120} nanotorous is a good candidate for H_2 storage with moderate adsorption energy. One pending task is to probe that even for a periodic nanotorus system coated with Be or Sc atoms, the wt % could be maintained as high as the above given result. The optimized structures of ScC_{120}-nH_2,

for n = 1-6, are shown in Figure 3. The geometry and energy information of scandium – nanotorous C_{120} nanostructure are presented in Table 5. The average C-C distances involving the C atoms closest to the Sc atom (C85 y C86) are 2.57 y 2.56 Å, respectively.

Table 4. Average adsorption energy per H_2 and consecutive adsorption energy (in parentheses) of H_2 for BeC_{120}-nH_2, n = (1-3) system.

System	Be	Be H_2	Be $2H_2$	Be $3H_2$
Average adsorption energy per H_2 (eV)	-	0.261	0.310 (0.359)	0.203 (-0.011)

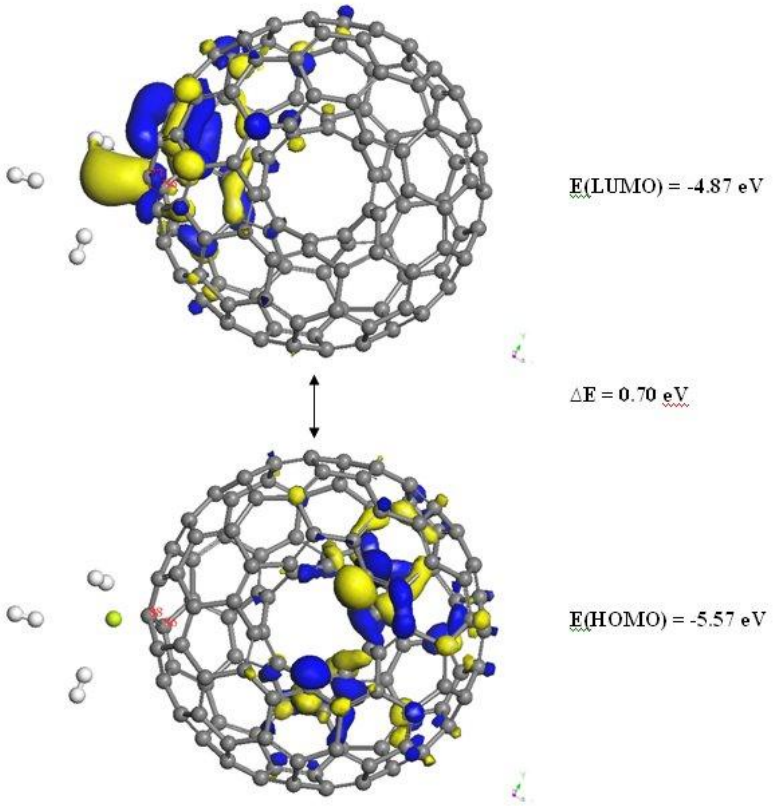

Figure 2. HOMO-LUMO for the BeC_{120}-nH_2 system, n =3.

All the Sc-H distances are in the range of 2.360-2.448 Å. On the other hand, the average H-H bond distances of the H_2 molecules located in the vicinity of the Sc atom slightly decreases from 0.780 to 0.776 Å, as the number of H_2 molecules increases from 1 to 6. On

the contrary the C85-C86 bond distance, slightly increases from 1.486 to 1.506 Å, as the number of H_2 molecules increases from 1 to 6.

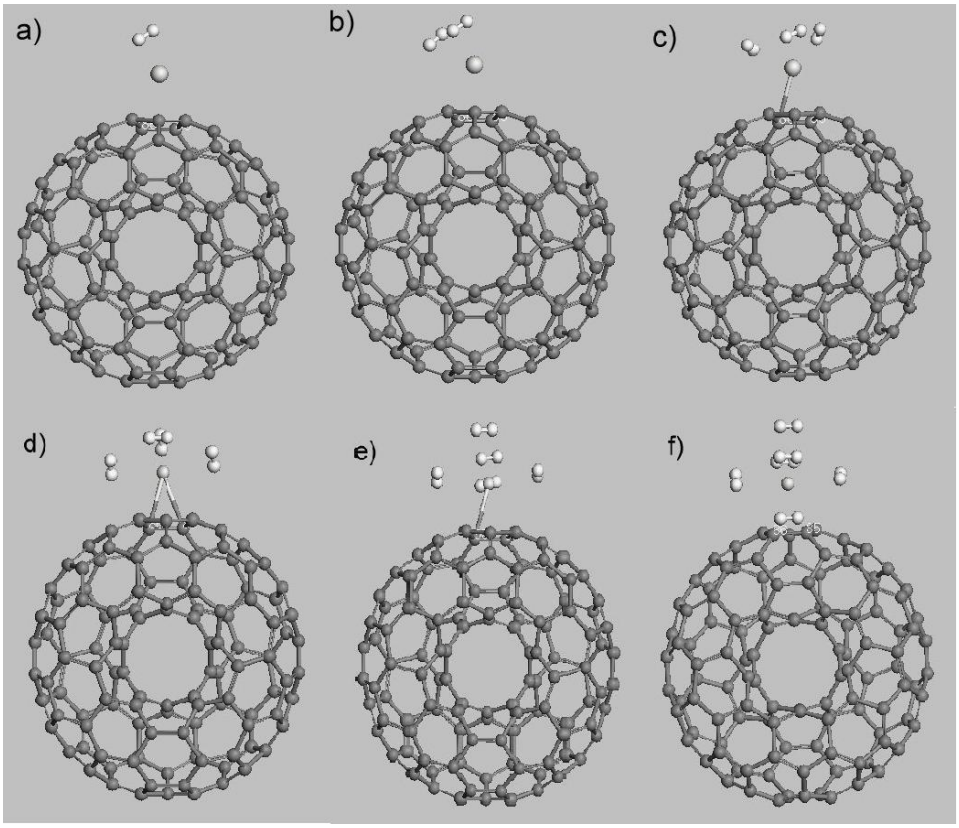

Figure 3 (a - f). Optimized structures of ScC_{120}-nH_2 systems, for n = (1-6) respectively.

Figure 4 show the geometry optimized system $10ScC_{120}$-$60H_2$. Total energy values for systems with 1 to 10 Sc atoms are reported on Table 6. In addition, the values HOMO-LUMO energy gaps (Δ) and geometric parameters of optimization are presented.

From values on Table 6, it is possible to conclude that as the number of Sc atoms increases from 1 to 10, the gap value decreases from 0.97 to 0.26 eV. This means that the chemical reactivity of the system increases. Regarding the distance we can observe that it is maintained within the same range, except the average of the H-H bond, that with a single Sc atom is of 0.776 Å and as the number of Sc atoms are increased the bond length increases slightly until the value 0.780 Å, with 10 Sc atoms.

Table 5. Total energy, average adsorption energy per H_2 and consecutive adsorption energy (in parentheses) of H_2, and geometric parameters of ScC_{120}-nH_2 n = (1-6) systems.

System	Total Energy (Ha)	Average adsorption energy per H_2 (eV)	Distances (Å)				Average H-H bond lengths (Å)
			C86-Sc	C85-Sc	Average Sc-H	C85-C86	
ScC_{120}	-4632.153487	--	2.577	2.568	--	1.486	--
ScC_{120}-H_2	-4633.329741	0.195	2.576	2.567	2.360	1.486	0.780
ScC_{120}-$2H_2$	-4634.507034	0.209 (0.223)	2.576	2.567	2.356	1.487	0.781
ScC_{120}-$3H_2$	-4635.683683	0.208 (0.205)	2.577	2.554	2.350	1.485	0.781
ScC_{120}-$4H_2$	-4636.860224	0.206 (0.202)	2.531	2.467	2.378	1.494	0.780
ScC_{120}-$5H_2$	-4638.035300	0.198 (0.163)	2.584	2.215	2.406	1.495	0.778
ScC_{120}-$6H_2$	-4639.210252	0.191 (0.159)	2.580	2.566	2.448	1.506	0.776

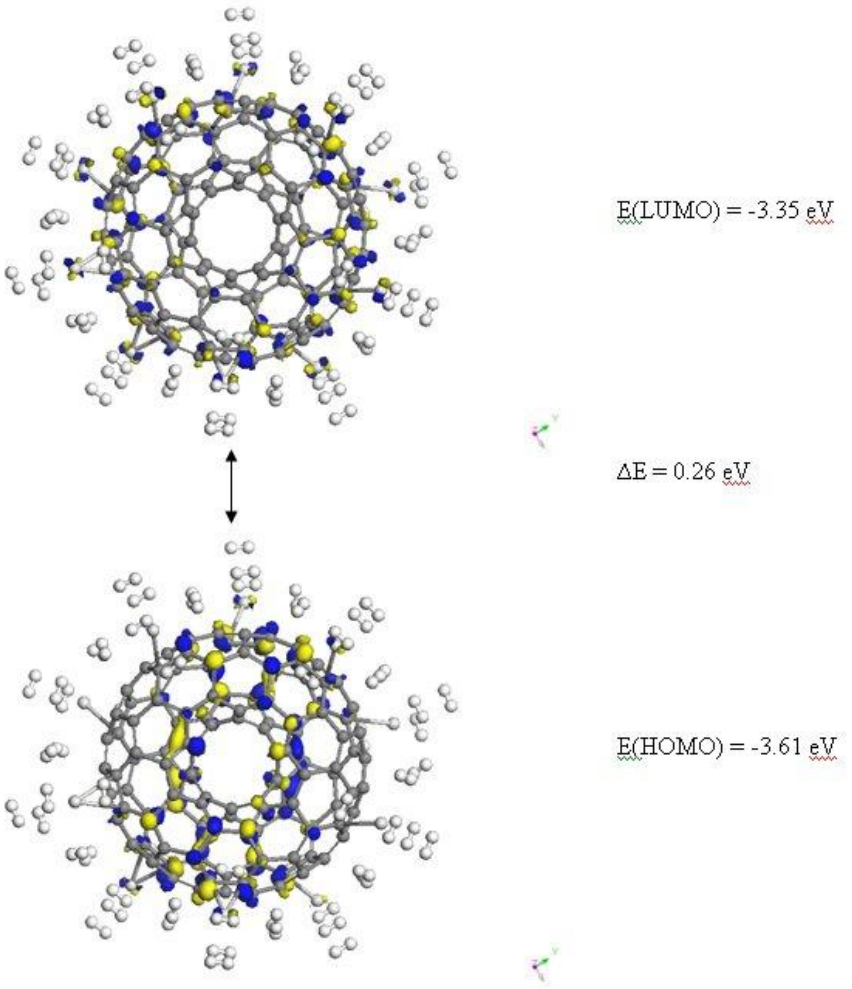

Figure 4. HOMO-LUMO energy gap (Δ) for the $10ScC_{120}$-$60H_2$ system.

Table 6. Total energy, HOMO-LUMO energy gap (Δ), and geometric parameters of 1-10ScC_{120}-6H_2 systems.

System	Total Energy (Ha)	(Δ) (eV)	Distances (Å)			Average H-H bond lengths (Å)
			Average C-Sc	Average Sc-H	C(1)-C(2)	
Sc	-4632.153487	0.97	2.572	--	1.486	--
ScC_{120}-6H_2	-4639.210252	0.97	2.573	2.448	1.506	0.776
2ScC_{120}-6H_2	-4704.717041	0.90	2.559	2.463	1.508	0.777
3ScC_{120}-6H_2	-4770.222553	0.86	2.558	2.466	1.505	0.777
4ScC_{120}-6H_2	-4835.727290	0.84	2.559	2.465	1.507	0.778
5ScC_{120}-6H_2	-4901.229882	0.84	2.550	2.480	1.507	0.778
6ScC_{120}-6H_2	-4966.729540	0.80	2.554	2.474	1.505	0.779
7ScC_{120}-6H_2	-5032.231204	0.05	2.559	2.481	1.505	0.779
8ScC_{120}-6H_2	-5097.729240	0.28	2.558	2.481	1.504	0.779
9ScC_{120}-6H_2	-5163.230647	0.26	2.559	2.474	1.504	0.780
10ScC_{120}-6H_2	-5228.730051	0.26	2.557	2.492	1.504	0.780

Table 7. Mulliken population analysis of 1-10ScC_{120}-6H_2 system.

System	Mulliken charge (electron)		
	Sc atom Average	H atom Average	C atom Average
Sc	0.550	--	-0.076
ScC_{120}-6H_2	0.330	0.0250	-0.187
2ScC_{120}-6H_2	0.339	0.0167	-0.190
3ScC_{120}-6H_2	0.338	0.0147	-0.189
4ScC_{120}-6H_2	0.336	0.0129	-0.189
5ScC_{120}-6H_2	0.338	0.0106	-0.190
6ScC_{120}-6H_2	0.340	0.0094	-0.184
7ScC_{120}-6H_2	0.340	0.0077	-0.184
8ScC_{120}-6H_2	0.341	0.0064	-0.183
9ScC_{120}-6H_2	0.336	0.0057	-0.183
10ScC_{120}-6H_2	0.340	0.0041	-0.184

We have computed the Mulliken populations for all the studied systems. The Mulliken charges on the Sc atom, H atom and C atom are shown in Table 7. We can conclude from this table that for the system with a single Sc atom without H_2 molecules, there is a net charge transfer of 0.550 electrons from the Sc atom towards the closer C atoms. This means a net average charge of -0.076 electrons for those C atoms around the Sc atom. For the systems with several Sc atoms and H_2 molecules around, there is also a charge transfer from the Sc atoms (0.338 average electrons transferred) towards the C atoms (being - 0.180 the average electron transferred to the nearest C atoms) keeping all the values within the

same range. In the case of the hydrogen atoms, it's observed that the average transfer charge decreases as the Sc atoms increases.

4. Conclusions

We have studied the hydrogen adsorption capabilities of a carbon C_{120} nanotorous structure with a Be atom or a single transition metal (Sc) externally attached to the nanotorous, which is demonstrated to be a good candidate for hydrogen storage with moderate H_2 adsorption energy. The maximum number of H_2 molecules that are expected to be adsorbed near the Sc atom is six. The nanotorus with 10 Sc atoms can adsorb up to 60 hydrogen molecules, which represents 6.01 wt %, which fulfils the current requirement of 6 wt %, for year 2010, specified by US Department of Energy (DOE).

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