Journal of New Materials for Electrochemical Systems 14, 223-228 (2011)

Hydrogen Storage on Scandium-Coated Toroidal Carbon Nanostructure C_{120} modeled with Density Functional Theory

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Received: December 21, 2010, Accepted: May 09, 2011, Available online: June 30, 2011

***Abstract**: Ab initio density functional calculations were performed on a toroidal carbon C_{120} nanostructure doped from one to ten Sc atoms bonded to its outer surface. These calculations are based on DFT with the generalized gradient approximation PW91 (Perdew and Wang) as implemented in the Materials Studio v.4.3 code. The Dmol^3 module was used to calculate, among others, total energies, charge density, HOMO-LUMO and Mulliken population analysis. On the basis of these results, it is possible to propose that a single Sc atom is able to adsorb up to 6 H_2 molecules. Therefore the study was extended for a system with 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 toroidal carbon C_{120} nanostructure is a good candidate for H_2 storage with moderate adsorption energy.*

Keywords: Toroidal C_{120} Carbon Nanostructure, Density Functional Theory, Hydrogen storage, Scandium-Coated Toroidal Carbon Nanostructure.

1. INTRODUCTION

A toroidal carbon nanostructure with six-fold rotational symmetry was proposed by Dunlap in 1992 by connecting six straight nanotube segments [1]. Carbon nanostructures with toroidal geometry are expected to have unusual physical properties that make them attractive for technological applications. To take advantage of the large surface area of the torus geometry, in this work we study the all-carbon five-fold symmetric C_{120} torus as a good candidate for a hydrogen storage system. Development of novel nanostructured materials for efficient hydrogen storage is of current technological interest because hydrogen is expected to replace hydrocarbons as energy source in the near future.

Ihara and coworkers [2] describe how the C_{120} nanotorus can be constructed from 12 inequivalent carbon atoms. In this work, we report calculations of total energies, charge density, Mulliken population analysis and highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps for the C_{120} nanotorus. Optimized geometry of C_{120} yields 4.159 and 11.740 Å for the inner and outer diameters, respectively, with a nearly circular cross section with diameter 4.623 Å. In a theoretical study, Guangfen Wu et al [3], investigate the feasibility of bare and metal-coated boron buckyball B_{80} with M = Li, Na, K, Be, Mg, Ca, Sc, Ti, and V for hydrogen storage using density functional theory approach. They find that M = Ca or Sc are best candidates for hydrogen storage with moderate adsorption energy of H_2 and without clustering of Sc or Ca on B_{80} surface. Qiang Sun et al [4], based on gradient corrected density functional theory, show that Li decorated B doped heterofullerene ($Li_{12}C_{48}B_{12}$) has properties of a hydrogen storage material. On the other hand, Qian Wang et al [5], by means of first principles calculations based on gradient corrected density functional theory and molecular dynamics simulations of Ca decorated fullerene yield some results, such as, $C_{60}Ca_{32}$ can absorb up to 62 H_2 molecules in two layers. In addition, T. Yildirim et al [6], performed a study about molecular and dissociative adsorption of multiple hydrogen molecules on transition metal decorated C_{60}, once the metal atoms are adsorbed on

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C_{60}, each one can bind up to four hydrogen molecules. In this work, we perform DFT calculations on C_{120} nanotorus with Dmol^3 code [7, 8] implemented in the Materials Studio program [9]. As a first step, the stability of the isolated C_{120} nanotorus and of each one of the scandium-coated nanotori with $n$$H_2$ molecules (n=1-6) was investigated. The closed structure and large specific surface area of the C_{120} toroidal geometry gives room to up to 10 Sc atoms, each of which can bond to up to 6 H_2 molecules, suggesting that they should be efficient H_2 storage systems.

2. METHOD

As Ihara and coworkers [2] describe, coordinates of the 120 carbon atoms of the nanotorus were obtained from a set of 12 inequivalent carbon atoms by successive five-fold rotations followed by a reflection and final rotation of $\pi/5$ radians. The structure consists of ten pentagonal, forty hexagonal and ten heptagonal rings. Five- and six-member rings follow the *isolated pentagon rule* [10, 11].

We use the generalized gradient approximation of DFT implemented in the Materials Studio v.4.3 code, as proposed by Perdew and Wang (PW91) [12]. The Dmol^3 module was used to calculate, among others, 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**. This methodology has been proven to be efficient to study similar systems [13].

3. RESULTS AND DISCUSSION

This section of the work has been organized in two parts. The first one is devoted to study the capacity of C_{120} doped with a single Sc atom externally attached to adsorb H_2 molecules. It was found that the maximum number is 6, based on the corresponding average adsorption energy per H_2, (Table 1). Based on this result, the second part of this section consists on the study of C_{120} doped with 10 Sc atoms, each of them associated with 6 H_2 molecules. The study was performed adding one Sc atom (and its 6 H_2 molecules) at a time, and optimizing the geometries of each system before adding the next Sc atom.

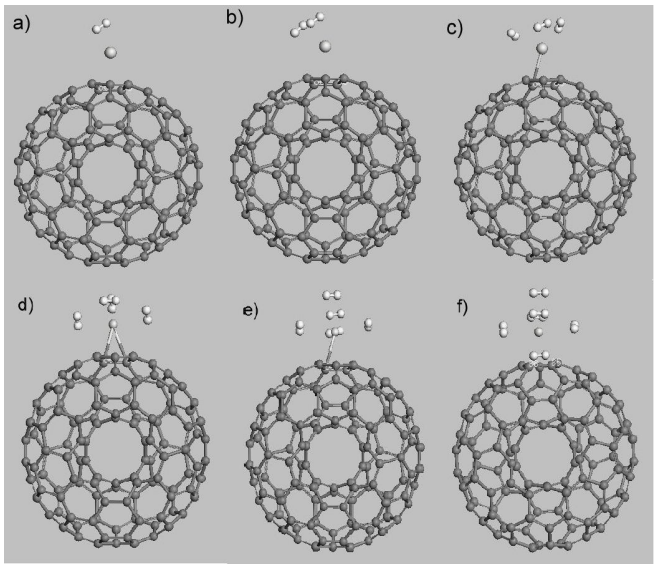

Figure 1. Optimized structures of ScC_{120}-$n$$H_2$ systems, for n = (1-6) respectively.

3.1. Study of the C_{120} system doped with a single Sc atom

Consequently, first we study hydrogen adsorption capabilities of the toroidal carbon C_{120} structure with a single Sc atom externally attached. Although metal atom can occupy different sites of toroidal carbon C_{120} nanostructure, we consider Sc atom adsorbed between carbon atoms labeled 85 and 86, which neighbors in a pentagonal and hexagonal ring and the respective bond length is 1.486 Å. The optimized structures of ScC_{120}-$n$$H_2$, for n = 1-6, are shown in Figure 1. The geometry and energy information of scandium-toroidal carbon C_{120} nanostructure are presented in Table 1. The average C-C distances involving the C atoms closest to the Sc atom (C85 and C86) are 2.57 and 2.56 Å, respectively. 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

Table 1. Total energy, average adsorption energy per H_2 and consecutive adsorption energy (in parentheses) of H_2, and geometrics parameters of ScC_{120}-$n$$H_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

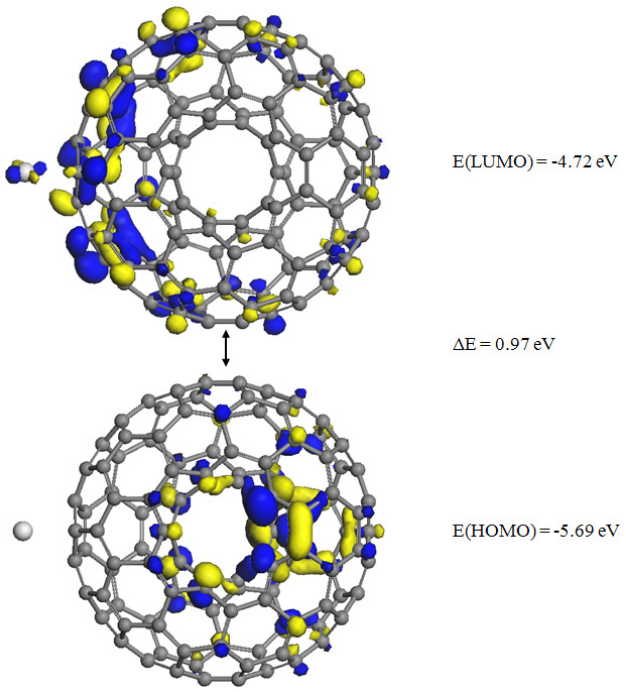

Figure 2. HOMO-LUMO energy gap (Δ) for the ScC_{120} system.

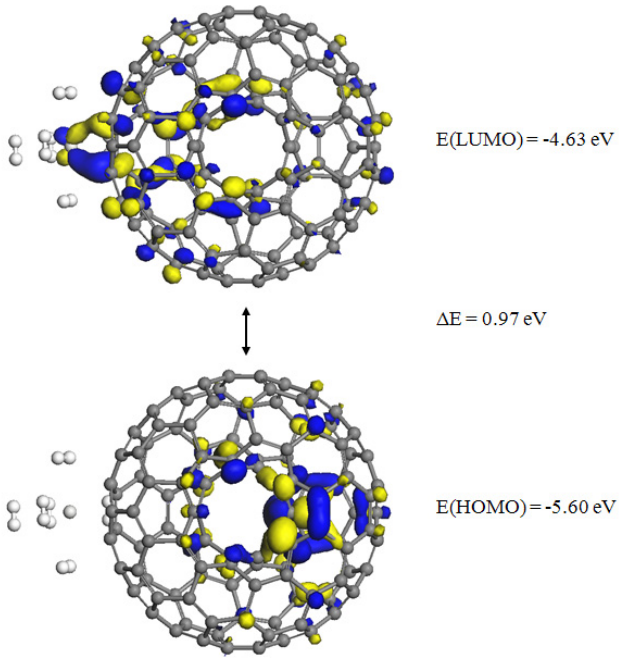

Figure 3. HOMO-LUMO energy gap (Δ) for the ScC_{120}-$6H_2$ system.

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.

The binding energy E_b of the Sc atom adsorbed on the outer surface of the bare nanotorus is defined as [14].

$$E_b=E_t(Sc)+E_t(C_{120})-E_t(C_{120\text{-}Sc}) \quad (1)$$

where E_t (Sc), E_t (C_{120}) and E_t ($C_{120\text{-}Sc}$) are the total energies of a free Sc atom, the pure C_{120} and the $C_{120\text{-}Sc}$ system, respectively. *E*b was found to be equal to 3.304 (eV), which indicates that the C_{120}-Sc system is strongly bonded. The strength of the interaction is consistent with the formation of a C-Sc bond, which indicates that the whole system can be considered as one single species.

We have also computed the average adsorption energy per H_2, [3].

$$E_{ave} = \{E[ScC_{120}] + nE[H_2] - E[ScC_{120}\text{-}nH_2]\}/n \quad (2)$$

and consecutive adsorption energy of H_2

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

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

Although the adsorption energy of the first H_2 on ScC_{120} reaches up to 0.195 eV, that of the second H_2 is 0.223 eV. The stronger binding of H_2 to ScC_{120} and the relatively larger HOMO-LUMO gap of ScC_{120}-H_2 imply that this structure is of high stability. Thus, the second H_2 is very easily adsorbed. For the other H_2 molecules the value of adsorption energy slightly decreases from 0.223 for two H_2 molecules to 0.159 eV, for 6 H_2 molecules. However, even for the latter there is a strong binding of H_2 to ScC_{120}. Accordingly the system ScC_{120}-$6H_2$ is stable and is expected to be a good alternative for hydrogen storage.

The spatial HOMO-LUMO distributions for the bare ScC_{120} and hydrogenated ScC_{120}-$6H_2$ system are shown correspondingly in Figures 2 and 3, respectively. Blue lobes show the positive and yellow lobes show the negative values of the wave function.

In Figure 2, the density distribution in the LUMO of ScC_{120} systems is mainly located in the neighborhood of the Sc atom, indicating that the adsorption of the first H_2 molecule is expected to take place in this region. Figure 3 shows the ScC_{120}-nH_2 system with n = (6). The LUMO density is also concentrated in the vicinity of the Sc atom, suggesting that the second molecule of H_2 would also be absorbed in this region.

The HOMO-LUMO energy gaps (Δ) for the systems ScC_{120}-nH_2 n = (1-6) are reported in Table 2. They are very similar for all the

Table 2. HOMO-LUMO gap (Δ) of ScC_{120}-nH_2 n = (1-6) system.

System	HOMO (eV)	LUMO (eV)	(Δ) (eV)
ScC_{120}	-5.69	-4.72	0.97
ScC_{120}-H_2	-5.67	-4.71	0.96
ScC_{120}-$2H_2$	-5.66	-4.69	0.97
ScC_{120}-$3H_2$	-5.63	-4.67	0.96
ScC_{120}-$4H_2$	-5.63	-4.67	0.96
ScC_{120}-$5H_2$	-5.61	-4.64	0.97
ScC_{120}-$6H_2$	-5.60	-4.63	0.97

Table 3. Mulliken population analysis of ScC_{120}-nH_2 n = (1-6) system.

System	Mulliken charge (electron)		
	Sc atom	H atom Average	C atom
ScC_{120}	0.550	--	C85 -0.076 C86 -0.077 C88 -0.078 C89 -0.084
ScC_{120}-H_2	0.531	0.033	C85 -0.074 C86 -0.078 C88 -0.077 C89 -0.085
ScC_{120}-$2H_2$	0.508	0.030	C85 -0.077 C86 -0.077 C88 -0.077 C89 -0.083
ScC_{120}-$3H_2$	0.492	0.020	C85 -0.074 C86 -0.067 C88 -0.085 C89 -0.089
ScC_{120}-$4H_2$	0.436	0.020	C85 -0.125 C86 -0.110 C88 -0.034 C89 -0.052
ScC_{120}-$5H_2$	0.377	0.020	C85 -0.139 C86 -0.118 C88 -0.017 C89 -0.033
ScC_{120}-$6H_2$	0.330	0.025	C85 -0.190 C86 -0.184 C88 0.038 C89 0.036

reported systems with values ranging from 0.96 to 0.97 eV.

The values for the Mulliken population analysis are reported on Table 3. According to them, for the system without H_2 molecules and only one Sc atom, the value is 0.550 electrons, which indicates that there is a very high charge transfer from this atom to the C atoms that are closer and labeled with numbers 85, 86, 88 and 89. For the rest of the Sc atoms, as the number of H_2 molecules increases the value of its charge transfer lowers from 0.531 for one H_2 molecule to 0.330 electrons for 6 hydrogen molecules.

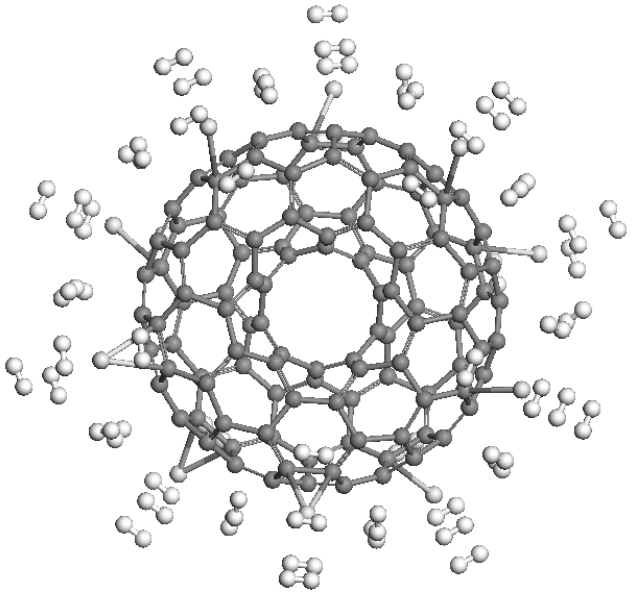

Figure 4. Optimized structure of $10ScC_{120}$-$60H_2$ system.

From Table 3 it is also possible to observe that when 1 to 3 H_2 molecules are adsorbed, the charge transfer to these carbon atoms is almost the same for all (-0.079 electrons in average). But when the number of hydrogen molecules increase to 4, 5 and 6, then the charge transfer also starts to increase towards the carbon atoms labeled with numbers 85 and 86 (-0.144 electrons in average). Regarding the hydrogen, these transfer their charge and stabilize in an average value of 0.025 electrons.

3.2. Study of the C_{120} system doped with ten Sc at-

Table 4. Total energy, HOMO-LUMO energy gap (Δ) and geometrics 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)	
ScC_{120}	-4632.153487	0.97	2.572	--	1.486	--
ScC_{120}-$6H_2$	-4639.210252	0.97	2.573	2.448	1.506	0.776
$2ScC_{120}$-$12H_2$	-4704.717041	0.90	2.559	2.463	1.508	0.777
$3ScC_{120}$-$18H_2$	-4770.222553	0.86	2.558	2.466	1.505	0.777
$4ScC_{120}$-$24H_2$	-4835.727290	0.84	2.559	2.465	1.507	0.778
$5ScC_{120}$-$30H_2$	-4901.229882	0.84	2.550	2.480	1.507	0.778
$6ScC_{120}$-$36H_2$	-4966.729540	0.80	2.554	2.474	1.505	0.779
$7ScC_{120}$-$42H_2$	-5032.231204	0.05	2.559	2.481	1.505	0.779
$8ScC_{120}$-$48H_2$	-5097.729240	0.28	2.558	2.481	1.504	0.779
$9ScC_{120}$-$54H_2$	-5163.230647	0.26	2.559	2.474	1.504	0.780
$10ScC_{120}$-$60H_2$	-5228.730051	0.26	2.557	2.492	1.504	0.780

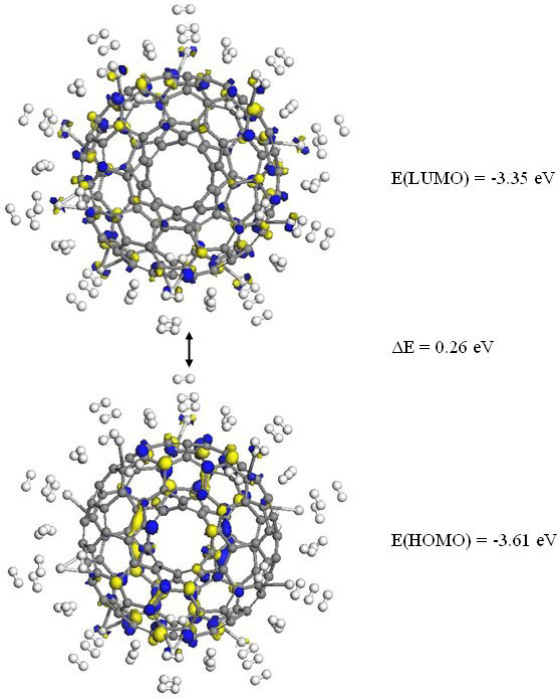

Figure 5. HOMO-LUMO energy gap (Δ) for the $10ScC_{120}$-$60H_2$ system.

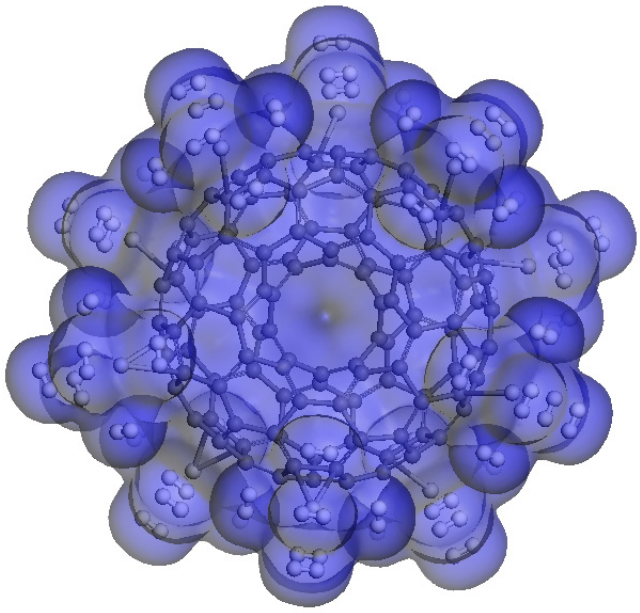

Figure 6. Top view of the calculated total charge density of $10ScC_{120}$-$60H_2$. The gray and dark-gray atoms are H and C, respectively. (Blue color isovalue = 0.017).

oms

Now that we know that a single Sc atom can adsorb up to 6 H_2 molecules, we proceed to the second part of our study which is cover the C_{120} with more Sc atoms and thus we find that the maximum number is 10, giving us a total of 60 H_2 molecules, this weight is in percentage 6.01, which complies with the U.S. Energy Department rule (6 wt %, at 2010, specified by US Department of Energy (DOE)), for materials designed to store hydrogen.

Figure 4 show the geometry optimized system $10ScC_{120}$-$60H_2$.

Table 5. Mulliken charges on the Sc, H and C atom for the studied systems.

System	Mulliken charge (electron)		
	Sc atom Average	H atom Average	C atom Average
ScC_{120}	0.550	--	-0.076
ScC_{120}-$6H_2$	0.330	0.0250	-0.187
$2ScC_{120}$-$12H_2$	0.339	0.0167	-0.190
$3ScC_{120}$-$18H_2$	0.338	0.0147	-0.189
$4ScC_{120}$-$24H_2$	0.336	0.0129	-0.189
$5ScC_{120}$-$30H_2$	0.338	0.0106	-0.190
$6ScC_{120}$-$36H_2$	0.340	0.0094	-0.184
$7ScC_{120}$-$42H_2$	0.340	0.0077	-0.184
$8ScC_{120}$-$48H_2$	0.341	0.0064	-0.183
$9ScC_{120}$-$54H_2$	0.336	0.0057	-0.183
$10ScC_{120}$-$60H_2$	0.340	0.0041	-0.184

The total energy values obtained for all systems from 1 to 10 Sc atoms are reported on Table 4. In addition, the values for the HOMO-LUMO energy gaps (Δ) and geometric parameters of optimization are presented.

From values in Table 4, it is possible to conclude that as the number of scandium atoms increases from 1 to 10, the gap value decreases from 0.97 to 0.26 eV, respectively. 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 is increased the bond length increases slightly to 0.780 Å for 10 Sc atoms. The HOMO and LUMO of the $10ScC_{120}$-$60H_2$ system are shown in Figure 5, where it can be observed that they are uniformly distributed on the external surface of C_{120}.

We have computed the Mulliken populations for all the studied systems. The Mulliken charges on the Sc, H and C atom are shown in Table 5. From this Table we conclude that for the system without H_2 molecules, but with a single Sc atom, there is a charge transfer of 0.550 electrons from Sc atom towards the C atom of -0.076 electrons (average of C atoms neighboring the Sc atom). For the systems with several Sc atoms that have H_2 molecules, there is also a transfer charge from the Sc atoms (0.338 average electrons) towards the C atoms (-0.180 average electrons), keeping all the values within the same range. In the case of the hydrogen atoms, it observed that the average transfer charge decreases as the Sc atoms increases. Finally, the total charge density for the system with 60 H_2 molecules is shown in Figure 6. The final equilibrium configuration for this case has a high symmetry distribution for all the atoms and in the charge density as well.

4. SUMMARY

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

5. CONCLUSIONS

Based on ab-initio density functional calculations, total energies, HOMO-LUMO, charge density and Mulliken population analysis are calculated for a toroidal carbon C_{120} nanostructure. In terms of these and other previous results [15], the scandium-coated toroidal carbon C_{120} nanostructure is theoretically a good candidate for H_2 storage with moderate adsorption energy. When doping this toroidal carbon C_{120} nanostructure with ten Sc atoms, results predicts the possible bonding and adsorption of a total of 60 H_2 molecules on the external surface of the system. The stability of each one of the studied systems and the amount of adsorbed or stored hydrogen is close to 6.01 wt %, close to the 2010 USDOE target for hydrogen storage. Experimental results are very desirable to prove or disprove the predictions and estimations about the real capability of the C_{120} nanotorus, with respect to hydrogen absorption and storage. Comparison of the results we obtained on the non coated and the coated C_{120} nanotorus show that the different mass of these atomic species is relevant to explain the greater average adsorption energy per H_2 for the Be coated system with respect to the Sc one. One task to be done about the geometry of the nanotorus is to see if in the border of the hexagonal and pentagonal rings for example, it could be possible to find quantum effects such as those observed for graphene under stress conditions [16].

6. ACKNOWLEDGMENTS

The authors would like to express their sincere thanks to Dr. Annia Galano for her valuable help. This work was possible thanks to the financing of CONACyT projects Numbers 25218 and 57262.

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