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Modelling carbyne C_{12}-ring calcium decorated for hydrogen storage

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We computationally investigate the hydrogen storage properties of C_{12} carbyne structure decorated with calcium (Ca) atoms adsorbed on its outer surface. The calculations are carried out on DFT-GGA-PW91 and DFT-GGA-PBE levels of theory as implemented in the modeling and simulation Materials Studio program. To account for the dispersion (van der Waals) interactions we also carry out calculations using DFT-D method of Grimme. Dmol^3 is used to calculate, total energies, charge density HOMO-LUMO and Mulliken population analysis. Based on these results, up to six H_2 molecules per Ca atom can be physisorbed with an average energy of 0.1890 eV (PW91) and 0.3204 (DFT-D) per H_2 molecule. This physisorption leads to 6.16 weight percentage (wt %) for the gravimetric hydrogen storage capacity. According to these results, the calcium-decorated carbyne C_{12} structure is a good candidate for hydrogen storage with application to fuel cells.

Keywords: Carbyne; hydrogen storage; calcium decorated; Dmol^3; physisorption.

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1. Introduction

Hydrogen has attracted much attention as a promising clean energy source that could one day replace fossil fuels to combat global warming [1-5]. One of the biggest challenges to reach that goal is the high-density hydrogen storage, to perform reversible hydrogen charging cycles at ambient conditions for automotive onboard applications [2,4,5].

A desired storage system must have a high gravimetric density (4.5 to 6.5 wt %) at moderate pressure, and should operate at delivery temperatures between -40 to 85°C, goal suggested by US Department of Energy (DOE) for the year 2020 [3,6,7]. In the past few decades, the carbon-based nanostructure materials, including nanotubes [8-11], fullerenes [8,11-12] and graphenes [8,13] were expected to be the promising candidate materials for hydrogen storage because of their high surface/volume ratios and high degree of reactivity between carbon and hydrogen [14]. However, physical sorption in these systems generally requires cryogenic temperature because of the small binding energy of ~ 0.05 eV, which makes it impractical for vehicular usage [15]. Desirable binding energy should lie in a range of $0.2 - 0.4$ eV per H_2 for the ambient condition storage [2,5,14-19].

In recent years, several first theoretical studies have been made to improve the hydrogen storage capacity of these carbon-based nanostructure materials by decorating atoms that can be transition metals (TM), alkaline metals (AM) or alkaline earth metals (AEM) [2,3,14-25]. Each TM (Sc, Ti) [18] or AEM (Ca) [2,15,21] atom can bind up to six hydrogen molecules per metal atom with a binding energy of $\sim 0.2 - 0.6$ eV [14,15,17].

However, a disadvantage shown by TM over AEM is that they have adsorption energies much larger than required, so not all hydrogen molecules might be adsorbed with the same energy since the first hydrogen molecules are strongly chemisorbed in atomic form, and the subsequent are physisorbed in molecular form [2,3,14,15]. This means that the total storage capacity cannot be carried out at a single operating temperature. On the other hand, the clustering of metal atoms will surely occur, due to the relatively large cohesive energy of these transition metals (≥ 4 eV per atom), which would further reduce the hydrogen storage capability [3,26,27]. Metal has a relatively small cohesive energy (≤ 2 eV per atom), so Ca atoms have a lower tendency to cluster on the host material once they are deposited. For instance, Ca-decorated graphene [20] and carbon nanotubes [19], the maximum hydrogen storage capacity can be as high as 8 and 5wt%, respectively. However, the binding energies of Ca on graphene and carbon nanotubes are only 0.632 and 0.88 eVCa^{-1}, respectively, which are much lower than the Ca-Ca cluster cohesive energy of 1.84 eV [14]. As a result, the Ca atoms prefer to form clusters on the carbon nanostructure, which may significantly reduce the hydrogen storage.

For this reason, the bonding energy of nanostructured decorated material must be greater than the cohesive energy to ensure there is no clustering between metals. On the other hand, Ca atom is expected to bind all hydrogen molecules reversibly by physisorption as well as being an abundant and low-cost element compared to metals such as Sc or Ti [3].

In this work, DFT calculations are performed in the carbyne C_{12}-ring structure decorated with Ca using Biovia Materials Studio Dmol^3 program to determine its capability for hydrogen storage. First, the carbyne type molecule used here is related to polyyne which is a single chain of carbon atoms with sp hybridization, formed with alternating single and triple bonds ($-C \equiv C-$), proposed by Tammann in 1921, the most common case is acetylene ($H-C\equiv C-H$) [28,29]. The C_{12}-ring is a variation of the linear chains of carbyne, where a decrease in the dimensions of the host materials is expected to increase the gravimetric capacity as well as volumetric capacity of hydrogen following the density increase of Ca atoms per volume or per C atom [15]. From this point of view, this kind of carbon may be utilized as a host material because of its perfect one-dimensional geometry, and consequently greater surface area.

We found a good behavior of C_{12}-ring as an adsorbent material of hydrogen through a dopant metal agent as calcium atom. The adsorption energy between C_{12}-ring and the dopant agent corresponds to chemisorption; however, according to the process of gas adsorption on a solid surface, we clearly found a physisorption between the dopant-metal in carbyne and the hydrogen molecules. The results show that up to six hydrogen molecules are physisorbed by the calcium atom with a desired binding energy 0.2 eV for hydrogen storage at ambient conditions and the hydrogen storage capability of 6.16 wt%. The HOMO-LUMO and Mulliken analysis show the areas with the greatest presence of electronic charge in the molecule; information that is compared with literature, making this molecule a suitable candidate to meet the requirements established by DOE.

2. Calculation method

In this work, DFT calculations are performed in the carbyne C_{12}-ring structure decorated with Ca using Biovia Materials Studio Dmol^3 program [30,31] to determine its capability of hydrogen storage. To calculate the adsorption energies, the generalized gradient approximation GGA-PW91 functional [32,33] for spin unrestricted was used. The interaction energies between the hydrogen molecules with a unit of C_{12}-ring are calculated by means of a set of double numerical bases (dnd), which has the advantage of being equivalent to the analytical base Gaussian 6-31 G*. All presented geometry optimizations are obtained until the maximum forces are lower than 0.004 Ha/Å. Here the effect of van der Waals (vdW) interactions is included explicitly by using the empirical correction scheme of Grimme (DFT-D) for periodic systems [34]. Standard values of the dispersion coefficients C_6 (0.14, 1.75, and 10.80 J nm^6 mol^{-1}, for H, C, and Ca, respectively), vdW radii (1.001, 1.452, and 1.474 Å), cutoff radius for pair interactions (30.0 Å), PBE global scaling factor S_6 (0.75), and damping factor d (20.0) have been used. We report both GGA-PW91 functional results and Grimme empirical correction scheme DFT-D method. In addition, the total energies, HOMO-LUMO electronic charge density and Mulliken population analysis are calculated.

3. Results and discussion

We performed the analysis of Ca-carbyne complex and found the most stable configuration from C_{12} carbyne molecule and Ca atoms adsorbed on its outer surface. First, carbyne molecule has been theoretically predicted to be a stable structure and it is possibly found in two phases: (i) energetically favorable polyyne phase $(-C\equiv C-)_n$ with alternation of triple (1.24 Å) and single (1.34 Å) bonds by Peierls distortion, called α-carbyne with an electronic configuration $((\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\pi_{2p_x}))^2(\pi_{2p_y})^2(\sigma_{2p_z})^2)_n$, and (ii) cumulene-type $(=C=C=)_n$ double bonds, as β-carbyne with an electronic configuration $((\sigma_{1s})^2(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^2(\pi_{2p_y})^2)_n$ [35,36]. We also found that carbyne rings can be created using an even number of carbons (polyyne), while cumulene rings can be designed with an odd carbons number. Figure 1(a) schematically shows the geometry optimization of carbyne C_{12}-ring, which corresponds to polyyne type used in this research. Second, we studied the case of a single Ca atom adsorbed to the carbyne surface separated at 2.48 Å and we analyze the stability of Ca-carbyne complex by evaluating the binding energy of Ca atom to the carbon ring from the following expression [6,15,16,23]:

$$E_b(\mathrm{Ca\ C_{12}}) = E(\mathrm{C_{12}}) + E(\mathrm{Ca}) - E(\mathrm{Ca\ C_{12}}) \qquad (1)$$

where $E(\mathrm{CaC_{12}})$, $E(\mathrm{Ca})$ and $E(\mathrm{C_{12}})$, are the total energies of the CaC_{12} system of one Ca atom and one carbyne molecule, respectively.

The binding energy (E_b) of CaC_{12} system shows a value of 2.95 eV and 2.23 eV with a GGA-PW91 and GGA-PBE functionals respectively, indicating that the system is strongly chemisorbed. Therefore, Ca atom will not tend to cluster if more calcium atoms are added to the system since the bonding energy is greater than the cohesive energy of the Ca-Ca bond (1.84 eV) [3,14,26,27]. Literature shows that typical chemisorption values are above 155 kJ/mol (1.6 eV) [37], therefore the CaC_{12} system can be considered as a single unit which we call decorated complex.

Figure 1(b), shows how the Ca atom tend to elongate the single bond of the carbyne molecule C_{12} to 2.210 Å. We found that the optimal position of Ca atom is at a bridge site of the carbyne (C-C) bonds as at this position optimally binds to the adjacent carbon atoms. In another position, with the Ca near a single carbon atom, the Ca atom disturbs the π-system creating a high energy radical.

In addition, we analyze the binding mechanism of Ca atom to carbyne molecule in this configuration. Figure 2 shows Total Density of States (DOS) for pure carbyne molecule C_{12}, and Fig. 3 shows the Partial Density of States

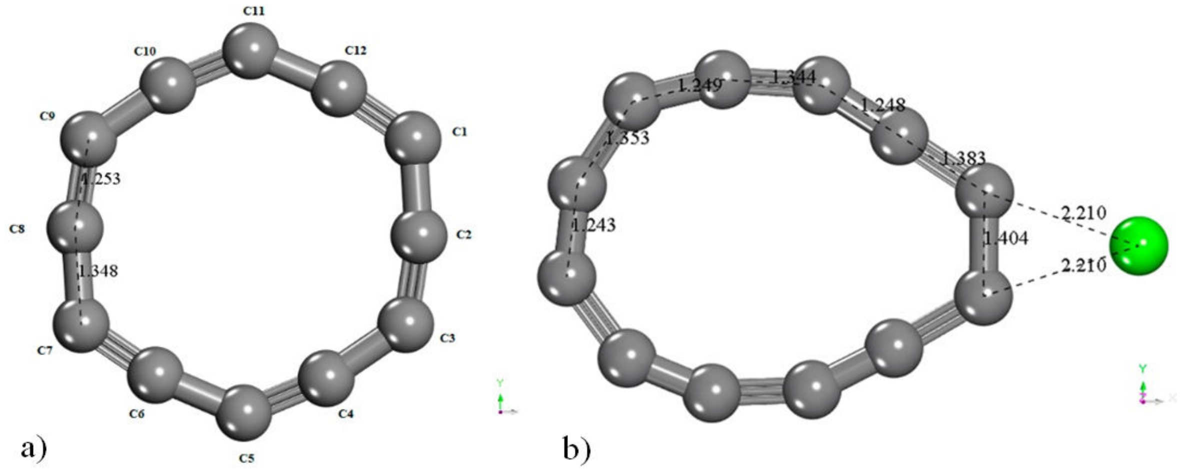

FIGURE 1. a) Carbyne C_{12}-ring with alternation of triple (1.25 Å) and single (1.34 Å) bonds. b) Geometry optimization of CaC_{12}, where the calcium atom tends to elongate the single bond at 2.210 Å.

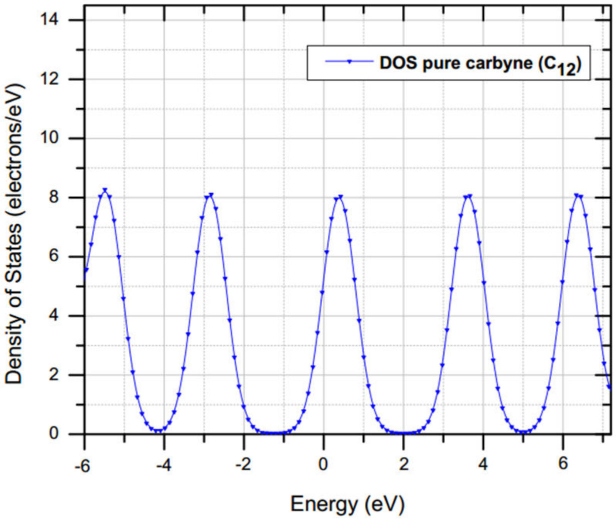

FIGURE 2. Density of States (DOS) of pure carbyne C_{12}-ring.

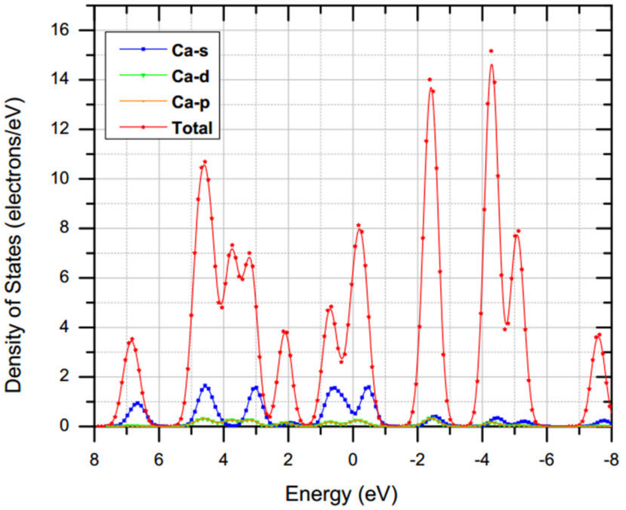

FIGURE 3. Ca-carbyne complex. The partial DOS of carbyne is presented by red line. The partial DOS of 4s, 4p and 3d Ca atom is presented by blue, orange and green lines respectively.

for the CaC_{12}. The 4s orbitals of the Ca atom play the main role in binding of Ca to C_{12}. This makes Ca atom to donate the s electrons due to their relatively low ionization potentials which leads to delocalization of the orbitals (Fig. 3). Also, the 3d orbitals of Ca atom and a small fraction of the 4p orbitals participate in bonding. There is a clear indication of charge transfer from s orbitals of Ca atom to carbyne π-system, and from carbyne π-system to the d orbitals of the Ca atom forming the donor-acceptor bond. Electron transfer from Ca to carbyne results in a positive charge on Ca atom (Mulliken charge +0.956e).

Once obtained CaC_{12} system in equilibrium, the next step is the adsorption analysis of H_2 molecules on the decorated complex. The H_2 molecules are added one by one over the Ca atom, reaching a maximum of six H_2 molecules adsorbed on it. We calculate the average energy of nH_2 molecules adsorbed on CaC_{12} complex using the Eq. (2) [6,15,16,23]

$$E_{ave} = \frac{[E(\mathrm{Ca\,C_{12}}) + nE(\mathrm{H_2}) - E(\mathrm{Ca\,C_{12}} - n\mathrm{H_2})]}{n} \tag{2}$$

where $E(\mathrm{Ca\,C_{12}})$ and $E(\mathrm{H_2})$ are the total energies of the complex CaC_{12} and of an isolated H_2 molecule, respectively. The $E(\mathrm{Ca\,C_{12}} - n\mathrm{H_2})$ is the total energy of the system with n molecules adsorbed on the doped complex.

The adsorption energy of the n-th of H_2 molecule is calculated using Eq. 3 [6,15,16,23].

$$\begin{aligned} E_{ad} = {} & E(\mathrm{Ca\,C_{12}} + (n-1)\mathrm{H_2}) + E(\mathrm{H_2}) \\ & - E(\mathrm{Ca\,C_{12}}) + nE(\mathrm{H_2}) \end{aligned} \tag{3}$$

where $E(\mathrm{Ca\,C_{12}} + (n-1)\mathrm{H_2})$ is the total energy of the CaC_{12} system with $(n-1)H_2$ molecules adsorbed on the decorated

TABLE I. Total energy DFT-GGA-PW91 and DFT-GGA-PBE (Grimme) (Ha), Average Energy (Eave) per H_2 molecule (eV) and Adsorption Energy (E_{ad}) of the nth H_2 molecule in a $CaC_{12} - nH_2$ system (eV), and weight percent (%wt) of $CaC_{12} - nH_2$ system.

System	Total Energy (Ha) GGA-PW91	Total Energy (Ha) GGA-PBE (Grimme)	E_{ave} and E_{ad} per H_2 GGA-PW91 (eV)	E_{ave} and E_{ad} per H_2 GGA-PBE-Grimme (eV)	%wt
H_2	-1.170096	-1.166029	—	—	—
Ca	-677.562931	-677.355188	—	—	—
CaC_{12}	-1134.496685	-1133.868382	—	—	—
CaC_{12}-H_2	-1135.67364	-1135.050485	(0.186)-(0.186)	(0.437)-(0.437)	1.0825
CaC_{12}-$2H_2$	-1136.850879	-1136.224976	(0.190)-(0.194)	(0.333)-(0.230)	2.1418
CaC_{12}-$3H_2$	-1138.02861	-1137.399998	(0.196)-(0.207)	(0.304)-(0.244)	3.1787
CaC_{12}-$4H_2$	-1139.204782	-1138.575493	(0.188)-(0.165)	(0.292)-(0.257)	4.1938
CaC_{12}-$5H_2$	-1140.381165	-1139.750244	(0.185)-(0.171)	(0.281)-(0.237)	5.1879
CaC_{12}-$6H_2$	-1141.558532	-1140.924903	(0.187)-(0.197)	(0.273)-(0.234)	6.1615

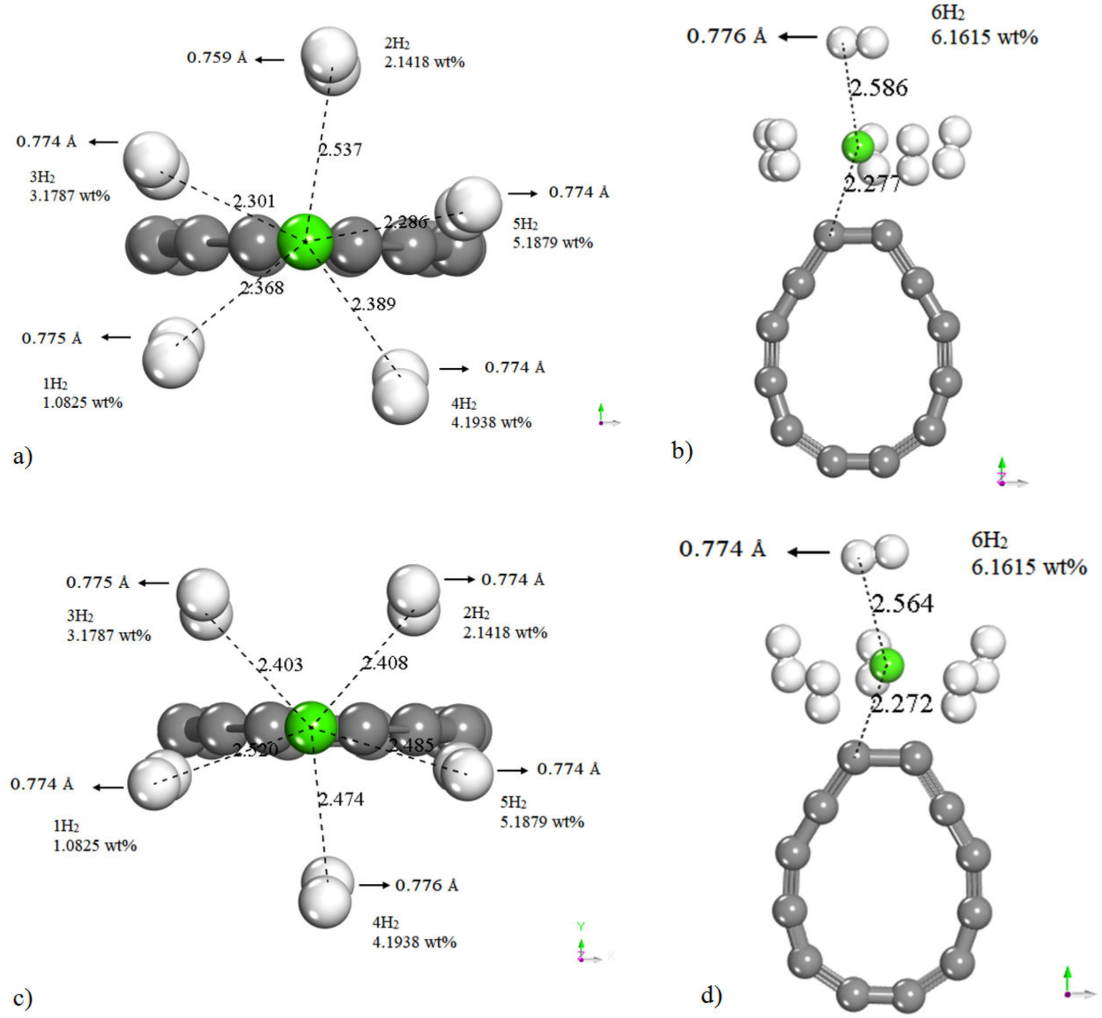

FIGURE 4. Geometry optimization scheme for the $CaC_{12} - nH_2$, with $n = 1 - 6$ H_2 molecules adsorbed onto the doped complex CaC_{12}. a, b) It shows the hydrogen adsorption on DFT-GGA-PW91 levels of theory. c, d) It shows the hydrogen adsorption on DFT-GGA-PBE levels of theory. The form of placement of the H_2 molecules in the doped complex is observed, the gray atoms are equal to the carbon atoms, the white atoms comprise the H_2 molecules and the green atom corresponds to the decoration Ca atom.

complex. The information of the optimized structures of $CaC_{12} - nH_2$, for $n = 1 - 6$ H_2 molecules, is shown in Table I.

To examine the hydrogen adsorption on the doped complex, more than 10 different configurations were simulated in the formation of H_2 molecules (linear and circular), thereby obtaining a formation at the time of reaching the six H_2 molecules. It was observed that the H_2 molecules tend to stay around the Ca atom, thereby obtaining a stable system (CaC_{12}-$6H_2$). In Fig. 4, it is clearly illustrated how the process of adding molecules to the doped complex is performed by placing one by one up to a maximum of six H_2 molecules; we show the first five H_2 molecules tend to be adsorbed around the Ca atom and the sixth H_2 molecule is adsorbed on top of the Ca atom.

The first H_2 molecule is adsorbed with an energy of $E_{ave} = 0.1866$ eV/H_2 and $E_{ad} = 0.1867$ eV/H_2 (PW91) on the doped complex, the average distance between H_2 molecules to Ca atom is 2.4101 Å and the bond distance among hydrogen molecules changes from 0.774 Å to 0.776 Å, which is due to the interactions between positively charged Ca atom and H_2 molecules. When the third H_2 molecule is adsorbed on decorated complex, the adsorption energy is 0.1962 eV/H_2, this value shows an increase of 5.14 % respect to the first H_2 molecule that is adsorbed on the doped complex. The additional H_2 molecules are maintained with an energy of 0.18 eV/H_2. The hydrogen storage capacity obtained in this study is 6.1615 wt% as seen in Table I, with an average energy of 0.1890 eV/H_2 and adsorption energy of 0.1871 eV/H_2 for the calculations with GGA-PW91 functional.

To account for the dispersion (van der Waals) interactions which are not included in GGA-PW91 functional used, we also carry out calculations using the DFT-D method of Grimme [34] with its default force-field parameters as implemented in Dmol^3, where Grimme's empirical correction scheme for common density functionals has been applied successfully to many chemical problems including molecular hydrogen [2,3,15,14]. It can be seen that the first H_2 molecule is adsorbed with an energy of $E_{\text{ave}} = 0.4373$ eV/H_2 and $E_{\text{ad}} = 0.4374$ eV/H_2 on the doped complex calculated from Eqs. 2 and 3. The average distance between H_2 molecules to Ca atom is 2.4756 Å and the bond distance among hydrogen molecules changes from 0.774 Å to 0.776 Å.

When the second H_2 molecule is adsorbed on the doped complex, it presents a decrease of 31% with respect to the first H_2 molecule resulting in an energy of 0.3338 eV/H_2. The following added molecules to doped complex presents an average decrease of 5.49% respect to the second molecule. Having thus an average energy of 0.3204 eV/H_2, and an average adsorption of 0.2736 eV/H_2, higher energies than the calculations with GGA-PW91. The hydrogen storage capacity obtained in this study is the same as for the results with PW91 (1.0825 to 6.1515) %wt (Table I). Thus, PW91 results can be taken as lower bounds for hydrogen storage energies whereas DFT-D results can be taken as higher bounds since they present better energies in the desirable range of 0.2 to 0.6 eV [14,15,17] for the hydrogen storage at ambient conditions as can be seen in Fig. 5.

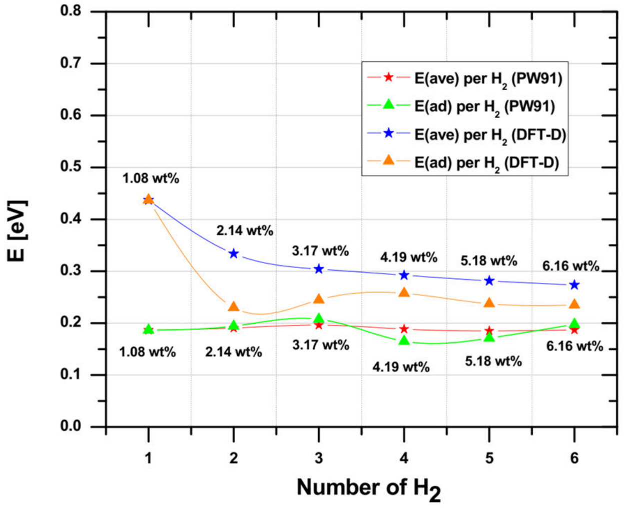

FIGURE 5. PW91 results taken as lower bounds and DFT-D results as higher bounds for hydrogen energies calculated from Eqs. 2 and 3 and weight percentage for all H_2 molecules adsorbed to the complex doped.

TABLE II. HOMO-LUMO energy difference or gap (Δ) of CaC_{12} and $CaC_{12} - nH_2$, $n = 1 - 6$ system in eV.

System	HOMO (eV)	LUMO (eV)	(Δ)
CaC_{12}	-4.360	-4.124	0.236
$CaC_{12}-H_2$	-4.248	-3.705	0.543
$CaC_{12}-2H_2$	-4.249	-3.714	0.535
$CaC_{12}-3H_2$	-4.258	-3.740	0.518
$CaC_{12}-4H_2$	-4.265	-3.758	0.507
$CaC_{12}-5H_2$	-4.273	-3.786	0.487
$CaC_{12}-6H_2$	-4.279	-3.807	0.472

Compared with results in the literature, some researches [15,18] obtain 0.24 to 0.07 eV as the range of binding energies for carbyne chains and 0.113 to 0.161 eV for the case of B_{80} decorated with calcium atoms, being in a range < 0.25 eV, making this system (CaC_{12}-$6H_2$) a good candidate for hydrogen storage since it has energies greater than 0.25 eV per H_2 only for calculations with DFT-D Grimme.

We performed the HOMO-LUMO spatial distribution analysis for the CaC_{12} and CaC_{12}-$6H_2$ systems shown in Fig. 6a,b, respectively. Blue lobes display positive values and yellow lobes negative values of the wave function. For CaC_{12} system (Fig. 6a) the distribution of electron density HOMO is on the single carbon bonds, the Ca atom is placed in front of the positive lobe since in this region there is an electron pair that can more easily yield or lose the carbyne molecule. The LUMO distribution can be seen to be located on the triple bonds, place of lower energy orbitals that are empty.

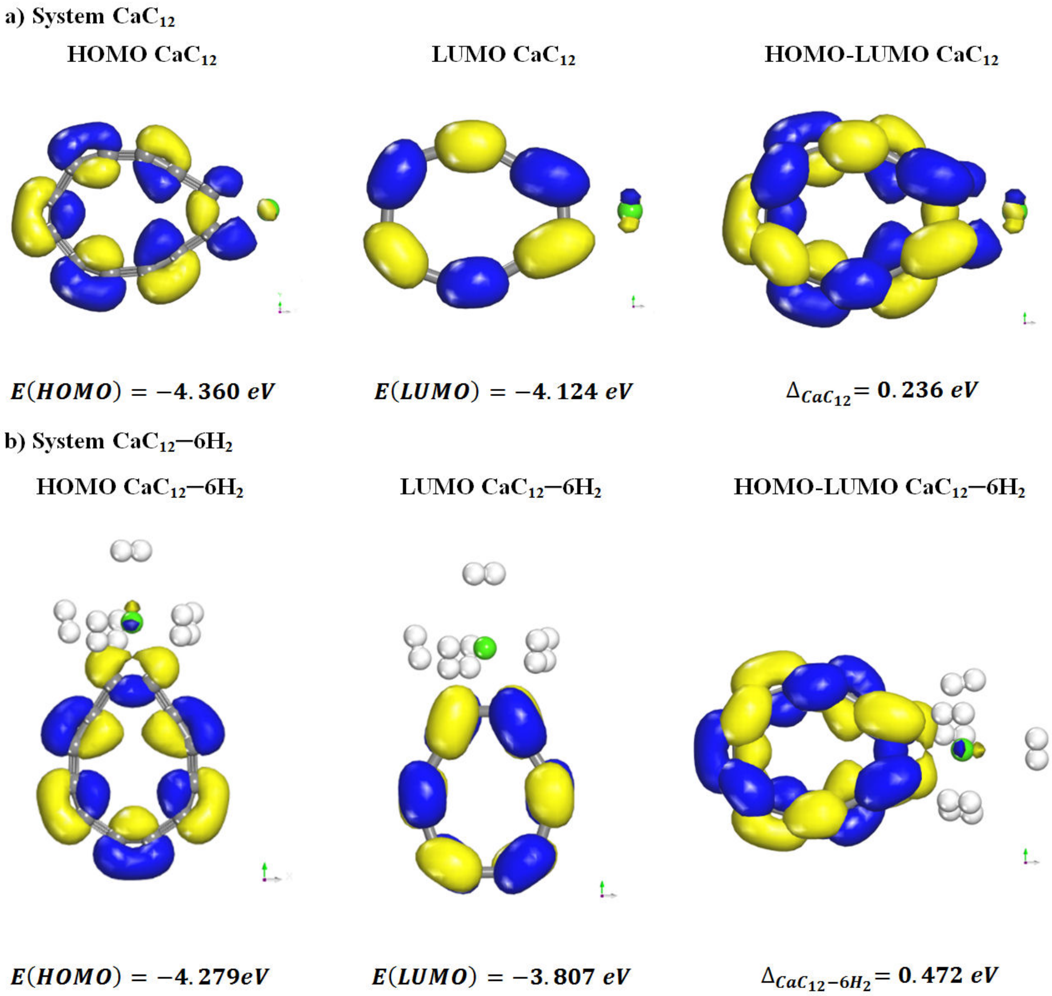

FIGURE 6. HOMO-LUMO spatial distribution analysis for CaC_{12} and $CaC_{12}-6H_2$ systems, blue lobes display positive values and yellow lobes negative values of the wave function. a) CaC_{12} system with an energy difference $\Delta_{CaC_{12}} = 0.236$ eV. b) $CaC_{12}-6H_2$ system with an energy difference of $\Delta_{CaC_{12}} - 6H_2 = 0.472$ eV.

TABLE III. Mulliken population analysis of CaC_{12} and $CaC_{12} - nH_2$ with $n = (1 - 6)$ system.

System	Mulliken charge (e)		
	C (atom)	Ca (atom)	H (atom average)
CaC_{12}	C1-0.399 C2 -0.399	0.956	—
$CaC_{12}-H_2$	C1- -0.405 C2 0.042	1.072	−0.078
$CaC_{12}-2H_2$	C1-0.403 C2 0.044	1.124	−0.078
$CaC_{12}-3H_2$	C1-0.409 C2 0.041	1.113	−0.091
$CaC_{12}-4H_2$	C1-0.416 C2 0.044	1.158	−0.090
$CaC_{12}-5H_2$	C1-0.406 C2 0.043	1.172	−0.090
$CaC_{12}-6H_2$	C1-0.408 C1-0.040	1.106	−0.081

Calculations of energy difference HOMO-LUMO or gap (Δ) for the $CaC_{12} - nH_2$ system, are summarized in Table II. It is observed that values of energy difference for the doped complex with 1 to 3 H_2 molecules give an average of 0.532 eV. Therefore, a higher than the latter is required to adsorb on the doped complex. Otherwise, for the doped complex with 4 to 6 hydrogen molecules, the average energy difference is 0.488 eV. This indicates that for the latter systems is relatively easier for adsorbing molecules to the doped complex. Likewise, the average energy difference HOMO-LUMO for $CaC_{12}-nH_2$ system is 0.5103 eV. Comparing this value with the binding energies of Table I, we have that the energy difference HOMO-LUMO is greater than adsorption energy for the doped complex with one to six H_2 molecules. This confirms the stability of the CaC_{12} system, providing a good physisorption alternative for hydrogen storage.

Mulliken population analysis is summarized in Table III, where we clearly observe the atomic charge +0.956e of Ca atom for CaC_{12} system, coming out from electrons donation of 4s orbitals plus a very small fraction of 4p and 3d orbitals of Ca atom, according to the graph PDOS vs Energy. This means that there is a charge transfer of the very high Ca atom to the nearest carbon atoms in the system. This calculation is in agreement with results obtained by Cruz-Torres *et al*. [23] where it can be observed that the atomic charge transfer of Ca atom into C_{12} system is +0.933e, having an overestimation of 2.46%, due to a lower number of carbon atoms in our system.

The whole $CaC_{12} - nH_2$ system values with $n \leq 6$ H_2 molecules are shown in Table III, where the average charge for Ca atom reaches a maximum value of +1.106e for six H_2 molecules, while the average charge for hydrogen atoms is -0.081e, increasing 15.69% with respect to the doped complex without hydrogen molecules. This physisorption process for a maximum number of hydrogen molecules on carbyne doped with calcium atom is stable as previously found [15], and easy for charge transfer in a mobile application system.

Likewise, it can be observed that the atomic charge on carbon atoms 1 and 2 (Fig. 1b) is maintained at an average -0.4078e on C1 atom, and 0.0423 on C2 atom. Reaching a maximum value when 5 H_2 molecules are adsorbed in the CaC_{12} system, with a charge transfer value on Ca atom of +1.172e, with an increment of 81% with respect to the +1.085e of CaC_{120}-5H_2 system [23], then the charge transfer decreases as the number of hydrogens increases. We also observe a decrease of 6.79% among CaC_{120}-5H_2 and CaC_{120}-6H_2 reported previously [23], in agreement with our study 5.96% among CaC_{120}-5H_2 and CaC_{120}-6H_2 reported by us. Then the addition of the sixth hydrogen molecule in a doped system proves a strong conservation charge transfer in the system.

Therefore, with the previous studies presented in this work, we can state that C_{12} carbyne molecule decorated with Ca atom can satisfactorily adsorb six H_2 molecules by physisorption with an average energy of 0.1903 eV (PW91) and 0.3204 (DFT-D) corresponding to 6.16 %wt, this storage capacity meets the requirements established by US Department of Energy by the end of the year 2020.

4. Conclusions

In summary, we performed the analysis of Ca-carbyne complex and found the most stable configuration from C_{12} carbyne molecule and Ca atom adsorbed on its outer surface, using Materials Studio Dmol^3 program. First, the carbyne molecule used in this work correspond to polyyne type with alternation of triple (1.34 Å) and single (1.24 Å) bonds. Second, we studied the case of a single Ca atom adsorbed to the carbyne surface, and we calculate the binding energy of the CaC_{12} system, showing a value of 2.95 eV (PW91) and 2.23 eV(PBE) indicating that the system is strongly chemisorbed.

The results show that up to six H_2 molecules are physisorbed by the Ca atom with an average energy of 0.1890 eV per H_2 (PW91). The first five H_2 molecules tend to adsorb around the Ca atom and the sixth H_2 molecule is adsorbed on top of the Ca atom.

To account for the dispersion (van der Waals) interactions which are not included in GGA-PW91 functional used, we also carry out calculations using the DFT-D method of Grimme, obtaining an average energy of 0.3204 eV per H_2. Thus, PW91 results are taken as lower limits and DFT-D results are taken as higher bounds since they present better energies in the desirable range of 0.2 to 0.6 eV for hydrogen storage at ambient conditions.

The hydrogen storage capacity obtained in this study 6.16 wt% agrees with objectives established by the US Department of Energy (DOE), and satisfactorily meets the target set for the year 2020.

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