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Research paper

Interaction of hydrogen with Pd- and co-decorated C_{24} fullerenes: Density functional theory study

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ABSTRACT

In this work, we have investigated the adsorption of a hydrogen atom and molecules on the Pd and Co-decorated C_{24} fullerenes by means of density functional theory. The hydrogen interaction mechanism with host cages by regarding the adsorption energy and charge density variations was studied. It is found that both Pd and Co atoms have a significant role to increase the adsorption energy as an exothermal process. This energy change is strongly dependent on the electrostatic potential variations around the Pd and Co atoms doped on the C_{24} fullerene. Also, the HOMO-LUMO gap (E_g) for C_{24} fullerene varies from 1.20 to 0.76 and 0.86 eV, after decorations of Co and Pd atoms, respectively. More consideration such as thermodynamics parameter, electronic density of states, and charge density analysis are discussed in the context.

1. Introduction

Hydrogen-based energy sources have been considered to be a highly important researches scope for future energy schemes because hydrogen is an appropriate, environmentally friendly and renewable energy. However, one of the main drawbacks is finding new materials capable of storing hydrogen effectively and safely at a low cost [1,2]. Each of the currently available hydrogen storage methods, including cryogenic liquid hydrogen, compressed gaseous hydrogen, complex hydrides and metal hydrides cannot meet all the requirements for mercantile applications [3–5]. Despite many technological developments in the hydrogen based fuel systems, it is still a challenge to have safe and efficient reversible hydrogen storage systems at high per mass quantities. One possible method is developing an efficient and controllable adsorption/desorption system for hydrogen production and storage. Thus, efforts have been made to develop new nanostructured materials, such as boron nitride nanotubes, fullerene, graphene, and carbon nanotubes [6–10]. Nanomaterial's which are related to fullerene based derivatives have possessed much attention due to their potential applications in hydrogen storage, biosensors, molecule electronic devices, biomedical science [11,12]. Because of the lack of unsaturated bonds in carbon-based fullerenes, they have various interactions with adsorbates. After synthesis of fullerenes [13], they attracted great interest because of their chemical and physical properties [14,15]. Among the smaller fullerenes, C_{24} is a desirable candidate for utilization in nanotechnology, molecular electronic devices and drug design [16–18]. Among the diverse hydrogen storage materials, transition metal decorated carbon fullerenes are known to have great potential due to their large surface areas, light weights and more interaction between the hydrogen molecules and host materials [19–23]. Moreover, the substitution of transition metal increases the binding ability of hydrogen by Kubas type interaction owing to empty d-orbitals [24]. Application of diverse transition metal decorated nanostructures for hydrogen storage has been widely examined using the theoretical study. For example, Romina Luna et al. showed the adsorption of hydrogen on pristine and Rh-decorated zigzag (8, 0) single-walled carbon nanotubes (SWCNTs) by using density functional theory (DFT) calculations. They found that the Rh-decorated (8, 0) SWCNT is a good candidate for hydrogen storage [2]. Lopez-Corral et al. investigated the SWCNTs with C-vacancies and the Pd decoration potency in a hydrogen storage system using the theoretical study [25]. They showed that the attendance of Pd atom on the C-vacancies of the (5, 5) SWCNT could

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develop interaction of hydrogen with SWCNT. Shokuhi Rad and Ayub investigated the adsorption of hydrogen on the $B_{12}N_{12}$ (BN) and Ni-decorated $B_{12}N_{12}$ using density functional theory [26]. Their results showed strong interaction between Ni-decorated $B_{12}N_{12}$ and the hydrogen molecule. In previous reports, transition metal decorated C_{24} were not documented as physisorption hydrogen storage. In this study, we used pure, Co- and Pd-decorated C_{24} for adsorption of hydrogen to further understanding of these fullerenes capacity for hydrogen storage usage.

2. Computational method

In this study, we calculated hydrogen adsorption by pure, Co- and Pd-decorated C_{24} fullerenes using density functional theory (DFT). All optimizations and energy calculations are investigated using Gaussian 03 software [27] at the PBE1PBE method and 6–311 + +G** basis set [28–30]. Previous reports indicated the PBE1 method is in good agreement with the experimental values [31,32]. For the Pd and Co atoms, the standard LANL2DZ basis set was used. LANL2DZ basis set uses an effective core for all atoms and is a popular standard choice for the theoretical methods involving transition metals and organometallic complexes [33]. The binding energy (E_b) of Pd and Co over the C_{24} fullerene was calculated with the following equations.

$$E_b\ (Pd\text{-}C_{24}) = E_{C24-Pd} - E_{C24} - E_{Pd} \quad (1)$$

$$E_b\ (Co\text{-}C_{24}) = E_{C24-Co} - E_{C24} - E_{Co} \quad (2)$$

where $E_{C24\text{-}Pd}$ and $E_{C24\text{-}Co}$ are the total energies of the C_{24} interacted with Pd and Co atoms, E_{C24} is the total energy of the pure C_{24} fullerene; E_{Pd} and E_{Co} are the total energies of the Pd and Co atoms, respectively.

The adsorption energy of hydrogen interaction with C_{24} nano-cage was defined by Eq. (3)

$$E_b = E_{C24} - E_{C24} - E_{H2} \quad (3)$$

where $E_{C24/H2}$ correspond to interaction energy of H_2 molecule with C_{24} fullerene, E_{C24} and E_{H2} are total energies of C_{24} and H_2 molecule, respectively.

The binding energy (E_b) of hydrogen onto Pd- and Co-decorated C_{24} fullerene is defined by Eqs. (4) and (5).

$$E_{b-Pd} = \frac{E_{nH2/Pd-C24} - E_{Pd-C24} - nE_{H2}}{n} \quad (4)$$

$$E_{b-Co} = \frac{E_{nH2/Co-C24} - E_{Co-C24} - nE_{H2}}{n} \quad (5)$$

where $E_{nH2/Pd\text{-}C24}$, $E_{nH2/Co\text{-}C24}$, $E_{Pd\text{-}C24}$, $E_{Co\text{-}C24}$, and E_{H2} are the total energy of the H_2 adsorption on the Pd-decorated C_{24}, H_2 molecule adsorption on the Co-decorated C_{24}, isolated Pd-decorated C_{24}, isolated Co-decorated C_{24} and the free hydrogen molecule, respectively, n corresponds to the number of H_2 molecules. Furthermore, we calculated geometric structures and quantum molecular descriptors as well [34–36].

3. Results and discussion

At first step, we calculate the possibility of the physisorption of H_2 molecule on the C_{24} surface while its binding energy is +1.54 eV and the distance of 3.20 Å top of the C_{24} cage (see Table 1). The H—H bond length is about 0.75 Å in this interaction. According to the previous reports, our calculations are close to the theoretical estimate (0.88 Å) [37] and experimental results (0.99 and 0.88 Å) [38,39]. The same situation can be seen in other fullerene cages with the same structure as Shokuhi Rad and Ayub reported the physisorption energy of H_2 molecule with the surface of $B_{12}N_{12}$ nano-cage with an amount of −0.02 eV [26]. Also, there is a theoretical report for a weak physical adsorption of H_2 molecule on the surface of $B_{12}C_6N_6$ nano-cage the adsorption energies that are −0.031 (B3LYP functional) and −0.039 eV (MP2 functional) [40]. Tian et al. reported the physisorption of H_2 molecule over the C_{20} fullerene to be about 1.57 kcal/mol in LDA method and 0.19 kcal/mol in PBE method [41]. The calculation demonstrates that the binding energy of H_2 molecule over the surface of C_{24} fullerene is very weak to meet the conditions of hydrogen storage. Our result also is in agreement with the previous reports that the pure carbon structures cannot be applied as hydrogen storage materials [42]. As displayed in Fig. 1, the HOMO and LUMO orbitals are located around the C—C bonds in C_{24} fullerene interacting with H_2 molecule.

Following the first step, the geometric and electronic properties of Pd- and Co-decorated C_{24} fullerenes were studied and optimized at PBE1PBE functional at 6–311 + + G** standard basis set. The relaxed geometries of Pd- and Co-decorated C_{24} fullerenes at the presence of H_2 molecule are displayed in Fig. 2. The C_{24} fullerene has C_4h symmetry and the Cs and C_4V symmetries belong to Pd- and Co-decorated C_{24} fullerenes, respectively. First, we investigated the adsorption of a single hydrogen atom on Co and Pd atoms, where the Pd or Co atoms are adsorbed on the bridge site (position directly on the C—C bonds). The distance between the palladium and the carbon atom of fullerene is about 2.08 Å and for Co atom with fullerene is about 1.95 Å. The analysis of the geometry of both structures demonstrate that the adsorption energy of Pd atom on the outer surface of C_{24} fullerene is about −0.76 eV, while the cobalt adsorption energy is about −0.54 eV. Liu et al. investigated the interaction between B_{40} fullerene and alkali metal (AM: Li, Na, and K atoms) using density-functional theory (DFT) calculations [43]. They found that the chemical adsorption between AM and B_{40} fullerene is quite stable with the values of −3.55, −2.71, and −2.64 eV for the Li, Na, and K atoms, respectively. The interaction of an Au atom binds to a four-coordinated Ti and O atoms from $(TiO_2)_{10}$ cluster was studied by Liu et al. They found that the adsorption energy value for Au atom on $(TiO_2)_{10}$ cluster is 0.78 eV (0.66 eV) using the PBE (HSE03) functional [44]. The study of Pd adsorption on the pure and a single vacancy (SV) defect Graphene was done by Choudhary and co-workers [45]. They have shown that the value of binding energy of a single palladium atom decorated on the pure and a single vacancy (SV) defect Graphene are −0.96 and −5.09 eV, respectively. Mulliken population analyses indicate that the positive charges on the Pd and Co-decorated C_{24} fullerenes are 0.194 and 0.108 |e|, respectively. The values of dipole moment after the Pd and Co decorations on the surface of C_{24} fullerene is increased from 0 to 3.40 and 5.76 Debye, while after adsorption of the hydrogen atom on the Pd and Co-decorated C_{24} fullerenes, the dipole moment values are reduced to 2.61 and 3.57 Debye, respectively.

As presented in Table 1, one hydrogen atom is bonded to the Pd and Co-decorated C_{24} fullerenes so that the distances of Pd-H and Co-H are about 1.90 and 1.87 Å and the binding energy values in these models are found to be −2.05 and −3.19 eV, respectively. We identify that the palladium and hydrogen atoms have charges about 0.212 and 0.045 |e| and the charges on cobalt and hydrogen atoms are about −0.155 and −0.058 |e|, respectively. Based on our results, the interaction of a single hydrogen atom over Pd and Co-decorated C_{24} fullerenes are very strong and the covalent bonds are formed between them. Our calculation shows that the binding energy of one hydrogen atom on cobalt atom is significantly larger than that in the Pd-decorated C_{24} fullerene. Another important observation that emerged from Table 1 is the dramatic changes of one or four pair's hydrogen molecule adsorbed on the surface of Pd and Co-decorated C_{24} fullerenes, for example, one compares the binding energy values for H_2/Pd-C_{24} (−0.64 eV) to that of $4H_2$/Pd-C_{24} fullerene (−0.25 eV). The charge transfer about 0.069e is occurring from Pd-decorated C_{24} fullerene to hydrogen molecule. The interaction energy of H_2 molecule on Ni-doped $B_{12}N_{12}$ nano-cage is reported and calculated with a value of −1.49 eV [26]. In other cases, we have observed that when a single H_2 molecule adsorbed over the Pd decorated single-walled carbon nanotube, the length of H—H bond was significantly weakened and it increases from 0.752 Å (in the free H_2

Table 1
The structural and electronic parameters and charge transfer of H and H_2 on the pure, Pd- ad Co-decorated C_{24} fullerenes.

Name	E_{ad} (eV)	$D_{Pdor\ Co\text{-}C24}$ (Å)	$D_{H\text{-}PdorCo}$ (Å)	$D_{H\text{-}H}$ (Å)	E_{HOMO} (eV)	E_F (eV)	E_{LUMO} (eV)	E_g (eV)	Q (e)	DM (Debye)
C_{24}	–	–	–	–	−5.69	−5.09	−4.49	1.20	–	0.00
C_{24}/H_2	+1.54	–	3.60	0.75	−5.69	−5.09	−4.48	1.21	0.005	0.03
C_{24}/Pd	−0.76	2.08	–	–	−5.26	−4.83	−4.40	0.86	0.194	3.40
C_{24}/Pd/H	−2.05	1.90	1.54	–	−5.09	−4.68	−4.27	0.81	0.045	2.61
C_{24}/Pd/H_2	−0.64	2.12	1.79	0.83	−5.31	−4.86	−4.42	0.89	0.069	2.86
C_{24}/Pd/$(H_2)_2$	−0.47	2.12	1.85	0.81	−5.12	−4.69	−4.27	0.85	0.105	4.44
C_{24}/Pd/$(H_2)_3$	−0.33	2.12	1.86	0.81	−5.13	−4.70	−4.28	0.85	0.010	4.38
C_{24}/Pd/$(H_2)_4$	−0.25	2.12	1.87	0.75	−5.14	−4.71	−4.28	0.86	0.062	4.31
C_{24}/Pd/$H_{2(Trap)}$	+2.35	2.07	4.23	0.71	−5.29	−4.87	−4.45	0.84	1.647	5.53
C_{24}/Co	−0.54	1.95	–	–	−5.15	−4.77	−4.39	0.76	0.108	5.76
C_{24}/Co/H	−3.19	1.87	1.44	–	−5.02	−4.62	−4.22	0.80	0.058	3.57
C_{24}/Co/H_2	−0.96	1.94	1.61	0.87	−5.33	−4.87	−4.40	0.93	0.009	3.24
C_{24}/Co/$(H_2)_2$	−0.75	2.00	1.61	0.86	−5.22	−4.81	−4.39	0.84	0.084	2.83
C_{24}/Co/$(H_2)_3$	−0.76	1.98	1.65	0.80	−5.03	−4.61	−4.18	0.85	0.171	5.13
C_{24}/Co/$(H_2)_4$	−0.57	2.00	1.66	0.77	−4.98	−4.54	−4.10	0.88	0.193	5.69
C_{24}/Co/$H_{2(Trap)}$	+2.30	1.95	3.78	0.71	−5.20	−4.82	−4.44	0.76	1.749	5.84

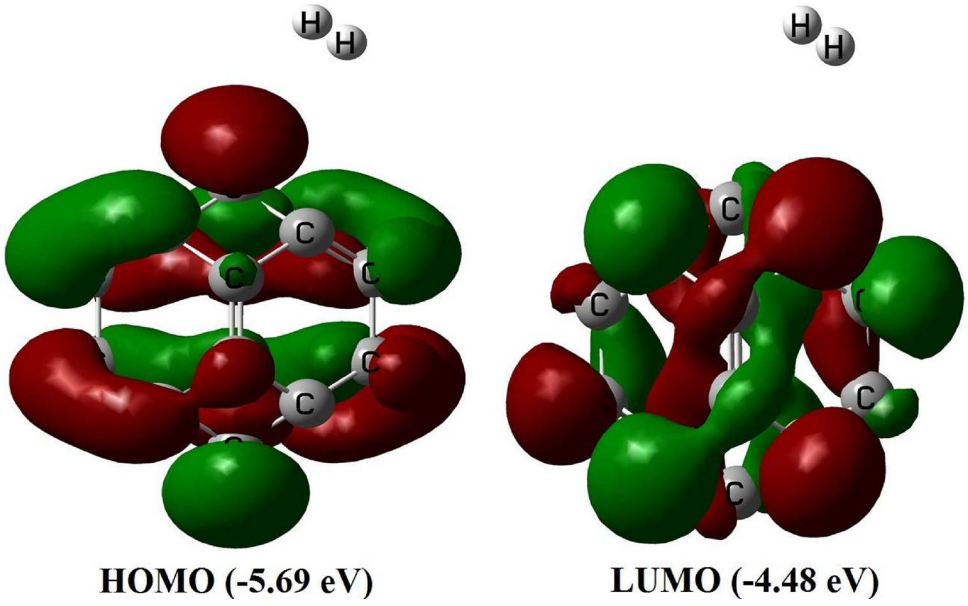

Fig. 1. FMO image of C_{24} fullerene interacting with the H_2 molecule.

molecule) to 0.83 Å, while the interaction distance between carbon atom and palladium atom was elongated from 2.08 to 2.12 Å, which is in agreement with results mentioned in other literatures [46,47]. By comparison of the interaction between the hydrogen molecule and Co-C_{24} fullerene, binding energy values have decreased for H_2/Co-C_{24} (−0.96 eV) to that of $4H_2$/Co-C_{24} fullerene (−0.57 eV). It is generally accepted that the binding energy values of hydrogen molecule over Co-C_{24} fullerene is the most stable in comparison with Pd-C_{24} fullerene. According to Mulliken population analysis (MPA), the charges on the H_2 molecule and Co atom of an adsorbent are about 0.004 and 0.065 |e| and the charges of 0.069 and 0.251 |e| belongs to H_2 molecule and Pd atom, respectively. Namely, d electrons of Pd and Co orbitals donate to H_2 σ*-antibonding orbitals. We have calculated also quantum molecular descriptors for the interaction of H and H_2 with Pd and Co-decorated C_{24} fullerenes. After the decorations of Pd and Co atoms, a decrement of the hardness (η) for C_{24} fullerene is observed with the values of 0.43 and 0.38 eV, respectively, that shows higher chemical activity for both systems [48,49]. The value of η for fullerene shows a slight increase when H or H_2 is adsorbed over Co-decorated C_{24} while this alteration for Pd-decorated C_{24} fullerene is very little (see Table 2). Lower electrophilicity (ω) index demonstrates the lower electrophilic strength of a system [50]. The increment in chemical reactivity is electrophilic in nature since the ω of Pd and Co-decorated C_{24} fullerenes are higher than the pure fullerene. In Table 2, the value of ω for H atom and H_2 molecule adsorbed upon Pd and Co-decorated C_{24} fullerenes is lower than that of the pure configurations as shown in Table 3. In addition, when H atom adsorbed on Pd-decorated C_{24} fullerene the value of softness (S) is slightly decreased to 0.20 eV^{-1}, while the S value for H atom adsorbed on Co-decorated C_{24} fullerene is slightly increased to 0.20 eV. The Pd and Co-decorated C_{24} fullerenes have S values of 0.22 and 0.19 eV^{-1}, respectively.

We demonstrated the evaluation of the adsorption nature of H/H_2 molecule on the Pd and Co-decorated C_{24} fullerenes by means of the total density of states (TDOS), partial population density of states (PDOS), and overlap population density of states (OPDOS) curves. In Fig. 3, the PDOS of H_2/Pd/C_{24} and H_2/Co/C_{24} systems, it is obviously seen that the H-s orbital and the Pd- or Co- d orbitals overlapped with each other around the Fermi level, suggesting the orbital hybridization occurs between metal atoms and hydrogen atom or molecule. The fragments 1 and 2 in each figure represent the interaction of H atom and H_2 molecule with Pd and Co-decorated C_{24} fullerenes, respectively. According to Fig. 3, there is a significant difference between H and H_2 interaction with both Pd and Co-decorated C_{24} fullerenes as we can see the HOMO state for H_2 interacting systems has a 0.2 eV shift toward the negative region of energy values. Regarding the OPDOS, we can see that significant bonding states around Fermi state. As a result, the

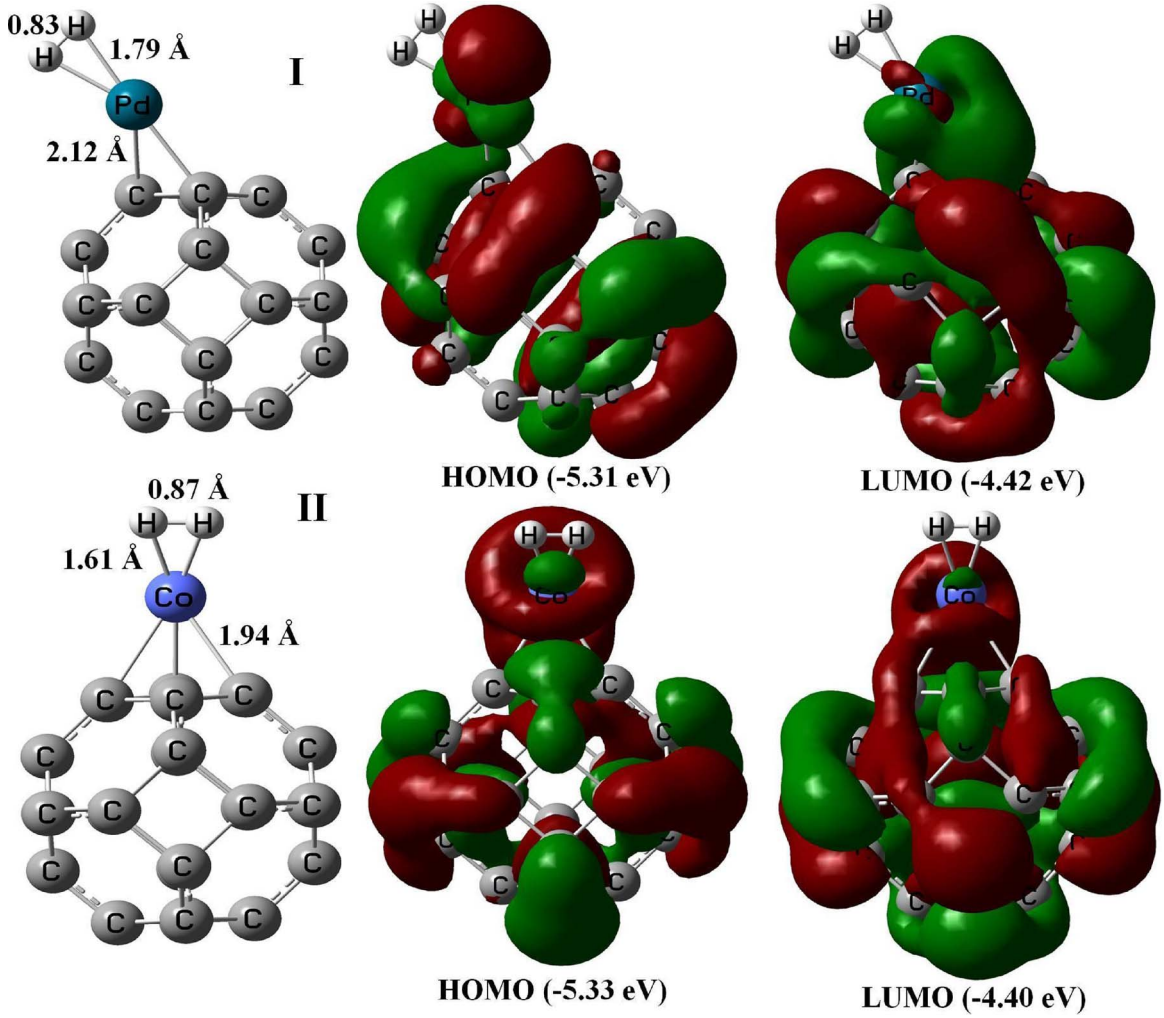

Fig. 2. Geometries and FMO images of Pd and Co-decorated C_{24} interacting with the H_2 molecule.

Table 2
Quantum molecular descriptors of H and H_2 adsorbed on the pure, Pd- ad Co-decorated C_{24} fullerenes.

Name	I/eV	A/eV	η/eV	μ/eV	S/eV^{-1}	ω/eV	χ/eV
C_{24}	5.69	4.49	0.60	−5.09	0.30	21.52	5.09
C_{24}/H_2	5.69	4.48	0.60	−5.09	0.30	21.44	5.09
C_{24}/Pd	5.26	4.40	0.43	−4.83	0.22	27.06	4.83
$C_{24}/Pd/H$	5.09	4.27	0.41	−4.68	0.20	26.87	4.68
$C_{24}/Pd/H_2$	5.31	4.42	0.44	−4.86	0.22	26.54	4.86
$C_{24}/Pd/(H_2)_2$	5.12	4.27	0.43	−4.69	0.21	25.82	4.69
$C_{24}/Pd/(H_2)_3$	5.13	4.28	0.43	−4.70	0.21	25.92	4.70
$C_{24}/Pd/(H_2)_4$	5.13	4.28	0.43	−4.71	0.21	25.90	4.71
$C_{24}/Pd/H_{2(Trap)}$	5.29	5.45	0.42	−4.87	0.21	28.22	4.87
C_{24}/Co	5.15	4.39	0.38	−4.77	0.19	29.99	4.77
$C_{24}/Co/H$	5.02	4.22	0.40	−4.62	0.20	26.71	4.62
$C_{24}/Co/H_2$	5.33	4.40	0.47	−4.87	0.23	25.34	4.87
$C_{24}/Co/(H_2)_2$	5.22	4.39	0.42	−4.80	0.21	27.53	4.81
$C_{24}/Co/(H_2)_3$	5.03	4.18	0.43	−4.61	0.21	24.90	4.61
$C_{24}/Co/(H_2)_4$	4.98	4.10	0.44	−4.54	0.22	23.49	4.54
$C_{24}/Co/H_{2(Trap)}$	5.20	4.44	0.38	−4.81	0.19	30.52	4.81

interaction kind of $H_2/Pd/C_{24}$ and $H_2/Co/C_{24}$ was covalent in nature. The HOMO-LUMO gap (E_g) for C_{24} fullerene is 1.20 eV using PBE functional, however, after decorations of cobalt and palladium atoms, the HOMO-LUMO gap decrease to 0.76 and 0.86 eV, respectively. Xu et al. [16] reported the HOMO-LUMO gap of the empty C_{24} fullerene to be about 1.79 eV using B3LYP functional and 6–31 + +G** basis set. The computed results demonstrate that the E_g of Co-decorated C_{24} is lower due to having electrons less than that of Pd-decorated C_{24} fullerene. As a result, the palladium-decorated C_{24} has a low chemical reactivity and is energetically undesirable to extract electrons from the HOMO or increase them to the LUMO in comparison with the Co-decorated C_{24} fullerene. The effect of the H_2 molecule upon the frontier molecular orbitals (FMOs) of Pd/C_{24} is different from that of Co/C_{24} system (see Fig. 2). When H_2 molecule adsorbs over Co-decorated C_{24} nano-cage, the HOMO energy (E_{HOMO}) is raised from −5.15 eV to −5.33 eV while the LUMO energy (E_{LUMO}) has insignificant change.

3.1. Thermodynamics analysis

The thermodynamic functions were performed via Gaussian 03 package at the level of density functional theory (DFT). All thermodynamic parameters such as Gibbs free energy (G), enthalpy (H), entropy (S), zero-point energy (ZPE) for H and H_2 interacting with the pure, Pd- and Co-decorated C_{24} fullerenes were presented in Table 3. The values of ΔH and ΔG for H_2 molecule interacting with C_{24} fullerene are found to be −0.05 and 0.21 eV, showing that the interaction between H_2 molecule and C_{24} fullerene is less stable too. The entropy values of the considered systems were calculated using below equation:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

As shown in Table 3, the most energy changes (ΔH, ΔS, and ΔG) have negative values. The changes in Gibbs free energy for Co-decorated C_{24} fullerene is more negative than Pd (−1.96 eV vs −1.83 eV)

Table 3
Thermodynamic parameters for H and H_2 interacting with the pure, Pd- ad Co-decorated C_{24} fullerenes.

Name	ΔH	ΔG	E0	E	S	G	H	CV	ZPE	υ_{min}	υ_{max}
C_{24}	–	–	−912.84	−912.83	95.99	−912.90	−912.80	51.2	82.99	359.13	1548.25
C_{24}/H_2	−0.05	0.21	−912.94	−912.92	96.11	−912.18	−912.08	51.3	83.12	19.82	4315.54
C_{24}/Pd	−2.32	−1.83	−1039.60	−1039.58	108.27	−1039.64	−1039.58	57.3	82.87	83.63	1543.28
C_{24}/Pd/H	−1.95	−2.57	−1040.17	−1040.17	109.98	−1040.21	−1040.16	58.0	86.64	36.64	2041.73
$C_{24}/Pd/H_2$	−0.56	−0.38	−1040.78	−1040.76	114.30	−1040.82	−1040.76	63.1	91.84	73.74	3224.77
$C_{24}/Pd/(H_2)_2$	−0.40	−0.31	−1041.94	−1040.92	119.07	−1041.98	−1041.92	69.6	100.52	81.15	3458.72
$C_{24}/Pd/(H_2)_3$	−0.27	−0.30	−1043.09	−1043.08	133.38	−1043.14	−1043.07	78.8	107.82	49.72	4195.26
$C_{24}/Pd/(H_2)_4$	−0.20	−0.14	−1044.25	−1044.23	148.87	−1044.30	−1044.22	88.2	114.94	44.73	4210.17
C_{24}/Co	−2.21	−1.96	−1057.90	−1057.89	105.95	−1057.94	−1057.89	56.8	80.66	46.46	1520.38
C_{24}/Co/H	−2.92	−1.62	−1058.51	−1058.49	106.05	−1058.55	−1058.49	58.7	88.10	107.63	2050.54
$C_{24}/Co/H_2$	−0.73	−0.24	−1059.08	−1059.07	110.19	−1059.12	−1059.07	60.9	91.35	84.69	2775.85
$C_{24}/Co/(H_2)_2$	−0.65	−0.07	−1060.26	−1060.24	116.08	−1060.29	−1060.24	68.1	100.22	80.61	2888.18
$C_{24}/Co/(H_2)_3$	−0.64	0.03	−1061.44	−1060.42	121.02	−1061.48	−1061.42	72.9	111.23	89.20	3592.63
$C_{24}/Co/(H_2)_4$	−0.47	0.04	−1062.59	−1062.57	130.27	−1062.63	−1062.57	81.5	119.03	83.95	3970.69

and the entropy changes for Co-decorated C_{24} fullerene is more positive than Pd (−0.83 eV vs −1.64 eV). These findings (ΔG < 0 and ΔS > 0) indicating that Co-decorated C_{24} fullerene has more stability than Pd-decorated C_{24} fullerene. Although the adsorption of hydrogen atoms on both Co- and Pd-decorated C_{24} fullerenes are thermodynamically feasible, two hydrogen atom adsorbed on Pd-decorated C_{24} fullerene induced the most negative Gibbs free energy changes (−2.57 eV) and the most positive entropy changes (0.62 eV) among all mentioned structures in Table 3. It's noteworthy that by adding hydrogen atoms to these structures, the values of thermodynamic parameters (especially ΔH and ΔG) were increased that indicating the role of Co and Pd-decorated C_{24} fullerenes in the adsorption of hydrogen, subsequently. In the most structures, due to the presence of the most negative values for enthalpy and entropy changes (ΔH and ΔS < 0), it can be deduced van der Waals and hydrogen-bond interactions play the main role in these structures. There is an exception in Pd-decorated C_{24} fullerene in the presence of mono hydrogen atom (C_{24}/Pd/H). The positive value for entropy (2.08 > 0) is a clear evidence for electrostatic interaction presence (ΔH < 0 and ΔS > 0) [51] that is in agreement with our previous calculation [52].

3.2. Electron density difference

Side view color-filled map of electron density (Fig. 4) between H_2 and Pd/Co-decorated C_{24} fullerenes (in the same position) were calculated to benefit the understanding of electron density properties. The electron density map shows a weak chemical interaction between the H_2 molecule and Pd/Co-decorated C_{24} fullerene as represented at Fig. 4, which demonstrates a slight charge transfer from the H_2 molecule to the Pd/Co-decorated C_{24} fullerene near the adsorption site. Overlap of electrons of molecular orbitals cause accumulation of electrons at the center of the bond which stands for a non-covalent bonding.

3.3. Electron localization function

In order to further confirm whether C_{24} and $\cdot H_2$ are bound together by the chemical bond, we compute electron localization function (ELF) which gives a good explanation of electron delocalization between

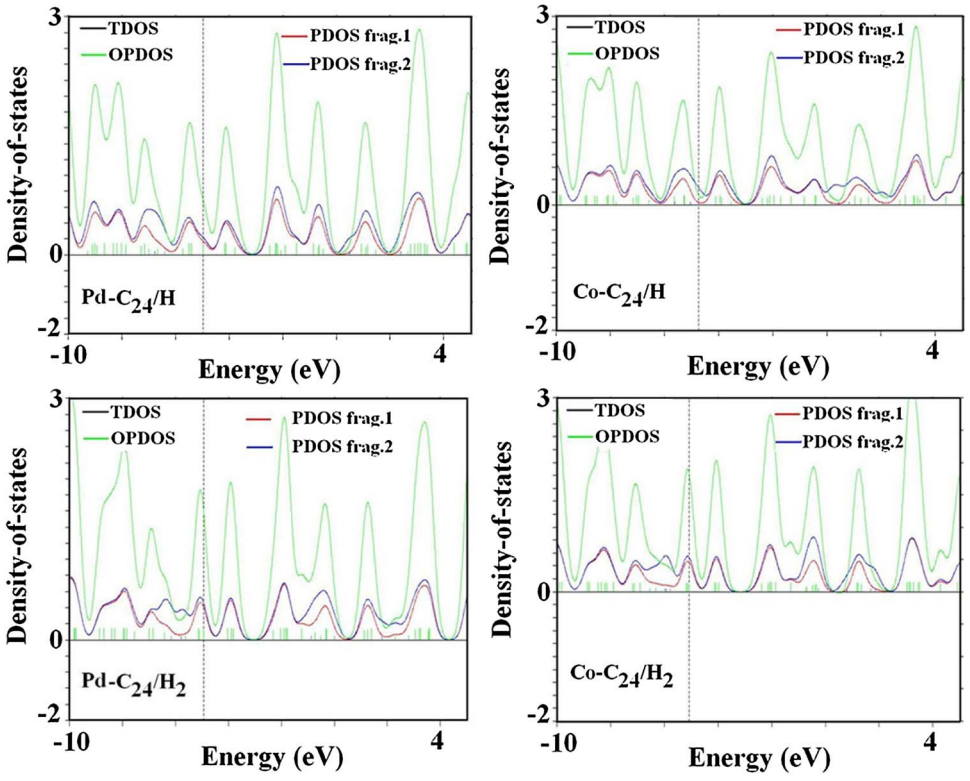

Fig. 3. Partial density of states spectrums for Pd (left) and Co (right) decorated C_{24} interacting with the H atom and H_2 molecule in most stable states.

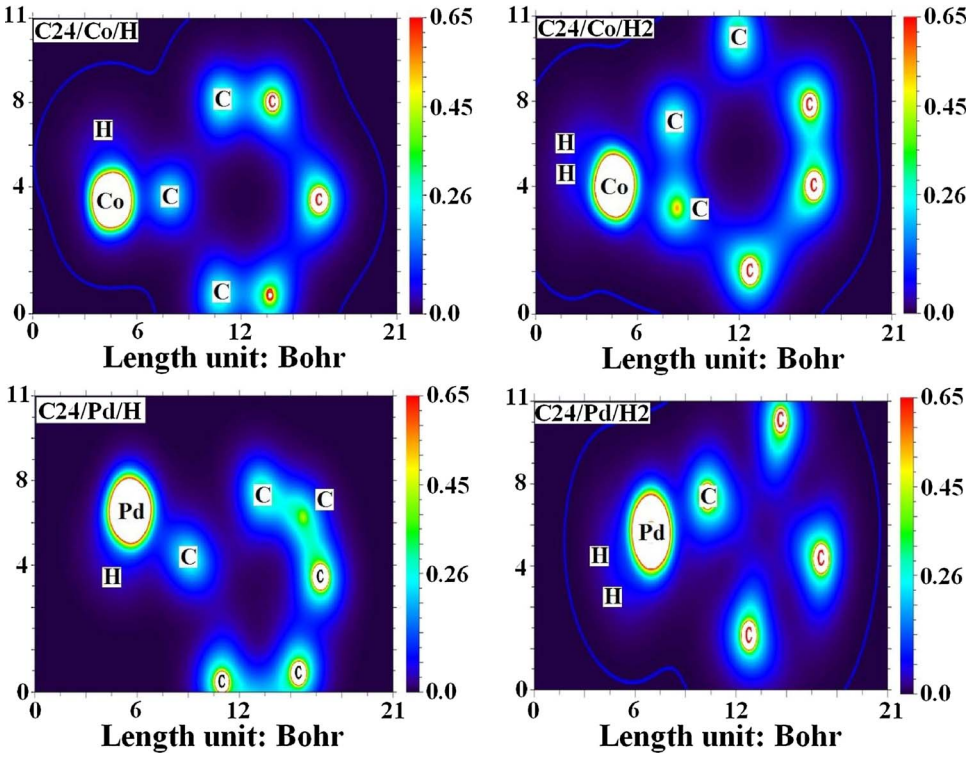

Fig. 4. Contour plots of charge density for the H and H_2 adsorbed on the outer surfaces of Pd- and Co-decorated C_{24} fullerenes.

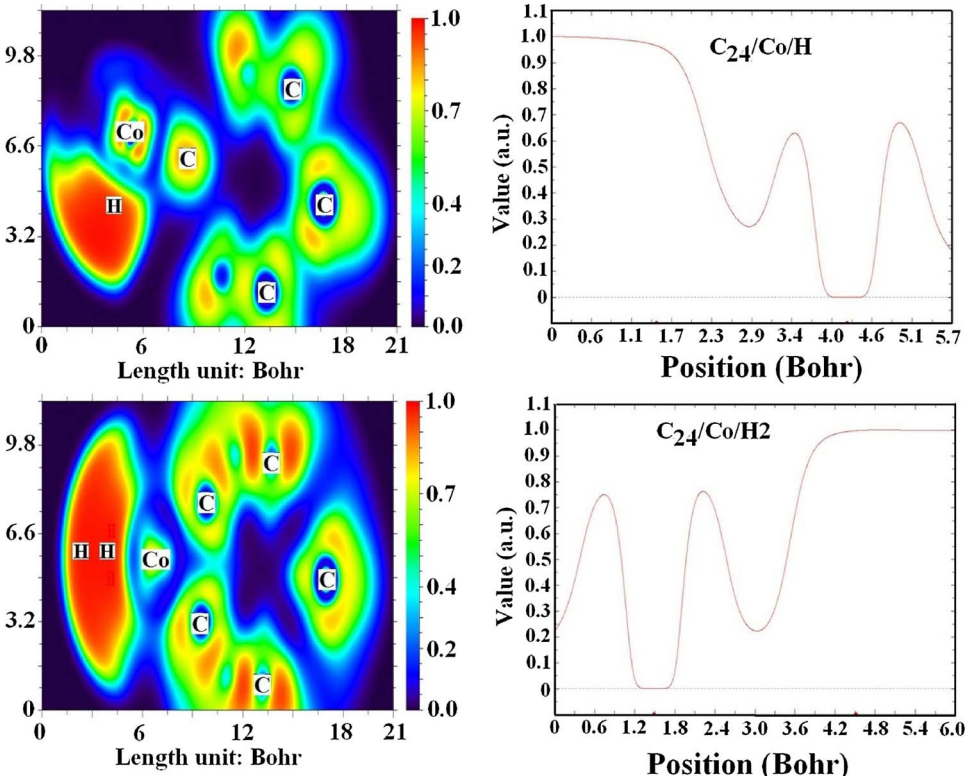

Fig. 5. ELF plots of H and H_2 adsorbed on Co-decorated C_{24} fullerene.

hydrogen molecules and C_{24} fullerene. The ELF specified in Figs. 5 and 6 refer to the jellium–like homogeneous electron gas and renormalizes the value to between 0.00 and 1.00. The values of 1.0 and 0.50 relate to the fully localized (red color) and fully delocalized electrons (green color), respectively [53], while the value 0.00 assign to very low charge density (blue color). As depicted in Figs. 5 and 6 the electrons are localized between the H/H_2 and Pd/Co-decorated C_{24} fullerenes. As shown in Figs. 5 and 6 larger ELF value ($Z \approx 1.0$) located on the H/H_2—Co and H/H_2—Pd bonds exhibit a non-covalent band must be formed in·hydrogen adsorption on Pd/Co-decorated C_{24} fullerene.

4. Conclusion

In this work we have investigated the adsorption of the hydrogen

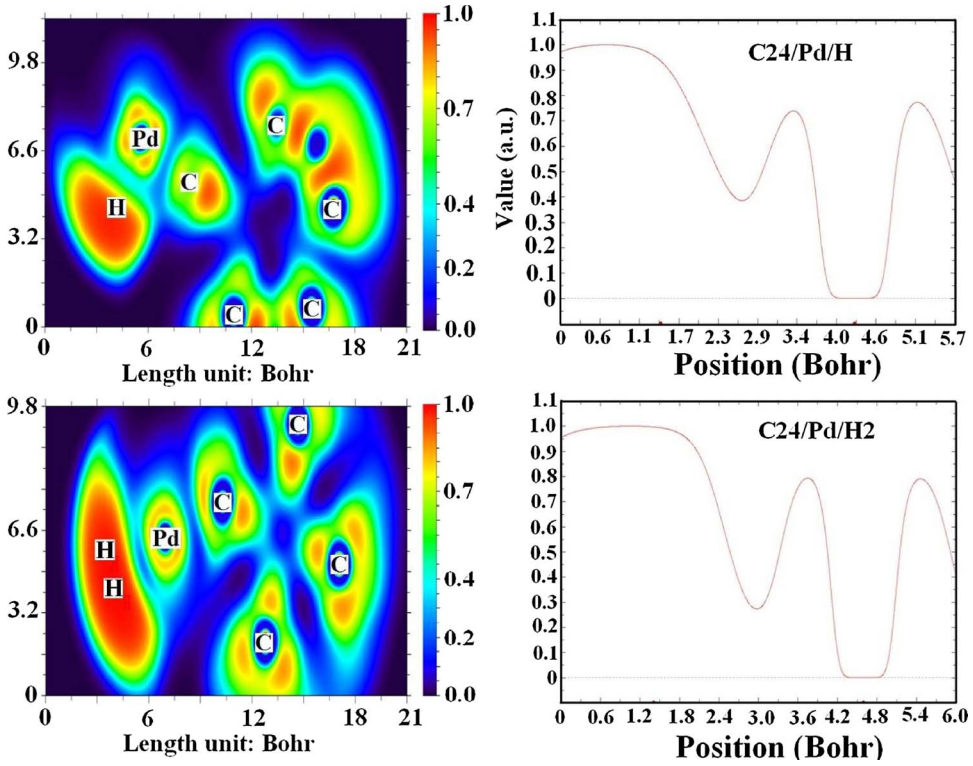

Fig. 6. ELF plots of H and H_2 adsorbed on Pd-decorated C_{24} fullerene.

molecules on the Pd and Co- decorated C_{24} fullerene by means of density functional theory. The hydrogen molecules interaction mechanism with host fullerenes with regarding the adsorption energy and charge density variations was studied. The interaction of H_2 molecule over the C_{24} fullerene is very endothermic and the binding energy is only +1.54 eV. According to our results, it seems that the both Pd and Co atoms have a significant role to increase the adsorption energy as an exothermal process. This change strongly is dependent on the electrostatic potential variations around Pd and Co atoms doped on C_{24} fullerene. Our calculations demonstrate that Co-decorated C_{24} fullerene has maximum hydrogen storage owing to very high binding energy compared with Pd-decorated C_{24} fullerene. The binding energy value of hydrogen molecule adsorbed on the outer surface of Pd- and Co-decorated C_{24} fullerenes are higher in comparison with the inner surface of C_{24} fullerenes. Also, the HOMO-LUMO gap (E_g) for C_{24} fullerene varies from 1.20 eV to 0.76 and 0.86 eV, after decorations of cobalt and palladium atoms, respectively. We anticipate that the results obtained in the present research are helpful to study the adsorption mechanism of the H_2 molecule in solid materials.

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