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Quantum chemical study of pure and transition metal (Ni, Pd, Pt) doped hydrogenated silicon nano cages

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ABSTRACT

The configurations, stability, and electronic structures of $TM@Si_nH_n$ cages where TM= (Ni, Pd, Pt) and N= (6-20 even once) have been investigated with density functional theory with the B3PW91 exchange-correlation functional using LANL2DZ as the basis set. As the first step of calculation, geometrical optimizations of the nanoclusters have been done. In the next step, these optimized geometries are used to calculate the binding energy and HOMO–LUMO gap (band gap) of the clusters.

Keywords- Nanoclusters, Electronic properties, Vibrational frequencies, DFT.

INTRODUCTION

The prediction and designing of metal-encapsulated caged clusters of silicon, germanium, tin and lead have suggested new approaches to develop different nanostructures of silicon and other materials that could be attractive for miniature devices and potentially useful in optoelectronic, magnetic, sensor, catalytic, and other applications. Both pure silicon and germanium clusters are chemically reactive. Guest atoms like transition metals (TMs) can be placed in the center to stabilize the empty silicon and germanium cages. This can prove to be a good method to fine tune the physical properties of devices based on different metal dopings which could be useful in different areas of optoelectronics, sensors and medical applications [1-14]. From the theoretical point of view, there have been several studies concerning the special stability of Si₁₅M and Si₁₆M cage clusters with this type of M impurity. The Si₁₆M (M= Ti, Zr, Hf, Fe, Ru, Os) and Si_nM (M= Cr, Mo, W; n = 14-17) clusters have been studied by Kumar and Kawazoe [15-16] using first principles calculations. Following this development, Zang *et al* [17] studied endohedral doping of neutral and cationic Li, Na, K, Be, Mg and Ca elements in a Si₂₀H₂₀ cage. It was found that due to the smaller interaction between the cages and the doping element, the cage can protect the magnetic moment of the doped atom. At the same time wide variations of band gaps in

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endohedral doping help in designing the desired optical and electronics properties. Keeping the progress made in this field in mind, much attention has been paid in the present work on the study of the variation of different properties of $TM@Si_nH_n$ (N = 6–20, TM = Ni, Pd and Pt) clusters. After optimization of different guess geometries, the optimized structures are then used to calculate the binding energy and band gap.

2. Computational methods

The theoretical methods used in this study were based on ab-initio methods within the density functional theory [18] approximation using the three-parameter hybrid functional B3PW91 [19-20] and LANL2DZ [21] as the basis set. The standard LanL2DZ basis as effective core potential with no symmetry constraint is employed in the present calculations. This basis set provides an effective way to solve two-electron integrals even in case of heavy elements. The previous calculations [22–25] revealed that LanL2DZ basis sets of the effective core potential theory proved to be reliable for the geometries, stabilities, and electronic properties of Si_nH_nTM (TM = transition metals) clusters. For all the Si_nH_nTM clusters, the spin-polarized geometry optimizations were carried out without any symmetry restrictions (*C*1 symmetry). To further check the stabilities, frequency analysis was employed for the optimized structures. All the calculations were implemented using the Gaussian 09 program package [26].

3. Results and discussion

Starting from various initial structures, we optimized the atomic positions of the cluster. Calculated optimized structures of different metal-doped silicon clusters $TM@Si_nH_n(TM = Ni, Pd and Pt)$ are shown in Fig. 1. Here we are discussing only lowest energy structures. Different parameters (dipole moment, band gap and binding energy) of the structures are presented in Table 1. The orbital distribution of endohedrally doped Si_nH_nTM clusters is shown in Figures 2, 3 and 4. The physical parameters and properties of the different structures are discussed as follows.

3.1 Electronic structures of the pure and doped clusters-

In the following section the structural changes of different pure and doped clusters SinHnTM (TM= Ni, Pd and Pt) will be discussed. The Bond length of Si-Si near the dopant atom is lower than the Bond length of Si-TM. It can be said that as the bond length of Si-TM increases the resultant bond strength decreases making these bonds vulnerable. The nearest-neighbor bond lengths in Si cages are given in Table 2. The variation of the bond lengths of Si-Si and Si-TM atoms is shown in Figure 5 and as it can be seen that the trend is almost the same in both the cases i.e, Si-Si and Si-TM.

3.1.1 Si₆H₆ & Si₈H₈.

Different structures obtained for Si_6H_6 are in the form of a plane benzene ring and like a prism. Since our aim is to study the cage-like clusters hence the planar structures are not considered in the present discussion. The selected prism-like structure with D3h point group symmetry is shown in Figure 1. This structure cannot absorb any element endohedrally because of its smaller size compared to the doped element. The structure obtained after doping the atom in the center does not lead to the minimum on the potential surface. All the elements make bonds with six silicons in the cluster and their orbital charge distributions have almost the same nature. As in the prism-like Si_6H_6 structure, here only the cubic Si_8H_8 cluster with Oh point group symmetry is considered. It is found that Ni, Pd and Pt move out from the cage, again through one of the sides of the cubic structure. Hence , it can be said that the initial structure was not a good choice and the $TM@Si_6H_6\,is$ not stable.

3.1.2 Si₁₀H₁₀ & Si₁₂H₁₂.

The optimized structures of pure and doped $Si_{10}H_{10}$ clusters are shown in Figure 1. Pure $Si_{10}H_{10}$ has a decahedral structure with D5h symmetry which is similar to the $Si_{10}H_{10}$ structure reported by Kumar and Kawazoe [27]. In the present calculation all transition metal elements (Ni, Pd and Pt) doped in $Si_{10}H_{10}$ clusters drift from the centre of the guest structure through the pentagonal surface and formed one-sided capped pyramidal structures as shown in Figure 1. The optimized $Si_{10}H_{10}M$ clusters are always bigger than the undoped $Si_{10}H_{10}$ cluster. In order to optimize the interaction energy, some of the Si–Si interaction bond elongated from 2.3719° A to a maximum of 2.5059°A in the doped cluster. The optimized structure of pure $Si_{12}H_{12}$ has two parallel hexagonal planes (D2h symmetry). Doping of the hexagonal $Si_{12}H_{12}$ is not much easier to understand. The doping of Ni, Pd and Pt distort the hexagonal structure.

3.1.3 Si₁₄H₁₄ & Si₁₆H₁₆.

Different combinations of Si–H are used with the aim of producing cage-like SinHn clusters. The first empty cage fullerene-like structure is obtained for Si₁₄H₁₄ with a threefold symmetric isomer. The structure can be understood after adding two Si–H pairs to a Si₁₂H₁₂ fullerene isomer. This has six pentagons and three rhombi. The threefold symmetric isomer with six pentagons and three isolated rhombi confirms that the structures with pentagons and isolated rhombi are more favourable due to lowest energy. The next fullerene-like structure has been obtained for Si₁₆H₁₆ with D4d symmetry. It has a football-like structure which is not the ground state and is not reported here. It is well established that the cluster with n = 16 is the most stable cage structure due to the combination of pentagons and two isolated rhombi. The doped atoms interact only with the diametric silicon atoms where the doped atoms are nearly at the centre.

3.1.4 Si₁₈H₁₈ & Si₂₀H₂₀.

A relatively less symmetric fullerene-like $Si_{18}H_{18}$ cluster, which is a combination of two rhombi, eight pentagons and one hexagon is the object of study. The doped atoms interact only with the diametric silicon atoms where the doped atoms are nearly at the centre. For n = 20, the calculated optimized $Si_{20}H_{20}$ structure is like carbon fullerene with Ih symmetry.

3.2 Binding energy (E_b) and HOMO–LUMO gap (E_g) -

The binding energy curves and HOMO–LUMO gap with cage size for a pure Si_nH_n and doped $TM@Si_nH_n$ clusters is shown in figure 6 and 7 respectively. The binding energy per atom of the pure cluster is defined by the following mathematical expression

$$E_{b} = - \underline{[E_{cluster} - nE_{Si} - nE_{H}]}$$
(2n)

Where $E_{cluster}$, E_{Si} and E_{H} are the optimized energy of the cluster, free silicon and hydrogen atoms. It is found that the binding energy curve linearly increases from n = 6 to 20 and then shows saturation behaviour for a pure cluster. The clusters for n = 6, 8 and 10 show a ground state that can absorb the guest atom exohedrally. Therefore $Si_{12}H_{12}$ is the first cluster that can be doped endohedrally with the present metal elements. In $Si_{12}H_{12}$, the isomer with hexagonal structure (D6h symmetry) has a relatively low energy compared to the other isomers. The behaviour of the binding energy curve is the same as that of Si_nH_n clusters as reported by Kumar and Kawazoe [31].

Similar behaviour is also found in doped clusters in the present calculations. The binding energy curve of doped clusters is different from that of pure clusters. In doped clusters the binding energy is defined as

$$\mathbf{E}_{b} = \underline{-[\mathbf{E}_{cluster} - \mathbf{n}\mathbf{E}_{Si} - \mathbf{n}\mathbf{E}_{H} - \mathbf{E}_{M}]}{(2\mathbf{n}+1)}$$

Where, E_M is the energy of the isolated doped atom. The variation of the binding energy is almost independent of the doping. Variation of the HOMO- LUMO gap with the size of the doped clusters is shown in Figure 7. The maximum binding energy per atom in a pure cluster is 6.72 eV, whereas in a doped cluster it is 3.84 eV(ref Table 1). The minimum value of the binding energy in doped clusters varies from 3.40 to 3.52 eV, whereas the minimum value of binding energy in a pure cluster is 6.05 eV per atom. Therefore, it is clear that the binding energy of the pure clusters does not change much. At the same time doping cannot increase the binding energy of the clusters. This is due to the strong bonding between the silicon and hydrogen atoms. We consider hydrogenated silicon cages for exploring endohedral doping. In small cages such as n=6-10 the guest atom generally comes out but in larger cages different atoms can be endohedrally doped. In the following section we describe these results. In the case of Ni doping, the cage has five fold rotational symmetry and Ni atom caps a pentagonal face of Si atoms. For Ni atom, it first increases from n = 6-10 and then decreases from n = 12-20. There is not much change in the gap between the clusters with n = 16-20. It is to be noted that the HOMO–LUMO gaps are always much higher than for Si_nH_n pure clusters, as reported by Kumar and Kawazoe [27]. The same trend can be found in doped clusters. For n = 16, the HOMO-LUMO gap of Ni@Si_nH_n clusters is lowest of all. So, it shows high chemical activity and a low chemical stability. Presumably, it also contributes to the decrease in the topological resonance energy. The calculated HOMO-LUMO gap of the doped clusters varies from 1.07 to 4.39 eV. In pure clusters it is much higher, and varies from 4.37 to 5.20 eV. It is found that the difference between the binding energies and the HOMO-LUMO gap of these pure and doped clusters follows the same trend.

3.3 Vibrational spectra-

The optical properties of the clusters are tested by calculating the vibrational (IR) spectra of the optimized geometries, and are given in table 3 for doped clusters only. The absence of imaginary frequencies in the spectrum show that the structure is a minimum and may be only a local minimum, of the potential surface in the given theoretical model. The high frequency regions in all clusters (the region where the frequency is greater than 300 cm^{-1}) are due to the vibration of the hydrogen atoms. The highest frequency with very high intensity is the breathing mode of hydrogen atoms in the cluster. In this mode all hydrogen atoms vibrate in the same phase whereas the cage remains static. The frequency region which is less than 300 cm^{-1} is mainly due to the vibration of the silicon atoms in the cage. The lowest frequency region is due to the vibrational modes of the doped atom indicates the weak binding between the doped atom and the cluster. Therefore the presence of hydrogen over the surface of the cage can make the cage stronger and the addition of transition metal atoms as a doped element cannot make it more stable than pure silicon clusters.

Clusters	Dipole Moment (D)	HOMO-LUMO Gap	Binding Energy	
		(eV)	(eV/SiH)	
Ni@Si ₆ H ₆	0.743	3.327	3.517	
Ni@Si ₈ H ₈	0.728	4.102	3.620	
$Ni@Si_{10}H_{10}$	0.708	4.396	3.742	
$Ni@Si_{12}H_{12}$	0.049	2.341	3.628	
$Ni@Si_{14}H_{14}$	0.674	2.753	3.824	
$Ni@Si_{16}H_{16}$	1.399	1.067	3.792	
$Ni@Si_{18}H_{18}$	0.260	1.813	3.745	
Ni@Si ₂₀ H ₂₀	0.136	1.816	3.677	
Pd@Si ₆ H ₆	1.113	3.055	3.400	
Pd@Si ₈ H ₈	0.954	2.959	3.525	
Pd@Si ₁₀ H ₁₀	1.158	4.022	3.661	
Pd@Si ₁₂ H ₁₂	0.032	2.567	3.563	
Pd@Si ₁₄ H ₁₄	1.095	3.946	3.762	
Pd@Si ₁₆ H ₁₆	2.329	2.859	3.737	
Pd@Si ₁₈ H ₁₈	0.671	4.082	3.765	
Pd@Si ₂₀ H ₂₀	0.4114	3.888	3.629	
Pt@Si ₆ H ₆	1.107	2.883	3.590	
Pt@Si ₈ H ₈	1.730	2.953	3.664	
$Pt@Si_{10}H_{10}$	1.289	3.658	3.769	
$Pt@Si_{12}H_{12}$	0.609	2.401	3.797	
$Pt@Si_{14}H_{14}$	1.234	3.832	3.843	
$Pt@Si_{16}H_{16}$	2.811	2.697	3.811	
Pt@Si ₁₈ H ₁₈	0.709	3.874	3.824	
Pt@Si ₂₀ H ₂₀	0.727	3.639	3.687	
Si ₆ H ₆	0.001	4.792	6.052	
Si ₈ H ₈	0.002	5.202	6.323	
$Si_{10}H_{10}$	0.003	5.001	6.455	
Si ₁₂ H ₁₂	0.001	4.832	6.576	
Si ₁₄ H ₁₄	0.002	4.372	6.652	
Si ₁₆ H ₁₆	0.755	4.604	6.710	
Si ₁₈ H ₁₈	0.002	5.855	6.721	
Si ₂₀ H ₂₀	0.215	5.204	6.720	

Table 1 Calculated dipole moment, binding energy and HOMO - LUMO gap for different lowest energy silicon cages in pure and doped forms

Table-2 Nearest-neighbor bond lengths in Å for Doped structures

Ν	Si-Si	Si-TM
6	2.27	2.54
8	2.48	2.79
10	2.33	2.56
12	2.26	2.48
14	2.32	2.54
16	2.35	2.51
18	2.25	2.57
20	2.25	2.64

Ni@Si ₆ H ₆		Ni@Si ₈ H ₈		Ni@Si ₁₀ H ₁₀		Ni@Si ₁₂ H ₁₂	
ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.
576	17.16	393	9.56	422	3.83	489	59.63
610	73.55	513	14.14	590	7.25	687	97.86
645	27.60	647	63.57	663	80.12	1995	300.5
2164	231.9	2164	175.1	689	128.7	2160	116.1
2198	129.5	2201	148.2	2198	329.8	2211	175.1
Ni@S	$i_{14}H_{14}$	Ni@Si ₁₆ H ₁₆		Ni@Si ₁₈ H ₁₈		Ni@Si ₂₀ H ₂₀	
ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.
540	10.30	517	10.42	690	95.48	577	16.06
642	27.59	698	256.2	732	201.2	691	82.87
703	196.5	2020	27.49	2144	100.8	728	561.1
2185	38.60	2162	86.51	2179	301.1	2202	230.5
2203	250.2	2202	212.1	2201	330.4	2216	274.8
Pd@	Pd@Si ₆ H ₆ Pd@Si ₈ H ₈		Si ₈ H ₈	Pd@Si ₁₀ H ₁₀		Pd@Si ₁₂ H ₁₂	
ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.
431	17.54	445	5.29	518	16.75	639	31.37
597	27.69	512	33.19	663	86.93	695	100.4
611	84.08	651	84.51	693	128.1	1998	327.1
2173	162.0	2158	180.6	2195	371.7	2161	131.9
2192	145.6	2199	148.5	-	-	2206	200.5
Pd@Si ₁₄ H ₁₄		Pd@Si ₁₆ H ₁₆		Pd@Si ₁₈ H ₁₈		Pd@Si ₂₀ H ₂₀	
ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.
647	28.13	640	30.62	693	241.0	550	25.60
690	157.3	697	220.6	721	218.1	693	71.89
704	190.3	2036	227.9	2179	52.81	735	137.3
2176	95.22	2160	92.02	2196	255.0	2198	75.90
2197	298.3	2200	261.3	2210	188.4	2214	312.9
Pt@Si ₆ H ₆		Pt@Si ₈ H ₈		$Pt@Si_{10}H_{10}$		$Pt@Si_{12}H_{12}$	
ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.
444	15.28	513	25.54	515	24.10	570	32.15
613	52.30	648	66.02	662	76.17	629	72.06
673	3.93	672	111.3	685	132.0	712	218.5
2165	186.5	2154	192.1	2174	124.5	2177	122.7
2188	290.9	2190	167.8	2197	196.2	2198	356.7
Pt@Si14H14		Pt@Si ₁₆ H ₁₆		$Pt@Si_{18}H_{18}$		Pt@Si ₂₀ H ₂₀	
ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.	ω (cm ⁻¹)	IR Int.
647	22.31	649	12.84	605	28.58	534	20.99
686	32.40	699	215.8	677	32.77	695	74.09
704	A A A A	1077	220.2	722	213.3	740	221.0
701	203.7	19//	230.5	122	215.5	740	221.0
2176	203.7 101.0	2161	100.5	2183	269.0	2198	85.85

Table 3 Dominant infrared (IR) frequencies and IR intensities for TM@Si_nH_n (*n*=6-20)



Figure 1- Optimized pure and transition metal doped hydrogenated silicon clusters of different sizes. Here 'TM' represents the doped metal atoms Ni, Pd and Pt.



Si18H18Pd

Fig-3 HOMO-LUMO orbital distributions of optimized transition metal (Pd) doped hydrogenated silicon clusters of different sizes.

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Fig-4 HOMO-LUMO orbital distributions of optimized transition metal (Pt) doped hydrogenated silicon clusters of different sizes.



Fig--5 Bond Lengths per SiH Unit

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Fig- 6 Binding Energy per SiH unit



Fig- 7 HOMO-LUMO Gap per SiH unit

CONCLUSIONS

In summary, we have reported ab initio calculation of transition metal (Ni, Pd and Pt) doped silicon clusters. Different properties of the optimized clusters such as binding energies, HOMO-LUMO gaps and vibrational spectra are discussed. With changing cluster size, the binding energy of the metal doped clusters initially increases and then shows a dip at n = 12 and then increases. At the same time the binding energy of an empty cluster is always higher than that of the same size doped cluster, indicating that the doping does not increase the binding energy because of strong binding between silicon and capped hydrogen's. The minimum value of the HOMO-LUMO gap shows the reactive nature of the clusters. The HOMO-LUMO gap shows the same variation for different doped atoms but for Ni when n = 16, it is different. It shows the highly reactive nature of nickel cluster. It is an important finding. IR spectra does not show any imaginary frequency in the optimized geometries. This can possibly help the experimentalists in identifying the structures of these clusters. Moreover, they show a number of dominant modes present in the IR spectra. Due to the strong binding between the Si and H atoms these clusters exhibit a symmetrical nature. With the increase in the size of the clusters, the binding energy of the cluster increases which is also evident from the shift of the dominant mode in the high frequency region. The character of HOMO and LUMO can also be modified so that it could arise either from the cage or the guest atom. This could make the endohedral species also attractive for sensor applications as well as for the development of derivatives. Our results should lead to the possibility of other new dopants. In general, about the behavior of dopants in Si cages for HOMO-LUMO character could lead to variations, which would be interesting for further study.

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