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REGULAR ARTICLE

Higher hydrogen uptake capacity of $C_2H_4Ti^+$ than C_2H_4Ti: a quantum chemical study

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Abstract Using density functionals theory, we show that gravimetric hydrogen uptake of C_2H_4Ti complex and its cation, $C_2H_4Ti^+$, differ by about 2 wt%. Six and five hydrogen molecules are found to be adsorbed on $C_2H_4Ti^+$ and C_2H_4Ti complexes thereby showing a hydrogen-uptake capacity of 13.74 and 11.72 wt%, respectively. All hydrogen molecules are adsorbed in molecular form on $C_2H_4Ti^+$ ion with an increase in metal bond strength, whereas in some cases, the hydrogen molecules are found to be dissociated on C_2H_4Ti neutral complex. The uptake capacity of neutral C_2H_4Ti complex shown in this work is in excellent agreement with that reported experimentally, Phillips and Shivaram (Phys Rev Lett 100:105505, 2008). The H_2 adsorption energy and its dependence on exchange and correlation functions in density functionals method were illustrated. Even after the adsorption of maximum number of hydrogen molecules on C_2H_4Ti and $C_2H_4Ti^+$ complexes, Ti and Ti^+ remain strongly bound to C_2H_4 substrate.

Keywords Hydrogen storage · Organometallic complexes and cation · Adsorption energy · Density functional theory

1 Introduction

Over the past few years, lot of work has been done on hydrogen storage capacity of different materials. Recent studies show that carbon-based nanostructures containing single transition metal be possible candidates for hydrogen storage [1–15]. From that point of view, hydrogen uptake capacity of single Ti atom containing neutral organometallic clusters has been extensively studied both theoretically and experimentally [10–16]. Recently, Phillips and Shivaram [15] have experimentally shown that Ti–ethylene complex is capable of storing 12 wt% of hydrogen which is well above the target specified by the Department of Energy (DOE)—by 2010 (6 wt%) and by 2015 (9 wt%). Barnes et al. [17] reported fluorescence spectra of metal–methylidyne complex and Vidal et al. [18] studied the nature of metal–carbon bonding in that complex. Recently, these metal–methylidyne organometallic complexes are suggested as possible hydrogen storage materials by Dong et al. [19]. To the best of our knowledge, hydrogen uptake capacity of charged organometallic clusters has not been tested so far. It is observed that first H_2 molecule dissociates upon adsorption on Ti containing organometallic clusters. Whether it also dissociates on Ti containing charged organometallic clusters? Whether the charge on a C_2H_4Ti compound enhances or reduces the H_2 uptake capacity? To answer these questions, we have performed a systematic computational study of hydrogen uptake capacity of neutral as well as charged Ti–ethylene complex using B3LYP and PBEPBE exchange and correlation functionals. In this contribution, we include Stuttgart–Dresden (SDD) effective core potential for Ti atom for incorporating relativistic effects and compared with nonrelativistic all-electron calculations.

In this paper, we show that the gravimetric hydrogen uptake capacity of $C_2H_4Ti^+$ ion is higher than that of neutral C_2H_4Ti complex. In neutral case, hydrogen molecules take electrons from metal atom and bind to it obeying the Pauli’s exclusion principle, occupying the antibonding

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orbital of the molecule. In contrast, in charged structures, hydrogen molecules do not take any electrons from the metal ion due to the fact that second ionization potential of metal atom is high. In this case, dipole formation leads the adsorption of H_2 molecules to metal ion. Here we found that metal ion, even after binding to a substrate, can trap more hydrogen molecules than its neutral counterpart. It is desirable that adsorption and desorption of H_2 molecules should occur at or somewhat above room temperature for vehicular applications. Whether H_2 adsorption is endothermic or exothermic can be predicted from averaged adsorption energy with Gibbs free energy correction. If it is positive at a particular temperature then H_2 adsorption is said to be energetically favourable at that temperature. We perform thermochemistry calculations to see whether H_2 adsorption on C_2H_4Ti and $C_2H_4Ti^+$ complexes is energetically favourable or not at room temperature.

This paper is structured as follows: Sect. 2 presents the computational details. Results are presented and discussed in Sect. 3. Conclusions are inferred in Sect. 4.

2 Computational details

The geometries of $C_2H_4Ti(nH_2)$ and $C_2H_4Ti^+(nH_2)$ are optimized using Becke's three-parameter hybrid functional combined with Lee, Yang and Parr correlation (B3LYP) [20–22] and PBEPBE [23, 24] functionals with accurate and larger all-electron density Gauss double-zeta valence polarization (DGDZVP) basis set and the valence double-diffuse and polarization function 6-311++G(d,p) basis set for all atomic species including Ti. For the sake of comparison with all-electron calculations, we used large-core relativistic Stuttgart–Dresden effective core potential (SDD) [25] basis for Ti atom and DGDZVP and 6-311++G(d,p) basis sets for C and H atoms. The vibrational frequencies are also obtained at the same levels of theory. All calculations are performed using Gaussian 03 suit of programs [26]. Basis set superposition error (BSSE) corrected interaction energy between any two molecules in a complex can be calculated as [27],

$$\begin{aligned}\mathrm{IE}_{\mathrm{AB}} = {} & E_{\mathrm{AB}}(\text{in a complex}) - E_{\mathrm{A}}(\text{in a complex}) \\ & - E_{\mathrm{B}}(\text{in a complex})\end{aligned}$$

where E_{AB} is the total energy of molecules A and B together in a complex and E_{A} and E_{B} the total energies of molecules A and B, respectively, in a complex.

3 Results and discussion

Figure 1 shows the optimized structures of $C_2H_4Ti(nH_2)$ ($n = 1$–5) and $C_2H_4Ti^+(nH_2)$ ($n = 1$–6) at B3LYP/DGDZVP level of theory. As can be seen for $n = 1$ and 2, one of the hydrogen molecules dissociates and adsorbs on C_2H_4Ti in dihydride form at B3LYP level whereas from $n = 3$ onwards, all the H_2 molecules are adsorbed in molecular form at that level. On the other hand, for $n = 1$–3, one of the H_2 molecules adsorbs dissociatively on C_2H_4Ti complex at PBEPBE level. In case of $C_2H_4Ti^+$ complex, all the H_2 molecules bound molecularly at all levels of theory used here. The binding energies of Ti atom to C_2H_4 are 0.88, 1.65 and 1.74 eV, whereas those of Ti^+ ion to C_2H_4 are 2.23, 1.54 and 2.28 eV at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. On the other hand, calculations of pseudopotential on Ti atom and DGDZVP basis set for C and H atoms provide fairly large binding energies of Ti atom to C_2H_4 viz. 4.15 and 5.90 eV at B3LYP and PBEPBE levels, respectively, whereas 4.60 eV at PBEPBE with 6-311++G(d,p) basis set for C and H atoms. In case of $C_2H_4Ti^+$ complex, using pseudopotential for Ti atom, binding energies of Ti^+ ion to C_2H_4 are 3.03 at B3LYP and 3.94 at PBEPBE with DGDZVP basis set for C and H atoms, whereas 3.87 eV at PBEPBE with 6-311++G(d,p) basis set for C and H atoms.

At all levels of theory used here, maximum five and six H_2 molecules are found to be adsorbed on C_2H_4Ti and $C_2H_4Ti^+$ complexes, respectively. This shows an uptake capacity of 11.72 and 13.74 wt% for the former and the latter, respectively. The calculated H_2 uptake capacity of C_2H_4Ti complex from this work is in agreement with the experimental determination of 12 wt% [15]. Due to removal of an electron from C_2H_4Ti to create $C_2H_4Ti^+$, the spin multiplicity of the latter is different from the former. For C_2H_4Ti, the spin multiplicity is 1 and that for $C_2H_4Ti^+$ is 2. This removal is from valence *d* orbital of Ti atom in C_2H_4Ti complex and is responsible for the adsorption of sixth H_2 molecule on $C_2H_4Ti^+$ complex.

The calculated adsorption energy per H_2 molecule on C_2H_4Ti complex without and with zero point energy (ZPE) corrections, $\Delta En = \{E[C_2H_4Ti(nH_2)] - E[C_2H_4Ti] - nE[H_2]\}/n$, and similarly, ΔEn^+ for $C_2H_4Ti^+$ complex are given in Table 1. Thermochemistry analysis has also been carried out to investigate the thermal stability of these complexes. The calculation of Gibbs free energy in the Gaussian 03 suite of program uses standard statistical thermodynamic formulae in order to obtain thermal-corrected free energy. The averaged adsorption energy with Gibbs free energy correction (at 298.15 K) is calculated as, $\Delta G = \{G[C_2H_4Ti] + n\,G[H_2] - G[C_2H_4Ti(nH_2)]\}/n$ with successive addition of a H_2 molecule from $n = 1$–5 of the C_2H_4Ti complex. Here, $G[X]$ stands for the total energy of X with Gibbs free energy correction. This energy correction mainly stems from translational and rotational entropies of reactant H_2 molecules in gas phase, which reduced the

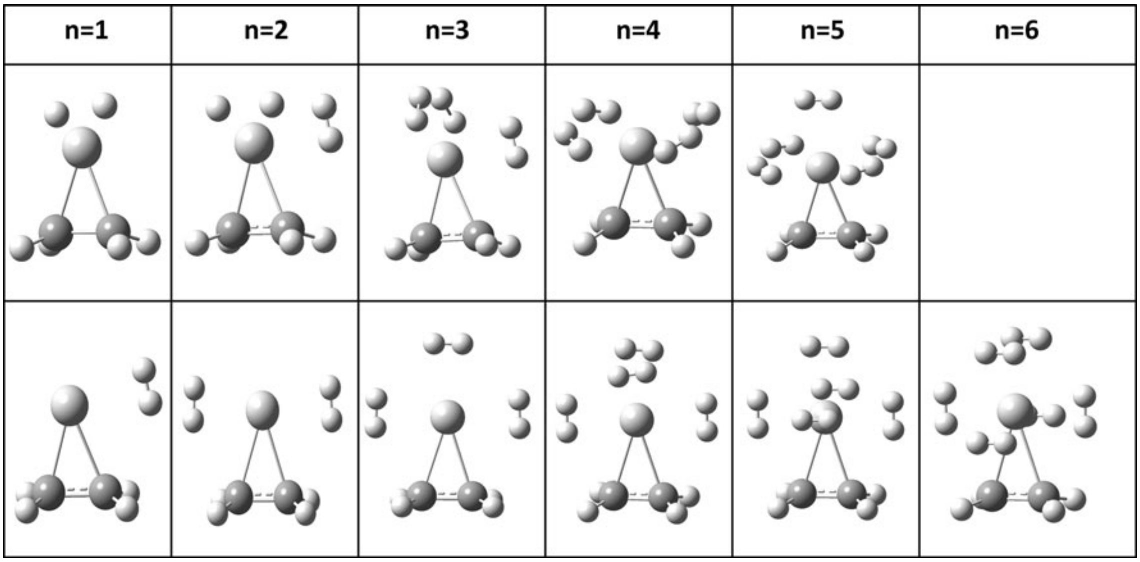

Fig. 1 Optimized geometries of $C_2H_4Ti(nH_2)$ (n = 1–5; *first row*) and $C_2H_4Ti^+(nH_2)$ (n = 1–6; *second row*) complexes with successive addition of H_2 molecule

adsorption energy. Similarly, values of ΔG^+ for $C_2H_4Ti^+$ complex are also inferred in Table 1. The adsorption energies are found to be larger for the cases where the H_2 molecules are adsorbed dissociatively. Using all-electron nonrelativistic calculations, it is found that B3LYP calculation provides smaller adsorption energy than PBEPBE calculation for neutral as well as cation case which elucidate the effect of exchange and correlation functional on the adsorption energy. On the other hand, using relativistic approach, the opposite is true. However, ΔG values for the cation at B3LYP and PBEPBE methods indicate that H_2 adsorption is not energetically favorable on cation complex at these levels at room temperature with as well as without relativistic approach using DGDZVP basis set. Thus, instead of changing the method, we have changed the basis set and used 6-311++G(d,p) basis set with same PBEPBE level. We found that H_2 adsorption on neutral as well as cation complex is energetically favorable at PBEPBE/6-311++G(d,p) level since ΔG (298.15 K) is positive at this level with and without pseudopotential on Ti atom. The averaged H_2 adsorption energy is considerably affected by the exchange–correlation functional employed in DFT-based calculations and basis set. Among all levels of theory used here, hydrogen adsorption at PBEPBE with relativistic and nonrelativistic approaches for both neutral as well as cation complexes are energetically favourable. Okamato also obtained energetically favourable H_2 adsorbed complexes using density functional method (PBE) than B3LYP and MP2 [16]. At this level of theory, the bond length (0.75 Å) of H–H for isolated H_2 molecule is also in agreement with the experimental determination.

The geometries are found to be similar at B3LYP and PBEPBE levels (except at $n = 3$ as shown in Fig. 2) without and with pseudopotential on Ti atom. Since there are no large changes in structural parameters with and without pseudopotential on Ti atom, here, we discuss the structural parameters from nonrelativistic calculations only. The structural parameters for $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes at all the levels of theory used here are tabulated in Table 2 with and without pseudopotential on Ti atom. The study of these parameters reveals that with successive addition of H_2 to C_2H_4Ti complex, the bond lengths of Ti–H (molecular H_2's) as well as Ti–C vary. The bond between Ti and atomic hydrogen is stronger than that between Ti and molecular hydrogen. The bond distance between Ti and atomic H in neutral complexes is 1.74, 1.75 and 1.74 Å at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. On the other hand, the bond distance between Ti and molecular hydrogen varies with 'n' in $C_2H_4Ti(nH_2)$ and $C_2H_4Ti^+(nH_2)$ complexes. Here 'n' represents number of H_2 molecule(s) adsorbed. For the former it varies as 1.85–2.13, 1.89–2.06 and 1.88–2.05 Å, whereas for the latter it varies as 1.93–2.20, 1.86–2.14 and 1.86–2.14 Å at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. There is no large change in carbon–carbon bond with successive addition of H_2 molecules.

In $C_2H_4Ti(5H_2)$ complex, four molecules surround the Ti atom whereas the fifth molecule is adsorbed on its top as shown in Fig. 1. In the following discussion, the values in parentheses are obtained with SDD pseudopotential on Ti

Table 1 Calculated adsorption energies per H_2 molecule without and with ZPE corrections ($\Delta En/\Delta En^{+}$) in eV and the corrected Gibbs free energies ($\Delta G/\Delta G^{+}$), at 298.15 K, in eV of $C_2H_4Ti(nH_2)$ ($n = 1$–5) and $C_2H_4Ti^{+}(nH_2)$ ($n = 1$–6) complexes at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels of theory

n	B3LYP/DGDZVP			PBEPBE/DGDZVP			PBEPBE/6-311++G(d,p)		
	$\Delta En/\Delta En^{+}$ without ZPE	$\Delta En/\Delta En^{+}$ with ZPE	$\Delta Gn/\Delta Gn^{+}$	$\Delta En/\Delta En^{+}$ without ZPE	$\Delta En/\Delta En^{+}$ with ZPE	$\Delta Gn/\Delta Gn^{+}$	$\Delta En/\Delta En^{+}$ without ZPE	$\Delta En/\Delta En^{+}$ with ZPE	$\Delta Gn/\Delta Gn^{+}$
$C_2H_4Ti(H_2)_n$									
1	2.84(2.88)[a]	2.76(2.81)[a]	2.48(2.54)[a]	3.09(0.80)[a]	3.01(0.76)[a]	2.75(0.49)[a]	3.06(3.07)[a]	2.99(2.99)[a]	2.71(2.71)[a]
2	1.52(1.10)[a]	1.23(0.99)[a]	1.12(0.78)[a]	1.69(1.01)[a]	1.59(0.91)[a]	1.30(0.63)[a]	1.72(1.71)[a]	1.60(1.59)[a]	1.32(0.92)[a]
3	0.44(0.81)	0.28(0.67)	0.44(0.40)	1.25(0.76)[a]	1.10(0.64)[a]	0.82(0.37)[a]	1.28(1.27)[a]	1.13(1.12)[a]	0.84(0.83)[a]
4	0.24(0.67)	0.21(0.52)	0.26(0.23)	0.89(0.53)	0.74(0.39)	0.45(0.10)	0.94(0.93)	0.78(0.77)	0.50(0.49)
5	0.20(0.57)	0.17(0.42)	0.15(0.13)	0.79(0.49)	0.63(0.34)	0.34(0.06)	0.82(0.81)	0.67(0.66)	0.38(0.37)
Avg	0.29(0.68)	0.22(0.54)	0.28(0.25)	0.84(0.51)	0.68(0.37)	0.39(0.08)	0.88(0.87)	0.72(0.72)	0.44(0.43)
$C_2H_4Ti^{+}(H_2)_n$									
1	0.30(0.31)	0.15(0.19)	−0.11(−0.10)[b]	0.29(0.34)	0.11(0.18)	−0.18(−0.08)[b]	0.80(0.46)	0.62(0.29)	0.36(0.01)
2	0.13(0.30)	0.05(0.13)	−0.25(−0.16)[b]	0.35(0.30)	0.18(0.16)	−0.11(−0.13)[b]	0.64(0.41)	0.47(0.24)	0.19(−0.04)
3	0.59(0.36)	0.44(0.20)	−0.09(−0.09)[b]	0.44(0.39)	0.27(0.23)	−0.01(−0.06)[b]	0.62(0.49)	0.44(0.31)	0.17(0.03)
4	0.25(0.36)	0.11(0.21)	−0.12(−0.07)[b]	0.44(0.42)	0.29(0.26)	−0.01(−0.01)[b]	0.61(0.51)	0.45(0.35)	0.17(0.08)
5	0.27(0.34)	0.16(0.19)	−0.11(−0.08)[b]	0.44(0.41)	0.28(0.26)	−0.01(−0.02)[b]	0.58(0.48)	0.42(0.33)	0.14(0.05)
6	0.05(0.29)	0.01(0.14)	−0.18(−0.15)[b]	0.40(0.38)	0.24(0.22)	−0.05(−0.07)[b]	0.52(0.45)	0.35(0.29)	0.06(−0.01)
Avg	0.26(0.33)	0.15(0.18)	−0.14(−0.11)[b]	0.39(0.37)	0.23(0.22)	−0.06(−0.06)[b]	0.62(0.47)	0.46(0.30)	0.18(0.02)

The values in *parentheses* are with SDD pseudo-potential for Ti atom with DGDZVP and 6-311++G(d,p) basis sets for the rest of lighter atoms

ΔEn and ΔEn^{+} are adsorption energies per H_2 molecule of $C_2H_4Ti(H_2)_n$ and $C_2H_4Ti^{+}(H_2)_n$, respectively, and their averages (Avg) of the complexes in which H_2 molecule found to be adsorbed molecularly

ΔGn and ΔGn^{+} are corrected Gibbs free energies of $C_2H_4Ti(H_2)_n$ and $C_2H_4Ti^{+}(H_2)_n$, respectively, and their averages (Avg) of the complexes in which H_2 molecule found to be adsorbed molecularly

[a] Energy of complex where one of the hydrogen molecule bound dissociatively

[b] *Negative sign* indicates that the adsorption is endothermic

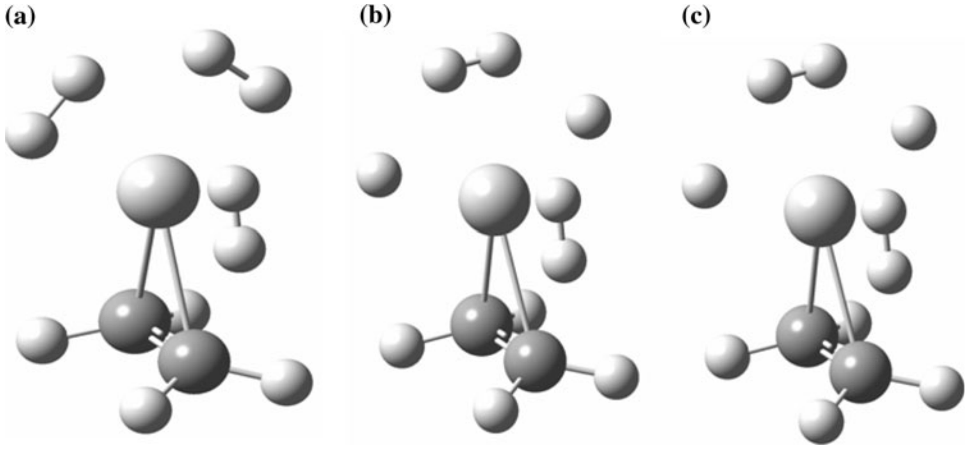

Fig. 2 Optimized geometries of $C_2H_4Ti(3H_2)$ or $C_2H_4Ti(H)_2(2H_2)$ at **a** B3LYP/DGDZVP, **b** PBEPBE/DGDZVP and **c** PBEPBE/6-311++G(d,p) levels

atom and all-electron basis set to C and H atoms (DGDZVP or 6-311++G(d,p)). This fifth molecule is loosely bonded to C_2H_4Ti with Ti–H distance of 2.13(2.16) Å at B3LYP/DGDZVP, 2.05(2.07) Å at PBEPBE/DGDZVP and 2.03(2.03) Å at PBEPBE/6-311++G(d,p) levels. The bond lengths of Ti–H_2 and Ti–C are in the range of 1.94–2.13(1.92–2.16) and 2.20(2.18) Å, respectively, at B3LYP level, whereas those bond lengths are in the range of 1.89–2.05(1.89–2.07) and 2.20(2.18) Å at PBEPBE level, respectively, with DGDZVP basis set. On the other hand, these bond lengths are in the range of 1.88–2.03(1.87–2.03) and 2.31(2.31) Å, respectively, at PBEPBE/6-311++G(d,p) level.

In case of $C_2H_4Ti^{+}(6H_2)$ complex, all the six H_2 molecules bound molecularly to $C_2H_4Ti^{+}$ complex (at $n = 6$) among which four are surrounding the Ti atom. Out of

Table 2 Structural parameters for $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes obtained at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels

Level	Complex	Position of H_2	Bond lengths (Å)							
			All-electron nonrelativistic approach				All-electron relativistic approach			
			Ti–H_2	H–H	Ti–C	C–C	Ti–H_2	H–H	Ti–C	C–C
B3LYP/DGDZVP	$C_2H_4Ti(5H_2)$	Top	2.13	0.77	2.20	1.42	2.16	0.76	2.18	1.43
		Side	1.94	0.81			1.92	0.81		
		Side	1.94	0.81			1.92	0.81		
		Side	1.94	0.81			1.92	0.81		
		Side	1.94	0.81			1.92	0.81		
	$C_2H_4Ti^+(6H_2)$	Near top par.	2.10	0.77	2.33	1.39	2.11	0.76	2.30	1.40
		Near top par.	2.10	0.77				2.11	0.76	
		Side par.	2.26	0.75				2.27	0.75	
		Side par.	2.26	0.75				2.27	0.75	
		Side perp.	1.93	0.80				1.94	0.79	
		Side perp.	1.93	0.80				1.94	0.79	
PBEPBE/DGDZVP	$C_2H_4Ti(5H_2)$	Top	2.05	0.79	2.20	1.43	2.07	0.79	2.18	1.43
		Side	1.89	0.85			1.89	0.85		
		Side	1.89	0.85			1.89	0.85		
		Side	1.89	0.85			1.89	0.85		
		Side	1.89	0.85			1.89	0.85		
	$C_2H_4Ti^+(6H_2)$	Near top par.	2.03	0.79	2.31	1.41	2.04	0.79	2.28	1.41
		Near top par.	2.03	0.79			2.04	0.79		
		Side par.	2.14	0.77			2.16	0.77		
		Side par.	2.14	0.77			2.16	0.77		
		Side perp.	1.89	0.83			1.89	0.83		
		Side perp.	1.89	0.83			1.89	0.83		
PBEPBE/6-311++G(d,p)	$C_2H_4Ti(5H_2)$	Top	2.03	0.80	2.21	1.43	2.03	0.80	2.19	1.43
		Side	1.88	0.85			1.87	0.85		
		Side	1.88	0.85			1.87	0.85		
		Side	1.88	0.85			1.87	0.85		
		Side	1.88	0.85			1.87	0.85		
	$C_2H_4Ti^+(6H_2)$	Near top par.	2.00	0.79	2.31	1.41	1.99	0.80	2.31	1.40
		Near top par.	2.00	0.79			1.99	0.80		
		Side par.	2.14	0.77			2.10	0.78		
		Side par.	2.14	0.77			2.10	0.78		
		Side perp.	1.88	0.83			1.86	0.84		
		Side perp.	1.88	0.83			1.86	0.84		

'*Par.*' and '*perp.*' indicate parallel and perpendicular orientations, respectively, of corresponding adsorbed H_2 molecule with respect to C–C bond length within the complex

these four surrounding H_2 molecules, two lie with their bond lengths perpendicular and other two lie parallel to the plane of C–C bond length in an organometallic complex. The remaining H_2 molecules are located near to the top of Ti atom with their bond length orientations parallel to the plane of the C–C bond at all the three levels. It is observed that relativistic treatment for Ti atom calculations give shorter bond lengths of Ti–C than its nonrelativistic treatment, at all levels of theory used here.

Next, we obtained the BSSE-corrected interaction energies between different molecules within the complexes and binding energy in which maximum hydrogen molecules are found to be adsorbed viz. $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes. The obtained results without and with SDD pseudopotential on Ti atom are inferred in Table 3. In this table, OM represents either C_2H_4Ti organometallic complex or its ion and H_i is the *i*th adsorbed H_2 molecule. The nature of interaction between C_2H_4Ti and

Table 3 BSSE-corrected interaction and binding energies (kcal/mol) for $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes using B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels

Interaction	Energy											
	All-electron nonrelativistic approach						All-electron relativistic approach					
	a^a	a^b	a^c	b^a	b^b	b^c	a^a	a^b	a^c	b^a	b^b	b^c
OM–H_1	−1.59	−7.99	−10.23	−7.15	−14.61	−18.57	−34.57	−5.77	−8.87	−15.33	−21.57	−26.18
OM–H_2	−1.59	−7.99	−10.23	−8.15	−9.87	−9.29	−34.57	−5.77	−8.87	−12.00	−18.49	−20.67
OM–H_3	−1.59	−7.99	−10.23	1.92	−2.65	−5.61	−34.57	−5.77	−8.87	−6.89	−11.65	−14.47
OM–H_4	−1.59	−7.99	−10.23	−7.15	−14.61	−18.58	−34.57	−5.77	−8.87	−15.33	−21.57	−26.18
OM–H_5	−0.82	−2.97	−4.11	−8.16	−9.87	−9.29	−9.40	−1.21	−3.28	−12.00	−18.49	−20.67
OM–H_6	–	–	–	1.96	−2.65	−5.61	–	–	–	−6.89	−11.65	−14.47
H_1–H_2	0.09	−0.06	−0.06	1.53	0.46	0.50	0.08	−0.08	−0.06	0.61	0.46	0.53
H_1–H_3	1.91	1.74	1.87	1.27	0.25	0.26	1.99	1.84	1.96	0.39	0.21	0.26
H_1–H_4	0.66	0.43	0.50	0.96	−0.06	−0.06	2.36	0.48	0.54	0.07	−0.07	−0.06
H_1–H_5	1.09	0.99	1.02	1.54	0.46	0.50	1.07	0.98	1.08	0.66	0.46	0.53
H_1–H_6	–	–	–	1.26	0.25	0.25	–	–	–	0.32	0.21	0.26
H_2–H_3	0.66	0.43	0.50	2.10	2.18	2.44	0.70	0.48	0.54	1.86	2.16	2.49
H_2–H_4	1.90	1.74	1.87	0.86	0.46	0.50	3.65	1.84	1.96	0.66	0.46	0.53
H_2–H_5	1.09	0.99	1.02	3.23	3.54	4.01	1.07	0.98	1.08	2.95	3.53	4.09
H_2–H_6	–	–	–	0.26	−0.05	−0.06	–	–	–	0.05	−0.06	−0.06
H_3–H_4	0.09	−0.05	−0.06	−0.71	0.25	0.25	1.74	−0.08	−0.06	0.32	0.21	0.26
H_3–H_5	1.09	0.99	1.02	−1.02	−0.05	−0.06	1.07	0.98	1.08	0.05	−0.06	−0.06
H_3–H_6	–	–	–	−1.05	−0.04	−0.04	–	–	–	0.03	−0.04	−0.04
H_4–H_5	1.09	0.99	1.02	1.54	0.46	0.50	1.07	0.98	1.08	0.61	0.46	0.53
H_4–H_6	–	–	–	1.27	0.25	0.26	–	–	–	0.39	0.21	0.26
H_5–H_6	–	–	–	2.10	2.18	2.44	–	–	–	1.86	2.16	2.49
Binding energy (kcal/mol)	−50.71	−76.81	−87.25	−44.59	−68.89	−83.23	−82.23	−72.17	−84.49	−52.67	−73.84	−89.04

OM represents $C_2H_4Ti/C_2H_4Ti^+$ and H_i the *i*th hydrogen molecule

[a] $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes, respectively, at B3LYP level

[b] $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes, respectively, at PBEPBE/DGDZVP level

[c] $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes, respectively, at PBEPBE/6-311++G(d,p) level

each adsorbed H_2 molecule in $C_2H_4Ti(5H_2)$ complex is attractive using all exchange and correlation functionals used here in density functional theory with and without pseudopotential on Ti atom except OM–H_3 and OM–H_6 interactions in $C_2H_4Ti^+(6H_2)$ complex at B3LYP/DGDZVP level. Out of five, four OM–H_i interaction energies are equal since these surrounding four H_2 molecules lie at the same distance of 1.94(1.92) Å at B3LYP/DGDZVP, 1.89(1.89) Å at PBEPBE/DGDZVP and 1.88(1.87) Å at PBEPBE/6-311++G(d,p) levels from Ti atom. The fifth H_2 molecule (H_5), which is loosely bonded molecule in a complex, lie on the top site of Ti atom at distances 2.13(2.16), 2.05(2.07) and 2.03(2.03) Å results in lower interaction energies −0.82(−9.40), −2.97(−1.21) and −4.11(−3.28) kcal/mol between OM and H_5 at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. In $C_2H_4Ti(5H_2)$ complex, the nature of interaction between any pair of H_2 molecules is repulsive at B3LYP level with and without pseudopotential on Ti atom. On the other hand, at PBEPBE level of theory, the nature of interaction between H_1–H_2 and H_3–H_4 pairs is attractive and that between any remaining pair of hydrogen molecules is repulsive. At PBEPBE/6-311++G(d,p) level of theory, the nature of interaction between C_2H_4Ti and all the H_2 molecules is attractive. The OM–H_i interaction energies at PBEPBE/6-311++G(d,p) level of theory are much higher than those obtained at B3LYP/DGDZVP and PBEPBE/DGDZVP levels, which indicate stronger bond between OM and adsorbed H_2 molecules without relativistic effect.

In $C_2H_4Ti^+(6H_2)$ complex, strong attraction is found between H_3–H_5 and H_3–H_6 pairs of H_2 molecules at B3LYP/DGDZVP level of theory, whereas it is repulsive with relativistic effects on Ti atom at the same level of theory. For these pairs of H_2 molecules, the nature of interaction is attractive as well at PBEPBE/DGDZVP and

PBEPBE/6-311++G(d,p) levels of theory without and with pseudopotential on Ti atom. The nature of interaction for other remaining pairs of molecules in $C_2H_4Ti^+(6H_2)$ complex is repulsive at all the levels of theory used here except for H_1–H_4 and H_2–H_6 pairs of molecules at PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels of theory without and with relativistic effect. The nature of OM–H_3 and OM–H_6 interactions is attractive with the relativistic effect but these interaction energies are lower than other OM–H_i interactions in the $C_2H_4Ti^+(6H_2)$ complex. The OM–H_i interaction energies are equal for the hydrogen molecules lying at same distance from Ti atom. However, the OM–H_i interactions are much stronger in $C_2H_4Ti^+(6H_2)$ complex than those in $C_2H_4Ti(5H_2)$ complex except the OM–H_i interactions at B3LYP level with relativistic effect on Ti atom. The binding energies of Ti to C_2H_4 are found to be 2.39(0.81), 3.17(5.69) and 3.11(5.53) eV in $C_2H_4Ti(5H_2)$ complex and that of Ti^+ to C_2H_4 2.18(1.46), 2.78(2.10) and 2.48(2.21) eV in $C_2H_4Ti^+(6H_2)$ complex at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. Thus, Ti and Ti^+ remain strongly bound to the substrate even after adsorption of hydrogen molecules. The binding energies of the $C_2H_4Ti(5H_2)$ complex are found to be −50.71(−83.23), −76.81(−72.17) and −87.25 (−84.49) kcal/mol, whereas those of the $C_2H_4Ti^+(6H_2)$ complex are −44.59(−52.67), −68.89(−73.84) and −83.23(−89.04) kcal/mol at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels without(with) relativistic effect, respectively.

Vibrational frequencies show that there are no soft modes for neutral and cation complexes which confirm the stability of these complexes. We now discuss selected vibrational modes in $C_2H_4Ti(5H_2)$ and $C_2H_4Ti^+(6H_2)$ complexes. The H–H stretching frequencies for adsorbed hydrogen molecules are in the range of 3016–3232(3012–3234), 2646–2887(2641–2889) and 2667–2896(2655–2884) cm^{-1} for the four H_2 molecules surrounding Ti atom in $C_2H_4Ti(5H_2)$ complex. The H–H vibrational frequency of top H_2 molecule is about 3937(4010) cm^{-1} at B3LYP/DGDZVP, 3533(3618) cm^{-1} at PBEPBE/DGDZVP and 3551(3552) cm^{-1} in PBEPBE/6-311++G(d,p) levels without(with) relativistic effect on Ti atom in the complex. The structural parameters, interaction energy and vibrational frequency show that top H_2 molecule is loosely bonded to neutral organometallic compound than the surrounding H_2 molecules at all levels of theory used here. On the other hand, the H–H stretching frequencies are in the range of 3411–4253(3473–4271), 2981–3968(3102–3995) and 2975–3905(2975–3915) cm^{-1} in $C_2H_4Ti^+(6H_2)$ complex at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. The H–H stretching frequencies for isolated H_2 molecules are 4,453, 4,355 and 4,319 cm^{-1} at B3LYP/DGDZVP, PBEPBE/DGDZVP and PBEPBE/6-311++G(d,p) levels, respectively. We also found a shift in C=C stretch with change in level of theory.

B3LYP and PBEPBE perform differently due to the fact that the former is hybrid functional and the latter is pure (nonhybrid) functional. B3LYP has HF contribution of 20% and PBEPBE has contribution from PBE exchange and PBE correlation terms. The 20% HF exchange contribution in B3LYP affects the bond strength of Ti–H_2 and ultimately the H_2 adsorption energy. The exchange and correlation functionals affect not only the Ti–H_2 bond but also the H–H bond for H_2 molecule. Thus, these exchange and correlation functionals were used here to see their effect on adsorption energy and structural parameters in a complex. Our findings on adsorption energies with Gibbs free energy correction using different methods are in good agreement with those by Okamato [16].

Lastly, we have obtained electronic configurations of isolated Ti and each atom in C_2H_4, C_2H_4Ti and $C_2H_4Ti(nH_2)$ of energetically favourable complexes and their cations (at PBEPBE/6-311++G(d,p) level). It was observed that Ti and Ti^+ donate about 0.8 and 0.4 electrons, respectively, to bind to C_2H_4 in an organometallic complex with all-electron basis sets calculations without any relativistic treatment for Ti atom. In complexes where one of the H_2 molecules dissociates viz. $C_2H_4Ti(H)_2$, $C_2H_4Ti(H)_2(H_2)$ and $C_2H_4Ti(H)_2(2H_2)$, we found that totals of about 0.3, 0.2 and 0.1 electrons, respectively, are transferred from Ti to each dissociated hydrogen atom in an organometallic complex. In contrast, totals of about 0.8 and 1.3 electrons are transferred from H_2 molecules to Ti atom in complexes where all the hydrogen molecules are adsorbed molecularly viz. $C_2H_4Ti(4H_2)$ and $C_2H_4Ti(5H_2)$ complexes, respectively. In case of cation, it is very difficult to take a charge from Ti^+ ion compared to Ti atom because second ionization potential of the metal atom bound to a substrate is higher than the first. In this case, H_2 molecules donate small amount of electrons to the Ti^+ metal ion bound to a C_2H_4 substrate. We found that totals of about 0.1, 0.2, 0.5 and 0.9 electrons are transferred from H_2 molecule to Ti^+ in $C_2H_4Ti^+(H_2)$, $C_2H_4Ti^+(2H_2)$, $C_2H_4Ti^+(3H_2)$, $C_2H_4Ti^+(4H_2)$ and $C_2H_4Ti^+(5H_2)$ complexes, respectively. In isolated hydrogen atom or H in isolated molecular hydrogen, the charge on H atom is unity. The charge of H atom in adsorbed H_2 molecule in $C_2H_4Ti^+(6H_2)$ complex does not remain unity but varies from 0.83 to 0.86 thereby transferring a total of about 1.8 electrons from these six adsorbed H_2 molecules to $C_2H_4Ti^+$ ion. On the other hand, all-electron calculations with relativistic treatment for Ti atom in the above complexes also show that the same amount of electron is transferred from Ti to dissociated hydrogen atom as well as from H_2

molecules to Ti atom in the respective neutral as well as cation complex. Thus, the Ti^+ ion in the considered cation complexes are in larger valence state than Ti atom in neutral complexes.

4 Conclusion

Our study predicts gravimetric hydrogen uptake capacity of $C_2H_4Ti^+$ is larger by about 2 wt% than that of C_2H_4Ti. The $C_2H_4Ti^+$ complex is a quantum mechanically stable structure and there is a strong interaction between different molecules in the complex. The uptake capacity is well above the target specified by DOE (9 wt% by 2015). Average Gibbs free energy correction is as large as 0.45 and 0.44 eV for neutral and cation complexes, respectively. Among the different levels of theory used here, the neutral as well as cation complexes are energetically favourable at PBEPBE/6-311++G(d,p) levels for H_2 adsorption. The averaged H_2 adsorption energy is considerably affected by the exchange–correlation functional employed in DFT and basis set. Significant changes in OM–H_i interaction energies are observed by the use of pseudopotential on Ti atom at B3LYP method. The B3LYP hybrid method has HF contribution of 20% which affects not only the bond lengths of Ti–H_2 but also the adsorption, interaction and binding energies.

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