H₂ Interaction with C₂H₂TM (TM = Sc, Ti, V) Complex Using Quantum Chemical Methods

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This work reports a comparative study of hydrogen uptake capacity of early transition metal atom (Sc, Ti and V) attached to light acetylene (C₂H₂) substrate. Using density functional theory and second order Møller–Plesset method, we predict that maximum of five, five and four hydrogen molecules will be adsorbed on C₂H₂Sc, C₂H₂Ti and C₂H₂V complex, respectively, with respective gravimetric hydrogen uptake capacity of 12.43, 12, and 9.48 wt%. All the interactions between hydrogen molecules and organometallic complex are found to be attractive. The highest occupied molecular orbital–lowest unoccupied molecular orbital gap shows that the maximum H₂ adsorbed complexes are kinetically stable. The average binding energies per H₂ molecule for these complexes are within the ideal range for hydrogen storage at ambient conditions. Even after maximum hydrogen molecules adsorption on C₂H₂TM complexes, transition metal atoms remain strongly bound to the C₂H₂ substrate. We have obtained temperature and pressure range over which H₂ adsorption on these three complexes is energetically favorable using the Gibbs free energy corrected H₂ adsorption energy.

1. Introduction

Search for novel materials to store hydrogen continues worldwide since hydrogen storage is one of the important issues for the advancement of hydrogen and fuel cell power technologies in transportation, stationary, and portable applications. There are various technical goals suggested for storage of hydrogen to develop and demonstrate viable hydrogen storage for vehicular transportation and stationary applications. Hydrogen storage is indeed a problem that needs special attention if hydrogen should become the future choice of energy source in vehicles. It is due to the very specific demands for safety, volumetric energy density, gravimetric energy density etc. There are different ways of storing hydrogen such as physisorption, storage in metal hydrides, storage in high pressure cylinders, storage as liquid hydrogen etc.; each with positive and negative sides. Various ways are being adopted to find out the novel materials, satisfying the target set by US Department of Energy (DOE) (5.5 wt% by 2020). Synthesis of a material first and then testing its hydrogen storage capacity is a time consuming and expensive job. Therefore, predicting the hydrogen uptake capacity of a material theoretically using molecular modeling techniques is one way to save time and money both. One can predict the hydrogen storage capacity of a material theoretically and if it is as per the US DOE target, one can go for its synthesis. The increase in computational power in recent years has opened up new possibilities for theoretical studies of hydrogen storage.

Small organometallic (OM) compounds in which transition metal is bound to organic substrate have attracted attention of researchers due to their high hydrogen storage capacity [1–23]. Experimentally, Phillips and Shivaram reported hydrogen storage on transition metal–ethylene and transition metal–benzene complexes [24–26]. There is an excellent agreement between the theory and experiment for the hydrogen uptake capacity and equilibrium isotope effect for the Ti–ethylene complex [8]. Most of these studies are focused on room temperature hydrogen storage. Suitability of a material for hydrogen storage at different temperature and pressure is predicted in very few investigations. Predicting hydrogen storage capacity of a material at room temperature and 1 atm pressure is not enough. We should also know the suitable temperature and pressure range over which the material favors hydrogen storage. It helps us to use the hydrogen storage material in different environment and applications. Interaction energy between adsorbed H₂ molecules and organometallic complex is also useful in deciding the nature of interaction between these two.

The aim of this work is to perform comparative study of hydrogen adsorption on acetylene–TM (TM = Sc, Ti, and V) complexes using density functional theory (DFT) method and second order Møller-Plesset (MP2) method. We report temperature and pressure dependent Gibbs free energy corrected hydrogen adsorption energies for these complexes, which give an idea about suitable temperature and pressure range over which H₂ adsorption on these complexes is possible. We considered C₂H₂TM complex in which H₂ binds to TM via so called "Kubas interaction" [27, 28]. Nature of interaction between hydrogen molecules and organometallic complexes and that between different hydrogen molecules within the complexes

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is also studied. The vibrational frequencies are obtained to confirm the stability of these complexes.

2. Computational details

The geometry optimization of $C_2H_2TM(nH_2)$ (TM = Sc, Ti, and V) complexes have been carried out with DFT by using Becke's three parameter hybrid functional with LYP correlation functional (B3LYP) [29–31] and MP2 method [32]. All calculations were performed using *Gaussian* 09 suit of programs [33] using larger DGDZVP basis set. The vibrational frequencies are also obtained at the same level of theory. The interaction energies between different molecules are obtained as suggested by Boys and Bernardi [34].

Binding energy of TM atom to C_2H_2 substrate (E_{TM}) is calculated as

$$E_{TM} = E[C_2H_2TM] - E[C_2H_2] - E[TM]. \quad (1)$$

Gain in energies with subsequent addition of H_2 molecule (ΔE_n) on C_2H_2TM are calculated as

$$\Delta E_n = E[C_2H_2TM(nH_2)]$$
$$- E[C_2H_2TM((n-1)H_2)] - E[H_2]. \quad (2)$$

Interaction energies between OM complex and i-th hydrogen molecule in a H_2 adsorbed complex are calculated using

$$E_{OM--H_i} = E[OM--H_i] - E[OM] - E[H_i]. \quad (3)$$

Interaction energies between i-th and j-th hydrogen molecule are calculated using

$$E_{H_iH_j} = E[H_iH_j] - E[H_i] - E[H_j]. \quad (4)$$

The averaged adsorption energy with Gibbs free energy correction (ΔE_G) is calculated as

$$\Delta E_G = \{E_G[OM] + (n * E_G[H_2]) - E_G[OM(nH_2)]\}$$
$$/n, \quad (5)$$

where $E_G[X]$ stands for the total energy of X with Gibbs free energy correction.

3. Result and discussion

Figure 1 shows the optimized geometries of maximum number of H_2 adsorbed C_2H_2TM complexes. As can be seen from Fig. 1, maximum five, five and four hydrogen molecules can be adsorbed on C_2H_2Sc, C_2H_2Ti and C_2H_2V complexes, respectively, with respective hydrogen uptake capacity of 12.43, 12, and 9.48 wt%. Though the hydrogen uptake capacity of C_2H_2Ti reported in this work is nearly the same as that of C_2H_4Ti reported by Philips and Shivaram experimentally [24], the material C_2H_2Ti is little lighter than C_2H_4Ti. Calculated binding energy (E_{TM}) of Sc, Ti and V to the C_2H_2 substrate is 1.82, 1.24 and 3.27 eV, respectively before H_2 adsorption. Structural parameters for the H_2 adsorbed complexes are presented in Table I.

n = 1: The first hydrogen molecule is adsorbed ($n = 1$) in molecular form on C_2H_2Sc and C_2H_2V organometallic complexes whereas it is adsorbed in diatomic form on C_2H_2Ti complex. The calculated gain in energies (ΔE_n) on first hydrogen molecule adsorption are
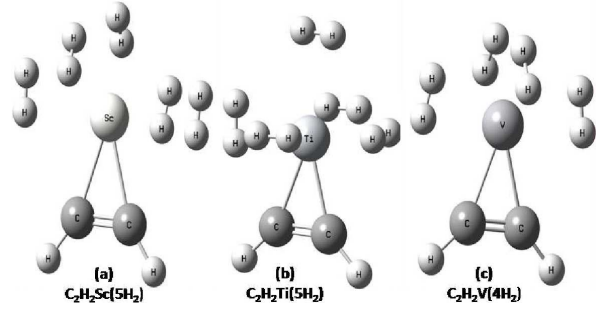

Fig. 1. Optimized geometries of (a) $C_2H_2Sc(nH_2)$ ($n = 5$) (b) $C_2H_2Ti(nH_2)$ ($n = 5$) (c) $C_2H_2V(nH_2)$ ($n = 4$) complexes at MP2/DGDZVP level.

TABLE I

Structural parameters for $C_2H_2TM(nH_2)$ (TM = Sc, Ti, V) complexes obtained at MP2/DGDZVP level. The values in parentheses represent the corresponding bond length before H_2 adsorption.

TM	Bond lengths [Å]		
	C=C	C–M	TM–H
Sc	1.36(1.37)	2.11(2.08)	2.38, 2.50, 2.31, 2.31, 2.38
Ti	1.33(1.31)	2.00(1.99)	1.96, 1.94, 1.94, 1.96, 2.35
V	1.36(1.31)	1.92(2.07)	1.85, 2.03, 2.03, 1.85

0.74, 1.44, and 0.08 eV for C_2H_2Sc, C_2H_2Ti, and C_2H_2V, respectively. The Sc–H, Ti–H and V–H bond lengths are 2.1, 1.8, and 2.2 Å, respectively.

n = 2: When the second hydrogen molecule is added on the C_2H_2Ti complex (at $n = 2$), it is adsorbed in molecular form and the first hydrogen molecule remains adsorbed in diatomic form. The molecular hydrogen is adsorbed towards side of the Ti-atom with orientation of H–H bond length perpendicular to the plane of the C = C bond of acetylene substrate. The second molecule on C_2H_2Sc and C_2H_2V is adsorbed in molecular form.

n = 3: For $n = 3$, all the three H_2 molecules are adsorbed in molecular form with H–H bond length perpendicular to the plane of the C = C bond length in $C_2H_2Sc(3H_2)$ and $C_2H_2V(3H_2)$ complexes. All the three H_2 molecules are adsorbed in molecular form on C_2H_2Ti. Two of the hydrogen molecules were adsorbed towards top site of Sc and V atom and the third molecule at the side. On the other hand, one of the H–H bond lengths orient perpendicular and remaining two have parallel orientations to the plane of C = C bond of a substrate in $C_2H_2Ti(3H_2)$ complex. Here the H–H distances are in a range of 0.75–0.77, 0.79–0.95, and 0.77–0.82 Å for $C_2H_2Sc(3H_2)$, $C_2H_2Ti(3H_2)$, and $C_2H_2V(3H_2)$ complex, respectively.

n = 4: All the four molecules are adsorbed in molecular form with their H–H bond length orientation perpendicular to the plane of C = C bond length in $C_2H_2Sc(4H_2)$, and $C_2H_2V(4H_2)$ complexes. In these complexes, two hydrogen molecules are adsorbed towards top site of the TM-atom and the remaining two at the

side. All the four H_2 molecules lie with their H–H bond length parallel to the C = C bond length forming a plane surrounding the Ti atom in C_2H_2Ti($4H_2$) complex.

n = 5: The fifth molecule adsorbed on the top site of Ti-atom on C_2H_2Ti complex at a distance of 2.35 Å, marginally longer compared to the other four hydrogen molecules adsorbed in the same complex. It indicates that the fifth H_2 molecule is loosely bonded to C_2H_2Ti complex. In C_2H_2Sc complex, all the five molecules are adsorbed with their bond length perpendicular to the plane of C = C bond and surrounding the Sc atom.

3.1. Binding and interaction energies

The first hydrogen molecule is adsorbed in dihydride form on C_2H_2Ti complex resulting in stronger C = C bond than that in isolated C_2H_2Ti complex. With successive addition of H_2 molecules, the C = C bond becomes weaker. Also, the TM–C bond length marginally increases with subsequent addition of hydrogen molecules.

Calculated binding energy of TM atom (E_{TM}) to the C_2H_2 substrate and gain in energies with subsequent addition of H_2 molecules (ΔE_n) using Eqs. (1) and (2) respectively are shown in Table II. The binding energy of Sc to C_2H_2 substrate decreases with successive addition of H_2 molecules. However the binding energy of Ti and V to C_2H_2 does not show a systematic change with successive addition of H_2 molecules. The average adsorption energies per H_2 molecule are found to be –0.03, 0.30, and 0.28 eV for C_2H_2Sc, C_2H_2Ti, and C_2H_2V, respectively. For C_2H_2Ti and C_2H_2V complexes, these average adsorption energies have the right order of magnitude (0.2 to 0.7 eV) for room temperature hydrogen storage but for C_2H_2Sc complex it is not so. Since the hydrogen molecules in maximum H_2 adsorbed complexes are adsorbed in molecular form, we expect fast adsorption and desorption kinetics.

We have obtained interaction energies between different molecules using Eqs. (3) and (4) and binding energy for C_2H_2TM(nH$_2$) complexes in which maximum hydrogen molecules are adsorbed. These energies are presented in Table III. In Table III, OM denotes organometallic complex and H_i is the i-th hydrogen molecule in a complex. In Table III, the interaction energies of organometallic complex with all the adsorbed H_2 molecules are attractive for all the three H_2 adsorbed OM complexes studied here. For C_2H_2Sc($5H_2$) complex, first and fifth H_2 molecules are at equal distance from Sc atom results in equal OM–H_1 and OM–H_5 interaction energies. Similar is the case for the third and fourth H_2 molecules. The OM–H_2 interaction energy is lower as compared to other OM–H_i energies for C_2H_2Sc($5H_2$) complex. In case of C_2H_2Ti($5H_2$) complex, out of five H_2 molecules, first four molecules are at nearly equal distance from Ti atom and show equal OM–H_1, OM–H_2, OM–H_3, and OM–H_4 interaction energy. The fifth H_2 molecule is loosely bonded to the C_2H_2Ti complex which results in negligible OM–H_5 interaction energy. For C_2H_2V($4H_2$) complex, first and fourth H_2 molecules

Calculated energy gains ΔE_n [eV] and binding energy E_{TM} (in [eV]) of single TM atom (TM = Sc, Ti and V) and C_2H_2 substrate by successive addition of H_2 molecules to C_2H_2TM(nH$_2$) complex at B3LYP/DGDZVP level of theory. The values in the parentheses are at MP2/DGDZVP level.

TM	n	ΔE_n	E_{TM}
Sc	1	0.42(0.74)	4.52(2.23)
	2	0.45(0.27)	4.36(2.16)
	3	0.17(0.12)	4.16(2.06)
	4	0.18(0.14)	3.93(2.07)
	5	0.05(0.09)	3.90(1.82)
Ti	1	1.12(1.44)	3.94(2.26)
	2	0.02(0.10)	4.22(2.22)
	3	0.07(0.69)	4.28(2.26)
	4	0.02(0.49)	3.93(1.92)
	5	0.13(0.16)	3.81(1.84)
V	1	1.46(0.08)	3.89(4.54)
	2	0.01(0.62)	3.61(2.52)
	3	0.10(0.31)	3.15(4.34)
	4	0.57(0.26)	3.20(4.41)

are also at equal distance from V. Hence, OM–H_1 and OM–H_4 interaction energies are equal. Similarly, OM–H_2 and OM–H_3 interaction energies are equal since H_2 and H_3 are at equal distance from V.

In Table III, all the H_i–H_j interactions are repulsive. The total H_i–H_j interaction energy increases from Sc to V. It is 3.63, 7.29, and 10.03 kcal/mol for C_2H_2Sc($5H_2$), C_2H_2Ti($5H_2$), and C_2H_2V($4H_2$) complexes, respectively. Total two-body interaction is attractive for the C_2H_2Sc($5H_2$) and C_2H_2Ti($5H_2$) complexes whereas it is repulsive for the C_2H_2V($4H_2$) complex. In C_2H_2Sc($5H_2$) and C_2H_2Ti($5H_2$) complexes, the OM–H_i interactions are dominant whereas in case of C_2H_2V($4H_2$), the H_i–H_j interactions are dominant.

3.2. Vibrational frequencies analysis

Selected vibrational frequencies for the three complexes are presented in Table IV. As can be seen from Table IV, adsorption of hydrogen molecules on an isolated organometallic complex leads to the change in their vibrational frequencies, which is an important tool to characterize interactions at atomic scale. We have compared the vibrational frequencies in an isolated OM complex with those for maximum H_2 adsorbed complex. The H–H stretching frequencies are ranging from 4349 cm^{-1} (for H_2 molecules near top site of Sc atom) to 4097 cm^{-1} (for side H_2) for the C_2H_2Sc($5H_2$) complex. In C_2H_2Ti($5H_2$) complex, out of five hydrogen molecules, the four are surrounding Ti atom with H–H stretch frequencies ranging from 3032 cm^{-1} to 3287 cm^{-1}. The vibrational frequency for the loosely bonded H_2 molecule in C_2H_2Ti($5H_2$) complex is found to be 4388 cm^{-1}. For the four H_2 molecules adsorbed on C_2H_2V complex, the H–H stretch frequencies are in a range of 3411–3944 cm^{-1}.

TABLE III

Interaction energies E_i and binding energy E_b (in [kcal/mol]) for TM–$C_2H_2(nH_2)$ complexes (TM = Sc, Ti and V) on which maximum hydrogen molecules are adsorbed at MP2/DGDZVP level of theory. OM represents organometallic complex and H_i is the ith adsorbed H_2 molecule.

Interaction	TM		
	Sc	Ti	V
OM–H_1	−25.04	−20.29	−0.75
OM–H_2	−1.05	−20.29	−2.45
OM–H_3	−1.66	−20.29	−2.45
OM–H_4	−1.66	−20.29	−0.75
OM–H_5	−25.04	−0.00	–
H_1–H_2	0.00	1.17	2.33
H_1–H_3	−0.01	1.17	2.33
H_1–H_4	1.00	−0.01	0.71
H_1–H_5	0.42	0.62	–
H_2–H_3	0.62	−0.02	0.00
H_2–H_4	0.62	1.17	2.33
H_2–H_5	0.00	0.70	–
H_3–H_4	−0.01	1.17	2.33
H_3–H_5	1.00	0.70	–
H_4–H_5	−0.01	0.62	–
E_b	37.67	34.52	25.61

On comparing the H–H stretching frequencies in H_2 adsorbed complexes and that for isolated H_2 molecules (4536 cm^{-1}), it can be said that the strongly bonded H_2 molecule to TM shows smaller H–H stretching frequency than that for the isolated H_2 molecule. The C–H symmetric and asymmetric stretching frequencies in all the three complexes are blue shifted than the corresponding mode in respective isolated OM complex indicating that the C–H bonds become stronger upon H_2 adsorption. The C = C stretching frequencies are red-shifted in $C_2H_2Sc(5H_2)$ and $C_2H_2V(4H_2)$ complexes than that for the respective isolated complex. The C = C stretching mode in $C_2H_2Ti(5H_2)$ complex is blue shifted than that for the isolated C_2H_2Ti complex.

3.3. Temperature and pressure dependence of Gibbs free energy corrected adsorption energies

Figure 2 shows temperature dependence of Gibbs free energy corrected H_2 adsorption energy (ΔE_G) calculated using Eq. (5) for all the three complexes at 1 atm pressure. As can be seen from Fig. 2, H_2 adsorption on C_2H_2Ti complex is energetically favorable for a wide range of temperature than that on C_2H_2Sc and C_2H_2V complexes. H_2 adsorption on C_2H_2Sc complex is energetically unfavorable even at very low temperature as can be seen from negative Gibbs free energy corrected H_2 adsorption energy for the $C_2H_2Sc(5H_2)$ complex. H_2 adsorption on C_2H_2Ti and C_2H_2V is energetically favorable below 180 and 110 K, respectively.

Figure 3 shows pressure dependence of Gibbs free energy corrected H_2 adsorption energy for the $C_2H_2Sc(5H_2)$, $C_2H_2Ti(5H_2)$, and $C_2H_2V(4H_2)$

TABLE IV

Selected vibrational modes (in [cm^{-1}]) for $C_2H_2TM(nH_2)$ complexes at MP2/DGDZVP level (a) — asymmetric, (b) — symmetric.

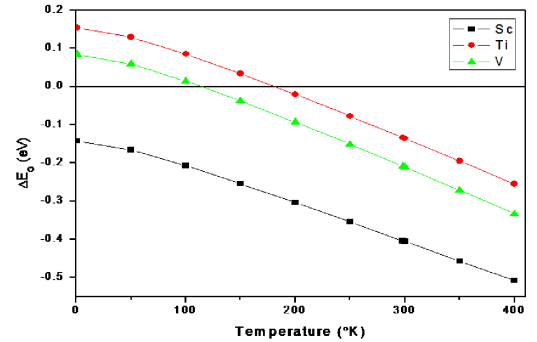| Stretch	$C_2H_2Sc(5H_2)$	$C_2H_2Ti(5H_2)$	$C_2H_2V(4H_2)$
C-TM-C (a)	575 (537)	618 (627)	748 (489)
C-TM-C (s)	598 (607)	594 (563)	713 (352)
TM-H_2 (s)	348/371/ 400/419/ 459	359/382/ 528 (top) 750/770 (side)	497/633/ 884/928
TM-H_2(a)	708/823/ 833/923/ 929	667 (top) 1375/1422/ 1454/1461 (side)	1163/1177/ 1479/1510
C = C	1449 (1426)	1578 (1819)	1775 (1612)
C-H (a)	3130 (3161)	3209 (3238)	3176 (3202)
C-H (s)	3158 (3186)	3246 (3281)	3204 (3240)
H–H	4097/4104/ 4220/4224 4349 (4536)	3032/3068/ 3234/3287 (side) 4388 (top) (4536)	3411/3896/ 3930/3944 (4536)

Fig. 2. Temperature dependence of Gibbs free energy corrected adsorption energies (ΔE_G) for $C_2H_2Sc(5H_2)$, $C_2H_2Ti(5H_2)$, $C_2H_2V(4H_2)$ at MP2/DGDZVP level.
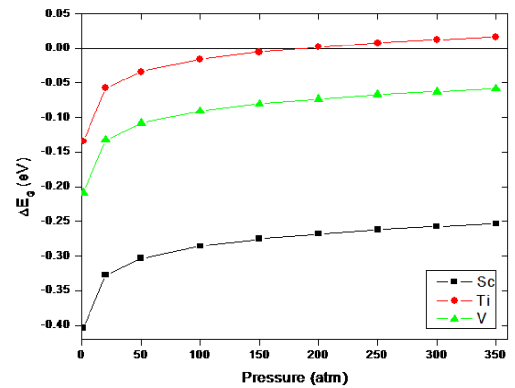

Fig. 3. Pressure dependence of Gibbs free energy corrected adsorption energies (ΔE_G) for $C_2H_2Sc(5H_2)$, $C_2H_2Ti(5H_2)$, $C_2H_2V(4H_2)$ at MP2/DGDZVP level.

complexes at 298 K. Similar to temperature dependence, H_2 adsorption on C_2H_2Ti complex is favorable over wide range of pressure. H_2 adsorption on C_2H_2Sc and C_2H_2V complexes is unfavorable for all the pressures considered here at room temperature.

3.4. HOMO–LUMO gap

The kinetic stability of these organometallic complexes is studied in terms of gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with successive adsorption of hydrogen molecules. Figure 4 shows the energy gap of respective complex with successive addition of hydrogen molecules using HF method. The HOMO–LUMO gap is also calculated at CAM-B3LYP level for comparison and is shown in Fig. 4. The energy gap for the isolated C_2H_2Sc, C_2H_2Ti, and C_2H_2V complexes is found to be larger than 4.5 eV, respectively. Figure 4 shows a common rise in the energy gap after adsorption of first hydrogen molecule for C_2H_2Sc and C_2H_2Ti complexes. In case of C_2H_2V complex, adsorption of subsequent hydrogen molecules decreases its kinetic stability. When the third hydrogen molecule is adsorbed on C_2H_2Ti complex, the first hydrogen molecule which was adsorbed in diatomic form becomes a hydrogen molecule which results in decrease in kinetic stability. The HOMO–LUMO gap of $C_2H_2Ti(1H_2)$ complex is found to be largest (9.49 eV) among all the complexes studied here due to adsorption of hydrogen in atomic form.
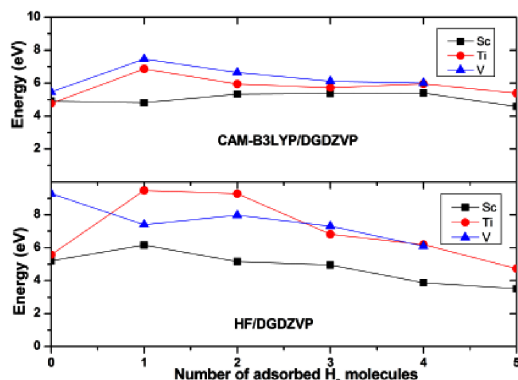

Fig. 4. Energy gap between highest occupied and lowest unoccupied molecular orbital for H_2 adsorbed complexes at HF/DGDZVP and CAM-B3LYP/DGDZVP levels.

Lastly, electronic configuration and natural population analysis of these energetically favorable complexes were scrutinized [35–41]. The amount of electron transfer (either partial or full) from Sc to the C_2H_2 substrate and H_2 molecules is computed. Here in isolated C_2H_2Sc, C_2H_2Ti, and C_2H_2V complexes, Sc, Ti, and V donates about 1.5, 1.3, and 1 electron respectively to the C_2H_2 substrate when these tend to bind the C_2H_2 substrate. Total of about 0.25, 0.5 and 0.6 electrons are transferred from H_2 molecules to Sc, Ti and V atom respectively

(back donation of electrons to the substrate) in respective $C_2H_2Sc(5H_2)$, $C_2H_2Ti(5H_2)$ and $C_2H_2V(4H_2)$ complex. The natural population analysis study reveals that the charge transfer from H_2 to metal atom dominates, reducing the charge on Sc, Ti and V atom with subsequent addition of H_2 molecules. The charge on Sc, Ti and V reduces from 1.362 to 0.955, 1.152 to 0.058, and 1.299 to –0.109 with successive addition of H_2 molecules in C_2H_2Sc and C_2H_2Ti, C_2H_2V complexes, respectively.

4. Conclusions

Using MP2 and B3LYP methods, we have performed a systematic study of H_2 adsorption on Sc, Ti, and V attached C_2H_2 complex. Hydrogen molecules bound strongly to C_2H_2Ti than C_2H_2Sc and C_2H_2V complexes. The average binding energy per H_2 molecule is 0.30 and 0.28 eV for C_2H_2Ti and C_2H_2V complex, respectively and has the right order of magnitude for room temperature hydrogen storage. The kinetic stability of H_2 adsorbed complexes is verified with their HOMO–LUMO energy gap. H_2 adsorption on C_2H_2Ti complex is energetically favorable over a wider range of temperature and pressure than that on C_2H_2Sc and C_2H_2V complexes. H_2 adsorption is energetically unfavorable even at very low temperature and low as well as high pressure on C_2H_2Sc complex. The C–H bond becomes stronger upon H_2 adsorption for all the three cases.

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