

Hydrogen Storage in C_2H_4V and $C_2H_4V^+$ Organometallic Compounds

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Received: June 10, 2009; Revised Manuscript Received: January 18, 2010

The hydrogen storage capacity of C_2H_4V organometallic complex and its cation was obtained using second order Møller–Plesset (MP2) and density functional theory methods with different exchange and correlation functionals. A maximum of five and six hydrogen molecules can be adsorbed on C_2H_4V and $C_2H_4V^+$ compounds with gravimetric H_2 uptake capacities of 11.32 and 13.28 wt %, respectively. The effect of temperature and different exchange and correlation functionals on the adsorption energy of $C_2H_4V(5H_2)$ and $C_2H_4V^+(6H_2)$ complexes was studied. The superiority of $C_2H_4V^+$ as a possible hydrogen storage material over C_2H_4V and other vanadium containing organometallic compounds was observed. Similar to isolated C_2H_4V and $C_2H_4V^+$, after adsorption of a maximum of H_2 molecules on C_2H_4V and $C_2H_4V^+$ also, V as well as V^+ remain strongly bound to the C_2H_4 substrate. Many-body analysis was carried out to study the nature of interactions between different molecules in a complex, and the contribution from different many-body energies to the binding energy of a complex.

I. Introduction

Energy is an indicator of growth, development, and prosperity. Globally, fossil fuels are increasingly becoming scarce. This calls for their efficient utilization and conservation. Increasing demand of energy is due to rising population, and limited natural energy sources (petrol, diesel, or gasoline) forces us to find out the compatible substitute energy source to the natural sources. In this type of scenario, hydrogen looks to be a more promising source of energy. There is a problem regarding production of hydrogen and of storage too. Though liquid hydrogen and gaseous hydrogen have fast kinetics, it is difficult to store them practically. For hydrogen to replace petrol or diesel, the current method of its production as well as storage system must be improved. Efficient and safe storage of hydrogen is crucial for the improvement of hydrogen energy economy.¹ We are in the search of a material that can store hydrogen with high gravimetric and volumetric density as well as with fast kinetics. Extensive work is going on in this direction. It includes chemical hydrides,^{2–4} nanomaterials^{5–20} such as nanotubes and fullerene, and so on.

Carbon based nanostructures have attracted attention because lightweight material is essential for achieving a high hydrogen storage weight percentage. However, hydrogen molecules bind loosely to these structures via van der Waals interaction. In order to overcome this problem, a novel concept of affixing a single metal atom to carbon nanostructures has been suggested.^{15–18,21–27} It was found that nanomaterials can adsorb hydrogen molecules with high gravimetric and volumetric density, but difficulties come while releasing the stored hydrogen.^{1,28–36}

To our knowledge, the hydrogen uptake capacity of C_2H_4V and its ions has not been reported so far. The aim of this work is to study hydrogen storage capacity of the C_2H_4V organometallic complex and its cation along with the nature of interactions between different molecules in a complex. It will be interesting to see the effect of ionization of C_2H_4V on its hydrogen uptake capacity and nature of interactions between different molecules

in a hydrogen adsorbed complex. We have used two hybrid functionals (B3LYP and PBE1PBE) and one generalized gradient approximation (PBEPBE) for our study to know the effect of exchange and correlation functionals on adsorption energy. We have also studied the hydrogen uptake capacity of these complexes using the Møller–Plesset (MP2) method. The hydrogen uptake capacity from this work and kinetic stability of these complexes are compared with those of a recently reported single vanadium containing organometallic complex.²⁶ These results should provide useful guidance for designing novel hydrogen storage materials with high hydrogen uptake capacity.

This Article is organized as follows: Computational approach is given in the next section. Results are presented and discussed in section III. Conclusions are given in the last section.

II. Computational Details

The geometries of $C_2H_4V(nH_2)$ ($n = 1–5$) and $C_2H_4V^+(nH_2)$ ($n = 1–6$) are optimized using Becke's three parameter hybrid functional combined with the Lee, Yang, and Parr correlation (B3LYP) functional as well as PBEPBE and PBE1PBE functionals.^{37–41} The geometries of the above complexes are also optimized using the MP2 method.⁴² An all-electron DGAuss double-zeta valence polarization (DGDZVP) basis set has been used for both, the density functional theory (DFT) as well as MP2 method. Basis set superposition error (BSSE) corrected relaxation energies and many-body energies for each complex were obtained using many-body analysis for both $C_2H_4V(5H_2)$ and $C_2H_4V^+(6H_2)$ complexes. In many-body analysis, the total energy of the n -body cluster can be written as the sum of one-, two-, three-, ..., n -body terms. Here, body represents a molecule in a cluster. Details of the decomposition of total energy of a complex into relaxation energies and many-body energies can be found in earlier published work.^{43–51} All calculations are performed using the Gaussian 03 suite of programs.⁵²

III. Results and Discussion

First, we optimized the geometries of $C_2H_4V(nH_2)$ ($n = 1–5$) and $C_2H_4V^+(nH_2)$ ($n = 1–6$) using MP2, B3LYP, PBEPBE,

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TABLE 1: Calculated Adsorption Energy per H_2 Molecule without (ΔE) and with Zero Point Energy Correction (ΔE -ZPE), and That with Gibbs Free Energy Correction (ΔG) in eV at 298.15 K for $C_2H_4V(nH_2)$ ($n = 1-5$) Complexes Using Different Levels of Theory

complex	B3LYP			PBE1PBE			PBEPBE			MP2		
	ΔE	ΔE -ZPE	ΔG	ΔE	ΔE -ZPE	ΔG	ΔE	ΔE -ZPE	ΔG	ΔE	ΔE -ZPE	ΔG
$C_2H_4V(1H_2)$	0.23	0.14	-0.12	0.34	0.24	-0.03	1.00	0.94	0.70	0.21	0.17	-0.11
$C_2H_4V(2H_2)$	0.48	0.36	0.08	0.57	0.45	0.17	0.93	0.81	0.53	-0.23	-0.39	-0.67
$C_2H_4V(3H_2)$	0.46	0.32	0.04	0.57	0.42	0.13	0.81	0.66	0.37	-0.08	-0.24	-0.53
$C_2H_4V(4H_2)$	0.45	0.29	-0.003	0.57	0.40	0.12	0.74	0.58	0.29	0.02	-0.18	-0.48
$C_2H_4V(5H_2)$	0.38	0.21	-0.08	0.52	0.34	0.05	0.64	0.47	0.18	0.22	0.01	-0.28

TABLE 2: Calculated Adsorption Energy per H_2 Molecule without (ΔE) and with Zero Point Energy Correction (ΔE -ZPE), and That with Gibbs Free Energy Correction (ΔG) in eV at 298.15 K for $C_2H_4V^+(nH_2)$ ($n = 1-6$) Complexes Using Different Levels of Theory

complex	B3LYP			PBE1PBE			PBEPBE			MP2		
	ΔE	ΔE -ZPE	ΔG	ΔE	ΔE -ZPE	ΔG	ΔE	ΔE -ZPE	ΔG	ΔE	ΔE -ZPE	ΔG
$C_2H_4V^+(1H_2)$	0.34	0.24	0.004	0.38	0.27	0.04	0.65	0.25	0.30	0.22	0.13	-0.12
$C_2H_4V^+(2H_2)$	0.39	0.25	-0.03	0.51	0.36	0.11	0.58	0.18	0.21	0.20	0.10	-0.17
$C_2H_4V^+(3H_2)$	0.46	0.29	0.01	0.54	0.37	0.09	0.69	0.26	0.28	0.24	0.10	-0.18
$C_2H_4V^+(4H_2)$	0.44	0.27	0.01	0.57	0.39	0.10	0.66	0.21	0.24	0.27	0.10	-0.19
$C_2H_4V^+(5H_2)$	0.44	0.27	-0.02	0.55	0.37	0.08	0.54	0.08	0.10	0.27	0.09	-0.20
$C_2H_4V^+(6H_2)$	0.38	0.19	-0.11	0.50	0.30	0.005	0.64	0.17	0.18	0.21	0.02	-0.27

and PBE1PBE methods and DGDZVP basis set. A maximum of six H_2 molecules can be adsorbed on the cation of C_2H_4V and five on neutral C_2H_4V organometallic complexes at all levels of theories used here. This corresponds to a maximum H_2 uptake capacity of 13.28 and 11.32 wt % for $C_2H_4V^+$ and C_2H_4V , respectively. The adsorption energies for $C_2H_4V(nH_2)$ ($n = 1-5$) and $C_2H_4V^+(nH_2)$ ($n = 1-6$) using different levels of theory are represented in Tables 1 and 2, respectively. The adsorption energy per H_2 molecule without Gibbs free energy correction is calculated as $\Delta E = \{E[OM] + E[nH_2] - E[OM(nH_2)]\}/n$ for each structure, where $E[X]$ is the total energy of X and OM (organometallic complex) is either C_2H_4V or $C_2H_4V^+$. Gradient generalized approximation (GGA) calculations give higher adsorption energies, whereas hybrid DFT gives lower adsorption energies. The adsorption energies obtained with the MP2 method are on a much lower side compared with the DFT method. Similar results were obtained for adsorption energy of $C_2H_4Ti_2(10H_2)$ by Okamoto using PBE and MP2 methods.⁵³ The author pointed out that H_2 adsorption is not energetically favorable on $Ti_2C_2H_4$ using the MP2 method but is favorable at the PBE level.

The adsorption energy per H_2 molecule with Gibbs free energy correction (ΔG) is calculated as $\Delta G = \{G[OM] + G[nH_2] - G[OM(nH_2)]\}/n$, where $G[X]$ stands for the energy of X with Gibbs free energy correction. ΔG values for $n = 5$ for $C_2H_4V(nH_2)$ complexes using B3LYP and MP2 method are negative, whereas they are positive for the PBEPBE and PBE1PBE methods. This indicates that adsorption of five hydrogen molecules at room temperature on the C_2H_4V complex is energetically favorable (exothermic) using PBEPBE and PBE1PBE methods and that it is energetically unfavorable (endothermic) using B3LYP and MP2 methods. This is in agreement with what was observed by Okamoto for the $Ti_2C_2H_4$ complex.⁵³ Similarly, adsorption of six H_2 molecules at room temperature on the $C_2H_4V^+$ complex is energetically favorable using PBEPBE and PBE1PBE methods and unfavorable using B3LYP and MP2 methods.

We have also studied the effect of temperature on ΔG to obtain the temperature range for which adsorption of " n " hydrogen molecules is energetically favorable on C_2H_4V and $C_2H_4V^+$ for all four levels of theory. The temperature depen-

dence of ΔG for $C_2H_4V(5H_2)$ and $C_2H_4V^+(6H_2)$ complexes is shown in Figure 2. Adsorption of five H_2 molecules on C_2H_4V is energetically favorable below temperatures 230, 340, and 450 K with B3LYP, PBE1PBE, and PBEPBE, respectively. The adsorption of six H_2 molecules on the $C_2H_4V^+$ complex is thermodynamically possible below 205, 310, and 420 K with B3LYP, PBE1PBE, and PBEPBE calculations, respectively. It was found that H_2 adsorption is energetically unfavorable for C_2H_4V and $C_2H_4V^+$ at the MP2/DGDZVP level, unless the temperature is very low (<50 K). This is also in agreement with H_2 adsorption on the $Ti_2C_2H_4$ complex.⁵³ Okamoto also pointed out that adsorption of 10 hydrogen molecules on $Ti_2C_2H_4$ at the MP2 level is possible only at very low temperature whereas it is possible at the PBE level for a wide range of temperatures.⁵³ Energetically favorable H_2 adsorption is possible for a wide range of temperatures at the PBEPBE/DGDZVP level for C_2H_4V as well as $C_2H_4V^+$ complexes. It is energetically favorable not only at room temperature but also at temperatures higher and lower than room temperature.

All the H_2 molecules are adsorbed in molecular form on C_2H_4V for all n at B3LYP level. At the PBEPBE level, the first H_2 molecule is adsorbed in dihydride form on C_2H_4V and it remains in dihydride form until the final structure ($n = 5$). In the case of PBE1PBE, all the hydrogen molecules are adsorbed in molecular form for $n = 1-4$ and one of the H_2 molecules is dissociated for $n = 5$. At the MP2 level, the first H_2 molecule is dissociated on C_2H_4V and all the subsequent H_2 molecules for $n = 2-4$ are adsorbed in molecular form. For $n = 5$, one of the H_2 molecules is dissociated at the MP2 level too. All the H_2 molecules are adsorbed in molecular form on $C_2H_4V^+$ for all n at all four levels of theory used here. The optimized structures of $C_2H_4V(5H_2)$ and $C_2H_4V^+(6H_2)$ are shown in Figure 1. For $C_2H_4V(5H_2)$, all five H_2 molecules are adsorbed in molecular form at the B3LYP level only, whereas at the MP2, PBEPBE, and PBE1PBE levels one of the H_2 molecules is dissociated. Unlike for DFT, the C_2H_4V structure at the MP2 level for $C_2H_4V(5H_2)$ is slightly distorted. The vanadium atom is equidistant from both of the carbon atoms in optimized structures by the DFT method, while it is not at the MP2 level. PBE1PBE and PBEPBE methods have similar geometries of $C_2H_4V(5H_2)$.

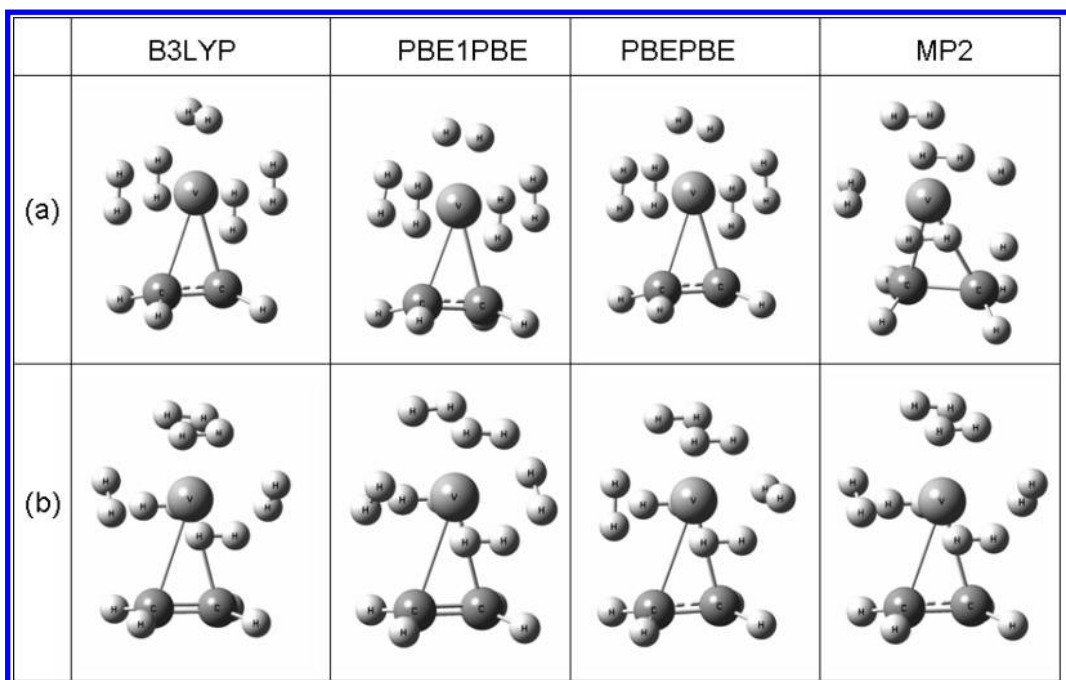


Figure 1. Optimized geometries of (a) $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$ and (b) $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ complexes.

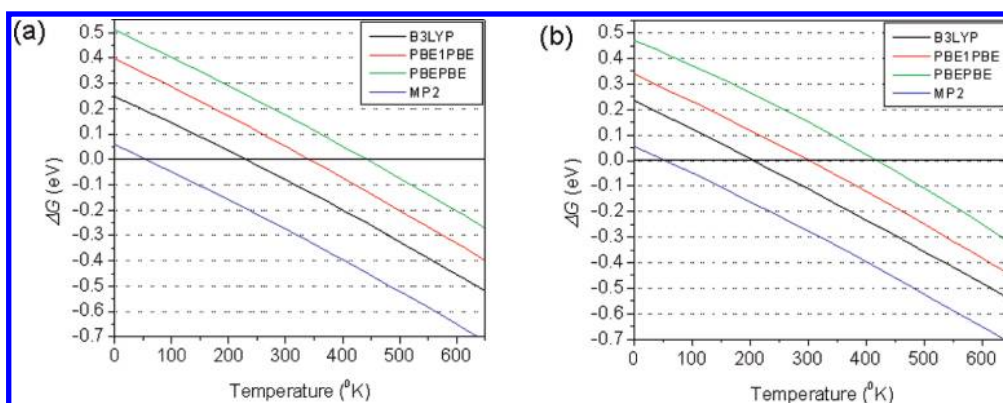


Figure 2. Temperature dependence of averaged H_2 adsorption energy (with Gibbs free energy correction) for (a) $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$ and (b) $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ complexes.

The $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ complex optimized at the B3LYP and PBE1PBE levels is similar with little difference in bond length. The H–H bond length for H_2 molecules adsorbed on the side of the V atom is 0.78 (0.79) Å, whereas it is 0.81 (0.84) Å for the H_2 molecule adsorbed on the top side of the V atom at B3LYP (PBE1PBE) level. The V atom is at a distance of 2.38 and 2.32 Å from both the carbon atoms at B3LYP and PBE1PBE levels, respectively. For $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ at the MP2 level, the C–V distance is of 2.23 Å and the H–H distance for the top H_2 molecule is 0.76 Å. The H–H bond length for the molecules adsorbed on the side of the V atom is in the range of 0.77–0.80 Å at the MP2 level. For $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ at the PBEPBE level, the vanadium atom is not equidistant from the carbon atoms. It is at a distance of 2.35 Å from one carbon and 2.29 Å from the other. Out of the six H_2 molecules, five molecules have parallel orientation whereas one has perpendicular orientation to the C–C bond axis.

A linear relation is obtained when the Mulliken atomic charge on the vanadium atom in the $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ complexes is plotted with averaged adsorption energy as can be seen in Figure 3. The more negative charge on vanadium, the larger is the adsorption energy. The Mulliken atomic charge on the vanadium atom is more negative for PBEPBE >

PBE1PBE > B3LYP > MP2 for both $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$ as well as $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$. The negative charge transferred from carbon to vanadium increases an attractive interaction between the H_2 molecule and $\text{C}_2\text{H}_4\text{V}/\text{C}_2\text{H}_4\text{V}^+$ substrate. Figure 3 shows that the negative charge on vanadium in $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ is greater than that in $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$. The kinetic stability of these systems is verified by means of the energy separation between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO–LUMO gap of the $\text{C}_2\text{H}_4\text{V}(n\text{H}_2)$ ($n = 1-5$) and $\text{C}_2\text{H}_4\text{V}^+(n\text{H}_2)$ ($n = 1-6$) complexes with successive addition of H_2 molecules is shown in Figure 4. The largest HOMO–LUMO gap is predicted for $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ complexes by all methods studied here. The intermediate complexes from $n = 2$ to $n = 5$ or 6 of these compounds are also more stable than the respective isolated organometallic substrates.

BSSE corrected interaction energies between different molecules and binding energy for the $\text{C}_2\text{H}_4\text{V}(5\text{H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(6\text{H}_2)$ complexes are obtained at the PBEPBE/DGDZVP level to know the nature of interactions between different molecules in these complexes. In Table 3, two-body interaction energies along with total three-body, total four-body, total five-body, total six-body, and total seven-body interaction energies, relaxation energies,

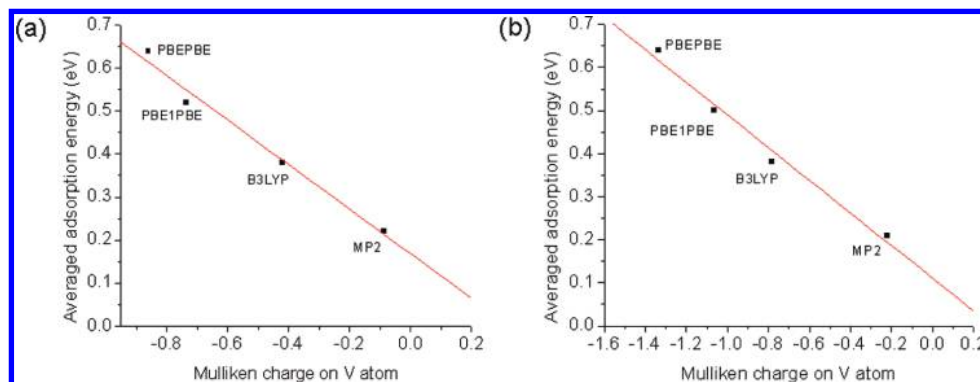


Figure 3. Mulliken atomic charge versus averaged H_2 adsorption energy of (a) $C_2H_4V(5H_2)$ and (b) $C_2H_4V^+(6H_2)$ complexes.

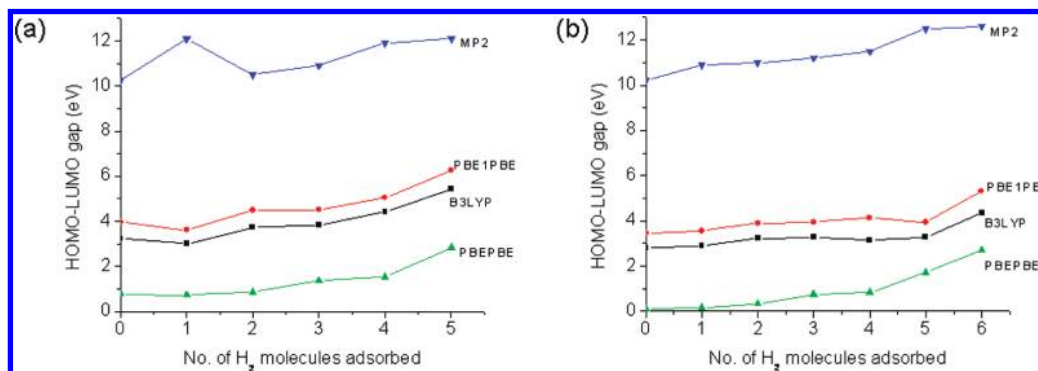


Figure 4. Energy gap between highest occupied and lowest unoccupied molecular orbitals for (a) $C_2H_4V(nH_2)$ ($n = 1-5$) and (b) $C_2H_4V^+(nH_2)$ ($n = 1-6$) complexes with successive addition of H_2 molecules.

TABLE 3: BSSE-Corrected Two-Body Interaction Energies and Total Many-Body Energies for $C_2H_4V(5H_2)$ and $C_2H_4V^+(6H_2)$ Complexes at the PBEPBE/DGDZVP Level^a

interaction energy term	energy (kcal/mol)		interaction energy term	energy (kcal/mol)	
	$C_2H_4V(5H_2)$	$C_2H_4V^+(6H_2)$		$C_2H_4V(5H_2)$	$C_2H_4V^+(6H_2)$
two-body					
OM-H1	-4.30	-21.4	H2-H4	—	1.38
OM-H2	-11.9	-10.4	H2-H4a	0.96	—
OM-H3	-4.30	-12.5	H2-H4b	0.96	—
OM-H4	—	-19.0	H2-H5	-0.04	-0.05
OM-H4a	-51.1	—	H2-H6	—	-0.06
OM-H4b	-51.1	—	H3-H4	—	1.60
OM-H5	-11.9	-12.5	H3-H4a	2.48	—
OM-H6	—	-10.4	H3-H4b	0.11	—
H1-H2	1.15	1.42	H3-H5	1.15	5.72
H1-H3	-0.06	1.45	H3-H6	—	-0.05
H1-H4	—	-0.07	H4a-H4b	-39.7	—
H1-H4a	0.11	—	H4-H5	—	1.60
H1-H4b	2.48	—	H4a-H5	0.96	—
H1-H5	1.15	1.45	H4b-H5	0.96	—
H1-H6	—	1.42	H4-H6	—	1.38
H2-H3	1.15	6.54	H5-H6	—	6.55
three-body					
$E_{relaxation}$				10.28	25.43
total two-body				-160.82	-55.99
total three-body				-22.23	-81.02
total four-body				49.61	-24.25
total five-body				-147.20	123.93
total six-body				120.61	-103.87
total seven-body				24.82	-0.04
BE				-124.93	-115.83

^a Higher many-body energies are given in the Supporting Information.

and binding energies for these complexes are represented. Three-body and higher many-body energies are given in the Supporting Information. In $C_2H_4V(5H_2)$ and $C_2H_4V^+(6H_2)$ complexes, all OM-Hi interactions are attractive. In $C_2H_4V(5H_2)$, interactions of atoms of the dissociated H_2 molecule with the OM complex

and nondissociated H_2 molecules are attractive and repulsive, respectively. The more negative charge on the vanadium atom in $C_2H_4V^+(6H_2)$ than in $C_2H_4V(5H_2)$ is due to the fact that more charge has been transferred from carbon to vanadium in the former than the latter. This causes stronger OM-Hi interactions

TABLE 4: Selected Vibrational Modes (in cm^{-1}) of $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ Complexes Using Different Methods with the DGDZVP Basis Set^a

assignments	B3LYP	PBE1PBE	PBEPBE	MP2
C–V–C stretch (sym)	364 (148)	400/450 (339)	431 (320)	—(417)
C–V–C stretch (asym)	562 (402)	482 (447)	461/613 (414)	410/532 (482)
V–H ₂ stretch (sym)	755/783/856/857/956 (574/630/701/715/955/977)	877/956/974/978 (1063/1078)	997/964/924/909 (804/807/110/1084)	894/907/1140/1417 (959/953/698/639/606/482)
V–H ₂ stretch (asym)	1378/1417/1454/1474/1739 (1215/1230/1259/1296/1514/1515)	1454/1472/1540/1581 (1350/1360/1378/1410/1641/1644)	1480/1508/1551/1597 (1424/1435/1444/1474/1654/1690)	1040/1514/1558/1882 (1495/1490/1282/1248/1001/992)
C=C stretch	1191 (1307)	1210 1314	1167 (1249)	1083 (1262)
C–H ₂ stretch (sym)	3103/3113 (3156/3161)	3131/3141 (3172/3178)	3047/3057 (3082/3091)	3112/3156 (3162/3169)
C–H ₂ stretch (asym)	3178/3200 (3248/3268)	3213/3233 (3270/3286)	3123/3141 (3175/3197)	3203/3242 (3266/3281)
H–H stretch	2041/3351/3372/3384/3446 (3207/3220/36813699/3707/3724)	3227/3241/3456/3480 (2933/2950/3497/3506/3519/3546)	2954/2978/3168/3202 (2510/2635/30903100/3145/3202)	4135/3540/3357/2845 (3385/3396/3836/3852/4103/4108)

^a The values in paranthesis are for the $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ complex.

in the former than in the latter, and H_2 molecules bound more strongly to $\text{C}_2\text{H}_4\text{V}^+$ than $\text{C}_2\text{H}_4\text{V}$. All two-body $\text{H}_i\text{--H}_j$ interactions in $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ are repulsive except H1--H4 , H2--H5 , H2--H6 , and H3--H6 . The $\text{H}_{i\text{a}}\text{--H}_{i\text{b}}$ interaction in $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ is attractive, whereas all $\text{H}_i\text{--H}_j$ interactions are repulsive except H1--H3 and H2--H5 . The H1--H3 and H2--H5 interaction energies in $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ complexes are very small and almost negligible. The total two-body energy has the highest contribution to the binding energy of the $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ complex. For $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ as well as $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$, not only two-body energies but higher many-body energies and relaxation energies have significant contribution to the binding energy of a respective complex except total seven-body energy for the $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ complex which is almost negligible as compared to other many-body energies.

The BSSE corrected binding energy for $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ complexes is -124.93 and -115.83 kcal/mol, respectively. It is observed that even after maximum hydrogen molecule adsorption on $\text{C}_2\text{H}_4\text{V}$ and $\text{C}_2\text{H}_4\text{V}^+$ complexes, the V as well as V^+ remain strongly bound to the C_2H_4 substrate with a very small change in the binding energy with respect to isolated $\text{C}_2\text{H}_4\text{V}$ and $\text{C}_2\text{H}_4\text{V}^+$ complexes. The BSSE correction for total energy is significant in the present system. It corrects the total energy of $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ by 1.26 and 0.09 hartree, respectively. This shows that BSSE correction is necessary for these complexes.

Different vibrational modes are obtained for $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ complexes. There are no imaginary frequencies for these complexes indicating that these complexes are quantum mechanically stable. Selected modes for these complexes are given in Table 4. We have compared these modes with respective modes in isolated organometallic complex. The C–V–C symmetric [asymmetric] stretching frequencies in $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ are red [blue] shifted than those for isolated organometallic substrate. The CH_2 symmetric and asymmetric stretching modes in $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ are blue-shifted compared to those in an isolated OM complex. The C=C stretching frequency is 1167 [1249] cm^{-1} for $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ [$\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$] which is 1054 [1164] cm^{-1} for isolated $\text{C}_2\text{H}_4\text{V}$ [$\text{C}_2\text{H}_4\text{V}^+$] organometallic complex at the PBEPBE level. At the MP2, PBE1PBE, and B3LYP levels, also the C=C stretching mode is blue-shifted in neutral as well as cation case compared to that of respective organometallic compounds. This indicates that the C=C bond becomes weaker upon maximum H_2 adsorption in both neutral as well as cation case at all levels of theories used here.

On comparing our results with those of other organometallic compounds containing a single vanadium atom, it is observed

that the uptake capacity from this work for both $\text{C}_2\text{H}_4\text{V}$ as well as $\text{C}_2\text{H}_4\text{V}^+$ is significantly higher than that of $\text{C}_4\text{H}_4\text{V}$, $\text{C}_5\text{H}_5\text{V}$, and $\text{C}_6\text{H}_6\text{V}$.²⁶ The uptake capacity of $\text{C}_4\text{H}_4\text{V}$, $\text{C}_5\text{H}_5\text{V}$, and $\text{C}_6\text{H}_6\text{V}$ reported earlier is 7.2, 6.4, and 4.4 wt %, respectively. The uptake capacity from this work is higher than that of these compounds by about 4 wt % for neutral and 6 wt % for cation complex. One similarity that can be seen between hydrogen adsorbed $\text{C}_2\text{H}_4\text{V}$, $\text{C}_4\text{H}_4\text{V}$, $\text{C}_5\text{H}_5\text{V}$, and $\text{C}_6\text{H}_6\text{V}$ complexes is that one of the H_2 molecules is adsorbed in the dissociated form on all of these complexes. Since enough charge is transferred from the metal atom to H_2 molecules to destabilize the dihydrogen state, neutral species have two hydrogens as hydride ligand plus the remainder as dihydrogen ligands.⁵⁴ On the other hand, due to the higher ionization potential of the V metal atom in the $\text{C}_2\text{H}_4\text{V}^+$ complex, it is difficult to take out charge from it; hence, all the H_2 molecules are adsorbed in molecular form on the $\text{C}_2\text{H}_4\text{V}^+$ complex. Since all H_2 molecules are adsorbed in molecular form on $\text{C}_2\text{H}_4\text{V}^+$ and one of the H_2 molecules is adsorbed in dihydride form on $\text{C}_2\text{H}_4\text{V}$, we expect faster adsorption and desorption kinetics in the former than in the latter.

IV. Conclusion

Different levels of theory are used to study the hydrogen uptake capacity of $\text{C}_2\text{H}_4\text{V}$ and $\text{C}_2\text{H}_4\text{V}^+$ organometallic compounds. The H_2 adsorption energy is affected by the exchange and correlation functionals employed in DFT calculations. The adsorption of the H_2 molecule on $\text{C}_2\text{H}_4\text{V}$ and $\text{C}_2\text{H}_4\text{V}^+$ is energetically favorable at room temperature using PBEPBE and PBE1PBE methods, whereas B3LYP and MP2 methods give thermodynamically unfavorable results at room temperature. The negative charge localization on the vanadium atom is responsible for the binding of H_2 molecules and which is more in the case of the charged substrate. All the H_2 molecules are adsorbed in molecular form on the $\text{C}_2\text{H}_4\text{V}^+$ complex, and we expect faster adsorption and desorption kinetics for $\text{C}_2\text{H}_4\text{V}^+$ than for $\text{C}_2\text{H}_4\text{V}$. Stronger attractive interaction is observed between the $\text{C}_2\text{H}_4\text{V}^+$ complex and adsorbed H_2 molecules than between the $\text{C}_2\text{H}_4\text{V}$ complex and adsorbed H_2 molecules.

Acknowledgment. Financial support from C.S.I.R., New Delhi (Grant No. 03(1115)/08/EMR-II) is gratefully acknowledged.

Supporting Information Available: Optimized geometries at different levels of theory and BSSE corrected many-body energies of $\text{C}_2\text{H}_4\text{V}(\text{5H}_2)$ and $\text{C}_2\text{H}_4\text{V}^+(\text{6H}_2)$ complexes at the PBEPBE/DGDZVP level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP910614N