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# Cooperative physisorption and chemisorption of hydrogen on vanadium-decorated benzene†

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3d TM-decorated carbon composites have been proved to be a new generation of hydrogen storage materials. However, detailed hydrogen storage mechanisms are still unclear. Investigation of the H<sub>2</sub> dissociation and H migration on the 3d TM-decorated six-membered carbocycles is very critical for better understanding the hydrogen storage mechanism. In this paper, the processes of chemisorption and physisorption of multiple H<sub>2</sub> molecules on synthesized VC<sub>6</sub>H<sub>6</sub> were simultaneously investigated for the first time. The Gibbs free energy calculations show that the optimal chemisorption pathway with the hydrogen storage capacity of 5.97 wt% is exothermic by 2.83 kcal mol<sup>-1</sup>. Both the continuous hydrogenation giving the product of VC<sub>6</sub>H<sub>11</sub>-3H and reverse dehydrogenation could run smoothly at room temperature. The physisorption with a hydrogen storage capacity of 4.48 wt% will be exothermic by 13.49 kcal mol<sup>-1</sup>. The H<sub>2</sub> molecules can be physisorbed at any temperature under 416 K and readily desorbed above 480 K at 1 atm. In summary, physisorption and chemisorption synergistically boost the hydrogen storage property of complex VC<sub>6</sub>H<sub>6</sub>. Our study provides a comprehensive picture of the interaction between hydrogen and VC<sub>6</sub>H<sub>6</sub> and opens a new window for optimizing the future hydrogen storage materials.

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## 1. Introduction

To satisfy the increasing global energy demands and solve serious environmental problems, renewable energy sources need to be researched to replace fossil-based fuels.<sup>1</sup> Hydrogen energy is reversible, recyclable, and pollution-free.<sup>2,3</sup> With the rapid progress of energy transformation, the value of hydrogen energy is further highlighted.<sup>4-9</sup> However, the hydrogen energy industry chain, especially the basic research on hydrogen storage links, faces many difficulties currently. Although many hydrogen storage methods<sup>10-12</sup> have their advantages in some aspects, they are not enough to meet the practical requirements of hydrogen energy in transportation. Generally, hydrogen is attached by physisorption or chemisorption. In physisorption, hydrogen remains in a molecular state and is weakly bound to the surface. In chemisorption, H<sub>2</sub> molecules dissociate into double H atoms and even migrate to the material forming chemical bonds, which are strong.<sup>6</sup> Kubas-type orbital interaction<sup>13,14</sup> is similar to physisorption, in which the H-H bond in an H<sub>2</sub> molecule is elongated but not broken. It improves the

hydrogen adsorption energy of transition metals (TMs)-decorated carbon composites (0.10–0.80 eV)<sup>6</sup> and makes most of the hydrogen gravimetric storage capacities satisfy the target of the U.S. Department of Energy (~6.5 wt%).<sup>15</sup> Then, TM-decorated carbon composites grew up to be a new generation of hydrogen storage materials.<sup>16-19</sup> Interestingly, the dissociation of the first H<sub>2</sub> was spontaneous on most of Sc/Ti/V-decorated carbon nanostructures.<sup>20-22</sup> The dissociation of the H<sub>2</sub> increases the probability of H migration. The question then arises: whether hydrogen molecules are adsorbed only or migrate to form C-H bonds? If dissociation and even migration take place and TM-H/C-H bond is formed, the adsorption of H<sub>2</sub> on transition-metal-decorated nanomaterials will change from physisorption to chemisorption. Investigation of the H<sub>2</sub> dissociation and H migration is very important for better understanding the hydrogen storage mechanism on the 3d transition metal-decorated carbon nanostructures. While physisorption was mainly focused on and chemisorptions was always neglected.

On the other hand, the spillover mechanism is another promising mechanism for enhancing the H<sub>2</sub> uptake in carbon-based materials.<sup>23-25</sup> Hydrogen spillover following three processes: (1) the dissociation of H<sub>2</sub> molecules on the TM sites; (2) the migration of the atomic hydrogen from TM sites to the carbon surface and (3) the diffusion of atomic hydrogen on the carbon surface eventually forming a stable C-H bond. Understanding these three key steps is necessary to fully understand the hydrogen spillover process. Most theoretical studies on the

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mechanism of hydrogen spillover on carbon adsorbent have been carried out on graphene.<sup>26–30</sup> The metal catalyst is an important factor affecting storage by hydrogen spillover. So far, the dissociation sources for hydrogen spillover have been long known for TMs such as Pt, Pd, Ru, Ni, and Ti.<sup>31–34</sup> The experimental progress of Kubas-type H<sub>2</sub>-storage materials always confirmed by V-containing polymers.<sup>35</sup> Then, could monatomic V be used as a source of dissociation sources for hydrogen spillover?

Six-membered carbocycle is an important linker in some metal organic frameworks<sup>36,37</sup> and covalent organic frameworks<sup>38</sup> but also a basic unit of C<sub>60</sub>,<sup>39,40</sup> graphene,<sup>41,42</sup> and carbon nanotubes.<sup>43–46</sup> In this regard, Ti/Sc/V-benzene complexes as representative units of high-capacity hydrogen storage materials have received great attention.<sup>47–50</sup> In this study, based on first-principles calculations, the adsorption behavior of hydrogen on the synthesized VC<sub>6</sub>H<sub>6</sub> (ref. 51–54) is focused on to further address the hydrogen storage mechanism. Previously, Weck,<sup>47</sup> Ajay,<sup>48</sup> and Li<sup>49</sup> reported that VC<sub>6</sub>H<sub>6</sub> could adsorb three hydrogen molecules, but the only physisorption was considered. Here, a systematic study of both physisorption and chemisorption is investigated. The mechanism of dissociative adsorption and even the migration of the H atoms on VC<sub>6</sub>H<sub>6</sub> is investigated. It was found that physisorption and chemisorption synergistically boost the hydrogen storage property of complex VC<sub>6</sub>H<sub>6</sub>. Most of our findings would have a great significance for the study of hydrogen storage on TM-decorated carbon composites.

## 2. Computational methods and details

All geometry optimizations were carried out by using the density functional theory (DFT) method at B3LYP<sup>55</sup>/6-31+G(d,p) level. The whole calculations employed the Gaussian 09 suite of programs.<sup>56</sup> The optimization was carried out without any symmetry constraint and different spin multiplicities were considered. The optimized geometric coordinates and energies were listed in the ESI.† Frequency calculations were performed to confirm that there was no imaginary frequency in the stable structure, and one imaginary frequency in the transition states. *Ab initio* molecular dynamics (MD) simulations based on atom density matrix propagation (ADMP)<sup>57–61</sup> were performed to confirm part of the favorable dissociation paths.

Consecutive adsorption energies with ZPEs ( $\Delta E_n$ ) and Gibbs free energy corrections ( $\Delta G_n$ ) at 298.15 K were obtained using the following formula:

$$\Delta E_n = E(\text{VC}_6\text{H}_6(\text{H}_2)_{n-1}) + E(\text{H}_2) - E(\text{VC}_6\text{H}_6(\text{H}_2)_n) \quad (1)$$

$$\Delta G_n = G(\text{VC}_6\text{H}_6(\text{H}_2)_{n-1}) + G(\text{H}_2) - G(\text{VC}_6\text{H}_6(\text{H}_2)_n) \quad (2)$$

where  $E(X)$  is the sum of electronic and zero-point energy,  $G(X)$  is the sum of electronic and thermal free energy of the corresponding structure at 298.15 K,  $n$  represents the number of H<sub>2</sub> molecules.

In the equilibrium state, various conformations of VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)<sub>*n*</sub> have different energy and proportion. The

proportion of conformation ( $P_i$ ) was calculated according to the Boltzmann distribution:

$$P_i = N_i \left( \sum_j N_j \right)^{-1} = e(-E_i/RT) \left( \sum_j e(-E_j/RT) \right)^{-1} = Q_i Q^{-1} \quad (3)$$

where  $N$  is the number of conformation,  $E$  is the energy of conformation,  $T$  represents the temperature (Kelvin),  $R$  is the ideal gas constant, and  $Q$  is the partition function.

Spin multiplicity, vibrational frequencies, ionization energy, and electron affinity of VC<sub>6</sub>H<sub>6</sub> were calculated to test the reliability of our calculations. The range-separated hybrid DFT method (wB97XD)<sup>57</sup> was used. The larger Pople-style orbital basis sets 6-311G++(3df,3pd) and diffuse functions in standard basis set aug-cc-pVTZ for C, H, and large-core relativistic Stuttgart–Dresden effective core potential (SDD)<sup>58</sup> basis set for V atom were included.

As shown in Table 1, both the results using B3LYP/6-31G+(d,p) and wB97XD/6-311G++(3df,3pd) show that VC<sub>6</sub>H<sub>6</sub> is quartet state and the vibrational frequencies of VC<sub>6</sub>H<sub>6</sub> are in good agreement with the experimental values.<sup>48</sup> The ionization energies and electron affinities of VC<sub>6</sub>H<sub>6</sub> in Table 2 using B3LYP/6-31G+(d,p), B3LYP/aug-cc-pVTZ and wB97XD/6-311G++(3df,3pd) are in good agreement with the experimental values in ref. 51 and 53. The C–C bond lengths and the C–H bond lengths of VC<sub>6</sub>H<sub>6</sub> using B3LYP/6-31+g(d,p) are 1.40–1.56 Å and 1.08–1.10 Å, respectively, which coincide well with the theoretical results by Duncan.<sup>54</sup> These values indicate the scheme of B3LYP/6-31+g(d,p) is a good compromise between accuracy and computational effort.

Moreover, the adsorption processes of H<sub>2</sub> molecules on TM decorated carbon nanomaterials include Kubas-type bonding, H<sub>2</sub> dissociation, H atom migration, and even strong C–H bonds producing. Both our previous researches<sup>52</sup> and other group's reports<sup>59–61</sup> prove that the B3LYP method is appropriate for obtaining both reliable structures and potential energy surfaces. Firstly, B3LYP functional is very valid for estimating the H<sub>2</sub> storage property of Ti-acetylene/ethylene compounds.<sup>59–61</sup> Secondly, the B3LYP method employing a 6-31+G(d,p) basis set was used to study the hydrogen storage capacity of alkali metal ion decorated boric acid.<sup>62</sup> Thirdly, the investigation of the stepwise adsorption energies of hydrogen on TiC<sub>6</sub>H<sub>6</sub> showed the M06-2X functional was not preferred and the B3LYP functionals with 6-31+g(d,p) basis sets gave an impressive agreement with the accurate results.

## 3. Results and discussion

### 3.1 Optimized configurations of VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)<sub>*n*</sub> (*n* = 1–4)

Optimized configurations of VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)<sub>*n*</sub> (*n* = 1–4) and relative free energies at 298.15 K and 1 atm are presented in Fig. 1, 3–5, respectively. Thermodynamic data show that the configurations in the quartet state are lower in energy than the corresponding doublet state except for **1c**. The most stable structure is the **1a(Q)**, which is 8.25 kcal mol<sup>−1</sup> lower in energy than the doublet state. **1a** with the dissociated H<sub>2</sub> molecule is mentioned in ref.



Table 1 Spin multiplicity, energy differences  $\Delta$  (in eV) between doublet state and quartet state, and vibrational frequencies of VC<sub>6</sub>H<sub>6</sub> (in cm<sup>-1</sup>)

Functional	Multi.	$\Delta$ (eV)	$\nu_{\text{o-p}}(\text{CH})^a$	$\nu_{\text{s}}(\text{CC})$	$\nu_{\text{i-p}}(\text{CH})$	$\nu(\text{CC})$
B3LYP/6-31G+(d,p)	2	0.07				
	4	0.00	769.05	956.3	1319.34	1420.15
B3LYP/6-311G++(3df,3pd)	2	0.30				
	4	0.00	734.10	924.20	1368.27	1507.34
B3LYP/aug-cc-pVTZ	2	0.11				
	4	0.00	679.54	928.29	1341.32	1500.48
wB97XD/6-311G++(3df,3pd)	2	2.64				
	4	0.00	760.51	947.81	1329.71	1426.20
wB97XD/aug-cc-pVTZ	2	1.61				
	4	0.00	781.87	974.09	1348.03	1506.89
Experiments <sup>54</sup>			758.00	958.00	1306.00	1460.00

<sup>a</sup> Vibrational modes:  $\nu_{\text{o-p}}(\text{CH})$  = C-H out of plane bending;  $\nu_{\text{s}}(\text{CC})$  = symmetric C-C stretching;  $\nu_{\text{i-p}}(\text{CH})$  = C-H in-plane rocking;  $\nu(\text{CC})$  = asymmetric C-C stretching.

Table 2 Ionization energy (eV) and electron affinity (eV) of VC<sub>6</sub>H<sub>6</sub>

Functional	Ionization energy (eV)	Electron affinity (eV)
B3LYP/6-31+G(d,p)	6.44	0.62
B3LYP/6-311G++(3df,3pd)	6.46	0.40
B3LYP/aug-cc-pvtz	6.44	0.65
wB97XD/6-311G++(3df,3pd)	6.59	0.65
wB97XD/aug-cc-pVTZ	5.98	0.70
Experiments	6.30 ± 0.50 (ref. 51)	0.62 ± 0.07 (ref. 53)

31 **1b** with the CH<sub>2</sub> group is more stable than the **1c** with molecular H<sub>2</sub>. It indicates hydrogen dissociation, H migration, and even formation of the C-H bond are favorable thermodynamically. Chemisorption forming C-H or V-H bonds is usually stronger than physisorption forming V-H<sub>2</sub> unit. Then, it's easy to understand that structure **1a** with V-H bonds and **1b** with a C-H bond is more stable than structure **1c**. The configurations of **1d**, **1e**, and **1f** have two CH<sub>2</sub> groups. The original C<sub>6</sub>H<sub>6</sub> has a little deformation and the longest V-C bond length increases

from 2.32 Å to 2.94 Å due to the formation of the CH<sub>2</sub> groups. Obviously, the forming of the C-H bond causes a great deformation of the C<sub>6</sub>H<sub>6</sub> unit. The preferred site of one H atom in VC<sub>6</sub>H<sub>6</sub> is determined by comparing the two structures in Fig. S2.† The binding energy of H to the V site is 2.83 eV, which is larger than that of H to the C site (1.82 eV). This indicates that the H atoms prefer to bind at the on-top V site. That's maybe why **1a** with the V-H bonds is more stable than **1b** with a C-H bond.

The dissociation of the first H<sub>2</sub> was spontaneous on most of Sc/Ti/V decorated carbon nanostructures.<sup>35–42</sup> To understand the dissociation process, Fig. 2 shows the partial orbital density state (PDOS) of V and adsorbed H<sub>2</sub> in **1c** (VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)), and **1a** (VC<sub>6</sub>H<sub>6</sub>(2H)). Effective intermolecular bonding leads to bonding orbits have lower energies. Two parts interact strongly when electrons filling in these bonding orbits. The three principles of effective bonding include matching symmetry, energy proximity, and maximum overlap between orbits. For **1c**, the orbital in the energy of -13.00 eV mainly comes from the s orbits of H<sub>2</sub> and the other orbitals of VC<sub>6</sub>H<sub>6</sub> are almost unaffected by the hydrogen molecule. The larger energy difference between the orbitals from V and the H<sub>2</sub> causes weak interaction. For **1a**, the localized 3d orbitals of V in VC<sub>6</sub>H<sub>6</sub> mix with s orbits from hydrogen atoms easily in energies of -6.00–7.50 eV. So, VC<sub>6</sub>H<sub>6</sub> has a strong interaction with the H atoms rather than a hydrogen molecule.

The structures in Fig. 3 include the configurations with one CH<sub>2</sub> group (**2d**), two CH<sub>2</sub> groups (**2e**, **2g**, **2h**), and three CH<sub>2</sub> groups (**2a**, **2f**, **2i**). The **2b** structure contains an activated hydrogen molecule and two V-H bonds, which was mentioned in previous literature.<sup>40</sup> **2a** and **2b** structures have an energy difference of only 0.14 kcal mol<sup>-1</sup> at the B3LYP level.

This little energy difference indicates **2b** inclines to form more stable **2a**. For the structure shown in Fig. 3, the bond length of the V-H bond is 1.67–1.74 Å for isomers with one H atom but is 1.90–1.95 Å for isomers with H<sub>2</sub>, which is longer than the former. This means that the single H atom has a stronger interaction with metal V. The distance of C-C neighboring CH<sub>2</sub> is lengthened to 1.50–1.56 Å. Besides, the V-C

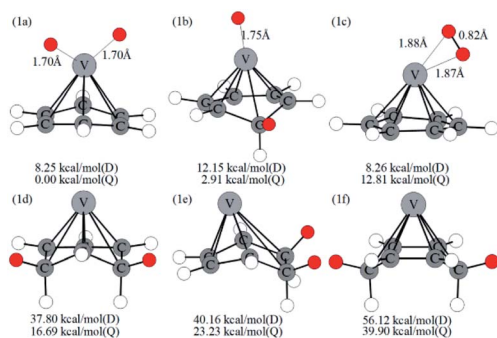


Fig. 1 Optimized configurations of VC<sub>6</sub>H<sub>6</sub>-H<sub>2</sub> at the B3LYP/6-31+G(d,p) level and relative free energies at 298.15 K (in kcal mol<sup>-1</sup>). D and Q represent the doublet state and quartet state, respectively. The red circle means adsorbed hydrogen.



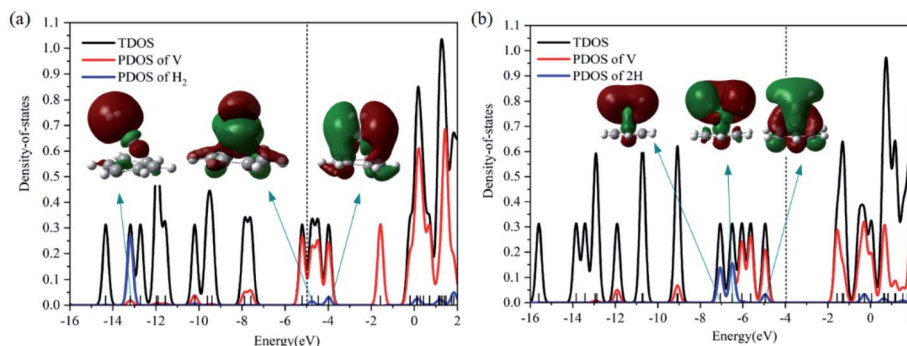


Fig. 2 The total DOS of (a) 1c(VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)), (b) 1a(VC<sub>6</sub>H<sub>6</sub>(2H)) and the PDOS of V and H<sub>2</sub>.

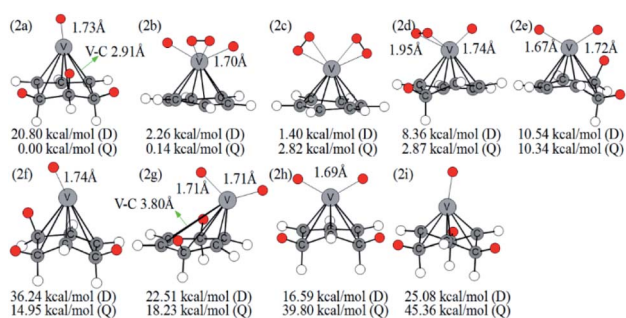


Fig. 3 Optimized configurations of various isomers of VC<sub>6</sub>H<sub>6</sub>-2H<sub>2</sub> at the B3LYP/6-31+G(d,p) level and relative Gibbs free energies at 298.15 K (in kcal mol<sup>-1</sup>). The red circle means adsorbed hydrogen.

bond adjacent to three CH<sub>2</sub> groups in 2a is stretched from 2.28 Å to 2.91 Å, and causing the metal V atom is tilted to one side.

The optimized VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)<sub>3</sub> are displayed in Fig. 4. Notably, the 3a with not CH<sub>2</sub> groups is the most stable doublet isomer

due to its higher symmetry (C<sub>3v</sub>). From the perspective of overlooking, it can be seen that the position of H<sub>2</sub> molecules corresponds to the C-C bond in the six-membered ring. There are two configurations with one CH<sub>2</sub> group (3e, 3f), six configurations with two CH<sub>2</sub> groups (3i, 3l, 3m, 3n, 3p, 3q), five configurations with three CH<sub>2</sub> groups (3d, 3g, 3j, 3o, 3r), and three configurations with four CH<sub>2</sub> groups (3b, 3h, 3k). Thus, the structures with the adjacent CH<sub>2</sub> groups are more stable.

A complex containing dissociated H<sub>2</sub> molecules (with V-H bond) is always more stable than the corresponding complex with activated H<sub>2</sub> molecules. For example, 1a with the dissociated H<sub>2</sub> molecule is more stable than the 1c with molecular H<sub>2</sub>; the 2b structure contains an activated hydrogen molecule and two V-H bonds is more stable than the 2c with two molecular H<sub>2</sub> and so on. However, the reverse appears in the VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>)<sub>3</sub> isomers. Firstly, calculations at different theoretical levels confirm our results. As shown in Table S2,<sup>†</sup> both the results

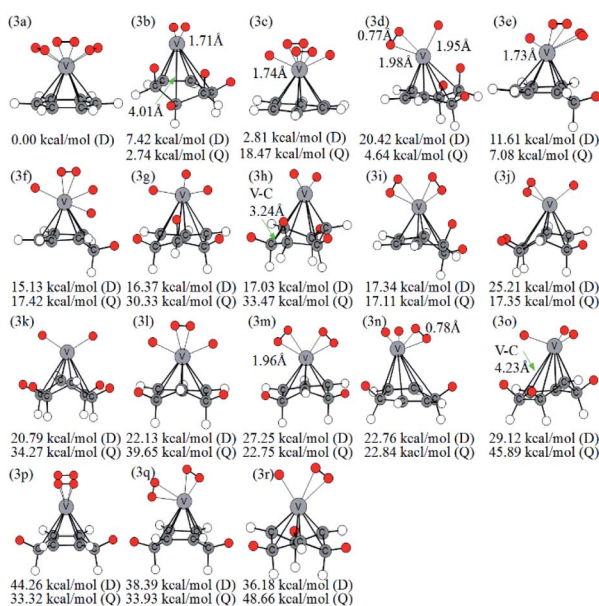


Fig. 4 Various configurations of VC<sub>6</sub>H<sub>6</sub>-3H<sub>2</sub> at the B3LYP/6-31+G(d,p) level and relative Gibbs free energies at 298.15 K (in kcal mol<sup>-1</sup>). The red circle means adsorbed hydrogen.

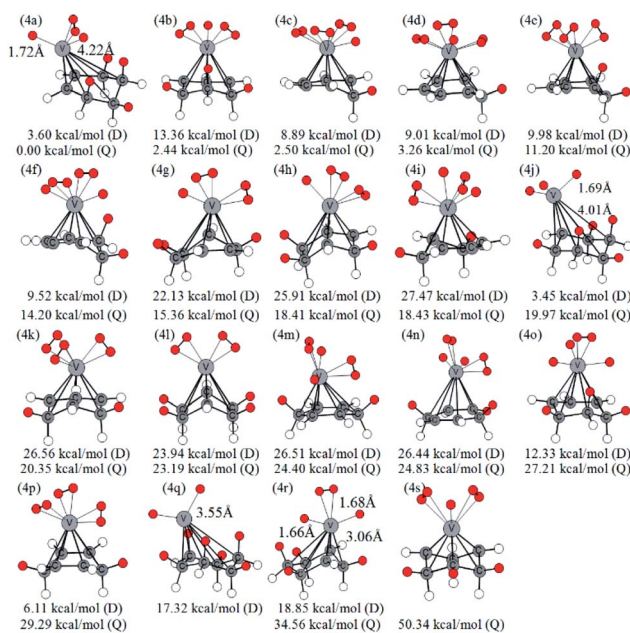


Fig. 5 Optimized configurations of various isomers of VC<sub>6</sub>H<sub>6</sub>-4H<sub>2</sub> at the B3LYP/6-31+G(d,p) level and relative Gibbs free energies at 298.15 K (in kcal mol<sup>-1</sup>). The red circle means adsorbed hydrogen.



using B3LYP/6-31G+(d,p), B3LYP/6-311G++(3df,3pd), B3LYP/aug-cc-pVTZ, wB97XD/6-311G++(3df,3pd) and wB97XD/6-311G++(3df,3pd) show that **3a** with three molecular H<sub>2</sub> molecules is more stable than the **3c** with the dissociated H<sub>2</sub> molecule. Secondly, detailed analyses of the symmetry and energy of deformation are carried out to comment on why this is the case. The symmetry of optimized VC<sub>6</sub>H<sub>6</sub>(D) is C<sub>6v</sub>. As shown in Table S2,† the VC<sub>6</sub>H<sub>6</sub> unit in structure **3a** is C<sub>6v</sub> symmetry while that in structure **3c** is C<sub>2</sub> symmetry. That's mean, after adsorbing 3H<sub>2</sub>, the VC<sub>6</sub>H<sub>6</sub> unit in structure **3a** is nearly no change. Therefore, the energy of deformation ( $\Delta G_R$ ) of VC<sub>6</sub>H<sub>6</sub> and hydrogen binding energy between the VC<sub>6</sub>H<sub>6</sub> unit and 3H<sub>2</sub> unit in **3a** and **3c** ( $\Delta G_H$ ) are defined.

$$\Delta G_R = G(\text{VC}_6\text{H}_6 \text{ unit in } \mathbf{3a}/\mathbf{3c}) - G(\text{VC}_6\text{H}_6)$$

$$\Delta G_H = [G(\text{VC}_6\text{H}_6 \text{ unit in } \mathbf{3a}/\mathbf{3c}) + G(3\text{H}_2 \text{ unit in } \mathbf{3a}/\mathbf{3c}) - G(\mathbf{3a}/\mathbf{3c})]/3$$

The values of  $\Delta G_R$  and  $\Delta G_H$  are listed in Table S3.† The deformation energy of **3c** is 0.28 eV, which is greater than that of **3a** (0.23 eV). When deformation energy is not taken into account, the hydrogen binding energy between the VC<sub>6</sub>H<sub>6</sub> unit in **3c** and 2H<sub>2</sub>-2H unit is 2.52 eV, which is greater than that between the VC<sub>6</sub>H<sub>6</sub> unit in **3a** and 3H<sub>2</sub>(0.72 eV). This is consistent with the common understanding.

Similarly, Fig. 5 lists several optimized isomers of VC<sub>6</sub>H<sub>6</sub>-4H<sub>2</sub> complexes. Notably, the structure with four activated hydrogen molecules is very unstable. The most stable configuration **4a** is composed of four adjacent CH<sub>2</sub> groups with an activated hydrogen molecule and two H atoms. Among many other configurations, **4c**, **4d**, and **4f** have one CH<sub>2</sub> group are, **4e**, **4i**, **4k**, **4m**, and **4p** have two CH<sub>2</sub> groups, **4b**, **4g**, **4h**, **4n**, **4o**, and **4s** have three CH<sub>2</sub> groups, **4a**, **4l**, and **4r** have four CH<sub>2</sub> groups, **4j** has five CH<sub>2</sub> groups, and **4q** has six CH<sub>2</sub> groups. The energy difference between **4g** and **4h** is 3.05 kcal mol<sup>-1</sup>, though both have three CH<sub>2</sub> groups and two activated hydrogen molecules. It indicates that the energy of structures also depends on the direction of the activated hydrogen molecule. **4q** and **4j** have six and five consecutive CH<sub>2</sub> groups, respectively, but their energy is not the lowest. This may be due to the steric hindrance effect formed by the consecutive CH<sub>2</sub> groups. For VC<sub>6</sub>H<sub>6</sub>-nH<sub>2</sub> (n = 1, 3), the most stable isomers have no CH<sub>2</sub> group. For VC<sub>6</sub>H<sub>6</sub>-nH<sub>2</sub> (n = 2,4), the most stable isomers have CH<sub>2</sub> groups, and in which CH<sub>2</sub> groups are adjacent. These prompt us to think strongly about whether the C-H bond could be formed easily.

### 3.2 The optimal chemisorption pathway of multiple H<sub>2</sub> molecules on the VC<sub>6</sub>H<sub>6</sub>

**3.2.1 Chemisorption of the first H<sub>2</sub> molecule.** As shown in Fig. 6, VC<sub>6</sub>H<sub>6</sub> adsorb the first H<sub>2</sub> in molecular form firstly. The single H<sub>2</sub> dissociates into two H atoms *via* the TS **1c/1a**. For the quartet state, the dissociation is exothermic by 13.22 kcal mol<sup>-1</sup>, and its barrier is only 2.72 kcal mol<sup>-1</sup>. For the doublet state, the dissociation is endothermic by 0.02 kcal mol<sup>-1</sup>, and its barrier is 6.53 kcal mol<sup>-1</sup>. It indicates

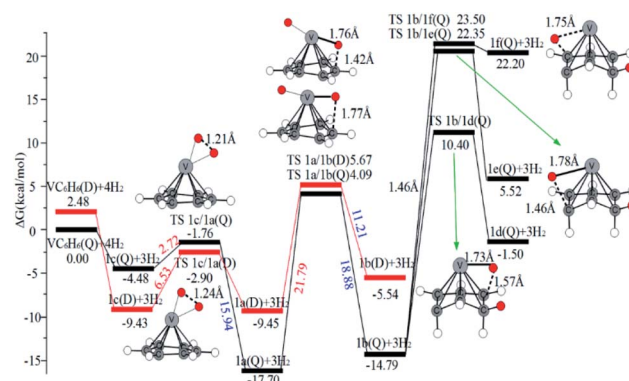


Fig. 6 The Gibbs free energy profiles of the first H<sub>2</sub> molecule adsorbed on VC<sub>6</sub>H<sub>6</sub>. The red and black lines represent doublet (D) and quartet (Q) states, respectively. The energy barriers are highlighted in red for the forward reaction and blue for the backward reaction.

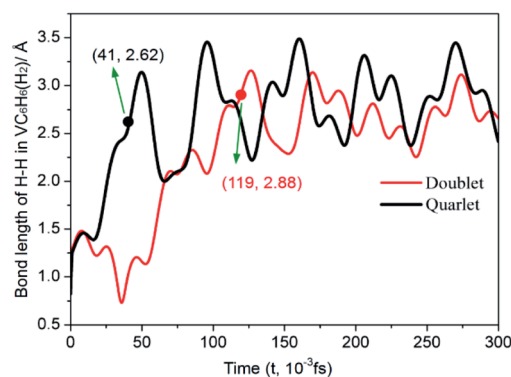


Fig. 7 Time evolution trajectories of the H-H in VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>) at 300 K. The bond lengths are given in Å.

that the H<sub>2</sub> dissociation in **1c(Q)** is more favorable than that in **1c(D)**, which is also confirmed by the first-principles molecular-dynamics MD simulations up to 0.3 fs. The time evolution trajectories of H-H in VC<sub>6</sub>H<sub>6</sub>(H<sub>2</sub>) at 300 K are presented in Fig. 7. After 0.04 fs, the H-H bond in **1c(Q)** elongates from 0.824 Å to 2.621 Å (the length of the H-H bond in **1a(Q)**). While H-H bond in **1c(D)** is shortened firstly and then elongates from 0.869 Å to 2.876 Å (the length of H-H bond in **1a(D)**) until 0.12 fs.

One of the dissociated H atoms in **1a(Q)** will migrate to form CH<sub>2</sub> group with a barrier of 21.79 kcal mol<sup>-1</sup>, which is endothermic by 2.91 kcal mol<sup>-1</sup> and slow. At 298.15 K, the overall conformation analysis shows that the **1a(Q)** and **1b(Q)** of VC<sub>6</sub>H<sub>6</sub>-H<sub>2</sub> are 99.3% and 0.70%, respectively. IR stability calculations ensure that the structures **1a(Q)** and **1b(Q)** are energy minima without imaginary frequency (see Fig. S4 of the ESI†). Two main H modes for **1a(Q)** are symmetric and anti-symmetric stretching vibrations, respectively corresponding frequencies of 1606.48 and 1645.80 cm<sup>-1</sup>. One main H mode vibration frequency for **1b(S)** is 1582.26 cm<sup>-1</sup>. The three unique modes should be present in the Raman/IR spectra of a successfully synthesized material.



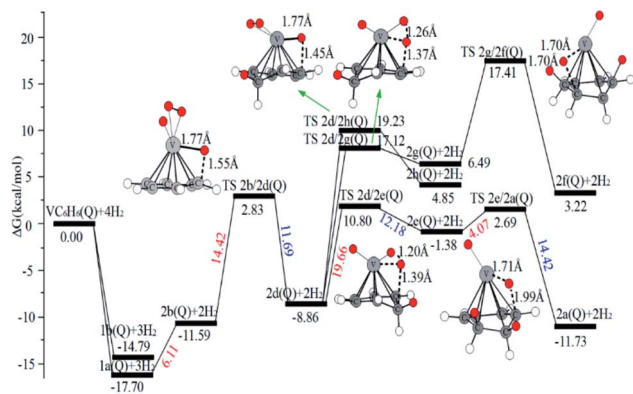


Fig. 8 The Gibbs free energy profiles of the second H<sub>2</sub> molecule adsorption on the VC<sub>6</sub>H<sub>6</sub> complex. The energy barriers are highlighted in red for the forward reaction and blue for the backward reaction.

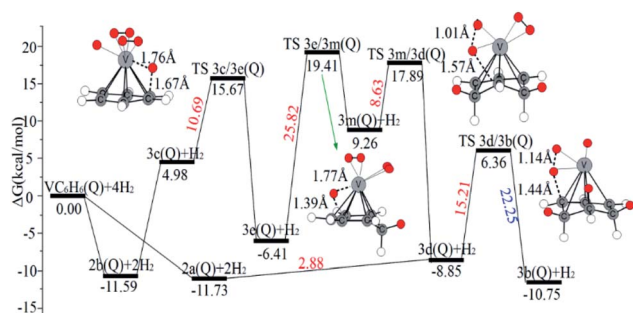


Fig. 9 The Gibbs free energy profiles of the third H<sub>2</sub> molecule adsorption on the VC<sub>6</sub>H<sub>6</sub> complex. The energy barriers are highlighted in red for the forward reaction and blue for the backward reaction.

**3.2.2 Chemisorption of the second H<sub>2</sub> molecule.** The intermediate **1a(Q)** is the precursor of the second H<sub>2</sub> molecule adsorption (Fig. 8). **2b(Q)** dihydrogen complex is formed by the H<sub>2</sub> molecule adsorption on V atom in **1a(Q)**. H atom in **2b(Q)** migrates to C atom through TS **2b/2d(Q)** with a barrier of 14.42 kcal mol<sup>-1</sup>. Another H atom on **2d(Q)** continues to migrate to form the other CH<sub>2</sub> group in **2e(Q)**. The reaction barrier of **2e(Q)** → **2a(Q)** is 4.07 kcal mol<sup>-1</sup>. The energy difference between **2a(Q)** and **2b(Q)** is 0.14 kcal mol<sup>-1</sup>, which is very small. Similarly, conformations population analysis at 298.15 K shows that **2a(Q)** and **2b(Q)** account for 55.83% and 44.17%, respectively, which indicates they can coexist. The formations of **2g**, **2h**, and **2f** are unfavorable due to they are endothermic.

**3.2.3 Chemisorption of the third and the fourth H<sub>2</sub> molecules.** There are a series of processes including hydrogen molecules adsorption, hydrogen molecules dissociate, and H atomic migration. It was observed in Fig. 9 that the process from **2b(Q)** to **3b(Q)** has energy barriers of 25.82 kcal mol<sup>-1</sup>. There is another easier pathway from **2a(Q)**, in which the H<sub>2</sub> molecule can be absorbed on the V atom to form **3d(Q)**. Compared with **2b(Q)** + H<sub>2</sub> → **3c(Q)**, **2a(Q)** + H<sub>2</sub> → **3d(Q)** is more favorable. The H<sub>2</sub> molecule in **3d(Q)** can be dissociated. At the same time, one H atom of the H<sub>2</sub> molecule migrates with the barrier of 15.21 kcal mol<sup>-1</sup>.

When the fourth H<sub>2</sub> molecule continues to approach the structure **3b(Q)**, the consecutive adsorption energies ( $\Delta E_{n\text{-ZPE}}$ ) is 2.18 kcal mol<sup>-1</sup> (0.09 eV). The **4a(Q)** forms **4j(D)** through a spin crossover. When **4j(D)** is used as a reactant, it is unfavorable to generate **4q(D)** (Fig. 10).

The optimal chemisorption pathways of H<sub>2</sub> molecules on VC<sub>6</sub>H<sub>6</sub> are shown in Fig. 11. (More detailed information regarding optimized cartesian coordinates and computed sum of electronic and thermal free energies of mentioned structures see the ESI†). When the pressure of hydrogen increases, H<sub>2</sub> molecules adhering to VC<sub>6</sub>H<sub>6</sub> can migrate continuously to form CH<sub>2</sub> groups, and finally VC<sub>6</sub>H<sub>11</sub>-3H (**4j**) is formed. Gibbs free energy calculations show that the whole reaction is exothermic by 2.83 kcal mol<sup>-1</sup> at 298.15 K. The generation of **4q(D)** is endothermic by 11.14 kcal mol<sup>-1</sup>, which is unfavorable in thermodynamics. The dissociation and migration of the second H<sub>2</sub> is the rate-determining step in the whole reaction with a barrier of 19.66 kcal mol<sup>-1</sup>. In turn, the complex VC<sub>6</sub>H<sub>11</sub>-3H will dehydrogenate continuously until VC<sub>6</sub>H<sub>6</sub> when the hydrogen pressure decreases. The energy barrier of the critical speed step (the migration of H atom in **3d(Q)**) is 17.11 kcal mol<sup>-1</sup>. Hence the hydrogen chemisorption adsorption and desorption on the VC<sub>6</sub>H<sub>6</sub> complex could run smoothly with the hydrogen storage of 5.97 wt%, simply regulated by increasing/decreasing the hydrogen pressure.

As the discussion above, the chemisorptions pathway of H<sub>2</sub> molecules on VC<sub>6</sub>H<sub>6</sub> at 298.15 K indicates that: (1) H<sub>2</sub> molecules attached to VC<sub>6</sub>H<sub>6</sub> can be dissociated, and H atoms migrate continuously to form CH<sub>2</sub> groups. (2) Spin crossover mainly occurs in the pathway of adsorption of the first and fourth hydrogen molecules. (3) The optimal chemisorption pathway should be VC<sub>6</sub>H<sub>6</sub>(Q) → **1c(D)** → **1a(Q)** → **2b(Q)** → **2d(Q)** → **2e(Q)** → **2a(Q)** → **3d(Q)** → **3b(Q)** → **4a(Q)** → **4j(D)** (VC<sub>6</sub>H<sub>11</sub>-3H). (4) Gibbs free energy calculations show that the overall reaction to give the hydrogenation product **4j** (VC<sub>6</sub>H<sub>11</sub>-3H) is exothermic by 2.83 kcal mol<sup>-1</sup> and has an energy barrier of 19.66 kcal mol<sup>-1</sup>.

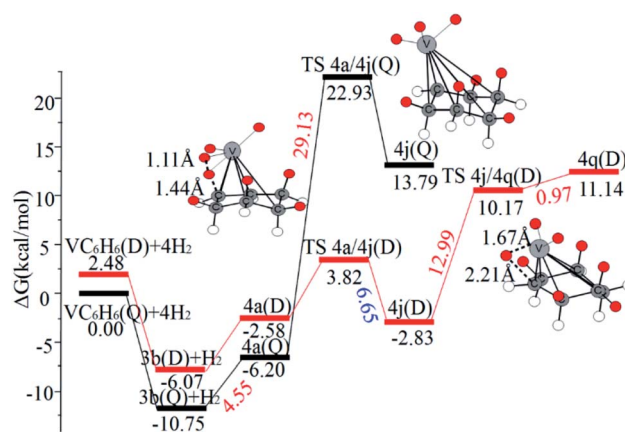


Fig. 10 The Gibbs free energy profiles of the fourth H<sub>2</sub> molecule adsorption on VC<sub>6</sub>H<sub>6</sub>. The energy barriers are highlighted in red for the forward reaction and blue for the backward reaction.



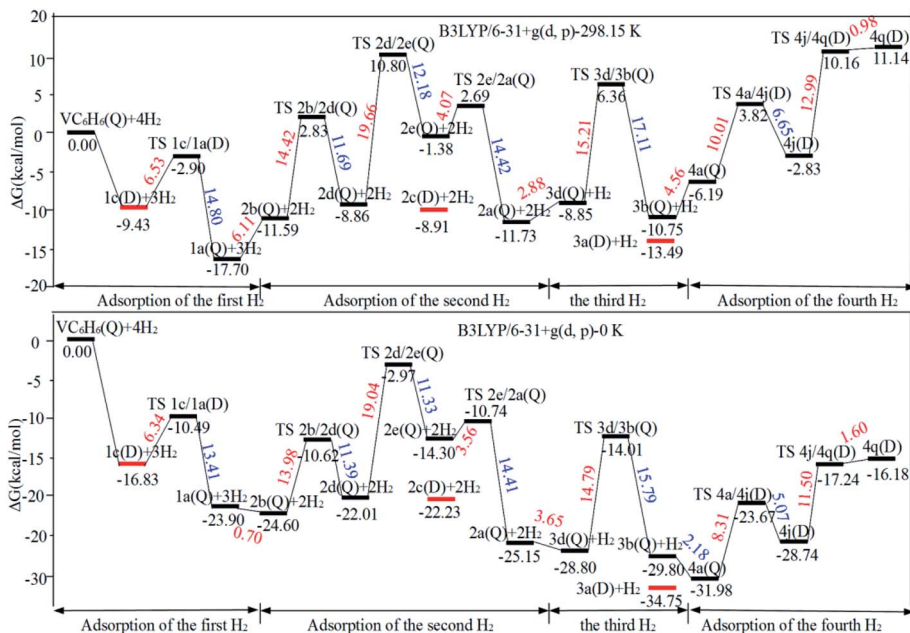


Fig. 11 The optimal chemisorption and physisorption pathways of  $\text{H}_2$  molecules on  $\text{VC}_6\text{H}_6$  at 298.15 K and 0 K. The energy barriers are highlighted in red for the forward reaction and blue for the backward reaction. The red line corresponds to the physisorption structures.

### 3.3 Physisorption of multiple $\text{H}_2$ molecules on the $\text{VC}_6\text{H}_6$

Fig. 12a shows the optimal physical adsorption path of multiple  $\text{H}_2$  molecules on the  $\text{VC}_6\text{H}_6$  complex. The free energy profile is shown in Fig. S5.† For  $n = 1$ ,  $\text{H}_2$  dissociates into two H atoms *via* the transition state TS. Though the single  $\text{H}_2$  dissociation on  $\text{VC}_6\text{H}_6$  is exothermic, the dissociation barrier is  $6.34 \text{ kcal mol}^{-1}$ . Moreover, **3a** is more stable than **3c**. So, the adsorption pathway along  $\text{VC}_6\text{H}_6 \rightarrow \mathbf{1c}(\text{D}) \rightarrow \mathbf{2c}(\text{Q}) \rightarrow \mathbf{3a}(\text{Q})$  pathway will be more favorable thermodynamically.

When all the three hydrogen molecules are adsorbed in molecular form, the consecutive adsorption energies are 0.50, 0.56, 0.45 eV, respectively. And the average hydrogen adsorption energy for  $\text{VC}_6\text{H}_6(\text{H}_2)_3$  is 0.50 eV, which is between physisorption and chemisorption (0.20–0.60 eV). As shown in Fig. 11, the physisorption of the three hydrogen molecules is exothermic by  $13.49 \text{ kcal mol}^{-1}$  at 298.15 K, and need no energy barrier. The hydrogen storage capacity of  $\text{VC}_6\text{H}_6$  is 4.48 wt%. Based on the van't Hoff equation:  $\text{TD} = (E_a/k_B)(\Delta S/R - \ln P)^{-1}$ ,<sup>63</sup>

the three  $\text{H}_2$  can be adsorbed at any temperature under 421 K and 1 atm. Notably, spin multiplicity and the Gibbs free energy correction fully considered here. The temperatures at which  $\Delta G = 0 \text{ eV}/\text{H}_2$  for **1c**(Q), **2c**(Q), **3a**(D) are 480 K, 462 K, and 416 K, respectively (Fig. 12b). It also indicates that three  $\text{H}_2$  molecules can be spontaneously adsorbed on  $\text{VC}_6\text{H}_6$  forming **3a** below 416 K. And three  $\text{H}_2$  can be readily desorbed above 480 K under atmospheric pressure.

## 4. Conclusions

TM-decorated carbon composites grew up to be a new generation of hydrogen storage materials. Most of these researches reported that the dissociation of the first  $\text{H}_2$  was spontaneous on most of Sc/Ti/V-decorated carbon nanostructures. As known that H migration easily occurs on metal sites. Then hydrogenation reaction would also occur during the hydrogen storage on 3d TM-decorated organic complexes. To further address this issue, the process of hydrogen adsorption on synthesized  $\text{VC}_6\text{H}_6$  is focused on answering the question that whether hydrogen molecules are absorbed only or migrate to form C–H bonds.

Optimized configurations of  $\text{VC}_6\text{H}_6(\text{H}_2)_n$  ( $n = 1-4$ ) and relative Gibbs free energies at 298.15 K and 1 atm were presented. For  $\text{VC}_6\text{H}_6-n\text{H}_2$  ( $n = 1, 3$ ), the most stable isomers have no  $\text{CH}_2$  group. For  $\text{VC}_6\text{H}_6-n\text{H}_2$  ( $n = 2, 4$ ), the most stable isomers have adjacent  $\text{CH}_2$  groups. The chemisorptions pathway of  $\text{H}_2$  molecules on  $\text{VC}_6\text{H}_6$  at 298.15 K indicates that  $\text{H}_2$  molecules attached to  $\text{VC}_6\text{H}_6$  can be dissociated, and H atoms migrate continuously to form  $\text{CH}_2$  groups. Gibbs free energy calculations show that the overall reaction giving the hydrogenation product **4j** (D) ( $\text{VC}_6\text{H}_{11}-3\text{H}$ ) is exothermic by  $2.83 \text{ kcal mol}^{-1}$  and has an energy barrier of  $19.66 \text{ kcal mol}^{-1}$ . Hence the

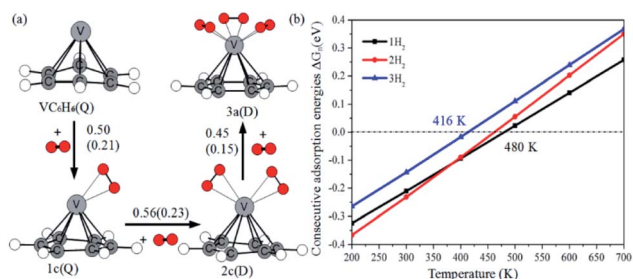


Fig. 12 (a) The consecutive adsorption energies  $\Delta E_n$  ( $\Delta G_n$ ) of multiple  $\text{H}_2$  molecules on the  $\text{VC}_6\text{H}_6$  (in eV), (b) temperature dependence of  $\Delta G_n$  at  $p = 1 \text{ atm}$ .



hydrogen chemisorption adsorption and desorption on the VC<sub>6</sub>H<sub>6</sub> complex could run smoothly with the hydrogen storage of 5.97 wt%, simply regulated by increasing/decreasing the hydrogen pressure. The physisorption along VC<sub>6</sub>H<sub>6</sub> → 1c(D) → 2c(Q) → 3a(Q) will be exothermic by 13.49 kcal mol<sup>-1</sup>. The three H<sub>2</sub> can be adsorbed at any temperature under 416 K and readily desorbed above 480 K at 1 atm. The corresponding hydrogen storage capacity is 4.48 wt%. In summary, both physisorption and chemisorption tend to occur in certain circumstances.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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- 63  $E_a$  is the average adsorption energy,  $k_B$  is the Boltzmann constant  $1.38 \times 10^{-23} \text{ J K}^{-1}$ ,  $R$  is the gas constant  $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $P$  is the equilibrium pressure 1 atm,  $\Delta S$  is the change of the  $\text{H}_2$  entropy from gas to liquid phase.

