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ELECTRONIC STRUCTURE

Quantum Mechanic Study of Hydrogen Chemisorptions on Nanocluster Vanadium Surface

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Abstract—In the present investigation, we have employed the adsorption of H–H at the bcc site of V (100) with use of an ab initio method. The most stable adsorption configuration has been found on transition metal surface with chemisorption energies. Although similar in type and energy, the adsorption on the V (100) surface shows a markedly different optimized geometry. The calculations have performed for small clusters representing three adjacent metal sites. Upon the adsorption, the molecule forms strong covalent bonds with the surface, whereupon the structure of nearby single H–H and H–V bonds change at various positions of top, bridge, and center sites in this model. We have predicted the existence of a new ordered structure comparable in stability to one proposed previously. We confirm the preference of the top approach of adsorption configuration suggested by experiment. Adsorption of H_2 from the top site goes through the same from the bridge and center sites, but the former has a higher energy.

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INTRODUCTION

For better understanding of the mechanism and selectivity of adsorption, it is important to know about the nature of the adsorbed species present under reaction conditions, particularly their role as reaction intermediates or poisoning species, and the adsorbate-metal interactions, particularly the resulting reaction configurations geometrically and electronically [1]. Transition metal surfaces catalyze numerous hydrogenation reactions; for example, hydrogen chemisorptions on Fe (110) [2] is particularly important, not only as a reactant in Fe-catalyzed ammonia synthesis [3], the Fischer–Tropsch reaction [4] (and many others), but also because hydrogen is known to embrittle steels [5, 6], causing fracture and ultimately failure of the steel component. Molecular hydrogen is found to adsorb dissociatively on these surfaces, and the process is strongly exothermic. The following survey of the literature focuses only on the surface adsorption of vanadium, which is the closest-packed surface of body-centered-cubic geometry (bcc).

A number of investigations are carried out on vanadium to examine the effectiveness of this kind of surface barriers on preventing hydrogen absorption and accelerating super permeation [7]. The results are, however, rather complicated and hence not well understood, because most of the experiments were done for polycrystalline specimens with different purities and pretreatments under various vacuum conditions. The calculation indicated that hydrogen adsorption takes place most easily via the on-top site of the atomic array in the [1 0] direction on the V (110) surface, and a hydrogen atom is stably adsorbed at the midpoint between the two vanadium atoms in the array. The adsorption of hydrogen at the V_2O_5 (010) surface was studied by K. Hermann et al. [8]. They confirm that hydrogen can adsorb at any of the five different surface oxygen sites forming a stable surface OH group. Later, Koller et al. studied the oxygen induced (1×5) reconstruction of V (100), achieving very good agreement between experimental and calculated data in finding the most stable adsorption structure [9]. Recently, the influence of carbon impurities on a d-like surface state of V (100) was studied [10].

Vanadium alloys are considered one of the most promising structural materials for fusion reactors because of their high temperature strength, high thermal stress factor, low activation property, and so on [11]. An important concern for this application is the adsorption of hydrogen molecules. Hydrogen is adsorbed on clean vanadium surfaces extremely fast, and then rapidly absorbed by the bulk because of the high diffusivity and solubility of hydrogen atoms in this material [12]. The purpose of our present effort is to undertake ab initio calculations for hydrogen adsorption for the V (100) by use of small nanoclusters consisting of several metal atoms as the models of crystal surfaces, to examine the validity of small nanostructure models, and to find effects of such barriers on the adsorption.

COMPUTATIONAL METHODS

Recent advances in methodology based on the technologies of the pseudo-potential and plane wave basis sets and high-speed computers have now made it possible to obtain quantitative information on surface phenomena. In this work, nanocluster models of the surface and periodic slabs is employed to simulate H_2 adsorbed on the V (100) surfaces. A given crystal is sliced to a slab comprising a set of given planes with several atomic layers. Then the slab was cut by a plane perpendicular or with a given angle to the plane to make a nanocluster consisting of several atoms. In this case, the mutual distances and angles among the atoms forming the cluster were set equal to those found in the crystal and kept constant; namely, no surface relaxation was accounted for surface formation and also hydrogen adsorption. All the models are calculated using the standard quantum-chemical ab initio method. Calculations are carried out at HF level of theory and the nanocluster fragments are considered as doublet molecules with partitioning of the basis sets for a hydrogen molecule described by the standard 6–31G* and 6–31G** basis sets, but for vanadium the standard LANL2DZ basis set is used. To study H_2 adsorption on the V (100) surface, we have modeled the surface with two layers of vanadium at the experimental lattice constant. Vanadium has the body-centered cubic structure with a lattice constant of a = 3.028 Å and two-layer model of the surface that contains fourteen vanadium atoms. The H_2 molecule, one per unit cell, is allowed to approach the vanadium surface along three different symmetrical sites: (1) directly on top of a V atom (top site), (2) on the middle of two nearest neighbor V atoms (bridge site), (3) in the center of the smallest unit structure of the surface (center site). As the smallest structure of V (100)-surface is a square, these three sites are the only symmetrically distinguishable sites. In addition to this, we have also considered some positions inside the vanadium two layers slab (interstitial positions). Then each of these positions are considered by two approaches of chemisorptions. They are as follows: (1) The H_2 molecule approaches vertically to the surface (Vertical approach), and (2) the H_2 molecule approaches parallel to the surface and the bcc lattice vectors (horizontal approach). It is obvious that for the horizontal approach, the hydrogen atoms are at the same distance from the vanadium surface, whereas for the vertical approach one hydrogen atom is closer to the surface than the other atom. For geometry optimization, the computations are performed with the Gaussian 98 package.

RESULTS AND DISCUSSION

The developments of modern surface science provide an opportunity to investigate the interaction between catalysts and molecules or atoms in the atomic scale. However, quantum chemical computations of molecules containing transition metal atoms have proven to be more difficult than those for first and second row atoms [13].

The interaction of hydrogen with transition metal surfaces is of great fundamental and practical interest in metallurgy. To understand fundamental roles of these surface barriers on hydrogen adsorption and super permeation, the adsorption of hydrogen molecules on the surfaces of vanadium, has studied from first principles in the present study.

The use of the stability condition established above (relation 1) enables us to determine the minimum energy of H_2 adsorption where the various configurations discussed in this study could be present at the surface of a V (100) sample, in equilibrium with the H_2 gas phase.

In the set of calculations reported here, the adsorption energy of the hydrogen molecule is computed as

$$\mathbf{Eads} = \mathbf{E}\,(H_2) + \mathbf{E}\,(\text{V-surface}) - \mathbf{E}\,(H_2/\text{V-surface}). \quad (1)$$

The third term in equation 1 is the total energy of the H_2/V-surface super molecule, and the first and second terms refer to the total energy of the separated fragments.

The nanocluster is used as a model of the crystal surface to evaluate the adsorption energy of a hydrogen molecule on the metal surface, where the distance between two hydrogen atoms and the height of H–H bond from the surface are calculated.

We start by describing the chemisorption process of H_2 at different sites on V-surfaces and calculating the geometry coordination. Vanadium has a body-centered cubic structure with a lattice constant of a = 3.032 Å, and there are three high-symmetry sites on V (100) (Fig. 1): (1) top site, (2) bridge site, and (3) center site. Consider first the top sites. In the top sites there are two different approaches for each site. The first, for the vertical top site (Fig. 1a), to H_2 molecule is allowed to approach the vanadium surface in different distances (1.54, 1.74, 1.94, 2.04, 2.09, 2.14) Å and their chemisorption energies are calculated at the HF/LANL2DZ,6–31G* and HF/LANL2DZ,6–31G** level of theory (Table 1). For every two basis sets approaches, the chemisorption distance (Rd) from the vanadium surface to the H_2 is 2.04 Å, while the chemisorption energies are 1.502 and 1.839 eV, respectively. In the next step, a chemisorption energy distance of 2.04 Å is calculated with an increase in the distance between the hydrogen atoms of (0.791, 0.841 and 0.941) Å. In this state, the chemisorptions of H_2 along the vertical approach behave differently for the HF/LANL2DZ, 6–31G*, and HF/LANL2DZ, 6–31G** cases. For the HF/LANL2DZ, 6–31G* case, H_2 remains as a molecule, while for HF/LANL2DZ, 6–31G** case, the H_2 molecule dissociates. The distance between the hydrogen atoms and chemisorption energy for HF/LANL2DZ, 6–31G** are 0.791 A and

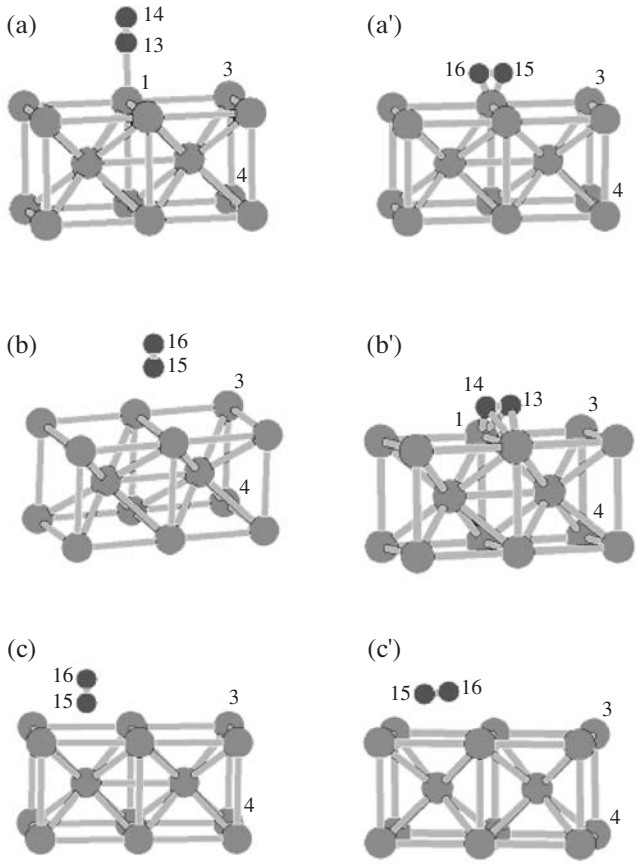

Fig. 1. Optimized structures of adsorption (a) vertical (a') horizontal top sites, (b) vertical (b') horizontal bridge sites, and (c) vertical (c') horizontal center sites on V (100)-surface.

2.125 eV, respectively, which implies partial dissociation of H.

For the horizontal top site (Fig. 1a'), the H_2 molecule is allowed to approach the vanadium surface in different distances (1, 1.54, 1.94, 2.04, 2.14, and 2.19) Å and their chemisorption energies are calculated at the HF/LANL2DZ,6–31G* and HF/LANL2DZ,6–31G** level of theory. For the HF/LANL2DZ, 6–31G* and HF/LANL2DZ, 6–31G** cases the chemisorption distances (Rd) from the vanadium surface to the H_2 are 1.94 and 2.14 Å, while the chemisorption's energies are 2.107 and 2.367 eV, respectively. In next step, chemisorption energies in distances of 1.94 and 2.04 Å are calculated with an increase in the distance between the hydrogen atoms (0.791, 0.841, 0.941, 1 and 2) Å. In this state, the chemisorptions of H_2 along the horizontal top sites approach behaved the same for the HF/LANL2DZ, 6–31G* and HF/LANL2DZ, 6–31G** cases, and in both cases H_2 remains a molecule; the chemisorption energies are 2.107 and 2.367 eV, respectively.

For the bridge site, the chemisorptions of H_2 along the horizontal and the vertical approaches behave the same and H_2 remains a molecule for both states. For the vertical bridge site, (Fig. 1b) at different distances (1.44, 1.49, 1.54, 1.60, 1.74, 1.84, 1.94and 2.04) Å, their chemisorptions energy are calculated. For the HF/LANL2DZ, 6–31G* and HF/LANL2DZ,6–31G** cases, the chemisorption distances (Rd) from the vanadium surface to the H_2 are 1.74 and 1.94 Å, and the chemisorption energies are 1.767 and 1.527 eV, respectively (Table 2).

In the horizontal bridge site, (Fig. 1b') different distances (0.45, 0.55, 0.65, 0.75, 0.85, 1, 1.15 and 1.26) Å are calculated and the chemisorption distances (Rd) from the vanadium surface to the H_2 are 1 and 1.15 Å, and the chemisorption energies are 0.606 and 1.205 eV, respectively.

In general, chemisorptions at the bridge site are considerably stronger than at the top site. This results from fact that hydrogen atoms are relatively much closer to the vanadium surface in bridge sites compared to the top sites. For the bridge site at the horizontal approach, hydrogen atoms are closer to the vanadium surface (Rd = 1 and 1.15 Å) than that of the top site (Rd = 1.94 and 2.14 Å), and the chemisorption energy is lower. The reason might be that the nearest V–H distances in the bridge site are smaller than the top site (Figs. 2a, 2a' and 2b, 2b').

In the center site, for the vertical center site (Fig. 1c), to the H_2 molecule is allowed to approach the vanadium surface at different distances (0.5, 1, 1.34, 1.54, 1.64, 1.74, 1.84) Å, and their chemisorption energies are calculated at the HF/LANL2DZ,6–31G* and HF/LANL2DZ,6–31G** levels of theory (Table 3). For both cases the chemisorption distances (Rd) from the vanadium surface to the H_2 are 1.64 and 1.74 Å and the chemisorption energies are 1.256 and 1.749 eV, respectively, and for the vertical approach (Fig. 1c'), like bridge sites, the chemisorptions of H_2 along the vertical approach with every two basis sets behave the same and H_2 remains a molecule for both states. But in the horizontal center site, to the H_2 molecule is allowed to approach the vanadium surface at different distances (0.55, 0.75, 0.95, 1.05, 1.15, 1.20, 1.25, 1.35, 1.55) 2Å, and their chemisorption energies are calculated at the HF/LANL2DZ, 6–31G* and HF/LANL2DZ, 6–31G** levels of theory. For both cases the chemisorption distances (Rd) from the vanadium surface to the H_2 are 1.20 and 1.15 Å and the chemisorption energies are 0.056 and 1.053 eV, respectively. In the next step, chemisorption energies at a distance of 1.20 and 1.15 Å are calculated with an increase in the distance between the hydrogen atoms (0.791, 0.841 and 0.941) Å. In this state, the chemisorptions of H_2 along the horizontal approach behaved differently for the HF/LANL2DZ, 6–31G* and HF/LANL2DZ, 6–31G** cases. For the HF/LANL2DZ, 6–31G** case, H_2 remains as a mole-

Table 1. Structural parameters and adsorption energies of H_2 onto the V (100) surface at the HF/LANL2DZ – 6–31G* or 6–31G** for vertical and horizontal top sites

Vertical top site

Rd[a]/Å	R(13,3)/Å	<(13, 3, 1) (Deg)	<(14, 13, 3) (Deg)	R(H–H)/Å	E[b]	E[c]	Eads[d]	Eads[e]
1.54	3.401	26.919	117.300	0.741	–26906.613	–26909.791	–2.288	0.767
1.74	3.496	29.847	120.229	0.741	–26907.344	–26909.630	–1.552	0.607
1.94	3.600	32.610	122.991	0.741	–26910.144	–26910.830	1.244	1.806
2.04	3.655	33.930	124.308	0.741	–26910.402	–26910.861	1.502	1.838
2.09	3.683	34.572	124.953	0.741	–26907.279	–26908.512	–1.621	–0.511
2.14	3.712	35.210	125.588	0.741	–26909.531	–26910.692	0.630	1.668
2.04	3.655	33.930	124.308	0.791	–26908.216	–26911.148	–0.684	2.125
2.04	3.655	33.930	124.308	0.841	–26910.219	–26908.223	1.319	–0.800
2.04	3.655	33.930	124.308	0.941	–26909.818	–26909.960	0.917	0.937

Horizontal top site

Rd[a]/Å	R(15,4)/Å	<(15, 4, 3) (Deg)	<(16, 15, 4) (Deg)	R(H–H)/Å	E[b]	E[c]	Eads[d]	Eads[e]
1	4.831	33.430	123.423	0.741	–26898.894	–26898.864	–10.006	–10.159
1.54	5.290	30.202	120.161	0.741	–26909.539	–26907.527	0.638	–1.496
1.94	5.640	28.164	118.127	0.741	–26911.008	–26906.735	2.107	–2.288
2.04	5.728	27.686	117.648	0.741	–26900.829	–26906.394	–8.072	–2.629
2.14	5.816	27.225	117.193	0.741	–26907.024	–26911.390	–1.88	2.367
2.19	5.860	27.032	117.015	0.741	–26906.724	–26906.735	–2.176	–2.288
1.94	5.627	27.934	117.938	0.791	–26910.394	–	1.493	–
1.94	5.616	27.704	117.674	0.841	–26910.586	–	1.685	–
1.94	5.593	27.261	117.260	0.941	–26910.227	–	1.327	–
1.94	–	–	–	1	–26907.958	–	–0.942	–
1.94	–	–	–	2	–26906.0351	–	–2.865	–
2.14	5.805	27.013	116.975	0.791	–	–26911.302	–	2.278
2.14	5.794	26.794	116.761	0.841	–	–26901.699	–	–7.325
2.14	5.772	26.342	116.296	0.941	–	–26908.554	–	–0.469

Note: [a] Distances of two hydrogen atoms from the surface.
[b] Adsorption energies (eV) of H_2 onto the V (100) surfaces at the HF/LANL2DZ/6-31G*.
[c] Adsorption energies of H_2 onto the V (100) surfaces at the HF/LANL2DZ/6-31G**.
[d] Eads = E (H_2) + E (V-surface) – E (H_2/V-surface) at the HF/LANL2DZ/6-31G*.
[e] Eads = E (H_2) + E (V-surface) – E (H_2/V-surface) at the HF/LANL2DZ/6-31G**.

cule, while for the HF/LANL2DZ, 6–31G* case, the H_2 molecule dissociates. The distance between the hydrogen atoms and chemisorption energy for HF/LANL2DZ, 6–31G* are 0.941 A and 0.134 eV, respectively, which implies partial dissociation of the H_2 molecule.

Table 2. Structural parameters and adsorption energies of H_2 onto the V (100) surface at the HF/LANL2DZ – 6–31G* or 6–31G** for vertical and horizontal bridge sites

Vertical bridge site

Rd[a]/Å	R(15,4)/Å	<(15, 4, 3) (Deg)	<(16, 15, 4) (Deg)	R(H–H)/Å	E[b]	E[c]	Eads[d]	Eads[e]
1.44	5.645	37.623	145.168	0.741	–26905.987	–26908.900	–2.913	–0.123
1.49	5.686	37.331	145.465	0.741	–26904.854	–26906.978	–4.046	–2.045
1.54	5.727	37.044	145.752	0.741	–26910.175	–26910.270	1.274	1.247
1.6	5.776	36.707	146.091	0.741	–26906.113	–26907.451	–2.787	–1.572
1.74	5.892	35.934	146.899	0.741	–26910.667	–26905.302	1.767	–3.721
1.84	5.975	35.406	147.354	0.741	–26906.059	–26907.004	–2.842	–2.019
1.94	6.059	34.888	147.906	0.741	–26905.275	–26910.55	–3.626	1.527
2.04	6.144	34.381	148.454	0.741	–26900.847	–26909.011	–8.053	–0.012
1.74	5.892	35.934	146.899	0.791	–26898.364	–	–10.537	–
1.74	5.892	35.934	146.899	0.841	–26906.840	–	–2.061	–
1.74	5.892	35.934	146.899	0.941	–26901.378	–	–7.522	–
1.94	6.059	34.888	147.906	0.791	–	–26907.686	–	–1.337
1.94	6.059	34.888	147.906	0.841	–	–26894.942	–	–14.082
1.94	6.059	34.888	147.906	0.941	–	–26901.350	–	–7.673

Horizontal bridge site

Rd[a]/Å	R(13,3)/Å	<(13, 3, 1) (Deg)	<(14, 13, 3) (Deg)	R(H–H)/Å	E[b]	E[c]	Eads[d]	Eads[e]
0.45	3.093	30.779	148.590	0.741	–26907.880	–26908.799	–1.020	–0.224
0.55	3.109	31.279	148.079	0.741	–26908.320	–26908.904	–0.580	–0.119
0.65	3.128	31.858	147.494	0.741	–26904.470	–26906.366	–4.430	–2.657
0.75	3.150	32.510	146.836	0.741	–26902.440	–26906.423	–6.461	–2.600
0.85	3.175	33.224	146.119	0.741	–26907.540	–26905.098	–1.360	–3.925
1	3.218	34.380	144.962	0.741	–26909.506	–26909.596	0.606	0.572
1.15	3.282	37.403	140.262	0.741	–26908.212	–26910.228	–0.688	1.205
1.26	3.307	36.611	142.738	0.741	–26906.219	–26906.912	–2.682	–2.111
1	3.197	34.631	144.713	0.791	–26905.704	–	–3.196	–
1	3.177	34.922	144.423	0.841	–26909.160	–	0.259	–
1	3.136	35.472	143.871	0.941	–26907.803	–	–1.097	–
1.15				0.791	–	–26906.752	–	–2.271
1.15				0.841	–	–26909.530	–	0.507
1.15				0.941	–	–26909.541	–	0.517
1.15				0.991	–	–26910.115	–	1.092
1.15				1.012	–	–26909.410	–	0.387

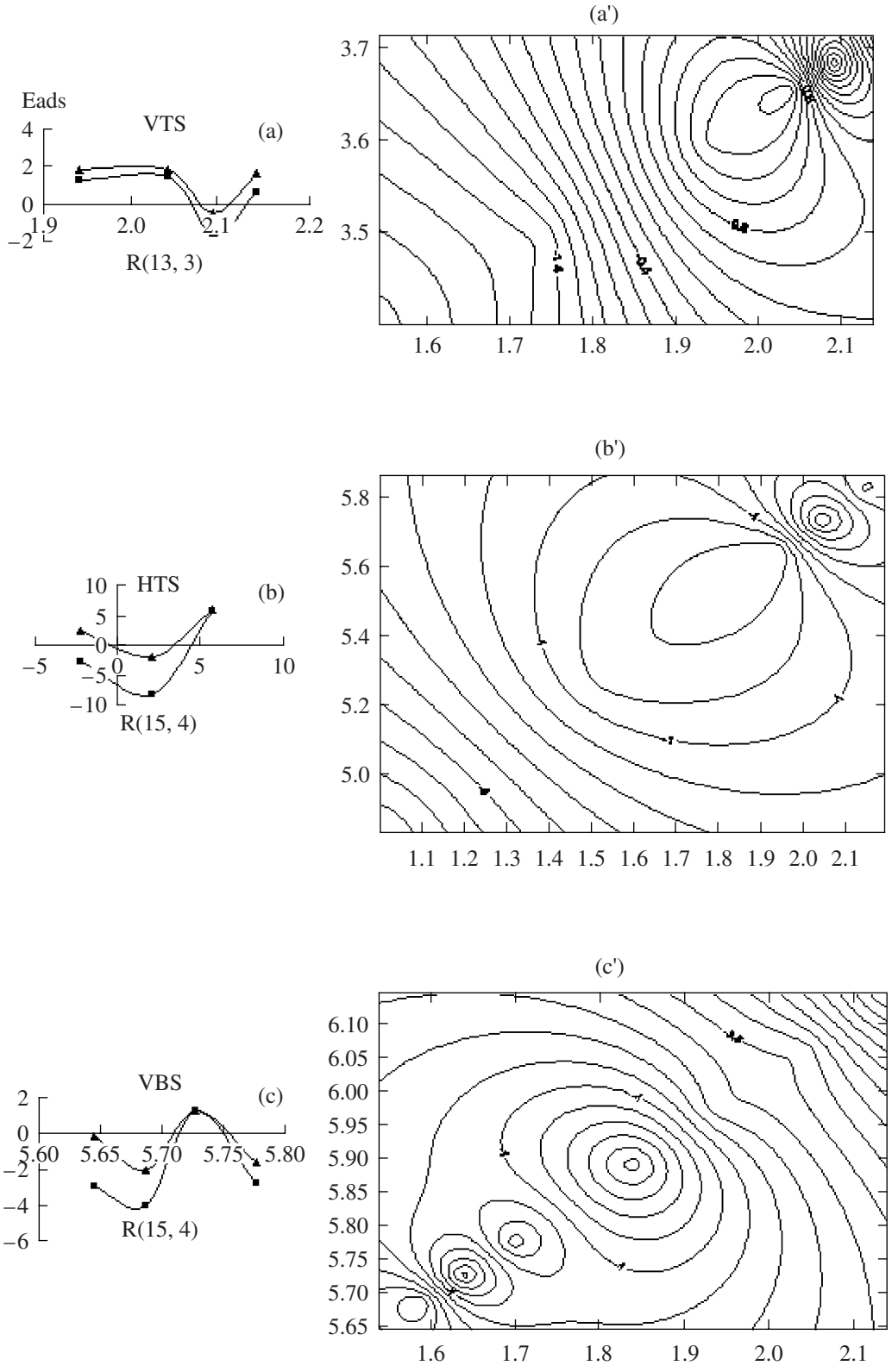

Fig. 2. Change of calculated stability energy (—■— 6–31G* and —▲— 6–31G** basis sets) versus R (V–H) optimized coordination (left is 2D curve and right is 3D plot). At each configuration (aa' bb' = top, cc' dd' = bridge and ee' ff' = center sites), vertical and horizontal approaches are indicated.

Table 3. Structural parameters and adsorption energies of H_2 onto the V (100) surface at the HF/LANL2DZ – 6–31G* or 6–31G** for vertical and horizontal center sites

Vertical center site								
Rd[a]/Å	R(15, 4)/Å	<(15.4,3) (Deg)	<(16, 15, 4) (Deg)	R(H–H)/Å	E[b]	E[c]	Eads[d]	Eads[e]
0.5	5.954	53.619	126.887	0.741	–26906.287	–26901.233	–2.613	–7.790
1	6.264	49.933	130.575	0.741	–26910.021	–29609.611	1.121	0.588
1.34	6.488	47.635	132.874	0.741	–26909.049	–26909.708	0.148	0.685
1.54	6.624	46.357	134.151	0.741	–26910.082	–26906.924	1.182	–2.099
1.64	6.694	45.738	134.771	0.741	–26910.156	–26908.148	1.256	–0.876
1.74	6.764	45.131	135.376	0.741	–26909.321	–26910.772	0.420	1.749
1.84	6.854	44.651	136.124	0.741	–26908.715	–26909.873	–0.186	0.850
1.64	6.694	45.738	134.771	0.791	–26905.153	–	–3.748	–
1.64	6.694	45.738	134.771	0.841	–26909.755	–	0.854	–
1.64	6.694	45.738	134.771	0.941	–26909.828	–	0.927	–
1.64	6.694	45.738	134.771	0.991	–26909.809	–	0.909	–
1.74	6.764	45.131	135.376	0.791	–	–26905.306	–	–3.718
1.74	6.764	45.131	135.376	0.841	–	–26909.407	–	0.384
1.74	6.764	45.131	135.376	0.941	–	–26910.081	–	1.058
1.74	6.764	45.131	135.376	0.991	–	–26904.597	–	–4.426
1.74	6.764	45.131	135.376	1.041	–	–26908.562	–	–0.462
Horizontal center site								
Rd[a]/Å	R(15, 4)/Å	<(15.4,3) (Deg)	<(16, 15, 4) (Deg)	R(H–H)/Å	E[b]	E[c]	Eads[d]	Eads[e]
0.55	6.271	55.164	38.288	0.741	–26906.396	–26909.391	–2.504	0.368
0.75	6.388	53.704	39.686	0.741	–26904.926	–26903.916	–3.974	–5.107
0.95	6.509	52.274	40.896	0.741	–26905.304	–26908.539	–3.597	–0.484
1.05	6.571	51.596	41.514	0.741	–26908.894	–26906.664	–0.006	–2.359
1.15	6.633	50.907	41.996	0.741	–26908.894	–26910.076	–0.0062	1.053
1.20	6.664	50.583	42.613	0.741	–26908.957	–26908.862	0.0560	–0.161
1.25	6.695	50.237	42.844	0.741	–26901.702	–26909.326	–7.198	0.303
1.35	6.759	49.893	43.428	0.741	–26908.607	–26909.208	0.048	0.184
1.55	6.893	48.343	44.448	0.741	–26908.607	–26906.155	–0.294	–2.868
1.20	6.600	49.943	40.477	0.791	–26903.240	–	–5.660	–
1.20	6.636	50.230	40.779	0.841	–26904.777	–	–4.123	–
1.20	6.550	50.682	40.935	0.941	–26909.035	–	0.134	–
1.15	6.558	50.188	40.136	0.791	–	–26910.071	–	1.048
1.15	6.594	50.459	40.249	0.841	–	–26909.415	–	0.391
1.15	6.665	51.015	40.704	0.941	–	–26909.683	–	0.660

The ab initio energy gain with two basis sets for hydrogen molecules as a result of the H–V interaction have been used to draw stability curves of the various surface configurations identified in this work (Fig. 2). The evolution of the surface V electronic states versus the H2 molecule has been followed.

The adsorption distances, Rd, are maximum for the top site, and the chemisorption energies are higher than the other two sites, except for the vertical top site approach (Figs. 2a, 2a' and 2b, 2b') with the HF/LANL2DZ,6–31G* level that the bridge site (Figs. 2c, 2c' and 2d, 2d') has a higher energy than the

top site. The reason might be that the nearest V-H distances in the top site are smaller than the bridge site and center site (Figs. 2e, 2e' and 2f, 2f').

From the above discussion, it is clear that the top site mode is the most stable site for hydrogen adsorption on the V (100) surface nanocluster. Comparing to the energies of these t configurations in the nanoparticle in Fig. 2, we have found that the vertical top site approach (Figs. 2a, 2a') with HF/LANL2DZ, 6–31G** and the horizontal center site approach (Figs. 2f, 2f') with the HF/LANL2DZ, 6–31G* level of theory are important for the chemisorption processes, because the H_2 molecule partially dissociate.

CONCLUSIONS

The most important results presented above can be summarized as follows. This study concerns the quantum chemical modeling behavior of H_2 on the (100) surface of a vanadium system using an ab initio method with HF level and LAN2DZ, 6–31G* and 6–31G** basis sets.

The V cluster has a two-layer slab and every layer contains five V atoms that are used to form the perfect V (100) surface. Three possible adsorption sites, top, bridge, and center, with two different approaches for each site (vertical and horizontal), are considered in the calculations. The predicted results show that the top site is the preferred site for hydrogen adsorbed on a V (100) surface energetically. The vertical top site approach with HF/LANL2DZ, 6–31G** and the horizontal center site approach with the HF/LANL2DZ, 6–31G* level of theory are important for the chemisorption processes, because the H_2 molecule partially dissociates. The geometry of V (100) surface has also been optimized theoretically in H_2 for various distances, and the adsorption distances, Rd, are minimal for the top site.

The present study should be considered a first step toward a complete understanding of the present system. Overall, structures and relative stabilities agree with experiment, suggesting that studies of nanostructures can be pursued with some degree of confidence with this level of theory.

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