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Quantum Theoretical studies of Nanostructures onto Hydrogen Adsorption on V-surface

F.Mollaamin[1, 2*], M. T. Baei[1, 3] and A. Kazemi Babaheydari[4]

1. Department of Chemistry, Science & Research Branch, Islamic Azad University, Tehran, Iran.
2. Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran.
3. Department of Chemistry, Azadshahr Branch, Islamic Azad University, Azadshahr, Iran
4. Department of Chemistry, ShahreKord Branch , Islamic Azad University, ShahreKord , Iran

ABSTRACT

We have studied the adsorption processes of H_2 on the V (100) surface of Vanadium using self consistent field theory.Dissociative adsorptions of H_2 are significantly favored compared to molecular adsorptions. There is a significant charge transfer from the first layer of the vanadium surface to the Hydrogen atoms. Three possible adsorption sites, top, bridge and center site, were considered in the calculations. The geometry of V (100) surface has also been optimized theoretically with Hartree-Fock method and the results show that the prediction from the HF/LANL2DZ, 6-31G* and HF/LANL2DZ, 6-31G** reproduce the experimental observation. These results indicate that two models of vertical top site and horizontal bridge site have short distances from surface and are more stable than other models, also the 6-31G* basis set give more optimized structures than 6-31G** basis set in calculations.

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[*] . Corresponding author:smollaamin@gmail.com

INTRODUCTION

The interaction of hydrogen with transition metal surfaces is a great fundamental and practical interest in both heterogeneous catalysis and metallurgy. Transition metal surfaces catalyze numerous hydrogenation reactions, for example hydrogen chemisorptions on Fe (110) [1] is particularly important, not only a reactant in Fe-catalyzed ammonia synthesis [2], the Fischer–Tropsch reaction [3] and many others, but also hydrogen is known to embrittle steels [4, 5], causing fracture and ultimately failure of the steel component.

A number of investigations are carried out on vanadium to examine the effectiveness of such kind of surface barriers on preventing hydrogen adsorption or accelerating super permeation [6].The adsorption of hydrogen on V (110) is investigated. The calculation indicated that hydrogen adsorption takes place most easily via the on-top site of the atomic array in [1 0] direction on 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 is studied by K.Hermann et al. [7]. Later, Koller et al. have studied the oxygen induced (1x5) reconstruction of V (100) achieving very good agreement of experimental and calculated data in finding the most stable adsorption structure [8]. Recently, the influence of carbon impurities on a *d*-like surface state of V (100) was studied [9].

Computational methods

In this work, cluster models of the surface and periodic slabs are 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 cluster consisting of several atoms. Calculations are carried out at HF level of theory and the cluster fragment is considered as a doublet molecules, with partitioning of the basis sets, for hydrogen molecule described by the standard 6-31G* and 6-31G** basis sets, but for Vanadium the standard LANL2DZ basis set is used.

Vanadium has the body-centered cubic structure with a lattice constant of a=3.028Å and in every the metal layer contain five V atoms. Our two-layer model of the surface contains nine V 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 structures of the surfaces (center site).

RESULTS AND DISCUSSION

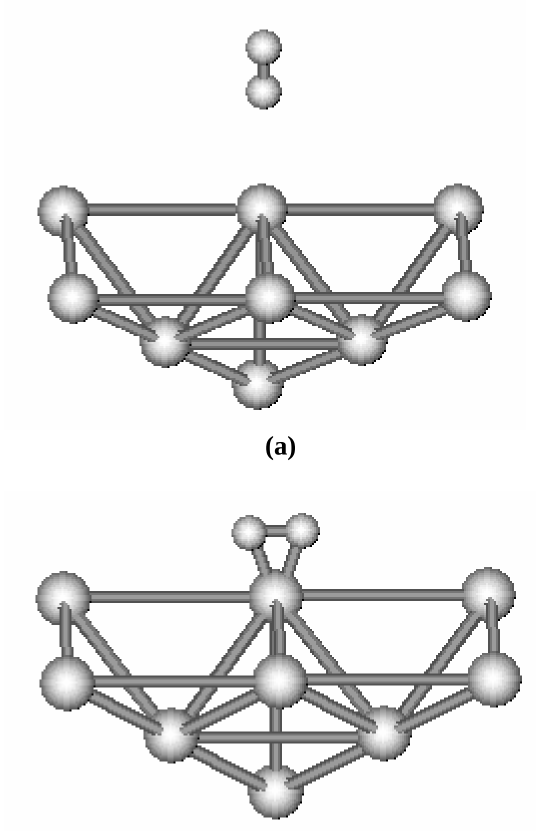
The adsorption of hydrogen on transition metal surface has been studied using a wide range of techniques and methods because of its interest for both basic and applied problems in surface science in the past several decades. The study is also important for the understanding of heterogeneous catalysis and metal corrosion. The adsorption of element onto metal surface forms the basic processes of catalytic reaction. Therefore, a comprehensive understanding of the bonding processes for the behavior of atom and valence electrons at the metal surface is important scientifically and technologically.

Hydrogen plays important roles in fields varying from bioelectronics, pharmacology, and to environmental chemistry and nanotechnology science. It has been found that, in general, molecular oxygen directly dissociates on the metal surface or does so after adsorption. Adsorption of atomic or molecular species on surface modified their electronic and atomic structural properties and hence the catalytic performance.

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. This is believed to be quite adequate considering that the hydrogen molecule is not expected to interact with atoms beyond the first two layers. The geometry and electronic structures of hydrogen adsorption onto clean V (100) surface using cluster and periodic slab models within the framework of first principles self consistent field theory.

We start by describing the chemisorption's process of H_2 at the different sites on vanadium surfaces. Vanadium has the body-centered cubic structure with a lattice constant of a=3.032Å, that there are three high-symmetry sites on V (100): 1) top site 2) bridge site 3) center site.

Consider first the top sites. In the top site there are two different approaches for each site (Fig.1).



(a)

(b)

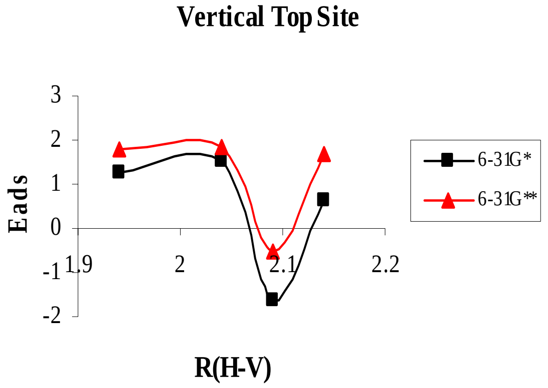
Fig. 1. High symmetry of H_2 adsorption **(a)** vertical and (**b)** horizontal top sites on V (100).

The first, for the vertical and horizontal top sites H_2 molecule is allowed to approach the vanadium surface in different distances and are calculated their chemisorption's energy with HF/LANL2DZ,6-31G* and HF/LANL2DZ,6-31G** level of theory .This results from fact that hydrogen atoms are relatively much closer to the vanadium surface in bridge sites compared to the top sites. The binding energies are also listed in table 1.

Table1. Optimized parameters of adsorption of H-H at vanadium-surface at the HF/LANL2DZ,6-31G* or 6-31G** for vertical and horizontal top sites.

R(H-V)/ Å	**R(H-H)/ Å**	**Eads(6-31G*)/ev**	**Eads(/6-31G**)/ev**
Vertical top site			
3.401	0.741	-2.288	0.767
3.496	0.741	-1.552	0.607
3.600	0.741	1.244	1.806
3.655	0.741	1.502	1.838
3.712	0.741	-1.621	-0.511
3.712	0.741	0.630	1.668
3.655	0.791	-0.684	2.125
3.655	0.841	1.319	-0.800
3.655	0.941	0.917	0.937
Horizontal top site			
4.831	0.741	-10.006	-10.159
5.290	0.741	0.638	-1.496
5.640	0.741	2.107	-2.288
5.728	0.741	-8.072	-2.629
5.816	0.741	-1.88	2.367
5.860	0.741	-2.176	-2.288
5.627	0.791	1.493	-
5.616	0.841	1.685	-
5.593	0.941	1.327	-
	1	-0.942	-
	2	-2.865	-
5.805	0.791	-	2.278
5.794	0.841	-	-7.325
5.772	0.941	-	-0.469
4.831	0.741	-10.006	-10.159

In vertical and horizontal top sites approach behave differently for 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 electron transfer from substrate to adsorbate as the hydrogen atom bound to vanadium (Fig.2).



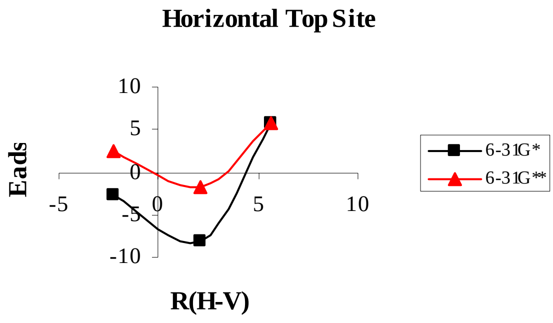


Fig.2. Theoretical calculations of Eads via R (H-V) on Adsorption of H-H at vanadium-surface at the HF/LANL2DZ, 6-31G* or 6-31G** for vertical and horizontal top sites.

For the vertical and horizontal bridge site, the chemisorptions of H_2 along the horizontal and the vertical approaches behave same and H_2 remains as a molecule for every two state. (Fig.3).

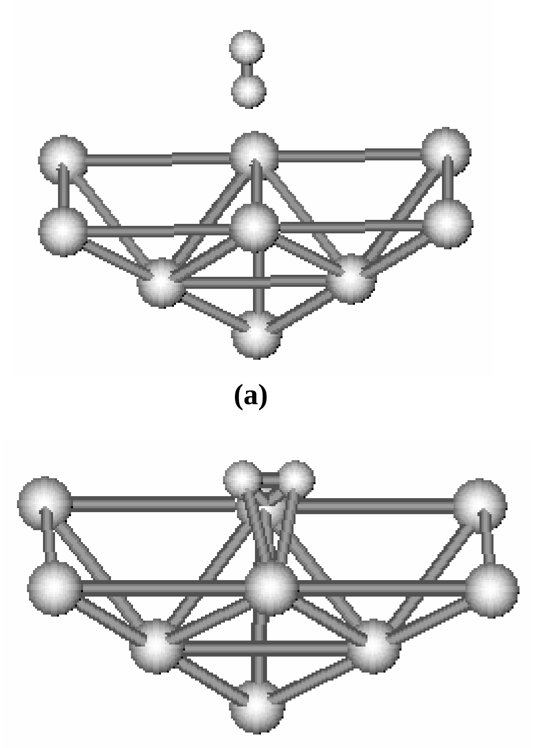


Fig.3. High symmetry of H_2 adsorption **(a)** vertical and **(b)** horizontal bridge sites on V (100).

The partial optimized structure obtained for the long-bridge uses as a starting point for a subsequent calculation where the adsorbed hydrogen molecule is free to move on the surface while its internal geometry is optimized. The geometric parameters for this structure are also reported in table 2.

Table2. Optimized parameters of adsorption of H-H at vanadium-surface at the HF/LANL2DZ, 6-31G* or 6-31G** for vertical and horizontal bridge sites.

R(H-V)/Å	R(H-H)/ Å	Eads(6-31G*)/ev	Eads(6-31G**)/ev
Vertical bridge site			
5.645	0.741	-2.913	-0.123
5.686	0.741	-4.046	-2.045
5.727	0.741	1.274	1.247
5.776	0.741	-2.787	-1.572
5.892	0.741	1.767	-3.721
5.975	0.741	-2.842	-2.019
6.059	0.741	-3.626	1.527
6.144	0.741	-8.053	-0.012
5.892	0.791	-10.537	-
5.892	0.841	-2.061	-
5.892	0.941	-7.522	-
6.059	0.791	-	-1.337
6.059	0.841	-	-14.082
6.059	0.941	-	-7.673
Horizontal bridge site			
3.093	0.741	-1.020	-0.224
3.109	0.741	-0.580	-0.119
3.128	0.741	-4.430	-2.657
3.150	0.741	-6.461	-2.600
3.175	0.741	-1.360	-3.925
3.218	0.741	0.606	0.572
3.282	0.741	-0.688	1.205
3.307	0.741	-2.682	-2.111
3.197	0.791	-3.196	-
3.177	0.841	0.259	-
3.136	0.941	-1.097	-
-	0.791	-	-2.271
-	0.841	-	0.507
-	0.941	-	0.517
-	0.991	-	1.092
-	1.012	-	0.387

For the two bridge-sites, the calculated adsorption energy of hydrogen on V (100) is small. This low adsorption energy is a sign of a small interaction with the surface as seen also from the large adsorbate to surface distance. The internal geometry of the adsorbate is practically the same of the gas-phase hydrogen molecule.

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 (Fig.4).

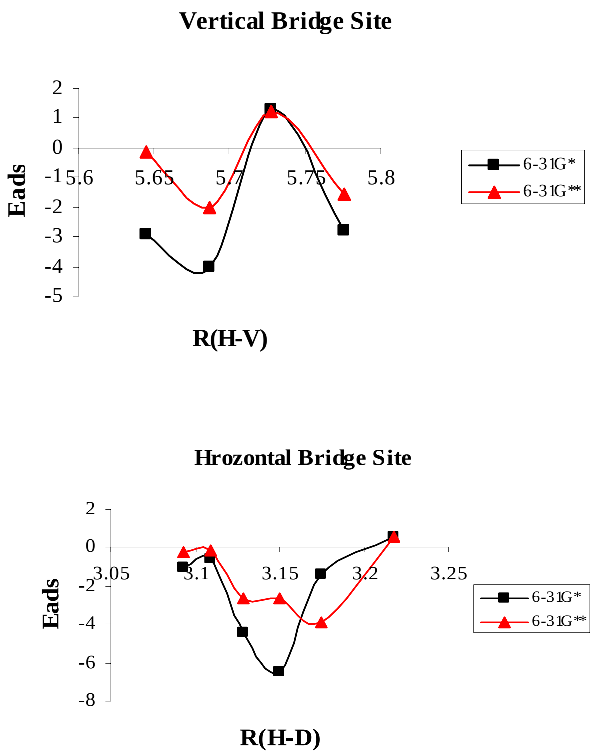
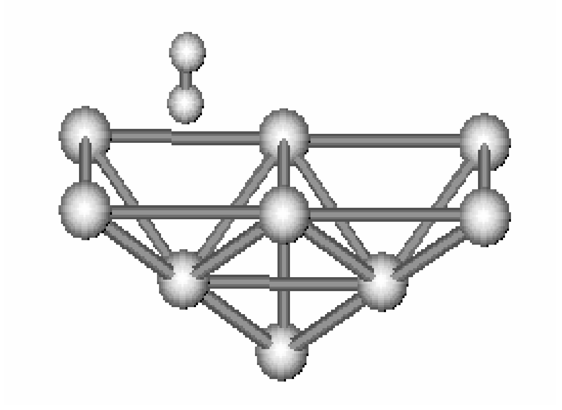
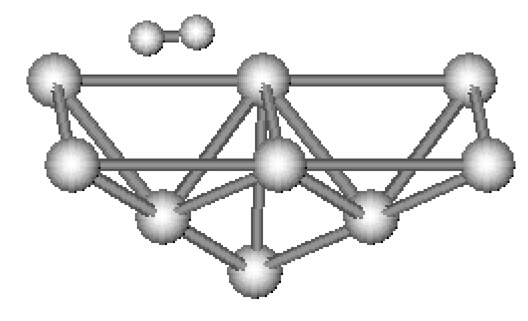


Fig.4. Theoretical calculations of Eads via R (H-V) on Adsorption of H-H at vanadium-surface at the HF/LANL2DZ - 6-31G* or 6-31G** for vertical and horizontal bridge sites.

In the center site, for the vertical and horizontal center site (Fig.5), H_2 molecule is allowed to approach the Vanadium surface in different distances and are calculated their chemisorption's energy with HF/LANL2DZ,6-31G* and HF/LANL2DZ,6-31G** level of theory (Fig.5).



(a)



(b)

Fig.5. High symmetry of H_2 adsorption **(a)** vertical and **(b)** horizontal center site on V (100).

For the center sites at Vertical approach, like bridge sites, H_2 dissociate completely and consequently the chemisorption's energy comprise in variant distances of H-H in table3.

Table3. Optimized parameters of adsorption of H-H at vanadium-surface at the HF/LANL2DZ, 6-31G* or 6-31G** for vertical and horizontal center site.

Vertical center site			
R(H-V)/ Å	**R(H-H)/ Å**	**Eads(6-31G*)/ev**	**Eads(/6-31G**)/ev**
5.954	0.741	-2.613	-7.790
6.264	0.741	1.121	0.588
6.488	0.741	0.148	0.685
6.624	0.741	1.182	-2.099
6.694	0.741	1.256	-0.876
6.764	0.741	0.420	1.749
6.854	0.741	-0.186	0.850
6.694	0.791	-3.748	-
6.694	0.841	0.854	-
6.694	0.941	0.927	-
6.694	0.991	0.909	-
6.764	0.791	-	-3.718
6.764	0.841	-	0.384
6.764	0.941	-	1.058
6.764	0.991	-	-4.426
6.764	1.041	-	-0.462
Horizontal center site			
6.271	0.741	-2.504	0.368
6.388	0.741	-3.974	-5.107
6.509	0.741	-3.597	-0.484
6.571	0.741	-0.006	-2.359
6.633	0.741	-0.0062	1.053
6.664	0.741	0.0560	-0.161
6.695	0.741	-7.198	0.303
6.759	0.741	0.048	0.184
6.893	0.741	-0.294	-2.868
6.600	0.791	-5.660	-
6.636	0.841	-4.123	-
6.550	0.941	0.134	-
6.558	0.791	-	1.048
6.594	0.841	-	0.391
6.665	0.941	-	0.660

From the above discussion, it is clear that vertical approaches where the H_2 adsorption is molecular are not the preferred approaches at any sites for the chemisorption's processes. They have significantly lower chemisorption's energies compared to the other cases where H_2 dissociates. Basically in molecular adsorption at vertical approach, one hydrogen atom closer to the vanadium surface is coordinated with vanadium surface atoms, while the other one is only bonded with hydrogen atom. This explains the much lower chemisorption's energies of the vertical approach despite of the fact that hydrogen atom is much closer to the surface. The surface basically interacts with the first atom, while the coordination with the second atom to the surface is screened by the first hydrogen atom. (Fig.6)

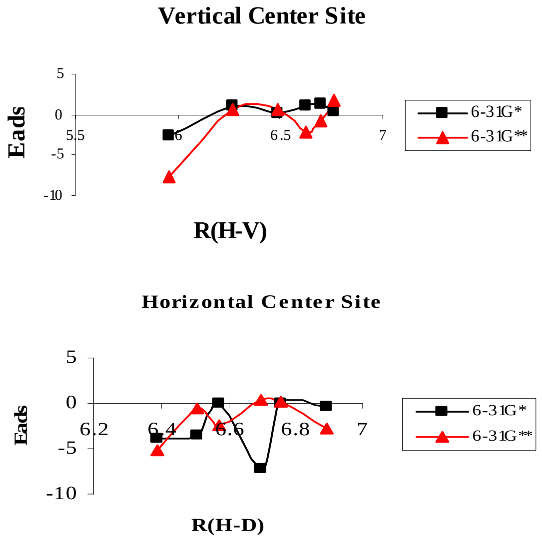


Fig.6. Theoretical calculations of Eads via R(H-V) on Adsorption of H-H at vanadium-surface at the HF/LANL2DZ - 6-31G* or 6-31G** for vertical and horizontal center sites

The adsorption distances are maximum for the top site, and the chemisorption's energies are higher than the other two sites except for the vertical top site approach with HF/LANL2DZ,6-31G* level of theory where bridge site has higher 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.

From the above discussion, it is clear that the top site mode is the most stable site for hydrogen adsorption on V (100) surface. The vertical top site approach with HF/LANL2DZ, 6-31G** and the horizontal center site approach with HF/LANL2DZ, 6-31G* level of theory are important for the chemisorptions' processes , because the H_2 molecule partial dissociates.

CONCLUSION

The adsorption of hydrogen on the surfaces of vanadium was modeled by simple clusters consisting of nine atoms and the potential energy surfaces were calculated by ab initio calculations using Gaussian 98 package.

The V cluster and a two-layer slab and in every the metal layer contain five V atoms are used to model the perfect V (100) surface. Three possible adsorption sites, top, bridge and center site that there are two different approaches for each site (vertical and horizontal) were considered in the calculations. The predicted results show that the top site is the prefer site for hydrogen adsorbed on V (100) surface energetically. The geometry of V (100) surface has also been optimized theoretically in H_2 various distance and the adsorption distances are maximum for the top site. The vertical top site approach with HF/LANL2DZ, 6-31G** and the horizontal center site approach with HF/LANL2DZ, 6-31G* level of theory are important for the chemisorptions' processes, because the H_2 molecule partial dissociate. The geometry of V (100) surface has also been optimized theoretically in H_2 various distance and the adsorption distances are maximum for the top site.

The present calculations were also showed that simple cluster models consisting of a few atoms can give useful information of the influence of crystal faces exposed to hydrogen. However, more accurate geometric models are necessary to obtain precise values of adsorption energies as well as structure of adsorption species.

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