ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2008, Vol. 82, No. 13, pp. 2354–2361. © Pleiades Publishing, Ltd., 2008.

PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

A DFT Study of Hydrogen Chemisorption on V (100) Surfaces

F. Mollaamin[a], M. T. Baei[b], M. Monajjemi[c], R. Zhiani[d], and B. Honarparvar[c]

[a] *Department of Chemistry, Qom Branch, Islamic Azad University, Qom, Iran*

[b] *Departments of Chemistry, Islamic Azad University of Azadshahr Branch, Azadshahr, Iran*

[c] *Department of Chemistry, Science and Research Campus, Islamic Azad University, Tehran, Iran*

[d] *Department of Chemistry, Islamic Azad University, Yazd, Iran*

e-mail: smollaamin@gmail.com

Received September 19, 2007

Abstract—In this study, hydrogen adsorption on the surface of vanadium at various positions (top, bridge, and central sites) was studied, and the binding energies of hydrogen species adsorbed on vanadium were calculated using density functional theory (DFT) within the generalized gradient approximation (GGA). The potential of the adsorption of hydrogen on vanadium was examined as a function of both surface coverage and adsorption site. Our results were in excellent agreement with the experimental values reported in the literature. The relative stabilities of hydrogen chemisorption were independent of both the transition metal surface and surface coverage. That is, hydrogen exhibited insignificant selectivity with respect to positions on the metal surface. Our data on H_2/V surface chemisorption revealed that the stablest model for hydrogen adsorption was that on the vertical bridge site. The adsorption energy for this model was lower than for the other sites. However, adsorption on bridge-hydrogen vacancies was strong.

DOI: 10.1134/S0036024408130323

INTRODUCTION

The chemisorption of atomic and molecular hydrogen on metal surfaces provides one of the simplest systems of interest in both surface science and heterogeneous catalysis [1]. Hydrogen diffusion on metals is a phenomenon of great fundamental and technological importance [2, 3]. Hydrogen adsorption has been widely studied because of its importance in such areas as the separation of hydrogen isotopes via adsorption on metals, damage of materials by H^+ ions, and heterogeneous catalysis [4]. Transition metal surfaces catalyze numerous hydrogenation reactions; for example, chemisorption of atomic hydrogen on Cu (001) [1], hydrogen chemisorption on Ni (111) and Co (0001) surfaces [5], and hydrogen chemisorptions on Fe (110) [6] are particularly important, not only as reactants in Fe-catalyzed ammonia synthesis [7] and the Fischer–Tropsch reaction [8], but also because hydrogen is known to embrittle steels [9, 10] causing fracture and, ultimately, failure of the steel component. Molecular hydrogen chemisorption is dissociative on these surfaces, and the process is strongly exothermic.

Several theoretical works on the quantum motion of hydrogen on metal surfaces demonstrated the accuracy and versatility of calculations based on density functional theory (DFT) [11–14]. DFT calculations are implemented in the Vienna ab initio simulation package (VASP) [15, 16], where electron–ion interaction is described by the projector augmented wave method [17], and the generalized gradient approximation (GGA) due to Perdew and Wang [18] is used for the exchange-correlation part. A profound illustration of this technique is the pioneering study of the diffusion of hydrogen isotopes on the Cu (001) surface by Lauhon and Ho [19].

Inspired by the experimental work of Krenn [20] to complete our theoretical studies of atomic oxygen [21] and carbon [22] adsorption on the V (100) surface, we investigated the adsorption behavior of atomic hydrogen on V (100) model. Recent experiments [20] reported the property of V to store hydrogen. The temperature-dependent behavior of the major impurities (C, O, and S) was similar to that of the V (100) single crystal surface [21].

Also, Adams et al. [23] first presented the structure of clean V (110) and reported the existence of the O–C (6×2) phase on V (110). These surface calculations were performed considering the calculated bulk lattice parameter, which was utilized throughout this work [18, 24].

Several studies were reported on vanadium to investigate the ability of surface barriers of this kind to hinder hydrogen absorption and stimulate superdiffusion [25]. Hermann et al. [26] studied the adsorption of hydrogen on the V_2O_5 (010) surface through the on-top site of the atomic formation in the [10] direction on the V (110) surface. The hydrogen atom was stably adsorbed at the midpoint between two vanadium atoms.

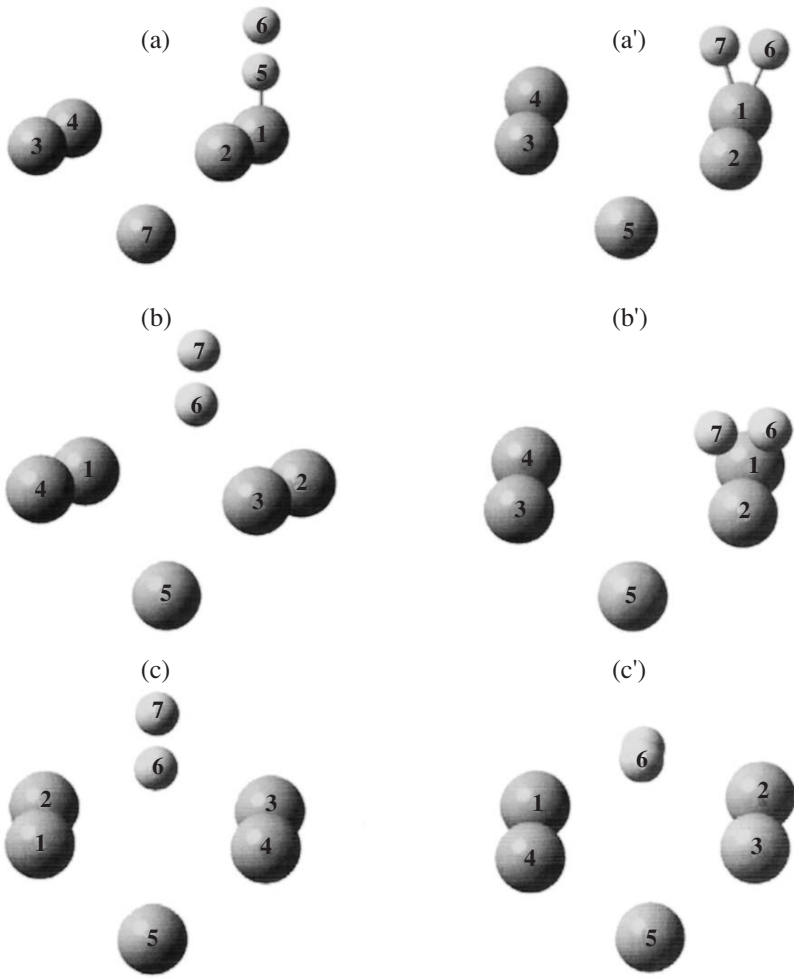

Fig. 1. Optimized structures of different adsorption models: (a) vertical and (a') horizontal top sites, (b) vertical and (b') horizontal bridge sites, and (c) vertical and (c') horizontal central positions on the vanadium (100) surface.

Koller et al. studied the oxygen-induced (1 × 5) reassemble of V (100) and obtained very good array of experimental and theoretical data on the stablest adsorption structure [27]. Lately, the effect of carbon impurities on a *d*-like surface state of V (100) has been studied [28].

The main goal of our current study was to use density functional theory calculations of hydrogen adsorption on the V (100) surface using a small nanocluster consisting of five metal atoms as a model of the crystal surface, evaluate the validity of small nanostructure models, and find effects of such limitations on adsorption. Unfortunately, a direct comparison of theory and experiment is often fairly difficult because of inherent uncertainties that appear because of adsorbate–adsorbate interactions and the presence of surface defects.

Since a real space image of the surface is obtained, it is even possible to determine the influence of the local environment on the behavior of a single adsorbent. Figure 1 displays three different high-symmetry V (100) sites, the top site, the bridge site, and the central site.

COMPUTATION DETAILS

This work is based on density functional theory (DFT). Despite the relative success of LDA, errors occur which are particularly striking when the electron density is strongly inhomogeneous, as for free atoms, molecules or surfaces, and localized states. This leads to the so-called overbidding effect resulting in too short bonds and too strong binding energies. For the treatment of electron exchange and correlation, it is well known that the generalized gradient approximation (GGA) is needed to obtain an accurate description of the magnetic properties and energies of bulk vanadium phases. Therefore, all calculations were performed with the GGA functional of Perdew. It uses a plane wave basis set, the ionic cores being represented by ultrasoft pseudo potentials [29].

In this study, a slab formed the V (100)-surface model. The equilibrium FCC parameter (a = 3.032 Å) was given by our computation on bulk V. The calculations included surface and subsurface H atoms. Geometry optimization included all degrees of freedom of the adsorbate and the V-surface, while the two lowest metal planes were kept fixed at the bulk geometry. The adsorption energy (E_{ads}) was calculated as the difference between the energy of the adsorbed molecule and the sum of the free surface and gas-phase molecule energies as

$$E_{ads} = E(\text{adsorbate-surface}) - E(\text{surface}) - E(\text{gas-phase molecule}). \quad (1)$$

Our DFT calculations show that the top site approach is the stablest one for all surface models, which is in disagreement with bridge positions on the V (100) surface model. We performed our calculations based on density functional theory (DFT) using the 6-31G*, 6-31G**, and LANL2DZ basis sets for the hydrogen molecule and vanadium surface, respectively. Because of the importance of electron exchange and correlation, we used the generalized gradient approximation (GGA).

Further, we modeled the adsorption of H_2 on the V (100) surface with five vanadium atoms using the experimental lattice constant of the body-centered cubic structure (a = 3.028 Å). The adsorption of the H_2 molecule can be oriented on the vanadium surface toward three different symmetrical sites (top, bridge, and central sites) at two adsorption orientations (vertical and horizontal). Hydrogen adsorbed on a stable site of a perfect crystal distorts the positions of surrounding substrate metal atoms.

In principle, any lattice distortions should be evaluated using the hydrogen density distribution. However, we found a finite extension of hydrogen density to have a very minor effect on the self-trapping energy value using an interatomic model potential for the H/Ni system [25]. This is also fully in agreement with the findings reported in [26] for hydrogen in bulk metals. When we optimized the atomic substrate sites in the self-trapped and classic saddle-point configurations, hydrogen was treated as a point particle.

RESULTS AND DISCUSSION

The basic concept of adsorption is that of acceptor or donor molecules, which induce a charge-transfer surface region. Although this is a simple mechanism, the details of the adsorption and charge transfer of specific molecules are complex, and more research is needed to gain fundamental understanding of the interaction of particular molecules with vanadium. However, our current research provides an overview of a considerable theoretical investigation of the interaction of the hydrogen molecule with transition metal surfaces. In particular, the interaction of hydrogen with vanadium attracted much attention because of its role in surface adsorption chemistry. Molecular interactions with vanadium surface are of importance because of their applications in studies of catalysts on the atomic scale. Also, modern surface science provides the opportunity to investigate such complex interactions. To facilitate the discussion of the results concerning the interaction of the H_2 molecule, we present our results in different subsections.

Clean V (100) model. The preparation of clean vanadium is in general a very difficult task because of the high reactivity of vanadium surface. Considerable effort was made by the experimental group [21] to prepare a surface as clean as possible. Vanadium is an element in the beginning of the 3*d* transition metal series; its bulk BCC lattice parameter (a = 3.028 Å) was determined. A quantum chemical study of interaction between transition metals and gaseous molecules is of great fundamental and practical interest in metallurgy. There are several theoretical studies in which this model was recently investigated in detail by density functional theory calculations (DFT), which were performed using the generalized gradient approximation (GGA) for the exchange–correlation energy at the P/LANL2DZ–6-31G* and 6-31G** levels of theory.

Investigation of adsorption sites on the model V (100) surface. Many chemisorbed molecules participate in charge transfer from solids to adsorbates. Hydrogen adsorption on metals is a phenomenon of great fundamental and technological importance. After the clean V(100) surface was studied, the relaxation energies were determined. In this work, the atomic adsorption of hydrogen and coadsorption are considered. Basically, we considered the most plausible adsorption sites on the V (100) surface, top, bridge, and central sites in vertical and horizontal orientations. In Figs. 1a, 1a', 1b, 1b', 1c, and 1c', various adsorption sites on the V (100) surface are displayed.

A study of H_2 adsorption on the V (100) model. A wide variety of applications to fundamental hydrogen studies and the simplicity of the system make it well suited for fundamental theoretical investigations of adsorption phenomena and facilitate comparison with the experimental data. In order to evaluate the dependence of binding energy on surface coverage, two hydrogen atoms were located on the V surface in vertical and horizontal orientations. The interaction of hydrogen with transition metal surfaces is of importance for understanding the fundamental roles played by these surface barriers in hydrogen adsorption and superpermeation. The adsorption of hydrogen molecules on the surface of vanadium was studied in this work from the first principles.

Supposing the stability position established above enables us to determine the minimum energy of H_2 adsorption, where various configurations discussed in this study could be present on the surface of the V (100) model at equilibrium with H_2 in the gas phase.

However, we observed that the H–V binding axis has a marked stabilization effect on the H_2 adsorption energy. This binding is important for the surface reaction, since it allows one of the H_2 atoms to approach the surface. According to the results obtained, we can predict a different mode of H_2 adsorption.

The binding energies of all possible adsorption sites were calculated to determine the most energetically favorable site. The calculated binding energy values change depending on hydrogen–vanadium bond lengths, surface coverage, and adsorption site. The corresponding data are summarized for the V (111) surface in Tables 1–3. As mentioned above, the binding energy corresponds to the adsorption of two hydrogen atoms. The adsorption energies of H atoms on different V (100) surface sites were calculated using density functional theory.

Models of H_2 adsorption derived from DFT calculations at the GGA level are presented in Figs. 1a, 1a', 1b, 1b', 1c, and 1c'. For the vertical top site (Fig. 1a), the H_2 molecule oriented toward the vanadium surface can be situated at different distances from the surface, (0.5–2.2) Å. The corresponding chemisorption energies were calculated at the P/LANL2DZ, 6-31G* and P/LANL2DZ, 6-31G** levels. At R_d = 1.8 Å, we obtained the highest stability for the horizontal top site (E_{ads} = –7.610 and –7.573 eV respectively) (Fig. 1a'). Various distances (0.5–2.2 Å) and their minimum chemisorption energies in the horizontal orientation were studied using both basis sets to obtain different optimized distances (R_d = 1.6–1.8 Å and E_{ads} = –8.942 and –6.777 eV for 6-31G* and 6-31G**, respectively) (Table 1). Vanadium adsorption was found to be strongest on the bridge hydrogen site.

For the vertical bridge site (Fig. 1b) with different distances (0.5–0.95 Å), chemisorption energies were calculated using the 6-31G* and 6-31G** basis sets, chemisorption distances (R_d) at chemisorption energies E_{ads} = –7.463 and –7.181 eV between the vanadium surface and H_2 were found to be 1.0 Å and 1.95 Å, respectively (Table 2). But for the horizontal bridge site (Fig. 1b') with a lower distance than in the vertical orientation (R_d = 0.75 Å), the minimum energy tends to increase to –9.205 eV for the 6-31G** basis set, (–8.588 eV at R_d = 0.85 Å with the 6-31G* basis set).

Next, we studied the central site, first the vertical central site (Fig. 1c), in which the H_2 molecule oriented vertically was situated at different distances from the vanadium surface (0.45–0.5 Å). The corresponding chemisorption energies were calculated at the

Table 1. Calculated optimized energies (eV) and geometric parameters such as distances (Å) obtained for H_2 adsorbed on the V (100) surface in both vertical and horizontal top sites at the P/LANL2DZ–6-31G* or 6-31G** level of theory

R_d, Å	R(H–H), Å	$-E_1$	$-E_2$	$-E_3$	$-E_4$
Vertical top site					
0.5	0.741	9560.921	–	–73.213	–
0.8	0.741	9616.530	9624.005	–17.604	–10.252
1.0	0.741	9630.732	9632.891	–3.402	–1.366
1.2	0.741	9638.287	9638.457	4.153	4.200
1.4	0.741	9640.408	–	6.274	–
1.6	0.741	9641.379	9639.076	7.245	4.819
1.75	0.741	–	9640.891	–	6.634
1.8	0.741	9641.744	9641.830	7.610	7.573
1.85	0.741	9638.706	9638.804	4.572	4.547
1.9	0.741	9637.911	–	3.776	–
2.0	0.741	9637.585	9636.610	3.450	2.353
2.1	0.741	9636.972	–	2.837	–
2.2	0.741	9637.585	–	3.451	–
1.8	0.791	9638.693	9641.523	4.559	7.267
1.8	0.841	9639.288	9639.380	5.153	5.123
1.8	0.941	9638.109	9638.087	3.974	3.830
1.8	1.041	9637.899	9637.630	3.765	3.373
1.8	1.2	9637.312	–	3.177	–
Horizontal top site					
0.500	0.741	9561.351	–	–72.783	–
0.800	0.741	9612.730	9613.340	–21.404	–20.917
1.000	0.741	9628.982	9629.470	–5.152	–4.787
1.200	0.741	9635.713	–	1.579	–
1.400	0.741	9636.053	9636.186	1.918	1.930
1.550	0.741	9640.904	–	6.769	–
1.600	0.741	9643.076	9637.688	8.942	3.431
1.650	0.741	9639.484	9640.954	5.350	6.697
1.70	0.741	–	9640.279	–	6.022
1.75	0.741	–	9640.279	–	6.022
1.80	0.741	9637.616	9641.034	3.481	6.777
1.85	0.741	–	9637.359	–	3.102
1.6	0.791	9637.826	–	3.692	–
1.6	0.841	9640.163	–	6.029	–
1.6	0.941	9638.960	–	4.826	–
1.6	1.500	9636.604	–	2.470	–
1.6	2.500	9641.337	–	7.203	–
1.6	3.500	9641.360	–	7.226	–
1.6	3.550	9641.316	–	7.181	–
1.6	3.600	9641.311	–	7.177	–
1.6	4.000	9640.776	–	6.641	–
1.8	0.791	–	9639.028	–	4.771
1.8	0.941	–	9638.546	–	4.289
1.8	1.200	–	9639.730	–	5.473
1.8	1.300	–	9638.779	–	4.522
1.8	1.450	–	9636.375	–	2.118
1.8	1.500	–	9640.529	–	6.272
1.8	1.530	–	9637.184	–	2.927
1.8	1.550	–	9640.840	–	6.583
1.8	1.600	–	9640.306	–	6.049
1.8	1.650	–	9636.683	–	2.427
1.8	2.500	–	9637.258	–	3.001

Note: R_d is the distance between hydrogen atoms on the surface; E_1 and E_2 are the adsorption energies of H_2 on the V (100) surface at the HF/LANL2DZ/6-31G* and HF/LANL2DZ/6-31G** levels of theory, respectively; E_3 and E_4 are $E_{ads} = E$ (H_2/V-surface) – E(H_2) – E (V-surface) at the P/LANL2DZ/6-31G* and HF/LANL2DZ/6-31G** levels of theory, respectively.

Table 2. Calculated optimized energies (eV) and structural distances (Å) obtained for H_2 adsorbed on the V (100) surface at the P/LANL2DZ–6-31G* and 6-31G** levels of theory for vertical and horizontal bridge sites

R_d, Å	R(H–H), Å	$-E_1$	$-E_2$	$-E_3$	$-E_4$	R_d, Å	R(H–H), Å	$-E_1$	$-E_2$	$-E_3$	$-E_4$
Vertical bridge site						Horizontal bridge site					
0.5	0.741	9636.332	9635.937	2.198	1.680	0.5	0.741	9636.802	9635.688	2.677	1.431
0.8	0.741	9636.332	9635.937	2.198	1.680	0.75	0.741	9640.038	9640.850	5.903	6.593
0.9	0.741	–	9635.788	–	1.531	0.8	0.741	9640.216	9638.390	6.081	4.133
0.95	0.741	9636.509	9641.117	2.374	6.860	0.85	0.741	9640.836	9636.317	6.702	2.060
1	0.741	9641.597	9637.365	7.463	3.108	0.9	0.741	9637.845	9637.799	3.710	3.542
1.05	0.741	9637.856	9636.977	3.721	2.720	1	0.741	9637.058	9636.868	2.924	2.611
1.2	0.741	9636.256	9637.207	2.122	2.950	1.2	0.741	9638.963	9637.676	4.829	3.419
1.4	0.741	9637.323	9638.795	3.189	4.538	1.3	0.741	9637.038	9636.533	2.904	2.277
1	0.791	9641.179	–	7.044	–	0.85	0.791	9639.668	–	5.534	–
1	0.841	9638.585	–	4.450	–	0.85	0.941	9639.774	–	5.640	–
1	0.941	9638.220	–	4.086	–	0.85	1.25	9641.011	–	6.877	–
1	1.25	9637.947	–	3.813	–	0.85	1.35	9639.345	–	5.211	–
1	1.45	9635.976	–	1.841	–	0.85	1.4	9642.708	–	8.574	–
1	1.6	9637.625	–	3.490	–	0.85	1.45	9639.417	–	5.283	–
1	1.8	9636.639	–	2.505	–	0.85	1.6	9639.983	–	5.849	–
1	2	9638.349	–	4.215	–	0.85	1.8	9640.764	–	6.630	–
1	2.35	9638.420	–	4.286	–	0.85	2.1	9640.958	–	6.823	–
1	2.4	9638.413	–	4.279	–	0.85	2.15	9642.544	–	8.409	–
1	2.45	9641.379	–	7.245	–	0.85	2.2	9642.722	–	8.588	–
1	2.5	9640.969	–	6.835	–	0.85	2.25	9641.459	–	7.325	–
1	2.55	9640.064	–	5.930	–	0.85	3	9642.587	–	8.453	–
1	3.45	9636.585	–	2.451	–	0.75	0.791	–	9640.614	–	6.357
0.95	0.791	–	9638.103	–	3.846	0.75	0.941	–	9640.365	–	6.108
0.95	0.841	–	9636.153	–	1.896	0.75	1.25	–	9642.500	–	8.243
0.95	0.941	–	9640.078	–	5.821	0.75	1.4	–	9640.316	–	6.059
0.95	1.45	–	9637.694	–	3.437	0.75	1.5	–	9640.356	–	6.099
0.95	2.35	–	9638.440	–	4.183	0.75	1.55	–	9640.474	–	6.217
0.95	2.45	–	9641.427	–	7.170	0.75	1.6	–	9643.461	–	9.205
0.95	2.5	–	9641.433	–	7.176	0.75	1.65	–	9640.689	–	6.432
0.95	2.55	–	9641.438	–	7.181	0.75	1.7	–	9642.286	–	8.030
0.95	2.6	–	9641.202	–	6.945	0.75	1.8	–	9642.848	–	8.592
0.95	3.45	–	9640.222	–	5.965	0.75	2	–	9641.330	–	7.073
						0.75	2.3	–	9641.536	–	7.279
						0.75	2.5	–	9639.511	–	5.254

P/LANL2DZ, 6-31G* and P/LANL2DZ, 6-31G** levels of theory for R_d = 0.5 Å (E_{ads} = –7.159 and –5.454 eV, respectively) (Table 3). In the horizontal central site (Fig. 1c'), over the range 0.5–1.2 Å and different chemisorption energies, we obtained the same adsorption distance with the two basis sets (1.2 Å), at which minimum energies at optimized geometries were higher than for the vertical orientation (E_{ads} = –7.193 and –7.220 eV, respectively). The chemisorption of H_2 in the vertical and horizontal orientations behaved similarly with both basis sets.

The relative adsorption energies of H_2 and H–V on the V (100) model surface are summarized in Tables 1, 2, and 3. The horizontal orientation is energetically favored on top, bridge, and central bridge sites.

According to our results, it is clear that the H_2 molecule is adsorbed weakly on V surfaces at the central site; its calculated adsorption energy is lower than for the other two sites. However, since the center of the surface remains constant, the binding energy does not reflect its surface coverage dependence. Adsorption energies of H_2 on the V surface are similar for the two models studied (top and bridge sites).

Stronger adsorption and stabilization energies are related to bridge-hydrogen vacancy sites. It is also obvious that a bridge hydrogen vacancy can bind two hydrogen atoms with one vanadium simultaneously. The binding energy of two hydrogen atoms should then be considered. We studied a monolayer coverage with hydrogen and found that complete orientation was always the most energetically favored adsorption model. The adsorption energies are shown in Figs. 2a, 2a', 2b, 2b', 2c, and 2c' for hydrogen adsorbed near the surface; H–V binding is facilitated when the hydrogen atom is adsorbed at the bridge position. The geometric parameter for the structure formed when the hydrogen molecule is located at the bridge site shows that the H–V axis is stronger because of the optimum distance between the two species. Atomic charge variations lead to charge transfer between hydrogen and metal surface atoms.

In fact, the required energies for H_2 formation decrease in the series V (100) on-bridge > V (100) on-top > V (100) on-center. These results can be related to the higher stability of various positions. The energy differences between the top, bridge, and central sites reveal that the barrier to hydrogen diffusion on these surfaces is quite small. These results are consistent with the high mobility of the hydrogen atom on the V (100) surface.

Despite this limitation, it is clear from the results reported above that the delocalized orbitals play a key role in hydrogen–metal binding. Because it is difficult to experimentally probe the dependence of binding energy on surface coverage and the site of interaction

Table 3. Calculated optimized energies (eV) and structural parameters such as distances (Å) obtained for H_2 adsorbed on the V (100) surface in vertical and horizontal central sites at the P/LANL2DZ–6-31G* or 6-31G** level of theory

R_d, Å	R(H–H), Å	$-E_1$	$-E_2$	$-E_3$	$-E_4$
Vertical central site					
0.450	0.741	9641.018	9637.592	6.884	3.335
0.500	0.741	9641.093	9639.711	6.959	5.454
0.550	0.741	9641.044	9637.451	6.909	3.195
0.600	0.741	9639.613	9639.473	5.478	5.216
0.700	0.741	9638.177	9638.339	4.043	4.082
0.800	0.741	9639.458	–	5.324	–
0.5	0.791	9639.604	–	5.470	–
0.5	0.841	9638.838	–	4.704	–
0.5	0.941	9639.462	–	5.327	–
0.5	1.041	9639.676	–	5.542	–
0.5	1.141	9638.755	–	4.621	–
0.5	1.241	9639.295	–	5.161	–
0.5	1.341	9639.342	–	5.207	–
0.5	1.441	9641.288	–	7.154	–
0.5	1.451	9641.294	–	7.159	–
0.5	1.500	9639.427	–	5.292	–
0.5	1.541	9636.980	–	2.846	–
0.5	1.600	9640.357	–	6.223	–
0.5	0.791	–	9637.485	–	3.228
0.5	0.941	–	9638.713	–	4.456
0.5	1.200	–	9638.810	–	4.553
0.5	1.250	–	9638.632	–	4.375
0.5	1.300	–	9639.405	–	5.148
0.5	1.350	–	9638.203	–	3.946
0.5	1.400	–	9637.015	–	2.758
0.5	1.500	–	9637.015	–	2.758
0.5	1.600	–	9638.847	–	4.590
Horizontal central site					
0.500	0.741	9638.694	9638.808	4.560	4.551
0.800	0.741	9640.407	9639.250	6.272	4.993
1.000	0.741	9639.108	9636.865	4.973	2.608
1.150	0.741	9641.327	9637.928	3.794	3.828
1.200	0.741	9641.327	9639.886	7.193	5.629
1.250	0.741	9639.815	9637.428	5.680	3.171
1.20	0.791	9635.611	–	1.477	–
1.20	0.941	9637.606	–	3.472	–
1.20	1.041	9639.871	–	5.737	–
1.20	1.091	9640.834	–	6.700	–
1.20	1.120	9639.180	–	5.046	–
1.20	1.141	9639.990	–	5.856	–
1.20	1.241	9638.059	–	3.925	–
1.20	1.341	9639.117	–	4.983	–
1.20	1.500	9639.180	–	5.046	–
1.20	2.500	9638.859	–	4.724	–
1.20	3.000	9640.966	–	6.832	–
1.20	0.791	–	9641.477	–	7.220
1.20	0.941	–	9639.926	–	5.669
1.20	0.991	–	9639.886	–	5.629
1.20	1.041	–	9640.737	–	6.480
1.20	1.091	–	9637.640	–	3.383
1.20	1.141	–	9636.430	–	2.173
1.20	1.241	–	9638.610	–	4.353
1.20	1.341	–	9638.775	–	4.519
1.20	3.000	–	9640.640	–	6.383

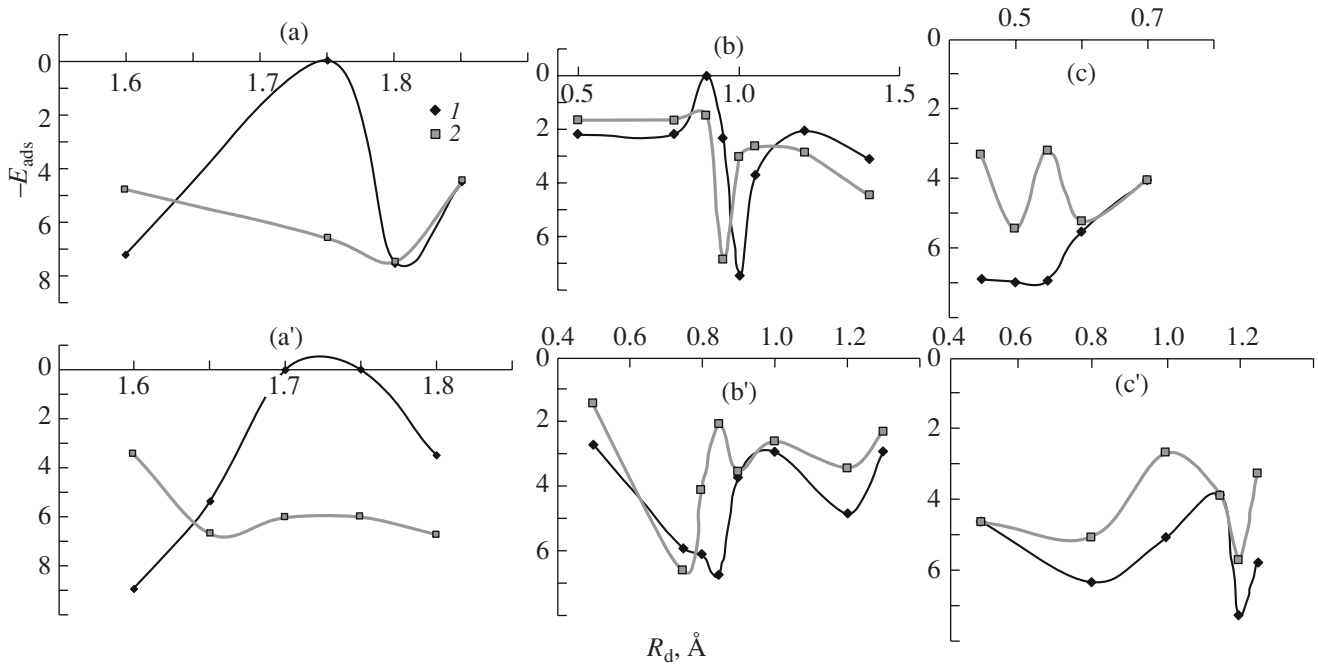

Fig. 2. Stability energies (E_{ads}) of calculated optimized distances of two hydrogen atoms from the surface (R_d). For each configuration ((a) vertical top site, (a') horizontal top site, (b) vertical bridge site, (b') horizontal bridge site, (c) vertical central site, (c') horizontal central site), the data of (*1*) 6-31G* and (*2*) 6-31G** calculations are shown.

simultaneously, the calculations reported provide comprehensive information for surface chemistry.

CONCLUSIONS

The quantum mechanical calculations performed significantly expand the database of structural and energy parameters describing the adsorption of hydrogen species on crystalline vanadium surfaces. From the results presented above, several qualitative observations follow.

Based on density functional theory calculations, we performed a theoretical investigation of the adsorption of H_2 on the V (100) model surface.

The energy values for a series of well-defined reaction paths were obtained using DFT and the GGA hybrid method.

In this work, we studied different interaction schemes starting with the H_2 molecule adsorbed on the bcc sites of the V (100) model. In all these interaction schemes, the final products were gas phase formaldehyde and adsorbed hydrogen. The main difference between these interactions concerns the surface site where the hydrogen atom is located and the extent of H–V axis binding. The different adsorption sites for adsorbed hydrogen interaction were the top, bridge, and central positions. The results obtained suggest that the most favorable chemisorption route is the one in which the H group is adsorbed with one hydrogen atom approaching the bridge site that connects BCC lattice vanadium atoms. The relative energies corresponding to the H_2–V (100) bridge model are higher than for the other two orientations.

According to the values reported in Tables 1, 2, and 3, the adsorption energies corresponding to the central site were slightly less favorable than the stablest surface site, the so-called hollow site or lattice vacancy. In this investigation, we calculated the relative adsorption energies and optimized distances for H_2 molecules adsorbed on the V (100) model surface. For each adsorption site, we focused on the energetically stablest model. This work revealed that the H–V binding axis yields a significant stabilization of adsorption energies. This result can be used to confirm the experimental evidence that minimum energy is required to establish a model in which hydrogen can approach three sites, top, bridge, and central sites, of the metal surface.

REFERENCES

1. D. Dominguez-Ariza, C. Sousa, and N. M. Harrison, Surf. Sci. **522**, 185 (2003).
2. J. V. Barth, Surf. Sci. Rep. **40**, 75 (2000).
3. T. Ala-Nissila, R. Ferrando, and S. C. Ying, Adv. Phys. **51**, 949 (2002).
4. M. Monajjemi, F. Mollaamin, M. R. Gholami, et al., Main Group Metal Chem. **26**, 6 (2003).
5. K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).
6. D. E. Jiang and E. A. Carter, Surf. Sci. **547**, 85 (2003).

7. G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).
8. R. B. Anderson, *The Fischer–Tropsch Synthesis* (Academic Press, Orlando, FL, 1984).
9. W. Zhong, Y. Cai, and D. Tomanek, Nature (London) **362**, 435 (1993).
10. J.-S. Wang, Eng. Fract. Mesh. **68**, 647 (2001).
11. T. R. Mattsson, G. Wahnstrom, L. Bengtsson, and B. Hammer, Phys. Rev. B: Condens. Matter **56**, 2258 (1997).
12. G. Källén and G. Wahnström, Phys. Rev. B: Condens. Matter **65**, 033406 (2001).
13. K. Nobuhara, H. Nakanishi, H. Kasai, and A. Okiji, Surf. Sci. **493**, 271 (2001).
14. S. C. Bădescu, P. Salo, T. Ala-Nissila, et al., Phys. Rev. Lett. **88**, 136101 (2002).
15. G. Kresse and J. Hafner, Phys. Rev. B: Condens. Matter **48**, 13115 (1993).
16. G. Kresse and J. Furthmüller, Phys. Rev. B: Condens. Matter **54**, 11169 (1996).
17. P. E. Blöchl, Phys. Rev. B: Condens. Matter **50**, 17953 (1994).
18. Y. Wang and J. P. Perdew, Phys. Rev. B: Condens. Matter **44**, 13298 (1991).
19. L. J. Lauhon and W. Ho, Phys. Rev. Lett. **85**, 4566 (2000); **89**, 079901(E) (2002).
20. G. Krenn, C. Eibl, W. Mauritsch, et al., Surf. Sci. **445**, 343 (2000).
21. R. Koller, W. Bergermayer, G. Kresse, et al., Surf. Sci. **480**, 11 (2001).
22. W. Bergermayer, R. Koller, C. Konvicka, et al., Surf. Sci. **497**, 294 (2002).
23. D. L. Adams and H. B. Nielsen, Surf. Sci. **107**, 305 (1981).
24. J. P. Perdew, J. A. Chevary, S. H. Vosko, et al., Phys. Rev. B: Condens. Matter **46**, 6671 (1992).
25. A. I. Livshits, F. Sube, M. N. Solovyev, et al., J. Appl. Phys. **84**, 2558 (1998).
26. K. Hermann, A. Chakrabarti, R. Druzinic, and M. Witko, Phys. Status Solidi A **173**, 195 (1999).
27. R. Koller, W. Bergermayer, G. Kresse, et al., Surf. Sci. **11**, 480 (2001).
28. A. J. Quinn, M. Schmid, J. Redinger, et al., Phys. Rev. Lett. **86**, 2396 (2001).
29. J. P. Perdew and Y. Wang, Phys. Rev. B: Condens. Matter **33**, 8800 (1986).