Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 4 (4) 229 -233**:** Winter 2008
(J.Phys.Theor.Chem.IAU Iran: Winter 2008)
ISSN: 1735-2126

CO Adsorption on the V (100) Surface: A Density Functional Study

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ABSTRACT

Adsorption of CO molecule on the Vanadium surface has been studied by using of the DFT method with LANL2DZ,6-31G* and 6-31G** basis sets by GGA approximation of theory. Using periodic first principles simulations we investigate the interaction of oxygen molecule with regular V (100) surface. The limitation of this approach is the use of thin metallic slabs with a limited range for their coverage by adsorbed oxygen. The advantage is the detailed modeling that is possible at an atomic level. On the regular V (100) surface, we have been able to follow the adsorption process from the approach of CO molecule to the surface, through the chemisorption and absorption of this compound, up to the formation of adsorption layers. In this work, in order to extract energetic information about the stability of adsorbed CO molecules, calculations were performed in the vacuum. The results obtained here are used to interpret experimental data. The computed geometry for adsorbed CO agrees with the structure proposed from a previous experimental work.

Keywords: Chemisorption; CO; V (100); GGA

INTRODUCTION

Experimental and theoretical studies of chemisorption on vicinal surfaces are of great current interest due to close connection to real catalytic substrates. Investigations about the adsorption of carbon monoxide on metal surfaces are prototypical in surface science, and the first studies on this subject date goes back at least 30 years ago [1]. The models for chemisorption based on density functional theory (DFT) are performs generally [2, 3] by the generalized gradient approximation (GGA) [4]. Much information is available regarding molecules and molecular fragments adsorbed on or scattering from surfaces.

But though there is reason to doubt the accuracy of GGA adsorption energies at the level of tenths of electron volts [5, 6] and though current implementations of DFT are known to overestimate the relative binding energies of compact structures [7] the sense of the literature is still that the GGA provides a reliable way to analyze and interpret surface chemical phenomena. [5, 8]. A large effort has been devoted in the past to study CO adsorption on Pt (111) [9] where CO also prefers to sit in the on-top site at low coverage, but standard ab-initio calculations predict the hollow site again.

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Besides the system CO/Pt (111) which is probably the best studied, there have also been various experiments on the system CO/Cu (111). The adsorption has been investigated with low energy electron diffraction (LEED) [10–12]. Vanadium alloys are considered as 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 [13]

In this work, we present a theoretical electronic and geometry studies of the change in the adsorption of CO onto V (100) surface. One of our interests is to investigate the effects of the approaches (cluster or slab) and the basis sets and DFT method selected for the cluster model calculation.

COMPUTATIONAL METHOD

The present work is devoted to the study of the interaction of CO molecule with the V (100) surface. 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 five atoms. Calculations are carried out at density functional level of theory (DFT) for consideration of electron exchange and correlation; it is well known that the generalized gradient approximation (GGA) is needed to give an accurate description of energetic of bulk V phases, and the cluster fragment is considered as a doublet molecules, with partitioning of the basis sets, for carbon and oxygen atoms 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 every metal layer contains five V atoms as shown in Fig.1. Our two-layers model of the surface contains nine V atoms. The CO 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).

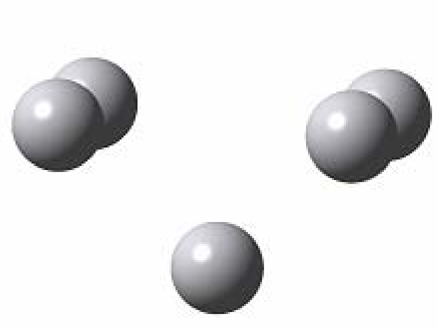

Fig.1. The body-centered cubic structure of V with a Miller plane (100).

RESULTS AND DISCUSSION

In this work, a slab approach is adapted to describe the metallic surface. The distance between the metals is 3.032 Å according to the theoretical bulk lattice parameter a V = 3.032 Å of bcc V. The structure of the clean V (100) surface is shown in Fig. 1. We consider CO molecules in unit cells that contain five vanadium atoms. Carbon Monoxide adsorption on the clean surface of vanadium was followed for V (100) surface. The CO 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. The various configurations discussed in this Study could be present at the surface of a V (100) sample, in equilibrium with the CO gas phase.

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

$$E_{ads} = E\,(CO/V\text{-surface}) - E\,(CO) - E\,(V\text{-surface}) \qquad (1)$$

The first term in equation 1 is the total energy of the CO/V-surface super molecule and the second and third 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 carbon monoxide molecule on the metal surface, where the distance between oxygen and carbon atoms and distance of C-O bond from the surface are calculated.

We start by describing the CO chemisorption process at the different sites on V-surfaces and calculating of geometry coordination. There are three high-symmetry sites on V (100), Consider first the top site (Fig. 2). In the top site (Fig.2), CO molecule is allowed to approach the vanadium surface in different distances (Rd: 0.8, 1, 1.2, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.05 and 2.1) Å and their chemisorption energy are calculated with P/LANL2DZ, 6-31G* and P/LANL2DZ, 6-31G** basis sets (Table 1).For two basis sets, energies and the chemisorption energies in along three different symmetrical sites are equal and optimized chemisorption distance (Rd) for vanadium surface-CO for top site is 2.05 Å while the chemisorption energy is -8.431eV.In next step, chemisorption energies in distance of 2.05 Å is calculated with increase of the distance between the oxygen and carbon atoms (RC-O: 1.24, 1.44, 1.64, 1.84, 2.04, 2.24 and 2.26) Å. In this state, the optimized R (C-O) is same 2.05 Å and the chemisorption energy of CO along the top site is without change, which implies CO remains as molecule.

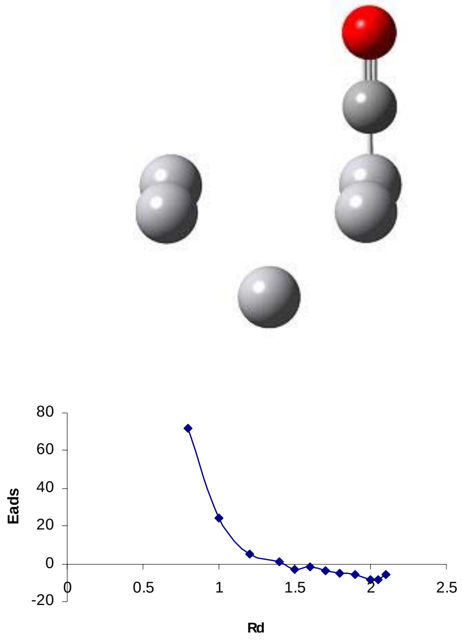

Fig.2. High symmetry of CO adsorption on V (100) top site (Eads) in terms of distances of monoxide carbon from the vanadium surface (Rd).

Table 1. Optimized parameters of adsorption of C-O at V (100) at the P/LANL2DZ,6-31G* or 6-31G** for top site

top site			
Rd^a/Å	**R(C-O)/Å**	**E^b/eV**	**Eabs^c/eV**
0.8	1.14	-12599.662	71.580
1	1.14	-12647.136	24.106
1.2	1.14	-12666.313	4.929
1.4	1.14	-12670.411	0.831
1.5	1.14	-12674.388	-3.146
1.6	1.14	-12672.596	-1.355
1.7	1.14	-12674.710	-3.468
1.8	1.14	-12676.062	-4.820
1.9	1.14	-12676.720	-5.478
2	1.14	-12679.596	-8.354
2.05	1.14	-12679.673	-8.431
2.1	1.14	-12677.000	-5.758
2.05	1.24	-12674.972	-3.730
2.05	1.44	-12674.400	-3.158
2.05	1.64	-12674.572	-3.330
2.05	1.84	-12673.016	-1.774
2.05	2.04	-12672.988	-1.746
2.05	2.24	-12671.900	-0.658
2.05	2.26	-12672.617	-1.376

[a] Distances of monoxide carbon from the vanadium surface.
[b] Adsorption energies (eV) of CO onto the V (100) surfaces at the P/LANL2DZ / 6-31G* or 6-31G**.
[c] Eads(eV) = **E** (CO/V-surface) - **E** (CO) - **E** (V-surface$_)$ at the P/LANL2DZ / 6-31G* or 6-31G**

For the bridge site (Fig. 3), CO molecule is allowed to approach the vanadium surface in different distances (Rd: 0.5, 0.8, 0.95, 1.1, 1.2, 1.4, 1.55, 1.6, 1.65) Å the optimized chemisorption distance (Rd) of the vanadium surface-CO is 1.6 Å (Table. 2) and the chemisorption energy is -8.132 eV while distance between the carbon and oxygen atoms is 1.19 Å, chemisorption energy is more (-8.590) which implies partial dissociation of CO molecule for this state.

In general, chemisorptions at the bridge site are considerably stronger than at the top site. This result is related to the fact that carbon and oxygen atoms are relatively much closer to the vanadium surface in bridge sites compared to the top sites. For the bridge site approaches, carbon and oxygen atoms are closer to the vanadium surface (Rd = 1.6 Å) than that of the top site (Rd = 2.05Å) and the chemisorption energy is lower.

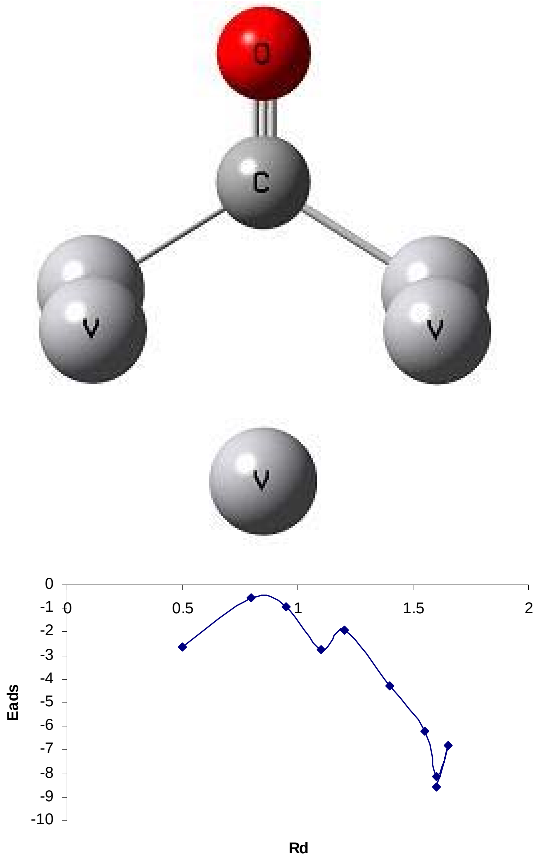

Fig.3. High symmetry of CO adsorption on V (100) bridge site (Eads) in terms of distances of monoxide carbon from the vanadium surface (Rd).

Table 2. Optimized parameters of adsorption of C-O at V (100) at the P/LANL2DZ, 6-31G* or 6-31G** for bridge site

Bridge Site			
Rd^a/Å	**R(O-O)/Å**	**E^b/eV**	**Eabs^c/eV**
0.5	1.14	-12673.871	-2.629
0.8	1.14	-12671.791	-0.549
0.95	1.14	-12672.192	-0.950
1.1	1.14	-12673.992	-2.750
1.2	1.14	-12673.146	-1.904
1.4	1.14	-12675.546	-4.304
1.55	1.14	-12677.438	-6.196
1.6	1.14	-12679.374	-8.132
1.65	1.14	-12678.060	-6.818
1.6	1.19	-12679.832	-8.590
1.6	1.24	-12679.368	-8.126
1.6	1.34	-12676.395	-5.153
1.6	1.44	-12676.879	-5.637
1.6	1.64	-12672.158	-0.916
1.6	1.84	-12669.588	1.654
1.6	2.04	-12673.375	-2.133
1.6	2.24	-12673.713	-2.471
1.6	2.44	-12671.169	0.073

In the center site, (Fig.4) to CO molecule is allowed to approach the vanadium surface in different distances (Rd: 0.45, 0.55, 0.65, 1.4, 0.75, 0.85, 0.9, 0.95, 1, 1.05) and their chemisorption energies are calculated with P/LANL2DZ,6-31G* or 6-31G** basis sets (Table 3). The optimized chemisorption distance (Rd) from the vanadium surface to the CO is 0.95 Å and the chemisorption energy is -5.835 eV. In next step, chemisorption energy in distance of 0.95 Å is calculated with increase of the distance between the oxygen and carbon atoms (RC-O: 1.19, 1.24, 1.44, 1.64, 1.84, 2.04, 2.24 and 2.44) Å. In this state, the optimized R (C-O) is same 0.95 Å and the chemisorption energy of CO along the top site is without change, which implies CO remains as molecule.

From the above discussion, it is clear that the bridge site mode is the most stable site for carbon monoxide adsorption on V (100) surface nanocluster. With comparing to the energies of these configurations in nanoparticle, we have gained bridge site approach are important for the chemisorption processes, because the CO molecule dissociate.

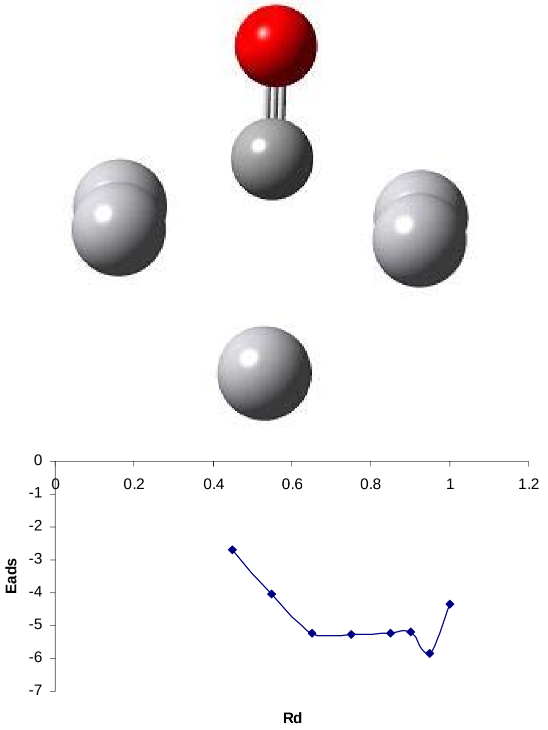

Fig.4. High symmetry of CO adsorption on V (100) Center site (Eads) in terms of distances of carbon monoxide from the vanadium surface (Rd).

Table 3. Optimized parameters of adsorption of C-O at vanadium-surface at the P/LANL2DZ,6-31G* or 6-31G** for center site

Center Site			
Rd^a/Å	**R(H-H)/Å**	**E^b/eV**	**Eabs^c/eV**
0.45	1.14	-12673.926	-2.684
0.55	1.14	-12675.269	-4.027
0.65	1.14	-12676.471	-5.229
0.75	1.14	-12676.514	-5.272
0.85	1.14	-12676.471	-5.229
0.9	1.14	-12676.420	-5.178
0.95	1.14	-12677.077	-5.835
1	1.14	-12675.576	-4.334
1.05	1.14	-12676.200	-4.958
0.95	1.19	-12674.987	-3.745
0.95	1.24	-12676.788	-5.546
0.95	1.34	-12676.427	-5.185
0.95	1.44	-12674.895	-3.653
0.95	1.64	-12673.878	-2.636
0.95	1.84	-12671.953	-0.711
0.95	2.04	-12674.885	-3.643
0.95	2.24	-12673.345	-2.103
0.95	2.44	-12672.410	-1.168

CONCLUSION

The most important results presented above can be summarized as follows. This study concerns about quantum chemical modeling behavior of CO on the (100) surface of vanadium system using density functional theory (DFT) method with P level and LAN2DZ, 6-31G* and 6-31G** basis sets.

The V cluster has five V atoms that are used to form the perfect V (100) surface. Three possible adsorption sites, top, bridge and center site are considered in the calculations. The predicted results show that the bridge site is the prefer site for oxygen adsorbed on V (100) surface energetically. The bridge site approach is important for the chemisorption processes, because the CO molecule dissociate.

The geometry of V (100) surface has also been optimized theoretically in CO various distance.

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